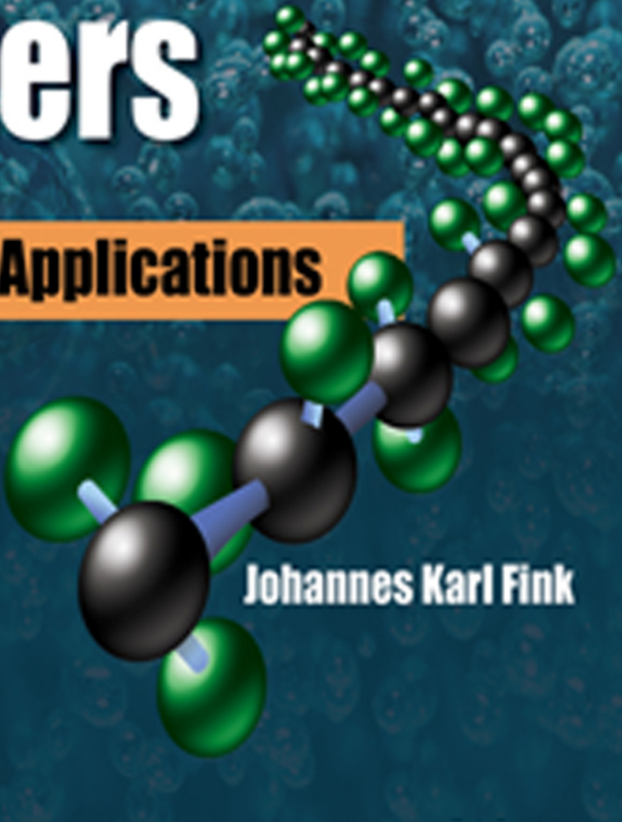
Marine, Waterborne, and Water Resistant Polymers

Chemistry and Applications



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Preface

This book focuses on the chemistry of marine polymers, waterborne polymers, and water resistant polymers, as well as special applications of these materials.

After an introductory section on the general aspects of the field, the types and uses of these polymers are summarized, followed by an overview of some testing methods.

In passing, as it so happens in the literature for these types of polymers, a lot of special organic compounds are used which for the ordinary organic and polymer chemist are not too familiar. Therefore, the structures of these organic compounds are reproduced in many of the figures.

The text focuses on the literature of the past decade. Beyond education, this book may serve the needs of industry engineers and specialists who have only a passing knowledge of these issues, but need to know more.

How to Use This Book

Utmost care has been taken to present reliable data. Because of the vast variety of material presented here, however, the text cannot be complete in all aspects, and it is recommended that the reader study the original literature for more complete information.

The reader should be aware that mostly US patents have been cited where available, but not the corresponding equivalent patents of other countries. In particular, in this field of science, most of the original patents are of Japanese origin.

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Index

There are three indices: an index of acronyms, an index of chemicals, and a general index. In the index of chemicals, compounds that occur extensively, e.g., *acetone*, are not included at every occurrence, but rather when they appear in an important context. When a compound is found in a figure, the entry is marked in boldface letters in the chemical index.

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I also want to express my gratitude to all the scientists who have carefully published their results concerning the topics dealt with herein. This book could not have been otherwise compiled.

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Johannes Fink
Leoben, July 15, 2015

1

Marine Polymers

An overview of the methods, applications, and products of marine biotechnology has been presented (1). A large portion of the surface of the earth is covered by the ocean. Therefore, more than 80% of living organisms can be found in aquatic ecosystems. Thus, these organisms constitute a rich reservoir for various chemical materials and biochemical processes.

The literature for marine natural products has been extensively reviewed (2–4). Compounds isolated from marine microorganisms and phytoplankton, green, brown and red algae, sponges, cnidarians, bryozoans, mollusks, tunicates, echinoderms, mangroves and other intertidal plants and microorganisms have been collected. Also, biosynthetic studies, and syntheses that lead to the revision of structures or stereochemistries, have been dealt with (4).

Biochemical materials and processes from marine sources make these materials available to applications in pharmaceuticals, cosmeceuticals or nutraceuticals, as well as for the production of biopolymers, bioenergy and biofuels (1). Also, biomaterials from marine-origin biopolymers have been reviewed (5).

1.1 Marine Microbes

The marine microbial biosphere is a large resource of biotechnological interest. The potential of marine microbes in biotechnology has been reviewed (6).

The biotechnological potential ranges from the synthesis of bioactive molecules to the production of biofuels, cosmeceuticals, nutraceuticals, and biopolymers.

Marine microbes can be used for biomedical purposes and also for the degradation of pollutants. Marine viruses have a great biotechnological potential. Marine archaea have been exploited for the isolation of enzymes. Also, bacteria and microbial eukaryotes are of importance for biotechnological uses (6).

1.2 Marine Microgels

The ocean plays a critical role in the global carbon cycle (7). It handles around 50% of the global primary production, yielding the world's largest stock of reduced organic carbon (ROC) that supports one of the world's largest biomasses. However, the mechanisms whereby ROC becomes mineralized remain unresolved. A review has been presented that focuses on laboratory and field observations that of dissolved organic carbon (DOC) self-assembles, and the formation of self-assembled microgels (SAGs).

Self-assembly has approximately 10% yield, generating an estimated global seawater SAG budget of some 1016 g carbon. The transects at depths of 10 to 4,000 m reveal concentrations of 10^6 to 3×10^{12} SAG l^{-1}, thus respectively forming an estimated ROC stock larger than the global marine biomass (7).

Because hydrogels have 1% solids, i.e., 10 $g\,l^{-1}$, whereas seawater DOC reaches only 10^{-3} $g\,l^{-1}$, SAGs contain 10^4 more bacterial substrate than seawater.

For this reason, microgels represent an unsuspected and huge micron-level ocean patchiness that could profoundly influence the passage of DOC through the microbial loop, with ramifications that may scale to global cycles of bioactive elements (7).

1.3 Polymer Production from Marine Algae

The broad class of polymeric materials includes polymers with excellent processability, chemical resistance, and mechanical properties. These properties allow polymers to be used to produce extrusion molded articles, injection molded articles, hollow molded articles, films, sheets, among many others.

Numerous polymers are derived from petroleum and natural gas. Actually, the market prices for these fossil fuels are increasing due to a number of factors, including a depletion of easily accessible deposits, growth of emerging economies, political instabilities, and environmental concerns. Therefore, polymer production methods that do not rely on fossil fuels are desirable (8).

The production of biopolymers from algae has already been described in 1975 (9). Long-chain polymers with flocculating properties have been produced.

The special issues of algae have been summarized (10). Algae are a very large and diverse group of eukaryotic organisms, ranging from unicellular genera and the diatoms to multicellular forms. An eukaryote is an organism whose cells contain a nucleus and other organelles enclosed within membranes (11).

Algae can produce 10–100 times more mass then terrestrial plants in the course of a year. Algae also produce oils and starches that may be converted into biofuels. Algae useful for biofuel production are also microalgae, consisting of small, often unicellular, types.

These algae can grow almost everywhere, but are most commonly found at latitudes between 40 degrees north and 40 degrees south. The algae can grow rapidly in nearly any environment, with almost any kind of water, including marginal areas with a limited or poor quality water. Micrographs from the algae are shown in Figure 1.1.

It has been found that certain algae species of the Isochrysis family produce polyunsaturated long-chain alkenones. In the studies, methyl and ethyl alkenones with 35–40 carbons having 2–4 double bonds have been detected.

Lipid-producing algae can include a wide variety of algae. Algae are classified as follows: diatoms are bacillariophytes, green algae are chlorophytes, blue-green algae are cyanophytes, golden-brown algae are chrysophytes, and phylum of algae are haptophytes. Most common algae are listed in Table 1.1.

Methods have been developed for producing polymers from algae. Such methods comprise (8):

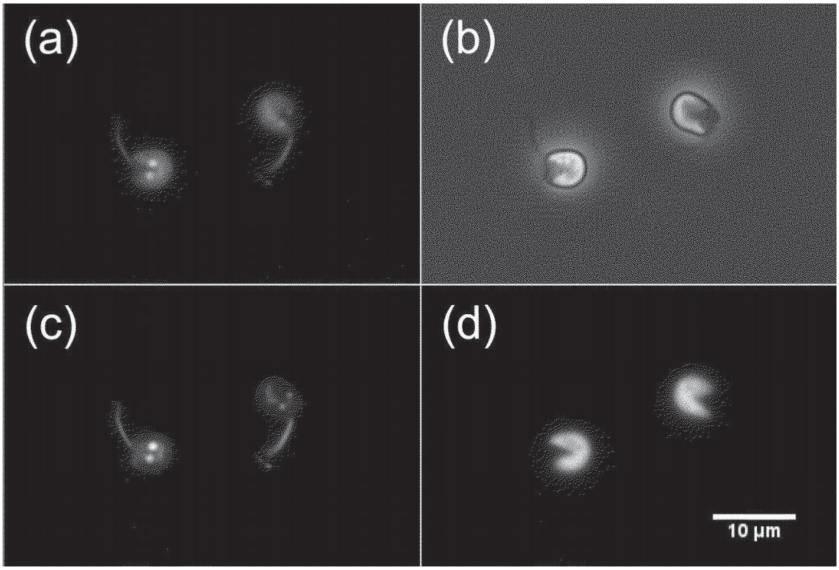


Figure 1.1 Micrographs from *Isochrysis sp.* (8): (a) merge of (c) and (d), (b) phase contrast image, (c) Nile Red stained image, (d) chlorophyll autofluoresence.

Table 1.1 Lipid-producing algae.

Bacillariophytes	Chlorophytes
Amphipleura	Ankistrodesmus
Amphora	Botryococcus
Chaetoceros	Chlorella
Cyclotella	Chlorococcum
Cymbella	Dunaliella
Fragilaria	Monoraphidium
Hantzschia	Oocystis
Navicula	Scenedesmus
Nitzschia	Tetraselmis
Phaeodactylum	
Thalassiosira	
Cyanophytes	**Haptophytes**
Oscillatoria	Isochrysis
Synechococcus	Pleurochrysis

1. Culturing an alkenone-producing alga under a growth condition sufficient to produce alkenones within the alga,
2. Optionally chemically modifying the alkenones to produce alkenone derivatives, such as acrylic acids, acrylic esters, alkenes, vinyl chloride, vinyl acetate, diacids, diamines, diols, or lactic acid, and
3. Polymerizing the alkenones or alkenone derivatives.

The alkenone-producing alga can be a species of the Isochrysis family, such as *Isochrysis galbana*, *Isochrysis sp. T-Iso*, and *Isochrysis sp. C-Iso*. The alkenones of the alga should be alkenones with a number of carbons of 35–40. The alkenones may be converted into hydrocarbons by catalytic hydroprocessing.

Eventually, the alkenones can be converted into a liquid fuel such as diesel and gasoline. Likewise, the alkenones may be processed into a gaseous fuel such as synthesis gas or methane, propane, and butane. The alga may also deliver fatty acid methyl esters.

The growth condition for culturing the alga may include a stationary growth phase, a high temperature, sufficient light, and nutrient limitation. The algae can also be directly converted into methane via a hydrothermal gasification process (8).

1.3.1 Recovery of Lipids Algae

Algae store lipids inside the cell body, sometimes but not always in vesicles (8). The lipids can be recovered in various ways, including solvents, heat, pressure, or depolymerization, such as by biologically breaking the walls of the algal cell or oil vesicles.

At least one of three types of biological agents may be used to release algae energy stores, for example, enzymes such as cellulase or glycoproteinase, structured enzyme arrays or system such as a cellulosome, a viral agent, or a combination of these agents.

A cellulase is an enzyme that breaks down cellulose, especially in the wall structures. A cellulosome is an array or sequence of enzymes or cellulases which is more effective and faster than a single enzyme or cellulase. In both cases, the enzymes break down the cell wall or lipid vesicles and release lipids from the cell.

Cellulases used for this purpose may be derived from fungi, bacteria, or yeast. Examples include cellulase produced by fungus

Trichoderma reesei and many genetic variations of this fungus, cellulase produced by the bacteria genus *Cellulomonas*, and cellulase produced by the yeast genus *Trichosporon*.

A glycoproteinase provides the same function as a cellulase, but is more effective on the cell walls of microalgae, many of which have a structure more dependent on glycoproteins than cellulose (8).

1.3.2 Conversion of Algal Lipids into Hydrocarbons

A process for converting the algal alkenones into hydrocarbons is catalytic hydroprocessing, or cracking (8). The catalytic hydroprocessing technology is well known in the art of petroleum refining and generally refers to converting at least large hydrocarbon molecules into smaller hydrocarbon molecules by breaking the carbon-carbon bonds (12).

The long chains of carbon in the alkenones produced by algae can be used to produce a wider range of biofuels or lubricating oils than those derived from glycerides (8).

1.3.3 Conversion of Algal Lipids into Polymers

The algal lipids can be used as feedstock in the industrial chemical field, particularly in the manufacture of polymers. The algal lipids can be polymerized, either directly or after some chemical modification (8).

Also, the algal lipids can be pyrolyzed or cracked into smaller molecules to permit the generation of standard monomers such as acrylic acids and esters, alkenes, vinyl chloride, vinyl acetate, diacids, diamines, diols, lactic acid, and others (8).

1.3.4 Crosslinking of Phenolic Polymers

It has been shown that a phenolic polymer extracted from *Fucus serratus* can be crosslinked using a vanadium-dependent bromoperoxidase (13). The methanol extracted phenolic polymer was adsorbed onto a quartz crystal sensor and the crosslinking was initiated by the addition of bromoperoxidase, KBr, and H_2O_2.

The decreased dissipation upon addition of the crosslinking agents, as measured with the quartz crystal microbalance with the quartz crystal microbalance dissipation (QCM-D), was interpreted as intramolecular crosslinks being formed between different phloroglucinol units in the phenolic polymer.

With surface plasmon resonance, it was shown that no desorption occurred from the sensor surface during the crosslinking reaction. UV/VIS spectroscopy verified the results achieved with QCM-D that all components, i.e., bromoperoxidase, KBr, and H_2O_2, were necessary in order to achieve intramolecular oxidative crosslinking of the polymer (13).

1.4 Marine Bioadhesive Analogs

Nature has evolved materials that possess mechanical properties surpassing many manmade composites. A nanostructured composite film that takes advantage of two different natural materials has been prepared (14). These materials are layered nacre and the marine adhesive of mussels.

L-3,4-Dihydroxyphenylalanine molecules impart an unusual adhesive strength to a clay composite and the hardening mechanism found in the natural cement plays an equally important role in the strengthening of the nanostructured nacre (14).

The in-situ molecular physicochemical characterization of bioadhesives at solid or liquid interfaces has been reviewed (15). The adhesion strategies that lie at the root of marine biofouling have been elucidated. Three major fouling organisms have been assessed: mussels, algae and barnacles.

The dispersal of these organisms, their colonization on the surfaces, and ultimately their survival are critically dependent on the ability of the larvae or spores of the organisms to locate a favorable settlement site and undergo metamorphosis. In this way their sessile existence is initiated.

Differences in the composition of the adhesive secretions and the strategies employed for their temporary or permanent implementation between the larval and adult life stages are obvious.

Until now, only a few adhesive secretions from marine fouling organisms have been adequately described in terms of their chemical composition. The presence of certain recurrent functional groups, specifically catechol, carboxylate, monoester-sulphate and -phosphate are used for this purpose. The binding modes of such functionalities to wet mineral and metal oxides surfaces have been described in detail.

A plausible explanation for the propensity of these adhesive functionalities to bind to hydrous metal oxide surfaces has been based on the basis of the hard and soft acids and bases principle, Hofmeister effects and entropic considerations.

From the in-situ analysis of marine organism bioadhesives and adsorption studies of functionalities relevant to the bioadhesion process, insights suitable for antifouling strategies and the synthesis of durable adhesive materials can be obtained (15).

1.5 Medical Applications

Marine organisms are constituted by materials with a vast range of properties and characteristics that may justify their potential application within the biomedical field (16). Moreover, assuring the sustainable exploitation of natural marine resources, the valorization of residues from marine origin, like those obtained from food processing, constitutes a highly interesting platform for the development of novel biomaterials, with both economic and environmental benefits.

In the last decade, many different biomaterials, like various types of polymers and bioactive ingredients, have been identified, isolated, and characterized. These biomaterials can be used in controlled drug delivery, tissue engineering, and diagnostic devices (17).

In this perspective, an increasing number of different types of compounds can be isolated from aquatic organisms and transformed into profitable products for health applications, including controlled drug delivery and tissue engineering devices.

The issues of marine structural proteins in biomedicine and tissue engineering have been reviewed (18). Actually, the development of biocompatible composites and vehicles of marine biopolymer origin for growth, retention, delivery, and differentiation of stem cells is of crucial importance for regenerative medicine.

Also, the current techniques for the isolation and characterization of polysaccharides, proteins, glycosaminoglycans and ceramics from marine raw materials have been reviewed (16). Specific compound classes for medical applications are listed in Table 1.2.

Table 1.2 Marine materials for medical applications (16).

Compound class	Compound class
Agar	Collagen
Alginates	Chondroitin sulfate
Carrageenans	Heparin
Chitin	Hyaluronic acid
Chitosan	Calcium phosphorous compounds
Glycosaminoglycans	Biosilica

Marine-derived bioactive compounds for breast and prostate cancer treatment have been reviewed (19). Marine-derived natural bioactive products, isolated from aquatic fungi, cyanobacteria, sponges, algae, and tunicates, have been found to exhibit various anticancer activities including anti-angiogenic, anti-proliferative, inhibition of topoisomerase activities and induction of apoptosis.

1.5.1 *Metalloproteinases*

Matrix metalloproteinases are endopeptidases which belong to the group of metalloproteinases that contribute for the extracellular matrix degradation and several tissue remodeling processes (20). An imbalance in the regulation of these endopeptidases may cause severe pathological complications like cancer, cardiac, cartilage, and neurological-related diseases (21).

Synthetic metalloproteinases have some shortcomings. Therefore, many of them cannot be used in clinical applications. Thus, a growing interest metalloproteinases from marine origin has been taking place. Potential matrix metalloproteinase inhibitors from edible marine algae have been reviewed (21).

An imbalance in the regulation of these endopeptidases eventually results in severe pathological complications like cancer, cardiac, cartilage, and neurological-related diseases.

1.5.2 Fucoidans

Fucoidans are a class of sulfated, fucose-rich polymers found in brown macroalgae (22, 23). They were identified in the early 20th century by Harald Kylin (24).

Subsequently, the class of these compounds was detailed (25,26). The systematic isolation of fucoidan from a number of different British seaweeds has been described (27).

Fucoidan was recognized as having a role in the biology of seaweed, and was examined over the next few decades for its activity in a number of biological systems.

The uses of fucoidan as a therapeutic target for cancer have been reviewed (28). Fucoidan was shown to induce a cytotoxicity of various cancer cells; it induces apoptosis, and inhibits invasion, metastasis and angiogenesis of cancer cells. The principle of apoptosis was already described in 1842. It is a process of programmed cell death (29,30). Apoptosis is a critical defense mechanism against the formation and progression of cancer and exhibits distinct morphological and biochemical traits. Targeting the apoptotic pathways has become an important strategy for the development of chemotherapeutic agents. Marine natural products have become important sources in the discovery of antitumor drugs. The effects of selected marine natural products and their synthetic derivatives on apoptosis signaling pathways have been reviewed (31).

Fucoidans from marine algae are also potential matrix metalloproteinase inhibitors. Inhibitory substances of metalloproteinases could be beneficial in the management of pathological events (20).

The current research interest in fucoidan is now global. Research in occurring in Australia, Japan, Korea, Russia and China, in addition to Europe and the American countries. The intensity of biological activities of fucoidan varies with species, molecular weight, composition, structure and the route of administration.

1.5.2.1 Drug Delivery

The literature concerning fucoidan drugs has increased considerably in the last decade. These algal-derived marine carbohydrate polymers present numerous valuable bioactivities.

The role of fucoidan in the control of acute and chronic inflammation via selectin blockade, enzyme inhibition and inhibition of the complement cascade has been reviewed (32–34). Most recent data on toxicology and uptake of fucoidan have been detailed together with a discussion on the comparative activities of fractions of fucoidan from different sources. The targets of of fucoidan-derived drugs include (34):

- Osteoarthritis,
- Kidney and liver disease,
- Neglected infectious diseases,
- Hemopoietic stem cell modulation,
- Protection from radiation damage, and
- Treatments for snake envenomation.

Sulfated fucans and galactans are strongly anionic polysaccharides that are found in marine organisms (33). Their structures vary among the various species, but their major features are conserved among phyla. Sulfated fucans are found in marine brown algae and echinoderms. In contrast, sulfated galactans occur in red and green algae, marine angiosperms, tunicates (ascidians), and sea urchins.

Polysaccharides with 3-linked, β-galactose units are highly conserved in some taxonomic groups of marine organisms and show a strong tendency toward 4-sulfation in algae and marine angiosperms, and 2-sulfation in invertebrates.

Marine algae mainly express sulfated polysaccharides with complex, heterogeneous structures, whereas marine invertebrates synthesize sulfated fucans and sulfated galactans with regular repetitive structures.

These polysaccharides are structural components of the extracellular matrix. Sulfated fucans and galactans are involved in sea urchin fertilization, acting as species-specific inducers of the sperm acrosome reaction. Galactan is a polysaccharide consisting of polymerized galactose.

The algal and invertebrate polysaccharides are also potent anticoagulant agents of mammalian blood and represent a potential source of compounds for antithrombotic therapies (33). α-*L*-Fucopyranose and galactose are shown in Figure 1.2.

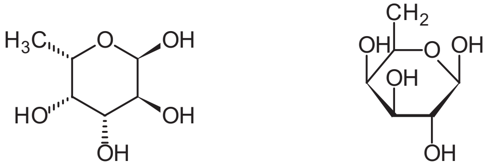


Figure 1.2 α-*L*-Fucopyranose (left), galactose (right).

1.5.2.2 Scaffold Compositions

The issue of marine organisms for bone repair and regeneration has been reviewed (35). Various types of polymer scaffolds have been described (36). Chitosan-alginate and chitosan-alginate with fucoidan, were developed by a freeze-drying method. Each of these materials was characterized as a bone graft substitute. The porosity, water uptake and retention ability of the prepared scaffolds showed a similar behavior.

The pore size of the chitosan-alginate and chitosan-alginate with fucoidan scaffolds were measured from scanning electron microscopy and found to be 62–490 μm and 56–437 μm, respectively.

It has been suggested that hydrogen bonding or ion-ion pair interaction between these components usually increases the uniform dispersion (37).

In-vitro studies revealed a more profound cytocompatibility, increased cell proliferation and enhanced alkaline phosphatase secretion in the chitosan-alginate with fucoidan scaffold in comparison to the chitosan-alginate scaffold (36).

Further, protein adsorption and mineralization were about two times greater in the chitosan-alginate with fucoidan scaffold than for the chitosan-alginate scaffold. Therefore, it has been concluded that chitosan-alginate with fucoidan will be a promising biomaterial for bone tissue regeneration (36).

1.5.3 Chitosan

Chitosan composites for bone tissue engineering have been reviewed (38). Bone contains considerable amounts of minerals and proteins. Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is one of the most stable forms of calcium phosphate and it occurs in bones in an amount of 60–65%, together with other materials such as collagen, chondroitin sulfate, keratin sulfate and lipids.

Chitosan has always played a major role in bone tissue engineering. It is a natural polymer that can be obtained from chitin, which forms a major component of the crustacean exoskeleton.

Considerable attention has been given to chitosan composite materials and their applications in the field of bone tissue engineering due to its minimal foreign body reactions, an intrinsic antibacterial nature, biocompatibility, biodegradability, and the ability to be molded into various geometries and forms such as porous structures, suitable for cell ingrowth and osteoconduction.

Composites of chitosan with hydroxyapatite is very popular because of their biodegradability and biocompatibility. Grafted chitosan polymers with carbon nanotubes have been incorporated into the compositions in order to increase the mechanical strength.

Chitosan and hydroxyapatite are among the best bioactive biomaterials in bone tissue engineering and are renowned for their excellent biocompatibility with the human body environment (39).

1.5.3.1 Nano-Chitins and Nano-Chitosans

The recent technological advances with regard to the isolation and manufacture of nanofibrillar chitin and chitosan have been reviewed (40). Chitin and chitosan are obtained either by mechanical chitin disassembly and fibrillation optionally assisted by sonication, or by electro-spinning. Nanosized materials have better performances.

Chemically modified or nanofibrous chitin and chitosan have been developed, and their effects on wound healing have been evaluated. These compounds are beneficial for the wound healing process (41).

The biomedical applications of chitin include hemostasis and wound healing, regeneration of tissues such as joints and bones, cell culture, antimicrobial agents, and dermal protection.

Other biomedical applications of chitosan are epithelial tissue regeneration, bone and dental tissue regeneration, and also protection against bacteria, fungi and viruses (40, 41). In addition, chitins and chitosans can be used as immunoadjuvants and nonallergenic drug carriers (42).

1.5.4 Collagen

Collagen is the most abundant protein of animal connective tissues (43). It is found in skin, bone or cartilage. Therefore, it is one of the key polymers for biomedical applications, i.e., tissue engineering and drug delivery.

Marine sponges are extremely rich in natural products and are considered a promising biological resource (44). Marine sponge collagen has unique physicochemical properties, but its application is difficult, due to the lack of availability because of inefficient extraction methodologies. The traditional extraction methods are time consuming since they involve several operating steps and large amounts of solvents.

An extraction methodology under mild operating conditions has been proposed, in which water is acidified with carbon dioxide to promote the extraction of collagen or gelatin from different marine sponge species (44).

Actually, there are various reasons to think about marine gelatin as an alternative to the terrestrian gelatin, for example, the risk of transmission of infectious diseases (45). So, an advantage of marine gelatin is that it has no risk associated with bovine spongiform encephalopathy. Practical applications for fish gelatins in the form of gels, films and composite materials have been discussed (45).

1.5.4.1 Tissue Engineering

Porous structures from marine collagen crosslinked with genipin under high-pressure carbon dioxide have been fabricated (46). Collagen from shark skin has been used to prepare pre-scaffolds by freeze-drying. The poor stability and the low mechanical properties require the crosslinking for scaffold uses.

In a dense carbon dioxide atmosphere, the crosslinking of collagen pre-scaffolds has been done for 16 h. Then, the hydrogels have been foamed and the thus obtained scaffolds showed a highly porous structure.

In-vitro cell culture tests using chondrocyte-like cell line showed a good cell adherence and proliferation. Therefore it has been suggested to use these materials in tissue cartilage (46).

1.5.4.2 Collagen Membranes for Drug Delivery

Industrial procedures to extract collagen use bovine and porcine as their main sources. A source of marine origin is one of the alternatives that has been explored through byproducts of fish processing.

In a study, collagen has been extracted from the skin of the shark *Scyliorhinus canicula*. The thus obtained collagen was evaluated as an alternative for dermal membranes, regarding the sustained release of drugs. The method used for the isolation, as well as the method used for membrane preparation have been described in detail (43).

For the preparation of membranes for drug delivery assessment, dexamethasone was added to the collagen solutions and membranes were prepared. The collagen membranes were characterized by the water contact angle, mechanical properties and their stability in phosphate-buffered saline. Collagen membranes showed more stability in phosphate-buffered saline as long as the degree of crosslinking is higher, which also influences their mechanical properties. The degree of crosslinking also affects the hydrophobicity of the membranes. The properties of the collagen membranes can be tailored by degree of crosslinking (43).

1.5.5 Shark Collagen for Cell Culture and Zymography

The use of shark collagen as a matrix for cell culture and as a substrate for zymography has been investigated (47). Zymography is an electrophoretic technique for the detection of hydrolytic enzymes, which is based on the substrate repertoire of the enzyme (48).

Fibroblasts were cultured on a gel matrix of shark type I collagen at 30°C. The collagen gel contracted by 4 *d* of incubation. Individual fibroblasts were visible against the transparent background of the contracted collagen as long, lean star-shaped cells (47). The matrix metalloproteinases from the fibroblasts secreted from the medium digested shark gelatin more easily than pig gelatin.

1.5.6 Glycosaminoglycans

Exopolysaccharides are high molecular weight polymers that are composed of sugar residues and are secreted by a microorganism into the surrounding environment (49).

Glycosaminoglycans are glycopolymers found in animal tissues and are composed of uronic acid and neutral or hexosamine residues (50). They are covalently bound to a core protein and are the major constituent of proteoglycans. Their carbohydrate backbone is unique for each cell type. Glycosaminoglycans are essential for the life of animals since they are involved in their development and organogenesis (51). Two glycosaminoglycan macromolecules are frequently used in various industrial fields, namely hyaluran and heparin (50).

Several exopolysaccharide-producing marine strains have been studied, which led to the discovery and isolation of new macromolecules (52).

An exopolysaccharide (HE800 EPS) is secreted by a deep-sea hydrothermal bacterium and displays an interesting glycosaminoglycan-like feature resembling hyaluronan (53). Hyaluronan is the new term for hyaluronic acid.

Its effectiveness in enhancing in-vivo bone regeneration and in supporting osteoblastic cell metabolism in culture has been demonstrated. in-vitro reconstructed connective tissues containing the HE800 EPS were achieved. This polysaccharide promotes both collagen structuring and extracellular matrix settle by dermal fibroblasts.

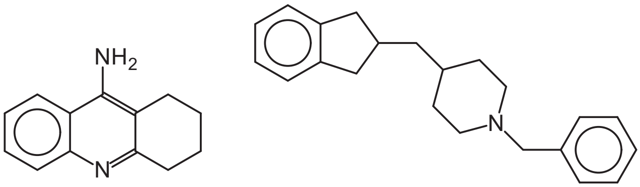
A low-molecular-weight sulfated derivative displays a chemical analogy with heparan sulfate (53). These derivatives can be obtained by means of free radical depolymerization of a native EPS followed by sulfating the resulting depolymerized derivatives (54).

Exopolysaccharides also find applications in environmental biotechnology where they are used for soil and water bioremediation, decontamination and detoxification processes (55, 56).

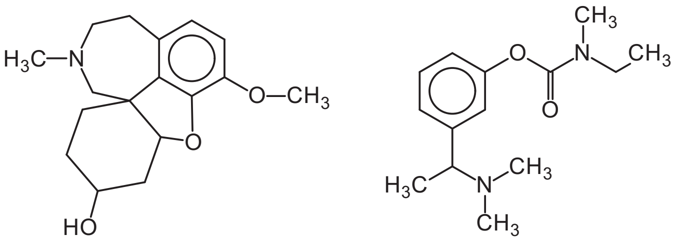
1.5.7 Anticholinesterase

Due to the diversity of biological activities in aquatic ecosystems, marine metabolites are of high interest with respect to drug discovery. Marine metabolites that inhibit the enzyme acetylcholinesterase have been reviewed (57). These compounds are of interest for the treatment of Alzheimer's disease in its early stage.

Seven classes of marine metabolites have been reported that exhibit an anticholinesterase activity. These metabolites were compared to clinically used acetylcholinesterase inhibitors. The results of a docking simulation indicate that several marine metabolites bind to regions of the acetylcholinesterase active site that are not bound by the clinically used drugs (57). These compounds are shown in Figure 1.3.



Tacrine Donepezil



Galanthamine Rivastigmine

Figure 1.3 Clinically used acetylcholinesterase inhibitors.

Marine metabolites vary greatly in structure, mass, and chemical composition. Only seven different classes of marine metabolites are reported to have an anticholinesterase activity: A sesquiterpene acetate (58, 59), a pyrrole derivative (60, 61), a tetrazacyclopentazulene (62), a bromotyrosine derivative (63, 64), plastoquinones (65), farnesylacetones (66), and alkylpyridinium polymers (67).

These metabolites have been found to exhibit a moderate anticholinesterase activity. They generate the inhibition by several different mechanisms (57).

1.5.8 Terpenoids

1.5.8.1 Bromoditerpenes

Bromoditerpenes isolated from the red alga, *Sphaerococcus coronopifolius*, show an antitumor and antimicrobial potential (68).

The structure of the bromoditerpenes was determined by spectroscopic analysis and comparison with the literature data. Five molecules were isolated and characterized that include a brominated diterpene belonging to the rare dactylomelane family, i.e., sphaerodactylomelol and four sphaerane bromoditerpenes.

The antitumor activity was assessed by cytotoxicity and anti-proliferative assays. The antimicrobial activity was evaluated against four pathogenic microorganisms: *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Candida albicans*.

The sphaerodactylomelol diterpene affected the inhibition of cell proliferation and cytotoxicity on HepG-2 cells (68).

1.5.8.2 Sesterpenoids

Natural products play a dominant role in the discovery of lead compounds for the development of drugs to treat human diseases (69). Terpenoids are by far the largest class of natural products. Within this class of compounds, sesterterpenes form a rare group of isoprenoids, which occur in widely differing sources. In particular, marine organisms have provided a large number of sesterterpenoids, possessing a novel carbon skeleton with a wide variety of biological activities.

The link between chronic inflammation and cancer has been explained. The most significant biologically active sesterterpenoids from marine organisms, grouped in a biogenetic sequence, have been detailed. The high potential for some of these products is suggestive in that they could be developed as drugs for the treatment of inflammation and cancer-related inflammation (69).

1.5.8.3 Triterpenoids

Triterpenoids are the most abundant secondary metabolites present in marine sponges (70).

A large number of triterpenoids are known to exhibit cytotoxicity against a variety of tumor cells as well as anticancer efficacy in preclinical animal models.

Therefore, it has been suggested that triterpenoids from marine sponges can be used in the pharmaceutical industry as new chemical classes of anticancer agents (70).

1.5.9 Membrane-Active Peptides

Some important membrane-active peptides, such as antimicrobial peptides, cell-penetrating peptides and peptide toxins from marine organisms, have been detailed (71).

Both antimicrobial peptides and cell-penetrating peptides play a role in membrane perturbation and exhibit an interchangeable role. The structural and functional characteristics of different classes of marine membrane-active peptides have been assessed. Antimicrobial peptides are considered as a potential remedy to antibiotic resistance acquired by several pathogens.

It has been found that peptides from marine organisms show novel post-translational modifications, such as cysteine knots, halogenation and histidino-alanine bridge, that enable these peptides to withstand harsh marine environmental conditions.

Such unusual antimicrobial peptides from marine organisms are expected to increase their life expectancy in living systems. This contributes to their increased bioavailability and stability when they are administered as a drug in in-vivo systems.

Also, marine toxins with membrane-perturbing properties could be assessed for their cytotoxic effect on various pathogens and their cell-penetrating activity across various mammalian cells (71).

1.6 Polymer Production from Marine Sponge

Large polymeric 3-alkylpyridinium salts have been isolated from the marine sponge *Reniera sarai* (72). They are composed of *N*-butyl(3-butylpyridinium) repeating subunits, polymerized head-totail, and exist as a mixture of two main polymers with molecular weights without counterion of about 5,520 and 18,900 *Dalton*.

The monomer analogue of the inhibitor, *N*-butyl-3-butylpyridinium iodide, has been synthesized. This molecule shows a mixed reversible inhibition of acetylcholinesterase. The polymers also act as acetylcholinesterase inhibitors and show an unusual inhibition pattern.

This may be caused by an quick initial reversible binding, followed by a slow binding or irreversible inhibition of the enzyme. This type of kinetics suggests that there are several affinity binding sites on the acetylcholinesterase molecule, where the polymer can bind. The first binding favors binding to other sites, which leads to an apparently irreversibly linked enzyme-inhibitor complex (72).

1.7 Chitin and Chitosan from Marine Origin

Chitin and chitosan can be produced from the shells of crabs and shrimps, and from the bone plates of squids (73).

Chitin is very similar to cellulose, a widespread fiber plant organic polymer, but there is an amine group on the C_2 position instead of a hydroxyl group (74).

The specific properties of these biopolymers, such as the appearance of the polymer, degree of deacetylation, and molecular weight, are of major importance for the fields of application.

Three marine sources of chitin from Tunisia were investigated (75). Structural differences between α-chitin from shrimp (*Penaeus kerathurus*) waste, crab (*Carcinus mediterraneus*) shells, and β-chitin from cuttlefish (*Sepia officinalis*) bones were studied.

It was shown that α-chitins were more crystalline polymorph than β-chitin. Shrimp chitin could be obtained in a good yield of 20% dry weight and no residual protein and salts. Chitosans, with a degree of acetylation lower than 20% and low molecular masses, could be prepared from the wet chitins. These materials were perfectly soluble in acidic medium. The chitin and chitosan characteristics depend on the chitin source (75).

The production of chitosan involves deproteinization, demineralization, and deacetylation (74). The deacetylation of chitin is shown in Figure 1.4.

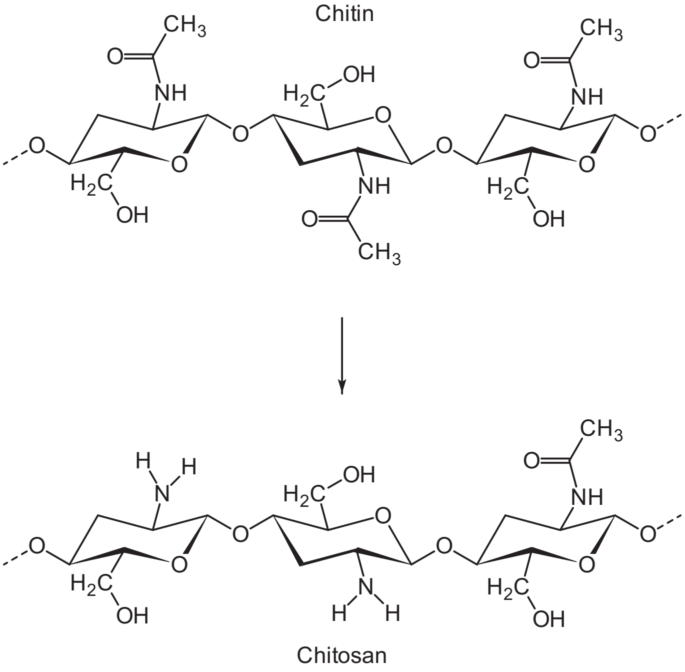


Figure 1.4 Chitosan by *N*-deacetylation of chitin.

For the production of 1 kg of 70% deacetylated chitosan from shrimp shells, 6.3 kg of HCl and 1.8 kg of NaOH are required (76,77).

Chitosan can also be isolated directly from the cell walls of certain fungi. However, commercially available chitosan is usually prepared from chitin. The enzymatic method could provide an alternative to the chemical production method because of environmental aspects (78). Chitosans can be degraded by enzymes and form various small molecular weight fragments. Chitosanase has been used for the preparation of small molecular weight chitosans.

The average molecular weight of chitosans obtained via the enzymatic method has been reported to be far greater than that obtained by chemical methods (78,79).

The characteristics of chitin and chitosan mainly depend on the process of production. The production processes for the production of chitin, chitosan, and related products have been reviewed (73).

1.8 Carbohydrates

Polysaccharides of carbohydrates play an important role in various fields such as pharmaceuticals, food production, cosmeceuticals, and so on. Marine organisms are good resources of nutrients, and they are rich carbohydrate in sulfated polysaccharide (80). The industrial applications of marine carbohydrates have been reviewed (81).

Marine organisms are good sources of polysaccharides and include seaweed (82), microalgae (83), bacteria, fishes, and mollusks. Seaweeds are used in the pharmaceutical industry (80).

The high biodiversity of these compounds and how they can be used in the biotechnological field have been discussed (84,85)

Structural characteristics, rheological properties and absence of pathogenicity of exopolysaccharides from extremophiles make these compounds attractive for uses in the food, pharmaceutical and cosmetics industries (52,86,87).

In particular, sulfated polysaccharides containing seaweed have potential uses in the blood coagulation system, antiviral activity, antioxidant activity, anticancer activity, immunomodulating activity, and antilipidepic activity (80).

In addition, various polysaccharides such as agar and alginates, which are extracted from marine organisms, have applications in food production and cosmetics (80).

1.8.1 Polysaccharides of Marine Origin

Polysaccharides are among the most abundant polymers on the earth (74). These polymers can be easily isolated from various marine resources such as algae, microorganisms and crustacean shells.

Marine biopolymers can be used for biomedical applications, such as in regenerative medicine and drug delivery, as well as for tailored biomaterials.

Seaweeds provide the most abundant sources of polysaccharides: Alginates, agar, agarose, carrageenans, and fucoidans. The original physicochemical and biochemical properties can be improved by chemical modifications (74). Important polysaccharide compounds isolated from the marine environment are listed in Table 1.3.

Polysaccharides play an important role in pharmaceutical science, in particular in the domain of nanotechnology. Modified polysaccharides can change the nanocomposite morphology and properties. Nanotechnology procedures may open up new horizons, and which include the use of polysaccharides found in the exoskeletons of crab, shrimp, prawn, lobster, squid pen, and other marine products (88).

1.8.2 Oligosaccharides

Oligosaccharides are relatively short compounds that are prepared from the longer polysaccharides or could also be found as such in nature. The potential bioactivity of marine polysaccharides is still considered underexploited and these molecules, including the derived oligosaccharides, are an extraordinary source of chemical diversity (89).

Sustainable ways to access marine oligosaccharides are particularly important in view of the huge list of the effects they have on cell events. Enzymatic tools, on which these sustainable ways are based, and modern techniques for purification and the investigation of chemical structures, have been reviewed (89). Some polysaccharidases from the marine environment are listed in Table 1.4.

Table 1.3 Polysaccharides from marine environment (90).

Compound	Source	Biological activity
Polysaccharide AJP	*Apostichopus japonicas*	Antioxidant
Fucoidan	*Ascophyllum nodosum*	Anti-proliferative, antitumor, anticancer, antimestastatic and fibrinolytic
Sulfated polysaccharide	*Sargasam wightii*	Anticoagulant activity
Rosacelose	*Mixylla rosacea*	Anti HIV
Spirulan	*Anthrospira platensis*	Antiviral
Fucan	*Cladosiphono kamuranus*	Inhibit the infection of BHK-21 cells with dengue virus type 2 (DENV-2)
Chitinase	*Streptomyces sp.*	Antifungal against A. niger and Candida albicans
Chitinase	*Craniella australiensis*	Antifungal against A. niger and Candida albicans
Polysaccharide YCP	*Phomaherbarum*	Antitumor
Polysaccharide (PS1-1, PS1-2, PS2-1)	*Penicillus sp.*	Antioxidant
Sulfated polysaccharide	*Sargassum swartzii*	Antioxidant
Sulfated polysaccharide	*Sargassum tenerrimum*	Antioxidant
Sulfated polysaccharide PK-G03	*Gyrodinium impudium*	Anti-influenza virus

Table 1.4 Enzyme class (89).

Class	References
Agarase	(91)
Xylanase	(92)
Chitinase	(93)
Carageenase	(94)
Laminarinase	(95)
Fucanase	(96)
Mannanase	(97)
Hyaluridonase	(98)

1.9 Poly(3-hydroxy butyrate) from Marine Bacteria

Poly(3-hydroxybutyrate) (PHB) is known to have applications as medical implants and drug delivery carriers (99).

PHB-producing bacteria from marine sources have been identified that can be effectively utilized for the synthesis of biopolymers (100). For isolation of PHB°-producing bacteria, the spread plate technique was followed using a mineralic medium. The structure of PHB is shown in Figure 1.5.

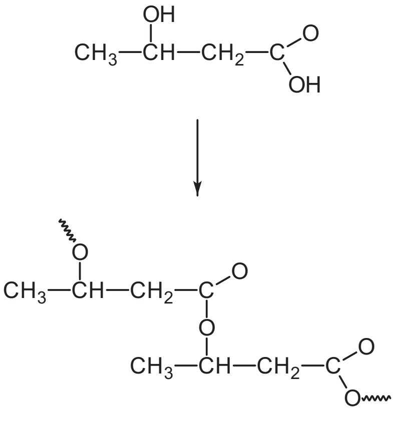


Figure 1.5 Poly(3-hydroxy butyrate).

After incubation, 32 strains could be isolated and identified from the sand dune plants of rhizosphere vegetation of the Chennai coast (100).

In another study, the possibilities of harnessing potential PHB-producing vibrios from marine sediments as a new source of PHB have been investigated (99).

Polyhydroxyalkanoate producing vibrios from marine sediments were assessed using a fluorescent plate assay followed by spectrophotometric analysis of the liquid cultures. Among 828 isolates, *vibrio sp. BTKB33* showed a maximum polyhydroxyalkanoate production of 0.21 $g\,l^{-1}$. The strain was identified as *vibrio azureus*. This strain also produces industrially important enzymes such as amylase, caseinase, lipase, gelatinase, and DNase.

The optimal submerged fermentation conditions for enhanced intracellular accumulation of the polyhydroxyalkanoate production were found to be 35°C, a pH of 7, and a NaCl concentration of 1.5%. Also, other parameters, such as agitation, inoculum properties and incubation time, were disclosed. The results indicated that *vibrio azureus BTKB33* has potential for the industrial production of PHB (99).

1.10 Metal Ion Absorption

The bioadsorption of $\mathrm{Pb}^{2+}\mathrm{Cu}^{2+}$ Cd^{2+}, and Zn^{2+} ions by marine alga *Sargassum filipendula* and by the alginate biopolymer extracted from this alga has been studied (101).

In this way, the importance of this biopolymer in removing different metallic ions by the marine alga *Sargassum filipendula* has been evaluated.

For Pb^{2+} and Cu^{2+} ions, when the alginates are isolated and are acting as bioadsorbents, adsorption capacities greater than those found for the alga themselves were observed, indicating that it is the main component responsible for the removal of metallic ions (101).

1.11 Fish Elastin Polypeptide

Photocrosslinked hydrogels reinforced with a microfibrillated cellulose have been prepared from a methacrylate-functionalized fish elastin polypeptide and microfibrillated cellulose dispersed indimethyl sulfoxide (DMSO) (102). A water soluble elastin peptide from the fish *bulbus arteriosus* was polymerized by *N*,*N*′-dicyclohexylcarbodiimide, a condensation reagent, and then modified with 2-isocyanatoethyl methacrylate in order to get the desired photocrosslinkable fish elastin polypeptide. The synthesis of *N*,*N*′-dicyclohexylcarbodiimide is shown in Figure 1.6.

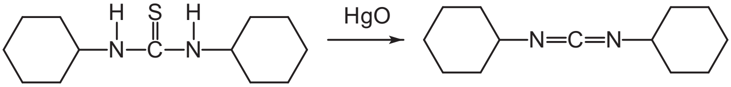


Figure 1.6 Synthesis of *N*,*N*′-dicyclohexylcarbodiimide.

The product was dissolved in DMSO and UV irradiated in the presence of a radical photoinitiator. Also, hydrogels could be obtained by substitution of the DMSO with water.

The addition of microfibrillated cellulose improved the tensile properties. The shape of the stress-strain curve of the composite gel became more similar to the typical shape of an elastic material with an increase of microfibrillated cellulose content.

Also, the elastic modulus of the composite gel increased with an increase of microfibrillated cellulose content. A cell proliferation test showed no toxicity (102).

1.12 Cosmetic Uses

Alteromonas macleodii subsp. fijiensis biovar deepsane is a deep-sea ecotype exopolysaccharide-producing bacteria. It has been isolated from the polychaete annelid *Alvinella pompejana*. The high molecular weight biopolymer HYD657 is produced by this strain. This was the first marine exopolysaccharide that was commercialized for cosmetic use (103).

To elucidate the complete structure of this exopolysaccharide and to synthesize potentially bioactive oligosaccharides it is necessary to depolymerize the structure. Enzymatic methods are useful for this purpose since they can specifically cleave glycosidic bonds and do not require harsh chemical conditions.

The HYD657 exopolysaccharide is structurally complex and no commercially available enzymes are able to effectively degrade it. An endogenous enzymatic depolymerization method of a marine exopolysaccharide has been developed.

The enzymatic activity was detected in the bacterial lysate and was able to decrease the apparent molecular size of the exopolysaccharide. Mainly oligosaccharides were released. The reduced form of the native polysaccharide showed a slightly modified osidic composition (103).

1.13 Protein Hydrolyzate

Marine protein hydrolyzate compounds are conventionally prepared by the enzymatic digestion of different proteases at controlled pH and temperature (104).

The marine biodiversity for the use of a protein hydrolyzate is of interest. This may have nutritional benefits and could play a significant role in functional ingredients for food industries.

The methods of preparation, purification and bioavailability of bioactive peptides from marine-based protein hydrolyzate compounds have been reviewed (104). Fractionated peptides may exhibit biological activities for health issues.

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2

Marine Applications

This chapter reviews the uses of marine polymers as well as conventional polymers in the marine environment, e.g., for coatings, antifouling and corrosion protection.

2.1 Marine Polymer Coatings

2.1.1 Dextrine-Modified Chitosan Marine Polymer Coatings

Partially acetylated chitosan marine polymers from crab or shrimp shells have been used as environmentally benign water-based coatings for aluminum substrates (1). Chitosan is shown in Figure 2.1.

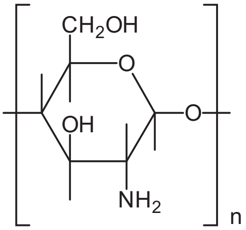


Figure 2.1 Chitosan.

The chitosan was dissolved in a solution of hydrochloric acid, then mixed with a corn starch-derived dextrine that contained cerium nitrate as an oxidizing agent in an aqueous medium.

This blend of polysaccharides was deposited on alumina surfaces using a dip-withdrawing method, and then heated up to 200°C to transform the liquid layer into a solid film.

The transition of the solution into a solid phase provided the changes in the molecular conformation of both chitosan and dextrine. Chitosan was transformed into deacetylated poly(*D*-glucosamine) and dextrine was responsible for the formation of cerium complexed carboxylate fragments.

In addition, the reactions between the amino groups in the deacetylated chitosan and the carboxylate fragments caused the formation of amide linkages. These are effective in grafting the dextrine fragments onto the chitosan.

Such coating films deduced from the proper proportions of chitosan to dextrine offer great film-forming performance, low susceptibility to moisture, and low ionic conductivity, conferring a salt-spray resistance of 720 h (1).

2.1.2 Marine Structure Coated with an Acrylic Water-Swellable Polymer

An attempt has been made to reduce the resistance developed on moving watercraft through water. In addition, simultaneous antifoulant compositions have been developed. It has been found that this can be achieved by the use of water-insoluble hydrophilic acrylate and methacrylate polymers as coatings for the underwater portion of watercraft and underwater structures in boats. Other underwater static structures include wharves, piers, pilings, or bridge substructures.

Antifoulant compositions are useful as marine coatings to render the structure resistant to fouling by marine organisms such as barnacles, algae, slime, acornshells, goose mussels, tubeworms, sea moss, oysters, brozoans, tunicates, and others.

The hydrophilic acrylic resins must be water insoluble. Otherwise they cannot be permanently applied to an underwater surface. The hydrophilic acrylic resin should be capable of absorbing at least 20% of its weight of water and preferably should not absorb more than 120% of water.

It has been found that linear polymers which are usually alcohol soluble are preferable, although crosslinked polymers can also be used. Such coatings effectively reduce the drag or the resistance developed on moving the coated surface through water.

It is believed that the mechanism of friction reduction is twofold: The coating absorbs a substantial percentage of water and the swollen coating exhibits a low contact angle with the water. In addition, the swollen coatings are soft, particularly if a linear polymer is employed. The softness can provide a hydrodynamic damping effect and thus reduces turbulence of the flow.

Hydrophilic monomers are summarized in Table 2.1. Some are shown in Figure 2.2. Typical examples of crosslinking agents are shown in Table 2.2 and in Figure 2.3.

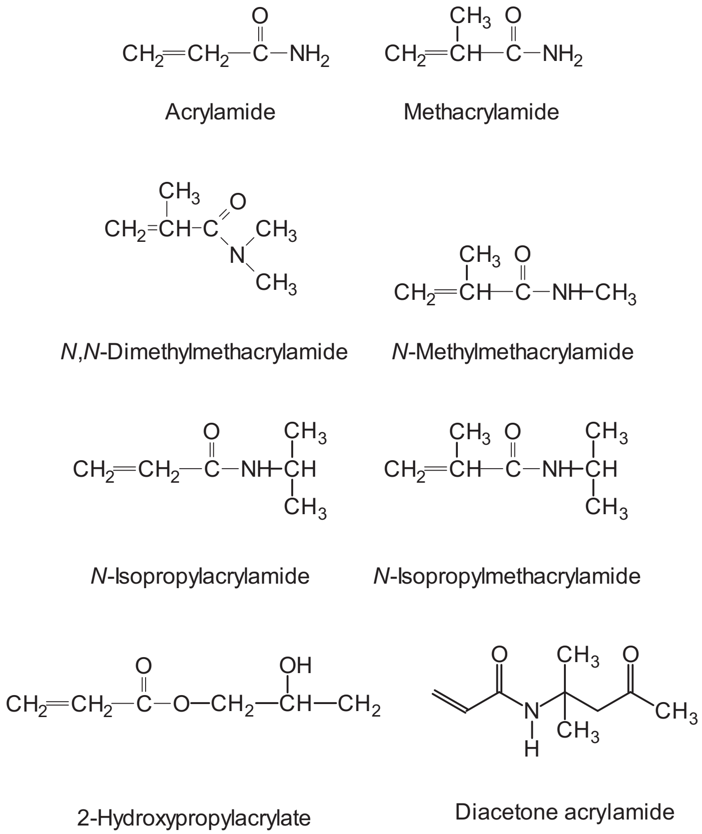
Table 2.1 Hydrophilic monomers (2).

Hydroxy monomers	Amide monomers
2-Hydroxyethyl acrylate	Methacrylamide
2-Hydroxyethyl methacrylate	*N*-Propylacrylamide
Diethylene glycol monoacrylate	*N*-Isopropyl acrylamide
Diethylene glycol monomethacrylate	*N*-Isopropyl methacrylamide
2-Hydroxypropyl acrylate	*N*-Propyl methacrylamide
2-Hydroxypropyl methacrylate	*N*-Butyl acrylamide
3-Hydroxypropyl acrylate	*N*-Methyl acrylamide
3-Hydroxypropyl methacrylate	*N*-Methyl methacrylamide
Dipropylene glycol monomethacrylate	Diacetone acrylamide
Dipropylene glycol monoacrylate	*N*-(2-Hydroxyethyl) acrylamide

Antifoulants can be incorporated into the hydrophilic polymers to prevent fouling by marine organisms. Typical examples of antifouling agents are shown in Table 2.3 and in Figure 2.4.

Polymers from these compounds can be prepared as casting syrups, as aqueous dispersions, by aqueous suspension polymerization, or as solutions in organic solvents, such as ethyl alcohol, methyl alcohol, propyl alcohol, isopropyl alcohol, formamide, dimethyl sulfoxide or other appropriate solvents.

Also, conventional pigments and fillers can be included, such as titanium dioxide, red lead, bone black, red iron oxide, talc, aluminum silicate, fullers earth, pumice, zinc oxide, or calcium carbonate.



Acrylamide

Methacrylamide

N,*N*-Dimethylmethacrylamide

N-Methylmethacrylamide

N-Isopropylacrylamide

N-Isopropylmethacrylamide

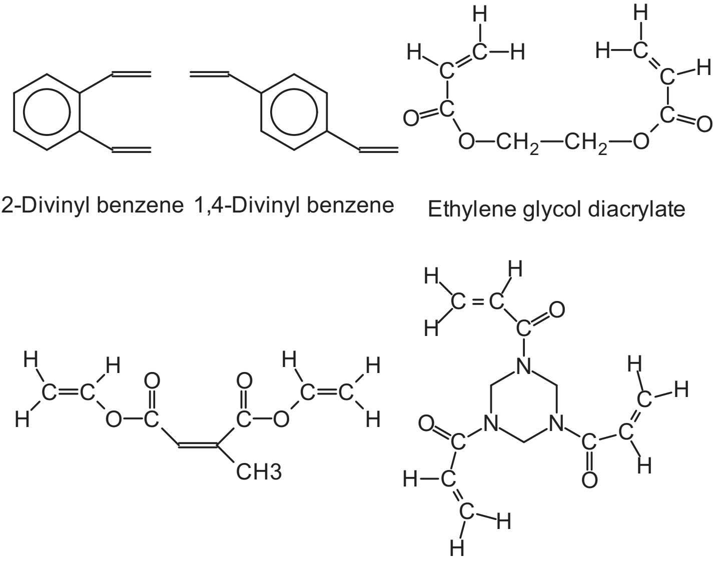
2-Hydroxypropylacrylate

Diacetone acrylamide

Figure 2.2 Acrylic compounds.

Table 2.2 Crosslinking agents (2).

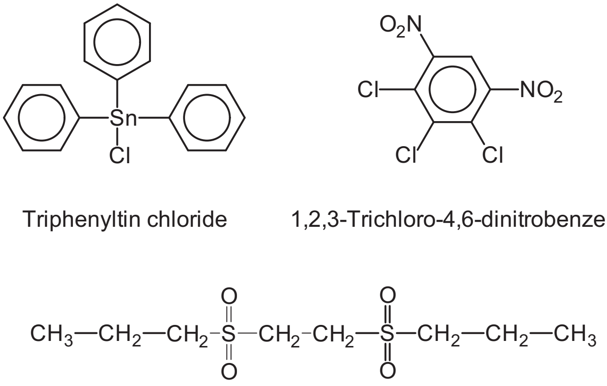
Compound	Compound
Ethylene glycol diacrylate	Ethylene glycol dimethacrylate
1,2-Butylene dimethacrylate	L,3-Butylene dimethacrylate
1,4-Butylene dimethacrylate	Propylene glycol diacrylate
Propylene glycol dimethacrylate	Diethylene glycol dimethacrylate
Dipropylene glycol dimethacrylate	Diethylene glycol diacrylate
Dipropylene glycol diacrylate	Divinyl benzene
Divinyl toluene	Diallyl tartrate
Allyl pyruvate	Allyl maleate
Divinyl tartrate	Triallyl malamine
N,N-Methylene bis-acrylamide	Glycerine trimethacrylate
Diallyl maleate	Divinyl ether
Diallyl monoethylene glycol citrate	Ethylene glycol vinyl allyl citrate
Allyl vinyl maleate	Diallyl itaconate
Ethylene glycol diester of itaconic acid	Divinyl sulfone
Hexahydro-l,3,5- triacryltriazine	Triallyl phosphite
Diallyl ester of benzene phosphonic acid	Polyester of maleic anhydride with triethylene glycol
Triallyl glucose	Pentaallyl sucrose
Sucrose diacrylate	Glucose dimethacrylate
Pentaerythritol tetraacrylate	Sorbitol dimethacrylate
Diallyl aconitate	Divinyl citraconate
Diallyl fumarate	



1,2-Divinyl benzene 1,4-Divinyl benzene Ethylene glycol diacrylate

Dicinyl citraconate Hexahydro-1,3,5-riacryltriazine

Figure 2.3 Crosslinking agents.



Triphenyltin chloride 1,2,3-Trichloro-4,6-dinitrobenzene

Bis-(*n*-propylsulfonyl) ethylene

Figure 2.4 Antifouling agents.

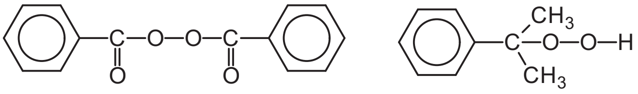
Table 2.3 Antifouling agents (2).

Compound	Compound
Cuprous oxide	Copper powder
Triphenyltin chloride	Triphenyltin bromide
Tri-*p*-cresyltin chloride	Tributyltin chloride
Phenyl diethyltin fluoride	Tri-(*p*-chlorophenyltin) chloride
Dibutyl ethyltin bromide	Tricyclohexyltin chloride
Triethyltin stearate	Triethyltin fluoride
Diphenyl ethyltin chloride	Triphenytin hydroxide
Triphenyltin thiocyanate	Triphenyltin trichloroacetate
Tributyltin acetate	Tributyltin neodecanoate
Tributyltin neopentanoate	Tributyltin oxide
Triphenyltin fluoride	Tripropyltin oleate
Tripropytlin neodecanoate	Tributyltin laurate
Tributyltin octanoate	Tributyltin dimethyl carbomate
Tributyltin chromate	Amyldiethyltin neodecanoate
Bis-(tributyltin) oxalate	Bis-(tributyltin) malonate
Bis-(ttributyltin) adipate	Bis-(tributyltin) carbonate
Triphenyl lead acetate	Trimethyl lead stearate
10,1-Oxybisphenoxazine	Triphenyl lead fluoride
Hexachlorophene	1,2,3-Trichloro-4,6-dinitrobenzene
Phenol mercuric acetate	Dichlorodiphenyl trichloroethane
Bis-(*n*-propylsulfonyl) ethylene	Tetrachloroisophthalonitrile

Two-component catalyst systems for effective curing at ambient conditions include peroxides together with such amine accelerators. Examples are shown in Table 2.4 and in Figure 2.5.

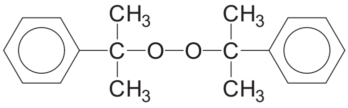
Table 2.4 Curing agents (2).

Peroxide	Accelerator
1-Butyl peroctoate	*N*,*N*-dimethylaminoethyl acetate
Dibenzoyl peroxide	*N*,*N*-dimethyl aniline
Isopropyl percarbonate	*N*,*N*-dimethyl aminoethanol
2,4-Dichlorobenzoyl peroxide	*N*,*N*-dimethyl toluidine
Methyl ethyl ketone peroxide	
Cumene hydroperoxide	
Dicumyl peroxide	



Dibenzoylperoxide

Cumene hydroperoxide



Dicumyl peroxide

Figure 2.5 Peroxides.

For example, a mixture of 89% dibenzoyl peroxide and 11% dimethyl aniline can be employed. In summary, the use of hydrophilic water-insoluble polymers reduces the problem of encapsulation of active antifoulants in impermeable resin systems due to the water-swellable nature of the hydrophilic film (2).

In other acrylic resins and in other types of resin systems, solid organic and organometallic antifoulants do not demonstrate any significant activity unless their concentration in the film exceeds a threshold of about 25% of the resin. In the systems an activity at much lower concentrations is noticed, indicating that the hydrophilic resin does not impermeably encapsulate the toxicant particles.

2.1.3 Styrene Copolymer Compositions

Two-phase styrene copolymer resins composed of a resin matrix and an elastomeric or rubber component are known to provide a number of useful properties (3). Such resins find use in a variety of applications in the building and construction markets, in marine components, outdoor furniture, and others.

Styrene copolymer compositions can be trimmed to an improved weatherability and color retention performance. The fabricated composites should have one interior layer which is thermoplastic and one exterior layer which includes weatherable styrene compositions (3).

2.1.4 Ethylene-Vinyl Acetate Emulsion Copolymers

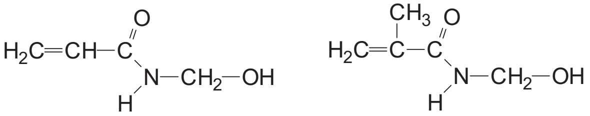
Highly functionalized ethylene-vinyl acetate emulsion copolymers have applications in marine coatings, among others. The preparation of ethylene-vinyl acetate polymers by emulsion polymerization is a well-known technique.

However, the incorporation of more than 5% of a functionalized comonomer is difficult in emulsion polymerization because of several reasons (4):

1. It is important to control the pH of the emulsion because functionalized monomer reactivity and emulsion stability vary with pH.
2. The polymerization of functionalized monomers in the aqueous phase can lead to high viscosity emulsions and grit formation.
3. The differences in the monomer reactivity ratios often result in nonhomogeneous copolymers.
4. The levels of acrylic acid higher than 1.5% inhibit the batch copolymerization reaction of ethylene and vinyl acetate.
5. The incorporation of large amounts of functionalized monomer in the growing polymer creates a polar micellar environment that discourages migration of gaseous ethylene to the micelles.

Various methods have been suggested to incorporate large amounts of functionalized monomers into ethylene-vinyl acetate copolymers. Physical blends of ethylene-vinyl acetate copolymers and polymers of acrylic acid have been suggested (5).

The use of acrylic monomers to overcome the reactivity ratio problem of acrylic acid has been proposed (6). Also, *N*-methylol acrylamide as a functional comonomer has been proposed (7). Such compounds are shown in Figure 2.6.



N-Methylol acrylamide *N*-Methylol methacrylamide

Figure 2.6 Unsaturated methylol amides.

However, this is not sufficient to synthesize ethylene-vinyl acetate aqueous emulsion copolymers that contain high concentrations of functionalized monomers (4).

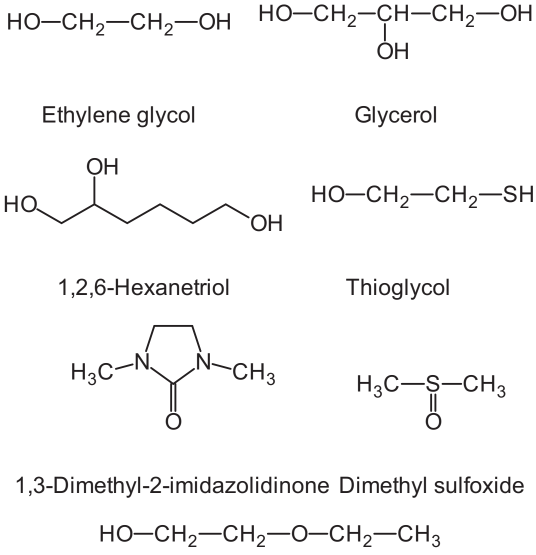
The published methods permit an incorporation of up to 60% functionalized monomers in ethylene-vinyl acetate copolymers without having high viscosity, grit, or sluggish reactivity. The functionalized ethylene-vinyl acetate polymers can also exhibit a pH sensitivity, have good emulsion stability, are water soluble or dispersible, cast clear and form tough films, redisperse readily in water after drying, and are post crosslinkable with suitable functional groups such as epoxides, aziridines, isocyanates, or multivalent ions.

A semi-batch process for preparing functionalized ethylene-vinyl acetate polymers has been developed (4). Minimizing the amount of acrylic acid and hydroxyethyl acrylate in the initial charge allows a substantial uptake of ethylene during the batch polymerization of the initial charge, which then carries over into the slow add portion of the reaction.

The amount of ethylene taken up during the slow add is controlled by the faster conversion rates built up by polymerization of the initial charge, by the rate of oxidizer or reducer addition during the slow add, by the rate of emulsified monomer addition and by the amount of buffer in the monomer emulsion (4).

Of course, the actual formulation of the ethylene-vinyl acetate aqueous emulsion copolymers containing high concentrations of functionalized monomers will vary depending upon the specific end use. Also, other ingredients may be incorporated into the aqueous emulsion copolymers as dictated by the nature of the desired composition. Examples of additives include plasticizers, tackifiers, thickeners, fillers, humectants, surfactants, defoamers, and wetting agents (4).

A humectant is a hygroscopic substance used to introduce moisture and to keep the moisture in compositions. Humectants are shown in Figure 2.7.



Ethylene glycol

Glycerol

1,2,6-Hexanetriol

Thioglycol

1,3-Dimethyl-2-imidazolidinone

Dimethyl sulfoxide

Ethylene glycol monoethyl ether

Figure 2.7 Humectants.

2.1.5 *Epoxy Coatings*

Curable compositions based on glycidyl compounds and amine hardeners are widely used in the coating industry for protective purposes, for instance, to coat metallic and mineral substrates (8).

For marine applications a rapid return to service or a shorter manufacture time is desirable. Therefore, accelerators are added in order to reach an appropriate curing rate.

Examples of accelerators are tertiary amines, acids, hydroxylamines, Mannich bases and phenols. Also, bisphenol A has been found to be suitable since it additionally improves the early water resistance of the cured thermoset due to its acceleration effect when used as accelerator. However, the disadvantages of bisphenol A is the high water susceptibility. This can result in a crystallization of the bisphenol A as a salt. Thus, most of these conventional systems, despite using accelerators, are still insufficient for marine paints (9).

Rapid setting coating systems have been developed. These coating systems are based on epoxy resins. As hardeners, blends of amines and novolac resins are used (8).

The coating compositions can be used as protective coatings for metallic and mineral substrates, in particular for marine, architectural and maintenance uses.

Curable compositions, based on glycidyl compounds and traditional poly(amine)s or poly(amidoamine)s, are widely used for ambient-cure-temperature epoxy systems in adhesives and coating application fields.

However, amines with a high reactivity and a fast cure rate become more and more indispensable for certain applications that require rapid return to service or shorter manufacture time.

For instance, the manufacturing of ships or the relining of water pipelines with rapid return to service are application areas, where requirements of rapid cure, especially at low temperature, are dominant.

Therefore, new hybrid curing agents based on amines and phenolic resins have been developed, which exhibit very fast cure rate in combination with epoxies, even at temperatures close to 0°C (8).

Depending on the amines or blends of amines mixed with the phenolic resin, the compositions show a surprisingly acceptable viscosity range.

In addition, the good chemical resistance of such cured epoxy systems is not altered by the introduction of phenolic resins into the epoxy/amine network. But the chemical resistance of such systems was even improved toward chemicals like acetic acid with concentrations of 5–10% in comparison to neat epoxy/amine systems. Epoxy compounds are summarized in Table 2.5.

Table 2.5 Glycidyl compounds (8,9).

Compounds
Diglycidylether of bisphenol A
Diglycidylether of bisphenol F
Polyglycidylether of polyhydric phenol or cresol novolacs
Mono- or polyglycidylether of mono- or polyhydric cycloaliphatic alcohols
Mono- or polyglycidylether of mono- or polyhydric aliphatic alcohols
Reactive diluents
Cresyl glycidylether
p-tert-Butyl-phenyl glycidylether
n-Dodecyl glycidylether
1,4-Butanediol diglycidylether
1,6-Hexanediol diglycidylether
Trimethyloipropane triglycidylether
Polyoxypropylene diglycidylether
Cyclohexane-dimethanol diglycidylether
Glycidylester of neodecanoic acid

The synthesis of a glycidyl ether is shown in Figure 2.8.

As curing agent, an adduct from an epoxy resin and a mixture of a volatile monoamine and a polyamine are also used. The volatile monoamine is removed from the reaction mixture after the completion of curing (9).

The novolac compounds can be prepared by reacting formaldehyde or paraformaldehyde with phenolic compounds such as phenol, cresol, or dimethylphenol. The synthesis of a novolac from bisphenol A and bisphenol F has been described in detail (8).

The molecular weights of the synthesized novolac resins were determined by gel permeation chromatography. The number average was approximately 1 $k\ Dalton$ and the weight average was approximately 2–3 $k\ Dalton$. The residual monomer content was around 12–15%.

The amines used may be of the aliphatic, cycloaliphatic or arali-

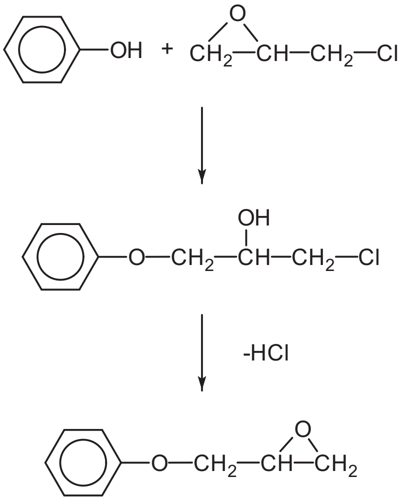


Figure 2.8 Synthesis of phenyl glycidyl ether.

phatic type. Examples are shown in Table 2.6 and in Figures 2.9, 2.10 and 2.11. Some anhydrides are shown in Figure 2.14.

The chemical resistance of the cured resins was tested on coatings applied approximately 500 μm thick on sand-blasted steel panels. Actually, the chemical resistance of the hybrid hardener blends were found to be superior in comparison to those of unmodified amine compositions (8).

2.1.6 Composites from Plant Oils

The synthesis of liquid molding resins derived from plant oils that are capable of curing to high modulus thermosetting polymers and composites have been described. The resins resemble unsaturated polyesters (UPs), vinyl esters, and epoxy resins (10).

Acrylated epoxidized triglyceride resins can be used as surface coatings. The triglycerides can be prepared from the crude plant oils by base extraction to remove free acids, and are heated and filtered to remove the gummy non-triglyceride residues.

The conversion of the plant triglycerides into epoxidized triglycerides can be accomplished by the reaction with hydrogen peroxide. The resulting epoxide can be polymerized in a number of ways.

Table 2.6 Amines for curing (8).

Compound
1,2-Diaminoethane
1,2-Propanediamine
1,3-Propanediamine
1,4-Diaminobutane
Neopentanediamine
Diethylaminopropylamine
2-Methyl-1,5-diaminopentane
1,3-Diaminopentane
2,2,4-Trimethyl-1,6-diaminohexane
2,4,4-Trimethyl-1,6-diaminohexane
1-Amino-3-aminomethyl-3,5,5-trimethylcyclohexane
1,3-Bis(aminomethyl)-cyclohexane
1,2-Bis(aminomethyl)cyclohexane
Hexamethylene diamine
Diaminocyclohexane
Bis(4-aminocyclohexyl)methane
Bis(4-amino-3-methylcyclohexyl)methane
Diethylene triamine
4-Azaheptane-1,7-diamine
1,11-Diamino-3,6,9-trioxundecane
1,8-Diamino-3,6-dioxaoctane
1,5-Diamino-methyl-3-azapentane
1,10-Diamino-4,7-dioxadecane
Bis(3-aminopropyl)amine
1,13-Diamino-4,7-10 trioxamidecane
4-Aminomethyl-1,8-diaminooctane
2-Butyl-2-ethyl-1,5-diaminopentane
N,*N*-Bis-(3-aminopropyl)methylamine
Triethylenetetramine
Tetraethylenepentamine
Pentaethylenehexamine
Bis(4-amino-3-methylcyclohexyl)methane
m-Xylylenediamine
5-(Aminomethyl)bicyclo[[2.2.1]hept-2-yl]methylamine
Dimethyldipropylenetriamine
Dimethylaminopropyl-aminopropylamine
3-Aminomethyl-3,5,5-trimethylcyclohexylamine
Diaminodicyclohexylmethane
2,2-Bis(4-aminocyclohexyl)propane
Bis aminomethyl-dicyclopentadiene

$H_2N—CH_2—CH_2—NH_2$

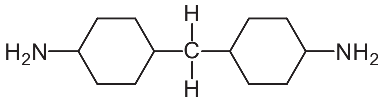
1,2-Diaminoethane

$CH_2—CH_2\text{-}CH_2—CH_2—NH_2$

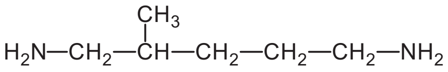
1,4-Diaminobutane

$H_2N—CH_2—CH_2\text{-}CH_2—CH_2\text{-}CH_2—CH_2—NH_2$

Hexamethylene diamine

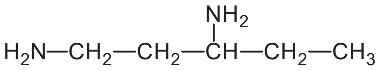


Bis(4-aminocyclohexyl)methane



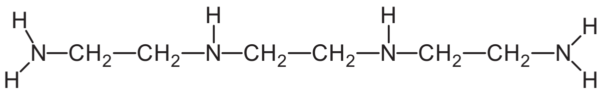
$H_2N—CH_2—\underset{}{\overset{\overset{CH_3}{|}}{C}}H—CH_2—CH_2—CH_2—NH_2$

2-Methyl-1,5-diaminopentane



$H_2N—CH_2—CH_2—\overset{\overset{NH_2}{|}}{C}H—CH_2—CH_3$

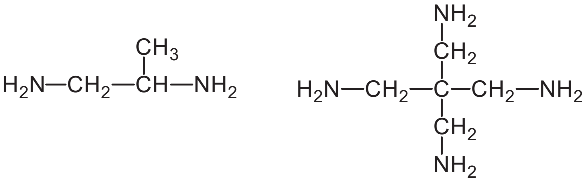
1,3-Diaminopentane



$H_2N—CH_2—CH_2—\overset{\overset{H}{|}}{N}—CH_2—CH_2—\overset{\overset{H}{|}}{N}—CH_2—CH_2—NH_2$

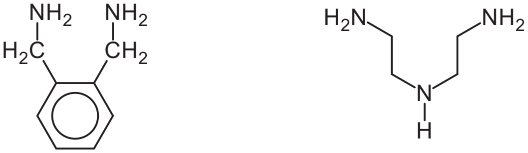
Triethylenetetramine

Figure 2.9 Amines for curing (8).



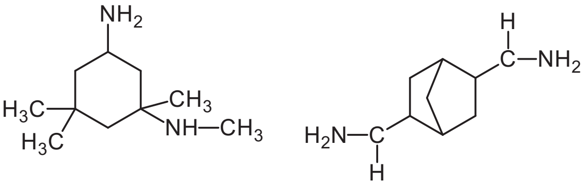
1,2-Propanediamine

Neopentanediamine



m-Xylylenediamine

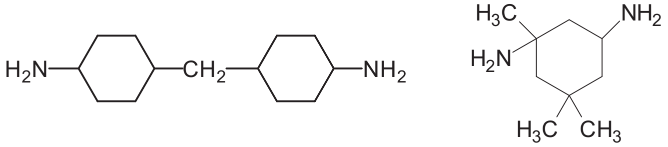
Diethylene triamine



1-Amino-3-aminomethyl-3,5,5-trimethylcyclohexane

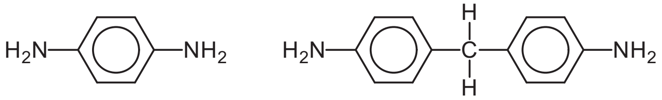
Norbornanediamine

Figure 2.10 Amines for curing (8).



Methylene dicyclohexyl amine

Isophorone diamine



p-Diaminobenzene

Methylene dianiline

Figure 2.11 Amines for curing.

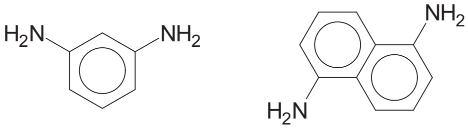
The epoxy groups were acrylated with acrylic acid and polymerized and crosslinked with free radical initiators in the presence of reactive diluents such as styrene, divinyl benzene, or methyl methacrylate. Benzoyl peroxide, methyl ethyl ketone peroxide, hydrogen peroxide, cumene hydroperoxide, or 2,5-dimethyl-2,5-di(2-ethylhexanoyl peroxy) hexane can be used as free radical initiators (11).

The residual epoxy groups can also be used to chain extend the acrylated base resin with reactive difunctional molecules, including diamines, alkyl and aromatic diols, anhydrides, carboxylic acids, alkoxides, hydroxides, and Lewis acids. Examples are summarized in Table 2.7.

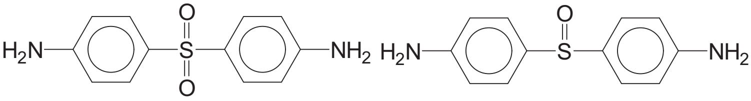
Some alcohols are shown in Figure 2.13 and some anhydrides are shown in Figure 2.14.

Several specific procedures, on how to modify the acrylated epoxidized triglycerides have been shown in detail (10). These substances have been used as varnishes, adhesives, protective coatings, ink vehicles, and high-gloss surface treatments.

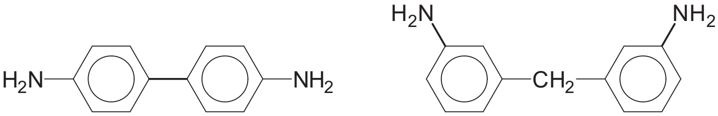
Certain modifications allow epoxidized triglycerides to be polymerized to higher molecular weights and higher crosslinking densities so that these resin types have structural strengths comparable to those of other liquid molding resins. Uses include aerospace,



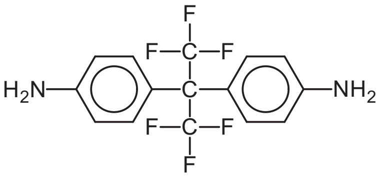
m-Phenyenediamine 1,5-Napthalene diamine



4,4'-Diaminodiphenylsulfone 4,4'-Diaminodiphenylsulfoxide

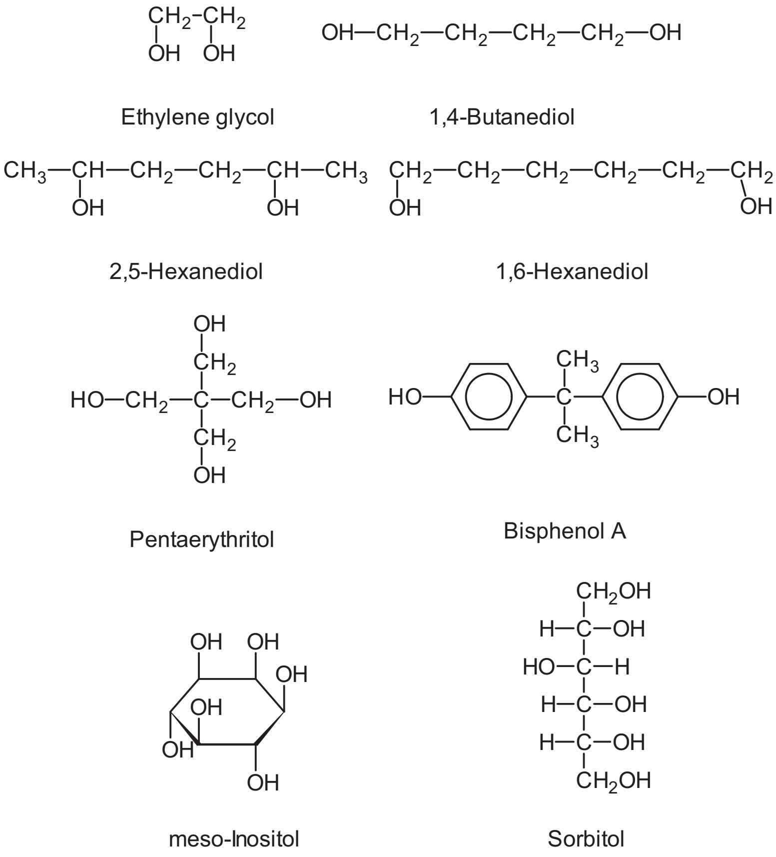


4,4'-Dianilinomethane 3,3'-Diaminodiphenylmethane



2,2-Bis(4-aminophenyl)hexafluoropropane

Figure 2.12 Aromatic diamines (12).



Ethylene glycol

1,4-Butanediol

2,5-Hexanediol

1,6-Hexanediol

Pentaerythritol

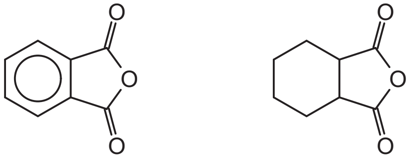
Bisphenol A

meso-Inositol

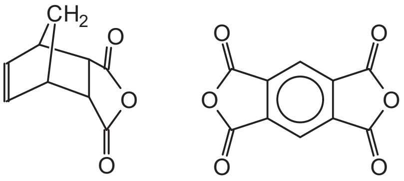
Sorbitol

Figure 2.13 Alcohols.

Succinic anhydride Maleic anhydride



Phthalic anhydride Cyclohexanedicarboxylic anhydride



Nadic anhydride Pyromellithic anhydride

Figure 2.14 Anhydrides.

Table 2.7 Chain extenders (10).

Amines	Alcohols
Methylene dicyclohexyl amine	Ethylene glycol
Triethylene tetraamine	2,5-Hexanediol
p-Diaminobenzene	1,4-Butanediol
Methylene dianiline	Pentaerythritol
Trimethyl hexamethylene diamine	Bisphenol A
Diethanolamine	1,6-Hexanediol
Propanediamine	Hydroquinone
Isophorone diamine	Sorbitol
	Inositol
Anhydrides	**Lewis acids**
Maleic anhydride	Sodium hydroxide
Phthalic anhydride	Potassium hydroxide
Pyromellitic dianhydride	Methoxide
Nadic anhydride	Isopropoxide
Succinic anhydride	Aluminum trichloride
Cyclohexanedicarboxylic anhydride	Boron trifloride

marine offshore, construction, bridge rehabilitation, automotive, or farming equipment (10).

2.1.7 *Inherently Metal Binding Poly(amine) Quinone Polymers*

Inherently metal-binding polymers are poly(amine) quinone polymers. These exhibit an unusual combination of properties that make them well suited as paints, coatings, binders and adhesives.

In particular, poly(amine) quinone polymers exhibit certain unusual characteristics, including (12):

- An extraordinary affinity towards all metals and their alloys, strong enough to displace water from wet, rusty metal surfaces,
- Total water-repellency when cured, either chemically or thermally,
- Excellent anticorrosive properties,
- Sufficient flexibility to allow a coated panel, cured with epoxy resins, to be bent on an 1/8"mandrel,
- Very good impact and abrasion resistance,

- The ability to bind to siliceous materials,
- The ability to be cast as free-standing films,
- A solubility in suitable organic solvents to provide paints and coatings, especially anticorrosive automobile and marine paints and coatings (13),
- The ability to metallize plastics (14),
- The ability to displace machine oils from metal surfaces,
- Good resistance to organic solvents,
- Resistance to short wavelength UV light,
- Nonflammability, and
- The ability to conduct heat.

These materials are generally formed by the reaction of quinones with poly(amine)s. Several methods are known for the preparation of poly(amine) quinone polymers.

One method involves the polymerization of poly(amines) together with quinones. This method works for both aliphatic and aromatic poly(amine)s and different quinones, but certain problems accompany this approach. Because the polymerization requires oxidative conditions to prevail and because the reactant quinone can act as the oxidizing agent, two thirds of the quinone is wasted as the oxidant, rather than being incorporated into the polymer product.

Further, when the oxidizing agent is benzoquinone, the reduction of benzoquinone during the polymerization reaction generates an equivalent quantity of hydroquinone, which can compete with the poly(amine) quinone polymer product for the binding sites on metals, thus decreasing the effectiveness of the poly(amine) quinone polymer coating. Therefore, the hydroquinone must be removed by an extensive washing process of the polymer.

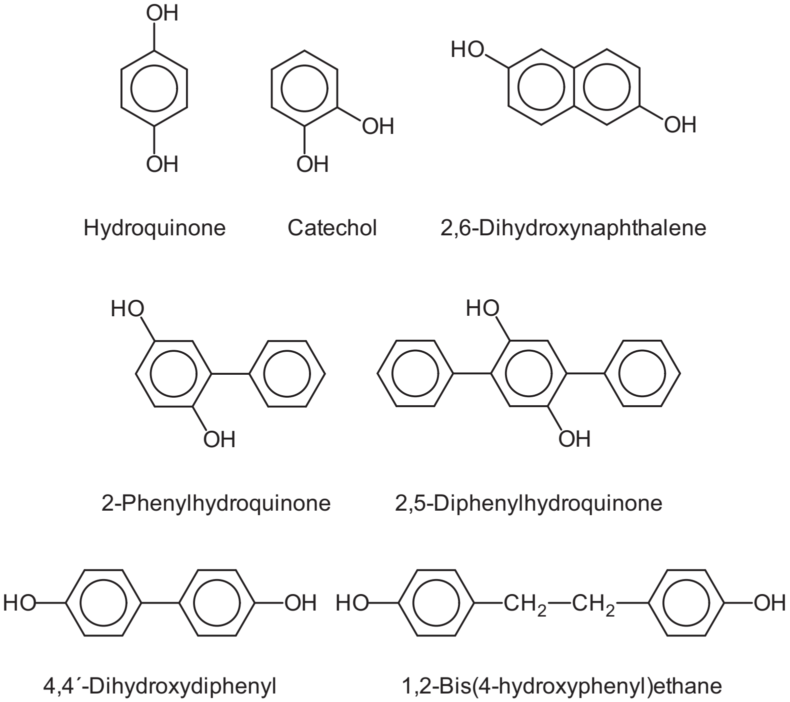
Another method for preparing similar polymers involves the substitution polymerization in *m*-cresol (15).

Here, the starting materials are 2,5-dichloro-benzoquinone, 2,5-dihydroxy-benzoquinone, or 2,5-dimethoxy-benzoquinone and aromatic amines. However, this method is limited to laboratory scale because of economic reasons.

A further method for preparing poly(amine) quinone polymers involves the reaction of stoichiometric ratios of poly(amine)s and quinones with an external oxidizing agent such as calcium hypochlorite (16).

This approach has disadvantages, since the quality of the oxidizing agent is critical. Even a slight amount of moisture reduces the efficiency of the reaction dramatically. In addition, this method cannot be used with aromatic diamines, because these compounds are preferentially oxidized, which results in unacceptable low yields. Also, when the reaction is complete, certain inorganic salts must be removed from the product.

A simple, efficient and economical method for the preparation of metal binding poly(amine) quinone polymers has been developed in which external oxidizing agents can be used (12). Examples of external oxidizing agents are sodium iodate, sodium chromate, or sodium chlorate. Aromatic diamines are summarized in Table 2.8. Chinones are summarized in Table 2.9 and the corresponding hydrochinones are shown in Figure 2.15.



Hydroquinone Catechol 2,6-Dihydroxynaphthalene

2-Phenylhydroquinone 2,5-Diphenylhydroquinone

4,4´-Dihydroxydiphenyl 1,2-Bis(4-hydroxyphenyl)ethane

Figure 2.15 Hydrochinones.

The method of the preparation of amine quinone containing

Table 2.8 Aromatic diamines (12).

Diamine compound
Phenylenediamine
m-Xylenediamine
m-Phenylenediamine
2,5-Dichloro-*p*-phenylenediamine
o-Phenylenediamine
Tetraaminobenzene benzidine
Diaminobenzidine
3,3′-Diaminodiphenyl 4,4′-diaminodiphenylether
3,3′-Diaminodiphenylether
4,4′-Diaminodiphenylsulfoxide
3-3′-Diaminodiphenylsulfoxide
4,4′-Diaminodiphenylsulfone
1,5-Diaminonaphthalene
4,4′-Diaminodiphenylamine
2,6-Diaminonaphthalene
3,3′-Diaminodiphenylamine
3,3′-Diaminobenzophenone
4,4′-Dianilinomethane
3,3′-Diaminodiphenylmethane
2,7-Diaminofluorene
2,4-Diaminophenyl-1,3,5-triazine
4,4′-Diaminophenylethane
tert-Butyltoluenediamine Bis-(*p*-aminophenoxy)diamethylsilane
Bis-(3-aminopropyl)tetramethyldisiloxane
4,4′-Diamino-1,1′-binaphthyl 2,4,6-triaminopyrimidine
1,3-Bis(3-aminophenoxy)benzene
2,2′-Bis(4-aminophenyl)hexafluoropropane
2,2′-Bis(3-amino-4-methylphenyl)hexafluoropropane
3,3′-Dihydroxy-4,4′-diamino-diphenyl
3,3′-Diamino-4,4′-dihydroxydiphenyl
3,3′,4,4′-Tetraaminodiphenyl
2,2′-Bis(trifluoromethyl)benzidine
2,2′Bis[4-(4-aminophenoxy)phenyl]propane
1,4-Bis(4-aminophenoxy)diphenylsulfone
1,3-Bis[2-(4-aminophenyl)propyl]benzene
1,4-Bis[2-(4-aminophenyl)propyl]benzene
2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane
Bis(4,4′-diamino-3,3′-dichlorophenyl)methane
2,2′-Bis[4-(4-amino-2-trifluorophenoxy)phenyl]hexafluoropropane

Table 2.9 Chinones (12).

Chinone compound	Precursor compound
p-Benzoquinone	Hydroquinone
o-Benzoquinone	Catechol
2-Phenylquinone	2-Phenylhydroquinone
2,5-Diphenylquinone	2,5-Diphenylhydroquinone
Diphenoquinone	4,4′-Dihydroxydiphenyl
Stylbenequinone	1,2-bis(4-hydroxyphenyl)ethane
Homostilbenequinone	1,4-Bis(4-hydroxyphenyl)butane
2,6-Naphthoquinone	2,6-dihydroxynaphthalene
1,4,5,8-Naphthodiquinone	1,4,5,8-Tetrahydroxynaphthalene
2-Methylquinone	2-Methylhydroquinone
Tetrahydroxyquinone	hexahydroxybenzene

polymers runs as follows (12):

1. Dissolving an aliphatic polyamine with a quinone or oxidizable quinone precursor,
2. Adding an external oxidizing agent enhancer such as a copper, nickel, or cobalt salt,
3. Adding an external oxidizing agent, i.e., oxygen or air
4. Eventually precipitating the polymer in water, or aqueous alcohols, and,
5. Recovering the polymer product and drying it in a vacuum oven.

Several examples of the preparation have been disclosed, among others, the preparation of poly(*tert*-butyltoluenediaminoquinone), 1,3-bis(3-aminophenoxy)benzene-*p*-benzoquinone, poly-(oxypropylene-diamine-benzoquinone), *o*-benzoquinone-trimethyl-hexamethylene-diamine polymer, poly-(2-phenyl-benzoquinone-1,12-diaminododecane), and *tert*-butyltoluenediamine-benzoquinone.

The polymers have a variety of industrial uses. In preparing paint and coating compositions for metal surfaces, the polymer may be dissolved in a suitable solvent or liquid carrier such as lower alcohols, dimethyl sulfoxide.

A marine or automotive paint, or anticorrosive coating composition can be prepared from the polymers and may also include other additives such as pigments, surfactants, and curing agents. The polymers can be also used, among other applications, as anticorrosive primers, water-displacing coatings, or water-resistant adhesion promoters (12).

2.2 Foams

2.2.1 Polyimide Foams

A fully imidized, solvent-free poly(imide) (PI) foam with excellent mechanical, acoustic, thermal, and flame-resistant properties can be produced as follows (17):

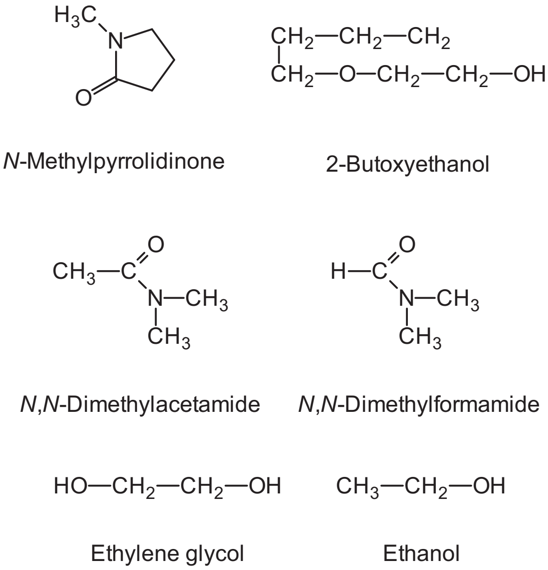
1. A solution with aromatic dianhydrides or derivatives of them together with aromatic diamines and blowing agents, dissolved in polar solvents is provided. This first solution may also contain catalysts, surfactants, and flame retardants.
2. The second solution contains isocyanates.

Examples of aromatic dianhydrides and aromatic diamines are summarized in Table 2.10 and in Figure 2.17. Examples of polar solvents and blowing agents are summarized in Table 2.11 and in Figure 2.16.

Table 2.10 Aromatic dianhydrides and diamines (17).

Aromatic dianhydrides	Aromatic diamines
Pyromellitic dianhydyride	4,4′-Oxydianline
3,3′,4,4′-Benzophenone tetracarboxylic dianhydride	*m*-Phenylenediamine
4,4′-Oxydiphthalic anhydride	*p*-Phenylenediamine
3,3′,4,4′-Biphenyl tetracarboxylic dianhydride	1,3-Bis(3-aminophenoxy)benzene
	4,4′-Diaminobenzophenone
	4,4′Diaminodiphenylsulfone

These solutions are rapidly and thoroughly mixed to produce an admixture, which is allowed to foam, e.g., in an open container or closed mold. Thus a foamed product is formed under ambient conditions. Eventually, this foamed product is cured by high frequency electromagnetic radiation or thermal energy.



N-Methylpyrrolidinone

2-Butoxyethanol

N,*N*-Dimethylacetamide

N,*N*-Dimethylformamide

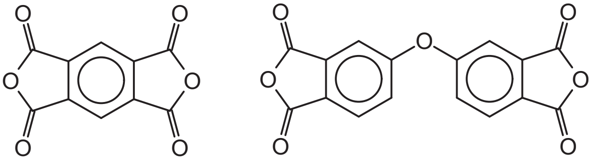
Ethylene glycol

Ethanol

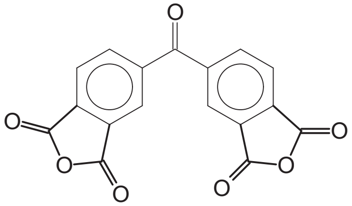
Figure 2.16 Blowing agents.

Table 2.11 Solvents and blowing agents (17).

Polar solvents	Blowing agents
N,*N*-Dimethylformamide	Water
N,*N*-Dimethylacetamide	Methanol
N-Methylpyrrolidinone	Ethanol
	2-Butoxyethanol
	Ethyl glycol butyl ether
	Ethylene glycol



Pyromellithic anhydride 4,4′-Oxydiphthalic anhydride



3,3′,4,4′-Benzophenone tetracarboxylic dianhydride

Figure 2.17 Aromatic dianhydrides.

The PI foams may find widespread applications in the aerospace, marine, automotive and building construction industries. An example for the preparation of a material for a marine vessel fuel tank that is effectively protected has been presented (17).

2.3 Antifouling

2.3.1 Fouling Problems

Fouling organism settlement and growth on submerged man-made structures cause significant material performance issues such as (18, 19):

- Reduction in the efficiency of heat exchangers, cooling towers, desalination equipment, filtration membranes, docks, and others,
- Fouling of ropes, cages, buoys and pontoons used in aquaculture,
- Interference with defective sensor responses, and

- Increased ship hydrodynamic drag.

In the case of ships, fouling can inhibit the performance of the vessel (19). Fouling may substantially increase the fuel consumption and may necessitate extensive and more frequent maintenance, all of which raise the overall costs of operation. Fouling may also reduce the ship speed and maneuverability.

Further, the attachment of regionally specific aquatic organisms on ships that traverse the world can lead to an unwanted invasion and infestation of these organisms to nonindigenous harbors. This can have severe adverse effects on the local aquatic ecosystems.

2.3.2 Mechanism of Fouling

Adult mussels bind to submerged surfaces by secreting a bundle of threads, known as byssus, from glands located in the foot organ (20,21). A total of 5 mussel foot proteins have been identified in the byssus plaque of the genus *Mytilus* (22,23)

The adhesion strategy of mussel veligers of *P. canaliculus* has been observed by scanning electron microscope. It was observed that the larvae can adhere to surfaces by secreting material from the posterior margin of the shell (24). Some 70 μm wide residual adhesive footprints were imaged on a glass surface. On the other hand, when the mussel larvae come into contact with a poly(tetrafluoroethylene) substrate they adhere to each other's shell, rather than settling onto the substrate. Thus, the differences in the settling behavior of the larvae can be attributed to surface properties of the substrate.

Algal species differ widely in their settlement mechanisms. They contain adhesives such as glycoproteins as in the case of *Ulva* (25,26) and *Palmaria* (27). Phenolic compounds are secreted by other brown and red algae which exhibit a non specific adhesion to a range of hydrophilic and hydrophobic substrates (28).

Cyprids are equipped with a pair of antennae with mechanical and chemical receptors. This allows cyprids to probe surfaces by forming temporary attachment points, resulting in an exploratory bipedal walking (29,30)

Young cyprids were more discriminating in settlement than old cyprids and they settled more on glass than on poly(styrene) (31).

During their surface temporary attachment, cyprids leave adhesive cuticular glycoproteins, consisting of aggregated and interconnected nanofibrils (32)

2.3.3 *Fouling Control*

Numerous attempts to minimize the effect of fouling on structures exposed to an aquatic environment have been performed. Coatings have been developed that can impede the attachment or the growth of aquatic organisms on such structures.

The most common approach to control marine fouling on the hulls of ships involves dispersing copper oxide particles in a degradable polymer matrix to produce an antifouling coating (19). The copper oxide serves as a biocide that deters settlement of marine organisms. Since the copper oxide is not chemically bound to the polymer matrix, it is gradually removed from the coating surface.

The slow degradation of the polymer matrix in an aqueous environment allows for replenishment of the coating surface with copper oxide to maintain biocidal activity. After about three years of service, the degree of degradation of the coating is severe enough that the ship must be dry docked and a fresh layer of coating applied. While this approach is effective, it is undesirable due to the release of copper oxide into the marine environment and the need for frequent dry docking.

Another approach involves the application of a nontoxic, nondegradable coating that allows the easy release of marine organisms that have settled on the coating. These coatings, commonly referred to as foul-release coatings, are typically silicone elastomers that possess a low surface energy.

So, the adhesion strength is comparatively low and the organisms can be readily removed by water jetting or moving the ship at high speed through the water. The primary disadvantage of this approach is that frequent cleaning of ship hulls is required and the coatings are easily damaged due to their low modulus (19).

2.3.4 Nontoxic Polymer Surfaces

Marine biofouling is the build up of microbial slimes, plants and animals on any surface immersed in seawater (33). Biofouling adds to the operational costs of shipping throughout the world. The additional drag on marine vessels caused by biofouling significantly increases operating and maintenance costs. For example, biofouling can raise fuel consumption by as much as 30%.

Because many traditional antifouling coatings containing metal-derived biocides have been linked to harmful effects on non-target organisms, environmentally friendly alternatives are being sought.

Recently, the research concerning surfaces that inhibit marine biofouling has focused on designing environmentally friendly materials due to current bans on toxic coatings.

The recent progress in the development and fabrication of surfaces that have antifouling or fouling-release properties has been reviewed (34). A comparison of the performance of materials against algal spore settlement has been reported. The efficacy of surface amphiphilicity and nanoscale phase segregation has been considered in detail (34).

2.3.5 Amphiphilic Polymers

Amphiphilic marine antifouling coatings have been developed by a chemical modification of triblock copolymers (33). Polystyrene-*b*-poly(ethylene-*ran*-butylene)-*b*-polyisoprene ABC triblock copolymers were modified by functionalizing the polyisoprene block with various side chains, such as hydrophilic poly(ethylene glycol) methyl ether, hydrophobic semifluorinated decyl alcohol, and amphiphilic ethoxylated fluoroalkyl side chains (33).

The general methods of making block copolymers have been reviewed (35). The method of sequential anionic polymerization of monomers seems to be useful. Because the types of monomers that undergo living polymerization are relatively limited for anionic methods, with the most favorable being conjugated diolefins and styrenes, partial hydrogenation of anionic block copolymers may be useful to obtain partially hydrogenated polymers that can act as precursors to the polymers of interest.

Polymers containing olefinic unsaturation or both aromatic and olefinic unsaturation may be prepared using anionic initiators or polymerization catalysts. Such polymers may be prepared using bulk, solution or emulsion techniques. The resultant polymers can be used to form a multilayer coating comprising (33):

1. A substrate, e.g., steel,
2. A primer, e.g., epoxy resin,
3. A functional block polymer layer to adhere to the primer for example, a maleated block copolymer,
4. A thick, tough elastomeric layer, for example, a polystyrene-poly(ethylene-ran-butylene)-block-polystyrene, and
5. A thin layer of a side-chain functional surface-active block copolymer.

The polymers show a resistance to the settlement and facilitate the removal of *Ulva* spores and *Navicula* diatoms. In the biofouling assays, a slight increase in spore settlement of the green alga *Ulva* was found on surfaces with greater incorporation of the hydrophobic semifluorinated decyl alcohol side chains, while the poly(ethylene glycol) methyl ether side chains inhibit the settlement. The lowest settlement for *Ulva* spores was observed for coatings with large amounts of poly(ethylene glycol) methyl ether side chains (33).

2.3.6 Fouling Release Properties of Metal Surfaces

The marine antifouling and fouling-release performance of titanium surfaces coated with a bio-inspired polymer was investigated (36). The polymer consisted of methoxy-terminated poly(ethylene glycol) (PEG) conjugated to the adhesive amino acid *L*-3,4-dihydroxyphenylalanine. This amino acid was chosen due its its successful resistance to protein and mammalian cell fouling.

Biofouling assays for the settlement and release of the diatom *Navicula perminuta* and settlement, growth and release of zoospores and sporelings of the green alga *Ulva linza* were done. The results were compared to glass, a poly(dimethylsiloxane) elastomer (Silastic® T2) and uncoated titanium.

The methoxy-terminated PEG modified titanium surfaces exhibited a substantial decrease in attachment of both cells of *Navicula perminuta* and the zoospores of *Ulva linza*.

The superior performance of this polymer over a standard silicone fouling-release coating in diatom assays and approximately equivalent performance in zoospore assays suggests that this bioinspired polymer may be effective in marine antifouling and fouling-release applications (36).

2.3.7 Copper Marine Cladding Composition

The difficulties encountered when fouling occurs on surfaces that are submerged in seawater, and the maintenance involved in keeping them free of marine growth are well known.

Numerous techniques have been proposed to retard or prevent fouling of the surfaces exposed to marine environments. Many approaches suggested have involved the use of toxic materials, many of which are being banned because of environmental considerations. The problem for the boat owner is a substantial one because it is common practice to haul pleasure boats once a year to renew the bottom paint surface.

Compositions that are free of environmental problems have been developed. These have been claimed to have other marked advantages. Once applied as directed they last for years. The formulations result in a hard, non-ablative surface which gives long life to the finish, unlike antifouling paints which are designed to ablate to renew the finish and must therefore be reapplied frequently.

It is known that barnacles do not grow on copper. However, cladding with copper has had distinct disadvantages because it is a highly noble, conductive element and therefore subjects other metals used in the construction of marine structures to galvanic corrosion. This problem can be overcome by a composition, as listed in Table 2.12.

Copper is utilized in a fine powder of a mesh size of 100–325. A bisphenol A epoxy resin composition is added with a molecular weight up to 3,000 *Dalton*. Preferably, the epoxy resins are normally liquid compounds or low molecular weight solid compositions that are soluble in ketones, esters, and ether alcohols or aromatic solvents such as xylene.

The poly(amido amine) and the aliphatic amine curing agent contain reactive hydrogen groups and amine-terminated polyamides, such as those formed through the condensation of unsaturated fatty

Table 2.12 Copper marine cladding composition (37).

Material	Amount/[%]
Copper	45 – 80
Bisphenol A epoxy resin	9 – 15
Polyglycol diepoxide	4 – 8
Glass fibers	0 – 10
Poly(dimethyl siloxane)	0.4 – 1.5
Poly(amido amine)	4 – 11
Amine curing agent	0 – 3

acids with aliphatic polyamines having at least three amino groups per molecule. Examples of useful amine-type curing agents are shown in Table 2.13.

Table 2.13 Amine-type curing agents (37).

Compound
Triethylene tetramine
m-Phenylenediamine
3-Diethylamino-1-propylamine
3-Isopropylamino propylamine
1,3-Diamino propane
1,2-Diamino propane, ethylene diamine
m-Xylylene diamine
3,3′-Iminobispropylamine
Tetraethylene pentamine
Diethylene triamine unsaturated fatty acid condensates

Inert diluents such as talc can be added to provide a greater viscosity. The ingredients without the curing agents are mixed at a temperature of above 20°C. Then, the curing agent is thoroughly admixed at the site.

The compositions with the curing agent are then painted on by a brush or roller. They can also be sprayed on using high pressure equipment. After application, a light sanding or abrasion of the surface of the clad is performed to expose the copper to the environment. Such a clad has a minimum electrical resistivity of 1 $M\Omega cm$.

The electrical resistivity is very important in the prevention of galvanic corrosion of less noble metals used in the fabrication of the clad structure (37).

2.3.8 Preventive Agents against Adhesion of Marine Organisms

An increasing number of marine organisms, especially *serpulidae*, have been observed adhering in semi-closed bays and maricultures (38). In some factories using seawater as cooling water, they adhere to the insides of tubes of heat exchangers, causing pitting or corrosion. In some maricultures, they sometimes do great damage to oyster farms.

Sometimes they adhere in large numbers to culture fish crawl nets, obstructing the flow of seawater and causing dissolved oxygen to become in short supply in the crawls, resulting in the death of bred fishes. When they adhere to the bottom of a ship, they reduce the speed of the ship, causing so much trouble that the ship must be docked for their removal.

Conventionally, for protecting seawater pipes, ships and fishing nets, a chlorine-based agent and an antifouling agent containing an organic tin compound or cuprous oxide have been used. Because such compounds are toxic to marine organisms and are slow to degrade in the environment and also accumulate in organisms, their use has been restricted to preserve the environment.

Higher aliphatic amine compounds are preventive agents against marine adherent organisms. They have potent effects in preventing the adhesion of mussels of *Mytilus edulis galloprovinciais*, and barnacles.

However, when used to prevent the adhesion of *serpulidae*, they must be poured into a seawater system at a high concentration and, when used as antifouling agent, they must be dispersed from antifouling coating at a high concentration. This may cause environmental contamination, which is not preferable from an economical viewpoint. Therefore, the development of an alternative safe antifouling agent is an important matter.

Safe preventive agents for use against adhesion of marine organisms, that can effectively protect seawater-drawing pipes, fishing nets, bottoms of ships and structures in the sea against fouling caused by marine organisms, especially *serpulidae*, have been developed (38). These are based on oligo amines. Exemplary formulations are shown in Table 2.14.

It has been concluded that the antifouling agents can efficiently avoid the damage caused by marine adherent organisms, especially by *serpulidae*, for a long time of more than 12 months (38).

2.3.9 Self-Polishing Paint

Self-polishing marine antifouling paint compositions have been developed. These compositions contain rosin, optional fibers, and polymeric flexibilizers (39).

The rosins are ammonium or metal salts of rosins having a low content of conjugated double bonds. Rosin is a very brittle material. Paints formulated with rosin as the main binder component show a very pronounced tendency to crack. Therefore, flexibilizer components must be added to the compositions.

The non-crystalline flexibilizer components have a glass transition temperature of −45 to +25°C and are preferably selected from copolymers and terpolymers of acrylate, methacrylate, acrylamide, vinyl ethers, and vinyl esters.

The fibers are preferably mineral-glass fibers, wollastonite fibers, montmorillonite fibers, tobermorite fibers, biotite fibers, atapulgite fibers, calcined bauxite fibers, volcanic rock fibers, bauxite fibers, rockwool fibers, and processed mineral fibers from mineral wool.

Metal biocides are copper, copper metal alloys, cuprous oxide and cupric oxide. Examples of pigments are shown in Table 2.15. Such materials are characterized in that they render the final paint coating non-transparent and non-translucent.

The pigments may further be selected from pigment-like ingredients such as fillers. Examples of fillers are calcium carbonate, dolomite, talc, mica, barium sulfate, kaolin, silica, perlite, magnesium oxide, calcite and quartz flour, etc.

These materials are characterized in that they do not render the paint non-translucent and therefore do not contribute significantly to hide any material below the coating of the paint. The paints have improved mechanical properties such as strength and resistance towards weathering (39).

Table 2.14 Adhesion preventive formulations (38).

Formulation 1	Amount/[%]
N-Coconut alkyl-propylenediamine	15
N-Beef tallow alkyl-tripropylenetetraamine	15
Hydrochloric acid	9
Isopropyl alcohol	10
Water	51
Formulation 2	Amount/[%]
N-Beef tallow alkyl-propylenediamine	25
N-Oleyl-tripropylenetetraamine	5
Acetic acid	2.5
Toxanon P-900 (HLB > 12)	25
Diethylene glycol monomethyl ether	42.5
Formulation 3	Amount/[%]
N-Octadecyl-dipropylenetriamine	10
Toxanon P-900 (HLB > 12)	30
Diethylene glycol monomethyl ether	40
Formulation 4	Amount/[%]
Dodecyldimethylamine	25
N-Coconut alkyl-dipropylenetriamine	5
Acetic acid	10
Isopropyl alcohol	10
Water	50
Formulation 5	Amount/[%]
N-Dodecyl-tripropylenetetraamine	25
Lactic acid	23
Toxanon P-900	7
Diethylene glycol monomethyl ether	40
Formulation 6	Amount/[%]
N-Oleyl-propylenediamine	10
Didodecylmethylamine	10
N-Coconut alkyl-dipropylenetriamine	4
Acetic acid	2
Toxanon P-900	18
Diethylene glycol monomethyl ether	56

Table 2.15 Pigments (39).

Compound	Compound
Titanium dioxide	Red iron oxide
Zinc oxide	Carbon black
Graphite	Yellow iron oxide
Red molybdate	Yellow molybdate
Zinc sulfide	Antimony oxide
Sodium aluminium sulfosilicates	Quinacridones
Phthalocyanine blue	Phthalocyanine green
Titaniumdioxide	Black iron oxide
Graphite	Indanthrone blue
Cobalt aluminium oxide	Carbazole dioxazine
Chromium oxide	Isoindoline orange
Bis-acetoaceto tolidiole	Benzimidazolon
Quinaphtalone yellow	Isoindoline yellow
Tetrachloroisoindolinone	Quinophthalone yellow

2.3.10 Copper-Nickel Epoxy Coating

Copper derivates and copper-nickel alloys are known to have marine antifouling properties. Bottom paints for boat hulls have been developed that contain copper complexes in a semi-water permeable paint. The copper complexes leach out of the paint into the surrounding water layer during use. While effective at inhibiting marine biofouling, these paints also are a source of undesirable toxic contamination for surrounding waters (40).

Improved bottom paint coatings have been developed which contain copper/nickel alloy particles suspended in a two-part epoxy resin mixture. These copper/nickel-epoxy mixtures have been found effective for potentially inhibiting marine biofouling, and also serve as corrosion inhibitors and mechanical protective coatings.

The pot life of conventional poly(amine)-based epoxy coatings has been found to be unsatisfactorily short. The premixed resin tends to rapidly increase in viscosity and may cure while still within the mixing container before application is complete. When the resin is dispersed by spraying, the resin may cure within the spray gun, resulting in the loss of expensive equipment.

Another drawback of poly(amine)-based systems is that once the liquid resin has been applied as a film, the curing of the resin film proceeds at a much slower pace. This is due to the decreased thermal mass of the sprayed film and conductive and convective heat losses.

A coating system has been developed based on an epoxy resin prepolymer, a poly(amide) (PA) curing agent. Preferably the PA is a PA adduct, e.g., an aliphatic poly(amino amide).

As antifouling agent, copper/nickel alloy particles are used. Volatile organic solvents are added in order to thin the mixed coating system to facilitate the use in spray applications.

When a PA curing agent is used, the pot life in the mixing container and the workable application time after mixing are substantially increased.

It has been found that the coating system shows an aggregation of the copper/nickel particles at the outer surface, with each particle being encapsulated within the epoxy resin matrix. This enables the coating to develop a copper oxide film, preventing substantial biofouling. The coating so produced may be used as a marine antifouling agent, for use in both seawater and freshwater applications.

Copper and nickel do not leach out of the coating at the levels experienced with water permeable paints. Thus, the contamination of the surrounding waters is minimized. Those organisms that do manage to grow or secure themselves to the coated surface may be easily removed by rubbing without requiring more extreme mechanical scraping (40).

2.3.11 Antifouling Paint

A marine antifouling paint has been developed that contains a film-forming binder which is gradually dissolved in seawater, a marine biocide and a pigment with a solubility in seawater of smaller than 10 ppm (41).

The binder is a resin produced by the reaction of rosin and an aliphatic poly(amine). Rosin is a carboxylic acid functional blend of terpene materials. Its major component is abietic acid. Also, a maleinized rosin and fumarized rosin type can be used.

Maleinized or fumarized rosin has two more carboxylic acid groups per terpene molecule than the original rosin. Rosin materials with an intermediate acid value can be prepared by partially esterifying maleinized or fumarized rosin with an alcohol (41).

Examples of monomers for polyamines are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, *N*-methyl ethylene diamine, *N*-hydroxyethyl ethylene diamine, or a poly(oxyethylene) diamine. The reaction product of the rosin and the poly(amine) results in an amido amine.

The pigment itself may be a marine biocide of the paint. Thus, the pigment is preferably a sparingly soluble pigment, for example, cuprous oxide, cuprous thiocyanate, zinc oxide, zinc chromate, zinc ethylene bis(dithiocarbamate), zinc dimethyl dithiocarbamate or zinc diethyl dithiocarbamate.

The sparingly soluble copper and zinc compounds are generally marine biocides. These pigments produce water soluble metal compounds by the reaction with seawater so that the pigment particles do not survive at the paint surface (41).

2.3.12 Cationic Poly(siloxane)s

Poly(amine) crosslinked poly(siloxane)s may be used in an antifouling composition to prevent the biological fouling in marine environments (19,42).

The polymer backbone may include a poly(siloxane) segment, such as from a dialkylsiloxane or a alkylhydrosiloxane, and a carbon polymer segment, such as acrylate moieties. Also, the polymer backbones may be entirely made of a polysiloxane polymer.

The use of siloxane moieties in the polymer backbone may be desirable to provide a rubbery characteristic to the antifouling material. A halide such as chlorine or bromine may be attached to the copolymer, either directly to the backbone or a pendant group or graft polymer.

The antifouling material may include multiple polymers that can be crosslinked using an ionene. Ionenes are any polymers with ionic groups as part of the main chain.

Such compounds were already synthesized in the 1930s (43). The unique physical and chemical properties of these polymers are the result of a judicious balance between multiple interactions, including hydrophobic, charge transfer and long-range electrostatic interactions (44). As for all polycations, besides the density and charge distribution along the backbone, the nature of the counterion, the molecular weight, flexibility and H-bonding capability of the polymer chain are also critical aspects that may markedly influence the conformation and dynamics of polymer chains.

The ionene bridge may be formed by reacting a poly(amine) with a halide group on the copolymer. The ionene bridge includes quaternary amines which couple adjoining copolymers together.

The ionene crosslinked copolymers may be prepared via the Menschutkin reaction between a dihalide and a ditertiary amine (19). The Menshutkin reaction converts a tertiary amine into a quaternary ammonium salt by the reaction with an alkyl halide (45).

The use of an ionene bridge may be desirable from a number of perspectives (42). The reaction that is used to form the quaternary amines in the inonene bridge may be reversible under shear stress, e.g., ship moving through water or pressure washer.

Because the quaternization reaction is reversible, a coating that uses such an antifouling material may slowly release the outer layer of the coating and thus prevent the fouling on the surface of the coating. Furthermore, quaternary and tertiary amines are toxic to organisms that cause fouling.

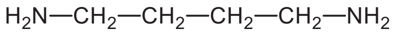
Thus, biocidal qualities of the ionene bridge and tertiary amines formed in the dequaternization reaction can also reduce fouling. Suitable poly(amine)s that may be used for crosslinking halide functionalized polymeric materials are shown in Table 2.16 and in Figure 2.18.

A variety of fouling inhibiting moieties may be attached directly to the copolymer backbone, to a polymer grafted to the copolymer backbone, or to the ionene bridge.

Fouling inhibiting moieties may include biocidal groups, fouling release groups, or texturizing groups. Examples of biocide groups are triclosan groups and pyridinium groups, as shown in Figure 2.19.

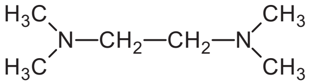
Table 2.16 Poly(amine)s for crosslinking (19).

Compound	Compound
1,4-Diaminobutane	Bis(dimethylamino)-dimethylsilane
1,3-Dipyridyl propane	1,3-Bis(*N*,*N*-dimethylamino)-butane
1,4-Bis(*N*,*N*-dimethyl-aminomethyl)-benzene	1,3-Di-(aminoethyl)-benzene
1,4-Bis(*N*,*N*-dimethyl-amino)-cyclohexane	1,4-Bis(*N*,*N*-dimethylaminomethyl)-cyclohexane
1,6-Dipyridyl hexane	1,4-Dipyridyl cyclohexane
N,*N*,*N*′,*N*′-Tetramethyl-propylenediamine	*N*,*N*,*N*′,*N*′-Tetramethyl-1,4-butanediamine
N,*N*,*N*′*N*′-Tetramethyl-ethylenediamine	*N*,*N*,*N*′*N*′-Tetramethyl-1,6-hexanediamine
N,*N*,*N*′*N*′-Tetramethyl-benzidine	*N*,*N*,*N*′,*N*′-Tetraethylethylenediamine
2,2′-Dipyridyl	4,4′-Dipyridyl

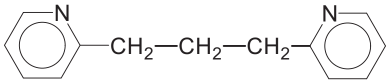


$H_2N—CH_2—CH_2—CH_2—CH_2—NH_2$

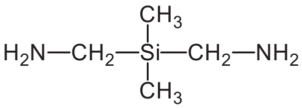
1,4-Diaminobutane



N,N,N′,N′-Tetramethyl-ethylenediamine

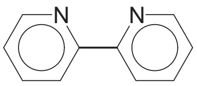


1,3-Dipyridyl propane

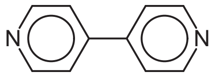


$H_2N—CH_2—Si(CH_3)_2—CH_2—NH_2$

Bis(dimethylamino)-dimethylsilane



2,2′-Dipyridyl



4,4′-Dipyridyl

Figure 2.18 Blowing agents.

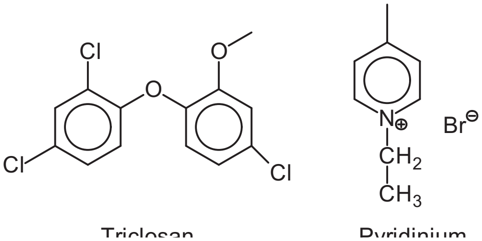


Figure 2.19 Biocide groups.

2.4 Electrochemical Impedance and Noise Data for Polymer Coated Steel

The degradation of various polymer coating systems on steel exposed to natural and artificial seawater has been monitored using electrochemical impedance spectroscopy and electrochemical noise analysis (46).

A new approach has been developed to obtain electrochemical impedance and noise data from external remote test sites via a modem. A multiplexer was used at the marine test sites to collect the data for the different coating systems subjected to the two electrochemical tests. The impedance data were collected once a week, while the noise data were collected twice a week.

The aim of the research was to determine the impact of microorganisms on the degradation of the protective properties of polymer coatings on steel during exposure to natural seawater (46).

2.5 Seawater Immersion Ageing of Glass-Fiber Reinforced Polymer Laminates

Glass-fiber reinforced polymer materials along with castings of their matrix resins have been aged in seawater in laboratory studies (47).

The water uptake behavior has been compared for polyester, phenolic, and vinylester glass-fiber reinforced polymers. The changes in their mechanical properties were assessed.

The phenolic glass-fiber reinforced polymer showed an anomalous uptake behavior. The water uptake by the polyester and vinylester laminates appeared to be affected initially by a suppression from fiber barrier effects and then later by an enhancement from interface effects. The flexural strengths declined by some 15–25% in the course of the experiments (47).

2.6 Post-Fire Mechanical Properties of Marine Polymer Composites

Glass-reinforced polymer composites are used increasingly in the construction of marine craft such as lifeboats, racing yachts, coastal patrol boats and naval mine-hunting ships. These composites are also used in marine structures such as radomes, sonar domes and submarine casings and are candidate materials for propellers, propeller shafts and masts.

The most common polymer used in marine composites are UP resins because of their low cost and good durability in the marine environment. Also, vinyl ester resins are sometimes used for marine composites because of their higher heat-distortion temperature, better water resistance and slightly higher mechanical properties.

A basic problem of using such composites in marine craft is that the polymer matrix can ignite within a short time when exposed to a fire. The poor fire resistance of the composites has been a contributing factor to their limited use in some marine craft such as large passenger ships and naval submarines. In particular, when composites are damaged by fire, their mechanical properties decline.

The changes of the tensile and flexure properties of marine-grade glass-reinforced polyester, vinyl ester and resole phenolic composites after exposure to radiant heat have been investigated (48).

The properties were determined at room temperature after the composites had been exposed to heat fluxes of 25–100 $kW\,m^{-2}$ for 325 s or to a heat flux of 50 $kW\,m^{-2}$ for increasing times up to 1800 s. The stiffness and failure load of all three composites decreased rapidly with increasing heat flux or time, due mainly to the thermal degradation of the resin matrix.

The post-fire tensile and flexural properties of the resole phenolic composite were similar to the properties of the other composites, despite its superior fire resistance.

Models have been presented for determining the post-fire mechanical properties of fire-damaged composites.

The models treat the layers as one layer being the char and the other layer being the uncharred composite. The mechanical properties are then treated as in a bilayer material. These models can be used to estimate the reductions in failure load of composite ship materials caused by fire (48).

2.7 Corrosion

2.7.1 Iron-Containing Substrata

The detection of microbiologically influenced corrosion on iron-containing substrata exposed in marine environments cannot be based solely on spatial relationships between large accumulations of bacterial cells and iron corrosion products (49).

The relationship between marine bacteria and localized corrosion on coated mild steel was elucidated. The distribution of bacteria was strongly influenced by the presence of iron corrosion products independent of coating combinations. In the presence of cathodic protection, coating defects were filled with calcareous deposits and few bacterial cells.

The results indicated that bacteria are preferentially attracted to iron corrosion products in coating defects, and the attraction is more influential than the topography in determining the spatial distribution of bacterial cells (49).

2.7.2 Polymethylenepolyamine dipropionamides

Polymethylenepolyamine dipropionamides are environmentally safe inhibitors of the carbon corrosion of iron (50).

A good inhibition of the carbonic corrosion of iron may be obtained with non-ecotoxic compounds of water soluble polymethylenepolyaminodipropionamide type having a very low marine ecotoxicity of 50–100 *ppm* on *Skeletonema costatum*.

The polymethylenepolyamino dipropionamide compounds can be readily obtained by the condensation of acrylamide with polymethylene-polyamine bases. Examples are diethylene triamine, triethylenetetraamine, and bis(propylamino)ethylenediamine (50).

2.7.3 Thioheterocyclic Rust and Corrosion-Inhibiting Agents

The primary function of lubricants is to decrease friction. Frequently, however, lubricating oils need additional properties, such as oxidation and corrosion resistance, to be used effectively (51). For example, lubricants used in the crankcases of large diesel engines, such as marine and railway diesel engines, are often subjected to operating conditions requiring special considerations. In particular, poor grade fuels, such as marine residual fuel, can be mixed with regular diesel fuel. However, engine performance problems, such as increased corrosion and poor oxidative stability, often arise.

Various additives have been used to improve the rust and corrosion inhibition of lubricants. For example, calcium sulfurized alkyl phenolates have been effective oxidation and corrosion inhibitors.

These compounds are typically made by processes including expensive recovery procedures and hazardous byproducts which are difficult to dispose of in an environmentally sound way. Alternatively, calcium sulfurized phenolates, made by a process using lime as the calcium source to avoid such processing problems, fail to provide a high level of rust and corrosion inhibition.

Lubricants used in the crankcase of a slow-speed crosshead marine engine must protect the engine parts from corrosion and especially rust. Rust is produced when ferrous metal engine components come in contact with water, typically through two avenues.

The first contact involves the internal combustion process where water is produced. The second contact comes from outside sources, that is, freshwater or saline water. In both cases, however, the net effect is identical: Rust and corrosion occur that reduce the engine efficiency and its lifetime.

A lubricant additive which imparts enhanced rust and corrosion resistance to engine lubricating oils has been provided (51). This additive contains basically polythiocyclic imide and a poly(ethylene-*co*-propylene-*g*-succinic anhydride).

2.7.4 Epoxy Compounds

A corrosion protection coating can be formed of a poly(amine) and an epoxy resin that can be applied either to virgin metal or to preexisting metallic items immersed below sea level, and a rigid cladding such as fiberglass reinforced pipe encapsulating the coating (52). The coating and cladding application can be conducted underwater by preceding the applications with an abrasive blasting of the surface to be protected.

For example, the coating should be a solvent-free epoxy PA adhesive. The formulations provide characteristics that displace water and create a strong molecular attraction or adhesive strength to the substrate. The cladding enables a uniform circumferential compression of the coating, squeezing out excess water and trapped air (52).

When the epoxy resin is mixed with the poly(amine) composition, a very high degree of molecular attraction to the steel substrate has been found to develop due to the exothermic polymerization. The phenomenon is sometimes termed as good wetting (53).

The surface of steel contains multiple layers of water molecules and the composition provides molecular attraction by diffusing through the water layers by emulsification, or disperses the water through the adhesive so that contact to the steel is accomplished. An essential step is that an adequate degree of adhesion is developed during the curing process (53).

Emulsification is attributed to the hydrophobic fatty acid portion of the poly(amine) molecules, which in combination with the hydrophilic portion of the molecule acts as the emulsifier. This contrasts with conventional poly(amine) products that are used for quick repair procedures that fail to develop an extraordinary molecular attraction.

2.7.5 Poly(aniline) Graft Copolymers

Water soluble and self-doped poly(aniline) graft copolymers can be prepared by grafting aniline onto a poly(styrenesulfonic acid-*co*-aminostyrene) backbone (54). Such a graft copolymer is useful for advanced applications, such as electrode manufacture, static electricity dissipation, metal anti-corrosion, electrochromic materials, sensors, functional film and marine-fouling prevention.

For example, *tert*-butoxycarbonyl-aminostyrene can be synthesized by the reaction of aminostyrene and di-*tert*-butyl dicarbonate. Then this is copolymerized with sodium styrenesulfonate.

Poly(styrenesulfonic acid-*co*-aminostyrene) can be prepared by the elimination of the *tert*-butoxy carbonyl groups and aniline can be graft copolymerized onto the poly(styrenesulfonic acid-*co*-aminostyrene). This results in water soluble and self-doped poly(styrene-*g*-aniline) polymers (54).

The synthesis has been detailed in several examples. Also, an electrochemical synthesis method has been described (54).

2.7.6 Imidazolines

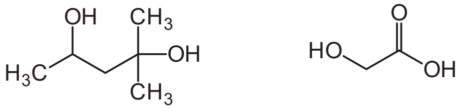
It has been reported that the corrosion rate of steel in the presence of H_2S is greatly decreased by the addition of imidazoline compounds or quaternary ammonium salts into the drilling fluids (55). Moreover, imidazoline can improve the rheological properties of a drilling mud.

Quaternized imidazolines with an amido unit can be used for corrosion-inhibiting formulations for oil and gas field applications. For aqueous systems that contain sulfides, a mixture has been described that consists of an aqueous solution of an alcohol such as diethylene glycol monobutyl ether, butyl cellosolve, additional orthophosphoric acid, a tall oil fatty acid, a substituted imidazoline, an ethoxylated fatty diamine, and a molybdate compound (56).

A modified variant uses amine products that contain only tertiary amino groups (57). These amines have favorable ecotoxicity levels in marine or freshwater environments. The ecotoxicity decreases with increasing substitutions on the nitrogen atoms present. It seems that tertiary groups are less toxic than secondary groups, which are in turn less toxic than primary groups.

Also, an ampholytic, substituted imidazoline has been described for inhibiting corrosion (58). This type of corrosion inhibitor is intended for a continuous treatment.

An imidazoline derivate can be prepared from a long-chain fatty acid and a poly(amine). This is dissolved in an aromatic solvent and dispersed with glycolic acid and hexylene glycol, c.f., Figure 2.20 (59).



Hexylene glycol Glycolic acid

Figure 2.20 Dispersants.

Poly(ester)s may be used instead of a fatty acid modifier for imidazoline (60). In this way, a corrosion inhibitor that forms persistent films can be produced by reacting a polybasic acid with a polyalcohol to form a partial ester. Then this partial ester is reacted with the imidazoline to give an ester salt.

2.8 Marine Ropes

A split poly(ethylene) (PE) stretched material can be used for marine ropes (61). It is known to mold an ultra-high molecular weight poly(ethylene) (UHMWPE) into a sheet or a tape and then stretch the sheet or tape to obtain a high-strength and high-modulus PE material. For example, an UHMWPE and a wax can be melt mixed, the resulting mixture is extruded, cooled, and then stretched. Also, compression molding processes have been used (62,63).

The UHMWPE sheets or tapes obtained by these processes are lightweight and have a high strength and excellent water resistance. Therefore, they are intertwisted to be used as marine ropes.

However, not only are these ropes high strength, but also high modulus, and therefore, lack flexibility. Moreover, the stretched materials, when laminated or used for a composite material, are unable to produce a sufficient adhesion strength because their area of contact with a resin or other material is limited (61).

These disadvantages can be overcome by providing a split PE stretched material having a tensile strength of at least $0.7\ GPa$ when twisted in the range of 50–500 times per meter (61).

This material can be produced by subjecting a PE having an intrinsic viscosity of 5–50 $dl\,g^{-1}$ at 135°C in decalin to stretching and then subjecting the stretched PE to splitting.

In the course of the production of the split PE stretched material, no solvent is used and stretching can be carried out in a solid state wherein melting is unnecessary, which results in excellent economy, enables stretching of high draw ratio and makes it possible to obtain a split polyethylene stretched material of high strength (61).

2.9 Marine Diesel Engine Lubricants

2.9.1 Dispersant Additive Composition

A dispersant additive composition for cylinder lubricant for marine diesel engines has been developed based on a borated dispersant and a high molecular weight poly(butene) (64).

Borated ashless hydrocarbyl succinimide dispersants can be prepared by reacting a hydrocarbyl succinic acid or anhydride with an amine. The hydrocarbyl group can be derived from a polymer such as a poly(isobutene).

On the isobutene moieties, there are 1 to 2 succinic groups attached. Preferred amines for forming the succinimide are ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, tetrapropylene pentamine, or pentaethylene hexamine.

This dispersant composition provides a lubricant with improved viscosity, wear, oxidation and deposit performance. It is possible to increase the kinematic viscosity of the engines (64).

2.9.2 Overbased Alkyphenates

Alkaline earth metals overbased sulfurized alkylphenate compositions, sometimes referred to as *overbased phenates*, are useful lubricating oil additives, which impart detergency and dispersancy properties to the lubricating oil composition, as well as providing for an alkalinity reserve in the oil. Alkalinity reserve is necessary in order to neutralize acids generated during engine operation. Without this alkalinity reserve, the acids so generated would result in harmful engine corrosion.

The preparation of lubricating oil additives in which a nitrogen-containing compound, such as a polyamine, involves the reaction of a metallic compound, a suspending agent, and a chalcogen compound such as carbon dioxide (65).

A problem has been encountered in the preparation of high overbased phenates (66): The problem occurs in the overbasing step, in which the carbon dioxide is added to the phenate to increase the Total Base Number (TBN) in the final product.

In general, highly overbased phenates are very sensitive to the addition of too much carbon dioxide. This is termed as overcarbonation. The result of adding too much carbon dioxide is the production of a product with varying quality.

Sulfurized alkylphenates could be formulated and prepared, which are substantially insensitive to overcarbonation (66). Such compositions are obtained by modifying the overbasing step by the inclusion of a poly(amine) concurrently with the carbon dioxide.

The combined neutralization and sulfurization reaction is conducted at temperatures of 120–200°C, depending on the particular metal and the promoter used. As promoters, short-chain organic acids, such as formic acid, acetic acid, or propionic acid, or alkylphenols can be used.

The reaction is also typically conducted in a compatible liquid diluent, preferably a low viscosity mineral or synthetic oil. The reaction should be conducted for a sufficient length of time to ensure the complete reaction of the sulfur. This is especially important where high TBN products are desired (66).

2.9.3 Overbased Metal Salts

Marine diesel engines are typically two-stroke or four-stroke compression-ignition engines commonly used in ships for main propulsion or auxiliary power generation applications, or in stationary land-based power generation applications (67).

Marine diesel engines are commonly designed to run on a variety of diesel fuels from good quality light distillate fuel with low sulfur and asphaltene content to poorer quality intermediate or heavy fuels like *Bunker C* or residual fuel oil with generally higher sulfur and asphaltene content.

Four-stroke engine designs have crankcase oil systems which can become contaminated with diesel fuel either through blowby or fuel leakage directly into the lubricating oil.

Certain overbased metal salts are useful as additives for lubricants for marine diesel engines (67). Overbased materials are single phase, homogeneous, usually Newtonian systems characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal.

As basic organic materials for preparing the overbased salts, propylene oligomer substituted phenols, poly(butene)-substituted phenols, and others can be used. These are esterified with a dicarboxylic acid, e.g., glyoxylic acid. Likewise, didecyl citrate can be used. Eventually, these organic acids or poly(acid)s are reacted with metal hydroxides in excess to get the overbased materials (67). The overbased metal salt has a stoichiometric metal ratio of at least 1.3.

Overbased materials provide improved detergency, antioxidant properties, or asphaltene suspension, in comparison to the same compositions, when the overbased material is absent (67).

2.9.4 Alkylsalicylate Lubricant Compositions

An improved poly(butene)-free lubricant composition for marine diesel engines has been developed (68). The composition contains a major amount of an oil of lubricating viscosity, a dispersant, overbased metal compounds, and antioxidants. As dispersants, a borated poly(isobutenyl) succinic anhydride poly(amine) is used. Tetraethylene pentamine serves as poly(amine).

Another class of dispersants are Mannich base condensation products. These can be prepared by condensing an alkyl-substituted hydroxy benzene with formaldehyde or paraformaldehyde, and poly(alkylene amine).

The overbased metal compounds should have a TBN of at least 300. The TBN is measured by ASTM D2896 (69). Preferrably, a calcium alkylsalicylate is used. Salicylic acids are typically prepared by the carboxylation of phenoxides and by the Kolbe-Schmitt process (70) of phenoxides. So, they will generally be obtained in an admixture with uncarboxylated phenol (68).

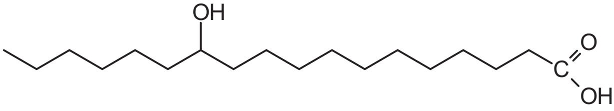
Antioxidants reduce the tendency of mineral oils to deteriorate in service. Evidence of such deterioration is, for example, the production of sludge and varnish-like deposits on metal surfaces, and an increase in viscosity. Suitable oxidation inhibitors include sulfurized alkyl phenols and alkali or alkaline earth metal salts, e.g., diphenylamines, phenyl-naphthylamines, and phosphosulfurized hydrocarbons (68).

2.9.5 Biodegradable Lubricants

Lubricant compositions for marine applications have been developed which are based on a biodegradable base oil, such as a polyol ester or poly(alkylene) glycol, a calcium sulfonate-based thickener and a naturally occurring phospholipid as an antiwear additive, such as lecithin for environmentally sensitive applications (71). An example of such a composition is presented in Table 2.17. 12-Hydroxystearic acid is shown in Figure 2.21.

Table 2.17 Biodegradable lubricant composition (71).

Ingredient	Function	Amount/[%]
Overbased Calcium Sulfonate	Thickener	11.15
Alkybenzene sulfonic acid	Thickener	0.60
Isopropyl Alcohol	Solvent	0.55
Acetic Acid	Thickener	0.20
Ester	Biodegradable base oil	74.40
12-Hydroxystearic acid	Thickener	3.70
Calcium Carbonate	Solid film lubricant	2.40
Lecithin	Antiwear additive	7.00



12- Hydroxy stearic acid

Figure 2.21 12-Hydroxystearic acid.

The lubricant submerges when dispensed on water avoiding formations of a surface sheen and biodegrades when submerged, resulting in a water eco-friendly lubricant (71).

2.10 Lubricant for Smoothing Caulking Joints

Caulking compound sealants are widely used in the construction, marine, automotive, aircraft, electronics, and manufacturing industries (72). Often a defined finished effect is desired in a dispensed caulking bead for both aesthetic and structural purposes. Tooling is usually recommended after dispensing of caulking compound sealants to correct all imperfections in the caulking bead, including (72):

- Smoothing of the exposed surface of the bead,
- Eliminating irregularities in the edges of the bead,
- Making the width and bed depth of the bead more uniform,
- Eliminating air bubbles within the bead, and
- Otherwise ensuring full contact of the caulking bead with a joint.

A water-based, phosphate-free, nontoxic, and biodegradable lubricant composition made from a combination of surfactants and stabilizers has been described (72).

2.11 Marine Well Applications

2.11.1 Marine Oil Spills Oil Separation and Disposal Systems

Marine oil spills present problems in (73):

- Gathering the oil from relatively large areas, where it has spread on the surface of a body of water,
- Separating the oil layer from water, and
- Handling the recovered oil to either store it or dispose of it in an efficient manner.

The recovery of oil that is floating on the surface of relatively calm bodies of water can be carried out using floating booms or barriers, which contain the oil and which also are effective in channeling the oil toward a separation system.

The problem is to handle relatively large volumes of oil-water mixtures and provide an effective separation of the oil from the water so that the water may be disposed of. Also, the disposal of the recovered oil is also a problem as such. If the oil has been exposed to atmospheric conditions for more than several hours, its usefulness as a refinery feedstock is diminished.

Further, if suitable storage and transport facilities are not available, the final disposal must be carried out without delay to avoid loss of the oil from a contained area on the body of water. Thus, the oil may eventually become a tarlike substance after the more volatile components of the oil evaporate, and the residue is likely to sink, thereby contaminating the sea bed.

2.11.1.1 Superabsorbents

An oil-water separation apparatus which can be used in conjunction with a unique oil recovery and disposal system for recovering oil from a marine oil spill has been developed (73).

The filter utilizes superabsorbents which are operable to absorb water but not oil and thereby effect separation of the water from oil at the recovery of oil from marine oil spills. Water-absorbent compositions are used that may include cellulose derivates, poly(acrylic acid) salts, or nonionic xerogellants (73).

2.11.1.2 Chemical Dispersants

Chemical dispersants can be used to reduce the interfacial tension of floating oil slicks so that the oils disperse more rapidly into the water column and thus pose less of a threat to shorelines, birds, and marine mammals. The action of oil spill treating agents goes beyond simply dispersing the spilled oil.

Special formulations have been developed that are suitable for various environments, such as marine, shoreline, freshwater and saltwater, tropic, and arctic environments. Functionalized copolymers from dienes and *p*-alkylstyrenes can serve as dispersants and viscosity index improvers. The functionalities are introduced via the aromatic units (74,75).

The polymers are selectively hydrogenated to produce polymers that have highly controlled amounts of unsaturation, permitting a highly selective functionalization. The dispersant substances may also include a carrier fluid to provide concentrates of the dispersant.

Corexit® 9580 consists of two surfactants and a solvent. It exhibits low fish toxicity, low dispersiveness, and effective rock cleaning capability. Experiments on mangroves to explore the potential use of Corexit 9580 to save and restore an oiled vegetation have been considered.

Such a dispersant formulation for dispersing oil contains a mixture of a sorbitan monoester of an aliphatic monocarboxylic acid, a poly(oxyethylene) adduct of a sorbitan monoester of an aliphatic monocarboxylic acid, a water-dispersible salt of a dialkyl sulfosuccinate, a poly(oxyethylene) adduct of a sorbitan triester or a sorbital hexaester of an aliphatic monocarboxylic acid, and a propylene glycol ether as solvent (76).

2.11.2 Marine Umbilicals

Marine umbilicals are used to transport materials between a processing facility such as a platform, surface vessel, or land-based installation, and an undersea oil wellhead (77). The umbilicals comprise a plurality of inner tubes encased in an outer casing.

Umbilicals often contain internal steel tubes encased in an outer polymeric pipe, where the steel tubes are used to convey chemicals such as hydraulic fluids, organic solvents, or hot water.

Although steel can be resistant to the chemicals and any elevated pressures used, it can have the disadvantages of high cost, high weight, and poor flexibility and fatigue strength. Flexibility and fatigue strength are particularly important in applications where the umbilical is subjected to stresses caused by ocean currents, waves, transportation, and the like.

PAs are often a desirable material to use for pipes and tubes because they have good chemical resistance, good physical properties, and are lightweight. However, many marine umbilical applications require that the inner tubes be exposed to nucleophiles, such as water and alcohols, at elevated temperatures. Under such conditions, the amide bonds of many PAs may be susceptible to hydrolysis and the rate of hydrolysis increases with temperature (77).

The hydrolysis of the amide bonds can cause a reduction in molecular weight and concomitant loss in physical properties that can result in failure of the pipe during use. Such a failure can be catastrophic, with the loss of fluid causing undesirable consequences ranging from the impairment of the performance of other components present in the umbilical, to contact of the fluid with the external environment if the outer pipe fails.

Special PAs have been investigated that do not suffer from the disadvantages described above. This are semiaromatic PAs. The constituents of such PAs are shown in Table 2.18 and in Figure 2.22.

Table 2.18 Monomers for semiaromatic poly(amide)s (77).

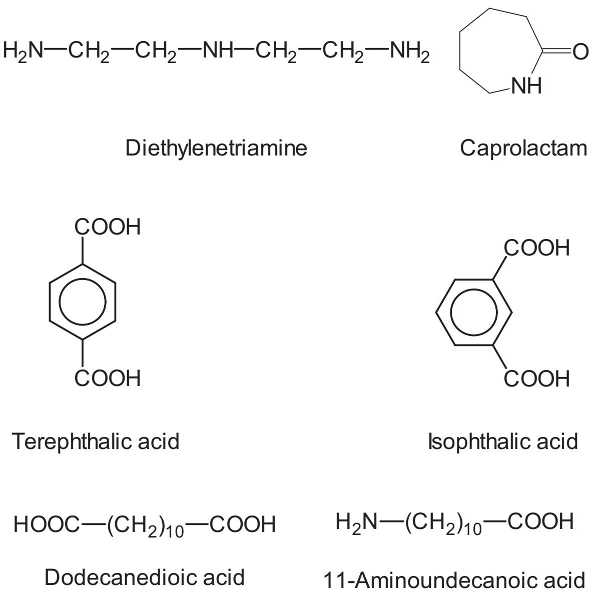
Acids	Amines
Terephthalic acid Isophthalic acid	Hexamethylene diamine
Nonanedioic acid	Hexamethylene diamine
Decanedioic acid	Hexamethylene diamine
Undecanedioic acid	Hexamethylene diamine
Dodecanedioic acid	Hexamethylene diamine
Tridecanedioic acid	Hexamethylene diamine
Tetradecanedioic acid	Hexamethylene diamine
Lactams	**Amino acids**
Caprolactam Laurolactam	11-Aminoundecanoic acid

The PA composition may optionally comprise additives, e.g., plasticizers. The plasticizer should preferably be miscible with the PA. Examples of suitable plasticizers are shown in Table 2.19 and in Figure 2.23.

Table 2.19 Plasticizers for semiaromatic poly(amide)s (77).

Compound
N-Butylbenzenesulfonamide
N-(2-Hydroxypropyl)benzenesulfonamide
N-Ethyl-*o*-toluenesulfonamide
N-Ethyl-*p*-toluenesulfonamide
o-Toluenesulfonamide
p-Toluenesulfonamide

The plasticizer may be incorporated into the composition by melt blending the polymer with the plasticizer or during the polymer-



Diethylenetriamine

Caprolactam

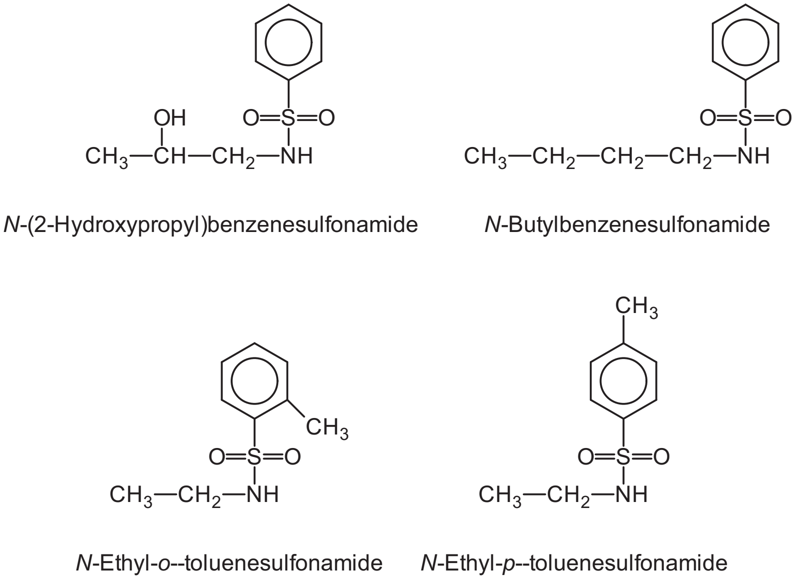
Terephthalic acid

Isophthalic acid

Dodecanedioic acid

11-Aminoundecanoic acid

Figure 2.22 Monomers for semiaromatic poly(amide)s.



N-(2-Hydroxypropyl)benzenesulfonamide

N-Butylbenzenesulfonamide

N-Ethyl-*o*--toluenesulfonamide

N-Ethyl-*p*--toluenesulfonamide

Figure 2.23 Plasticizers for semiaromatic poly(amide)s.

ization reaction. If the plasticizer is incorporated during polymerization, the PA monomers are blended with the plasticizer prior to starting the polymerization cycle and the blend is introduced to the polymerization reactor. Alternatively, the plasticizer can be added to the reactor during the polymerization cycle (77).

2.11.3 Hagfish Slime

Hagfish are marine craniates, also known as *Hyperotreti*. When captured they can secrete a slime, which expands into a gelatinous and sticky goo in combination with water.

An adult hagfish can secrete as much slime to turn a 20 *l* bucket of water into slime in a matter of several minutes. The slime may be mixed with seawater for and used as a drilling fluid (78).

2.11.4 Adhesive Compositions

Adhesive compositions can be used in subterranean formations to consolidate a loosely consolidated formation or to improve the structural integrity of a wellbore.

Adhesive compositions are ubiquitous among biological organisms due to their ability to effectively function in a variety of environments. Marine mussels and other marine organisms, in particular, are known for their ability to secrete adhesive proteins, i.e., bioadhesives that can form a coacervate in the mussels' aqueous habitat.

Adhesive proteins typically contain a 3,4-dihydroxyphenylalanine or a catechol type moiety within the polymer structure (79). Catechol type moieties are susceptible to oxidation, in particular in the presence of transition metal ions, thereby forming an *o*-quinone, which may undergo a crosslinking with another catechol in the polymer.

These adhesive proteins can be easily synthesized by biological organisms. On the other hand, biomimetic adhesive compositions have been synthesized (79). In comparison to protein-derived biomaterials these materials may provide more stability at elevated temperatures and in certain chemical environments. These polymers are based on 1,2-dihydroxybenzene and a biopolymer, such as chitosan, that can be crosslinked with the first polymer.

2.11.5 Bit Lubricants

2.11.5.1 Polymeric Alcohols

Synthetic poly-α-olefins (PAO)s are nontoxic and effective in marine environments when used as lubricants, return-of-permeability enhancers, or spotting fluid additives for water-based drilling muds (WBM)s.

Both poly(alkylene glycol) (80) and side-chain polymeric alcohols, such as poly(vinyl alcohol), have been suggested. These substances are comparatively environmentally safe.

An amine-terminated polyoxyalkylene with an average molecular weight from about 0.6–10 $k\,Dalton$ can be acylated with a succinic acylating agent, e.g., hexadecenyl succinic anhydride or a Diels-Alder diacid, obtained from an unsaturated fatty acid (81). Similarly, alkyl-aryl sulfonate salts can be used for lubrication purposes (82).

The pendant hydroxy groups of ethylene oxide–propylene oxide copolymers of dihydroxy and trihydroxy alcohols may be sulfurized to obtain a sulfurized alcohol additive. This is effective as a lubricant in combination with oils and fats (83).

2.11.5.2 Epoxides

2-Ethylhexanol can be epoxidized with 1-hexadecene epoxide. This additive also helps reduce or prevent foaming. These compositions are nontoxic to marine life, biodegradable, and capable of being disposed of at the drill site without costly disposal procedures (84).

2.11.5.3 Biodegradable Compositions

A biodegradable lubricating composition has been proposed. This composition is based on an aliphatic hydrocarbon oil and a fatty acid ester (85). The hydrocarbon should not be aromatic. Petroleum cuts with a high aromatic compound content present a risk to marine life due to their toxicity if they are released into the sea during offshore drilling.

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3

Waterborne Polymers

A waterborne polymer is a colloid system. According to the basic concepts of colloidal science, a waterborne polymer system, including the emulsion, microemulsion, nanoemulsion, latex, water dispersions, sol and gel, water-soluble resin, and water-reducible resin, have been discussed (1).

3.1 Analytical and Characterization Techniques

The typical characteristics of the different waterborne polymer systems were analyzed, and their similarities and differences were indicated.

The performance characteristics of waterborne polymers is characterized by the content of the soluble polar groups in the polymer, the molecular weight of the polymer, and the ratio of hydrophilic to hydrophobic groups (1).

Various analytical and characterization techniques at the macro or micro levels for waterborne polymers and coatings have become an important part of coatings science and technology (2). The application of modern analytical and characterization techniques in water-based polymers and coatings are discussed in terms of the analysis of raw materials, analysis of paint formations, characterization of the film formation process and structure, and the morphology of the waterborne polymer and coating films.

3.1.1 Surface Tension

A low dynamic surface tension is of great importance in the application of waterborne coatings (3). The issues of the surface tension in waterborne coatings and the dynamic surface tension in such coatings have been discussed.

The equilibrium and the dynamic surface tension were evaluated for several surface active agents. It is pointed out that low dynamic surface tension is an important factor in achieving a superior film formation in waterborne coatings. Dynamic coating application methods require surfactants with low dynamic surface tensions in order to prevent defects such as retraction, craters, and foam.

Thus, foam control is also of crucial importance in the application of many waterborne formulations, because foam generally leads to defects (3).

3.2 Synthesis Methods

3.2.1 Atom Transfer Radical Polymerization

Waterborne block and statistical copolymers have been synthesized using atom transfer radical polymerization (ATRP) (4).

ATRP provides one of the most efficient synthetic routes for the preparation of polymers with both controlled molecular weight and a desired complex architecture (5).

Homopolymers and pure block copolymers can be synthesized via ATRP in miniemulsion. Alkyl halides are used as initiators and transition metal complexes are used as activators. The activators are generated by electron transfer without involvement of initiating organic radicals (6). This method has a significant advantage over conventional ATRP, because it provides a simple route for synthesizing pure polymers with complex architectures such as star copolymers (7).

Forced gradient copolymers with a controlled distribution of the monomer units along the copolymer backbone have been prepared via ATRP in miniemulsion (8). The initiation technique using activators generated by electron transfer, is beneficial for the preparation of forced gradient copolymers, because all polymer chains are initiated within the miniemulsion droplets and the miniemulsion remains stable throughout the entire polymerization. Various monomer pairs with different reactivity ratios have been tested such as *n*-butyl acrylate/*tert*-butyl acrylate, *n*-butyl methacrylate/methyl methacrylate, and *n*-butyl acrylate/styrene. In each case, the added monomer diffused across the aqueous suspending medium and gradient copolymers with different forced distributions of comonomer units along the polymer backbone could be obtained. The shape of the gradient along the backbone of the copolymers is influenced by the ratio of the monomers used, the reactivity ratio of the comonomers, and by the feeding rate. Also, the relative hydrophobicity of the monomers affects the gradient.

The inverse miniemulsion ATRP allows the synthesis and functionalization of well-defined water soluble and crosslinked polymeric nanogel particles (9). The materials showed a higher colloidal stability, higher swelling ratios, and a better controlled degradability as compared to the corresponding counterparts that were prepared by conventional free radical polymerization in inverse miniemulsion.

The state of the art of ATRP methods using aqueous dispersed media has been reviewed (10). A better understanding of the ATRP mechanism and the development of new initiation techniques, such as activators generated by electron transfer, significantly facilitated the application of ATRP in aqueous systems.

Environmentally friendly ATRP methods have been reviewed (11, 12). Procedures to lower the concentration of the residual catalyst in polymeric products have been described, as well as how to develop highly active ATRP catalysts. Ionic liquids and other solvents of low volatility should be used. The introduction of degradable functionalities can be achieved by a radical ring-opening polymerization. The biodegradability can be improved by the introduction of disulfide moieties as well by the introduction of multiple degradable functionalities.

3.3 Aqueous Dispersions of Pigments

Aqueous dispersions of pigments have been used in various applications, such as (13):

- Inks for printing, in particular for inkjet printing,

- Waterborne paints and other coating formulations for vehicles, buildings and road markings,
- Cosmetics, and
- Pharmaceutical preparations.

Because pigments are often not soluble in an aqueous vehicle, the use of dispersing agents is required. Polymeric dispersants or surfactants can produce a stable dispersion of the pigment in the vehicle.

The recent advances in the synthesis of waterborne polyurethane and their application in water-based inks have been reviewed (14). Poly(ε-caprolactone) and poly(lactic acid) are versatile materials used in the synthesis of waterborne poly(urethane) (WPU) and these compounds supply a potential special performance. Reversible addition-fragmentation chain transfer (RAFT) polymerization and ATRP processes provide an opportunity to control the chain sequence of WPU to get products with the desired performance.

3.4 Waterborne Coatings

There is a wide variety of polymers that can be used in waterborne coatings. The most common polymers are acrylic polymers, polyvinyl acetate ethylene, vinyl acetate copolymers, and polymers of vinyl esters.

Most waterborne formulations require small amounts of organic solvents to aid in the coalescence of the polymer particles. Cyclohexanoic acid diesters of C_2–C_6 alcohols are useful as coalescing aids. These diesters have a number of unique properties which are often difficult to find in a single solvent (15):

1. Limited water miscibility,
2. Hydrolytic stability,
3. Proper evaporation rates, and
4. Strong solvency to coalescence the polymer particles.

Important in the formulation of a waterborne coating is the evaporation rate of the water/solvent mixture (15). As the coating dries, it is desirable that the water and solvent evaporate at rates such that the concentration of solvent increases over time.

Depletion of the solvent prior to the water leads to poor coalescence. The evaporation rates of the diesters may be controlled by selection of molecular weight to provide the flexibility to formulate efficiently and balance the impact of varying humidity levels.

Glycol ethers are commonly used as coalescers. These ethers are entirely or partially soluble in water, which has a negative effect on the coalescing power and leads to a poor hydrolytic stability.

Due to their low water solubilities, cyclohexane diesters will partition into the polymer phase, exhibiting excellent coalescing power. Due to water immiscibility and steric hindrance, the diesters exhibit good hydrolytic stability. These esters can be obtained from the corresponding phthalate esters.

The compounds can be advantageously used as coalescers in latex coatings (15).

3.4.1 Food Packaging

Waterborne coatings are often used to provide the paper, cardboard or paperboard used as packaging material for food with a barrier against water, water vapor, grease, and oil (16). The coated paper can be used to pack food such as sausages, fish, pizzas, and others.

Coating compositions for paper and paperboard have been described that are based on poly(vinyl alcohol) (PVA) and a fatty acid melamine wax (17).

Waterborne coating compositions based on hydrophobic polyester resins prepared from poly(ethylene terephthalate) (PET) have excellent water and oil repellency properties (18). The selection of these types of waterborne coating compositions is also advantageous from an environmental point of view, since waste PET such as bottles, sheet material, and textile wastes can be used for the preparation of these resins, and the coatings do not have a negative effect on the compostability of the coated material (16).

A waterborne coating composition based on a water soluble or water-dispersible polyester resin and a metal salt of a fatty acid for use as a coating for paper, cardboard, or paperboard, has been described (16).

The water-dispersible and hydrophobic polyester is based on a reaction product of 30–70% of a terephthalate polymer, 5–40% of a hydroxyl-functional compound, 1–20% of a carboxyl functional compound, and 10–60% of a fatty acid or triglycerides thereof.

It was found that the compositions are suitable for food packaging. In addition, the coated substrate exhibits good release properties, i.e., the food can be easily removed from the substrate, keeping its original appearance. The food does not receive an odor from the coating or packaging material. Furthermore, the coated substrate exhibits good grease-resistant properties.

Thus, this coating formulation is a suitable replacement for the undesirable silicon release aids and fluorocarbon grease barrier treatments. Another advantage of the coating compositions is that the formulation does not contain undesirable melamine components that are often used to cure polyester resins.

The water-dispersible resins can be synthesized by condensation polymerization of recycled PET. The following steps have been used to produce the resin (16):

1. Incorporation of a non-polar group from fatty acids or reactive silicones, blown paraffins.
2. Incorporation of a multifunctional hydroxyl component or components, such as pentaerythritol, sorbitol, or glycerol, by esterification or transesterification.
3. Esterification or transesterification of difunctional acids, such as terephthalic acid, and difunctional alcohols such as ethylene glycol.
4. Incorporation of an ionic group or groups needed for dispersing the resin in water. Examples of these groups are trimellitic anhydride, maleic anhydride, sulfo succinate, sulfonated isophthalic acid or its esters, and others.
5. Dispersing the resin in water containing an amount of base, if needed, to neutralize the pendant acid groups.

Eventually, the waterborne coating composition can be prepared by making a colloidal solution or a dispersion of the water-dispersible and hydrophobic polyester resin in water, in the presence of a base.

The addition of talc or other cationically charged minerals, like hydrotalcite, to the composition was found to be very effective at inhibiting foam formation even under high agitation and conditions that would promote air entrainment (16).

3.4.2 Unsaturated Polyesters

Waterborne unsaturated polyesters are mostly used for wood coatings (19). Usually, they are equipped with UV-sensitive initiator systems. The basic constituents are selected from ethylene glycol, 1,2-propylene glycol, diethylene glycol, and tetrahydrophthalic anhydride, terephthalic acid, and trimellitic anhydride. The vinyl monomer is trimethylolpropane diallyl ether. A preferred UV-sensitive compound is 2-hydroxy-2-methylphenylpropane-1-one.

When diluted with water, the resins exhibit a viscosity of 2,500 *cps*. The cured products show good tensile properties and weatherability.

Another method to make unsaturated polyesters (UPs) water soluble is the incorporation of polar hydrophilic groups, such as carboxylic and sulfonic groups. This ensures a good dispersibility in water. An exemplary compound is sodium 5-sulfonatoisophthalic acid. Also, instead of styrene, glycerol monoethers of allyl alcohol and unsaturated fatty alcohols can be used as vinyl monomers (20).

Diluted in water, such UP resins can be used for particleboards and fiberboards. Further, they can be modified with acrylonitrile and also used in mixtures with urea formaldehyde resins. A mixture of an UP resin with an urea formaldehyde resin allows the production of boards with better mechanical properties in comparison to those that are bonded exclusively with urea formaldehyde resins (21).

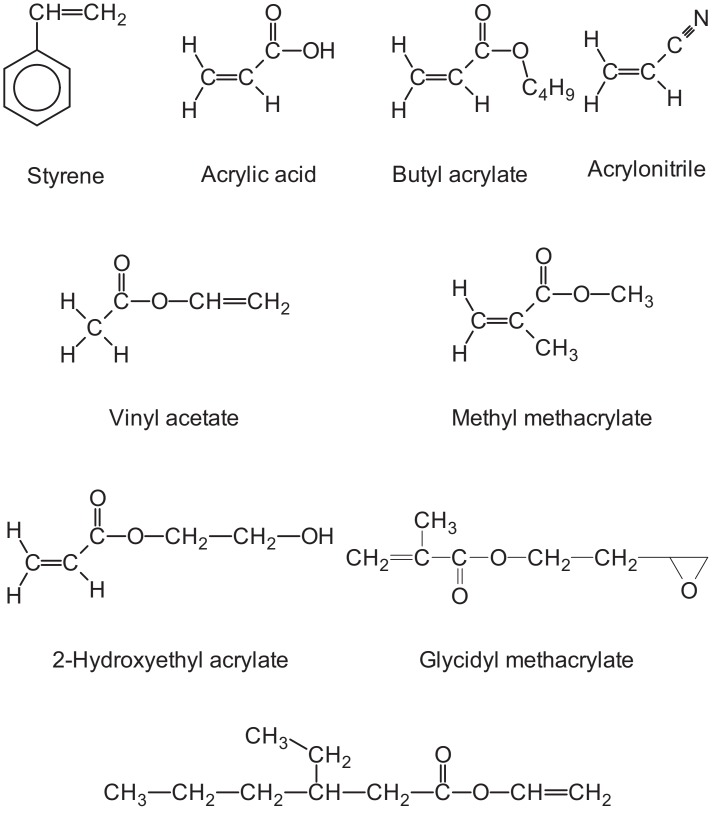
Biobased unsaturated polyesters were synthesized from itaconic acid and different diols which could be derived from renewable resources (22). Waterborne UV-curable networks based on these polyesters were manufactured. The UV cured polyester coatings exhibited high hardness, good water resistance and solvent resistance. These coatings combined the merits of biobased materials, UV curing process, and water distribution.

3.4.3 Coatings with Pendant Allyl Groups

The polymers contain pendant allyl groups, which are capable of effecting free radical flux when the compositions are applied to a substrate and exposed to oxygen. Coatings from these compositions are superior in solvent, print, and block resistance.

Aqueous emulsion polymers or latexes in both clear and pigmented form are well known. They are used for interior and exterior architectural coatings, general metal coatings, and adhesives.

Latexes can be formed by aqueous emulsion polymerization of styrene, *n*-butyl acrylate, methyl methacrylate, vinyl acetate, vinyl 2-ethylhexanoate, acrylic acid, acrylonitrile, glycidyl methacrylate, 2-hydroxyethyl acrylate, and others. These compounds are shown in Figure 3.1.



Styrene

Acrylic acid

Butyl acrylate

Acrylonitrile

Vinyl acetate

Methyl methacrylate

2-Hydroxyethyl acrylate

Glycidyl methacrylate

Vinyl 2-ethylhexanoate

Figure 3.1 Monomers for latexes.

When monomers that contain a polar functionality, such as a carboxyl group or a hydroxyl group, are used, there is a propensity for these groups to be found at or near the surface of the emulsion particles because of the affinity of these groups for the aqueous environment.

In addition, techniques for increasing the amount of any non-water reactive functional group near the surface of the emulsion particles are known.

The importance of the polymer gel fraction, the polymer swell ratio, and the choice of appropriate monomers for allyl survival in waterborne particles has been demonstrated (23).

The film properties can be greatly improved if the polymer film can be crosslinked after the formation of the film. The preparation of emulsion polymers containing pendant double bonds is a possible solution for a coating system, which crosslinks thermally and photochemically. However, this is difficult to achieve, since the emulsion polymerization process also involves the free radical polymerization with such double bonds.

While emulsion polymers can be prepared as high molecular weight polymers at low viscosity, waterborne polymer particles which contain unsaturation allow later crosslinking of the coating under a variety of cure conditions.

The use of allyl groups as vehicles to cure oil-based paints has been used in alkyd resin systems. Alkyd resins are esterified resins prepared from polyols, dicarboxylic acids, and fatty acids. Pendent double bonds in alkyd resins are present in the fatty acid portion of the resins.

The reaction of oxygen and allylic hydrogen atoms forms peroxides in the fatty acid portion of the resin and starts the crosslinking reactions. A so-called drier in the coating is typically a cobalt salt. This cobalt salt decomposes the peroxide into active hydroxyl and organic radicals already at room temperature.

The advantage of such a system is that it uses oxygen as an active agent in the crosslinking chemistry via a free radical mechanism.

Therefore, the coating formulation is stable until it is exposed to oxygen. Its obvious disadvantage is that organic solvents are liberated as the coating dries.

Examples of water-dispersible alkyd resins have been described (24). These resins have a tendency to become brittle and yellow (23).

In addition to alkyds, UPs are another class of resins which are prepared from the esterification of unsaturated dicarboxylic acids and polyols. The unsaturated moiety of the polymer is usually located in the backbone of the polymer molecule.

Although UPs can be oil-in-water emulsions, water-in-oil emulsions of UPs are typical. For example, a curable water-in-oil emulsion in which the oil phase contained a carboxylic acid-containing UP, a copolymerizable monomer such as styrene or methacrylic ester, nonionic emulsifiers, a thixotropic thickener, a basic neutralizing agent, a promotor-catalyst system composed of dimethyl aniline, an oil-soluble cobalt salt, and a thermal peroxide initiator has been reported (25). An emulsion can be obtained by adding water, while the oil phase is stirred.

A process for converting polymerizable water-in-oil emulsions into thermoset objects at room temperature has been described (26). The oil phase consists of a carboxylic acid-containing UP resin, polymerizable monomers, oil-soluble cobalt salts, and a promoter consisting of *N*-hydroxyl alkyl substituted, phenyl-substituted tertiary amines and dialkyl anilines. The water phase, which contains hydrogen peroxide, is stirred into the oil to obtain an emulsion which rapidly cures.

The effectiveness of a combination of catalyst and promoter can be enhanced when it includes a mixture of tertiary amines, where one of the tertiary amines has a hydroxyalkyl group attached to the amino group of the nitrogen, and the second amine is a dialkyl aniline. Further, the $-\mathrm{OH}$ group of hydroxyalkyl substituted amines coordinates with the cobalt, which enhances the effectiveness of the catalyst-promotor system.

A process for producing a pourable or pumpable thermosetting water-in-oil emulsion with water as the continuous phase, and an UP, a copolymerizable monomer, and a peroxide-cobalt-tertiary amine curing system in the oil phase has been described (27). UPs with molecular weights greater than 1800 *Dalton* give a water-in-oil emulsion with superior properties.

An approach to an emulsion particle which has dangling double bonds, which avoids the problem of polymerization of such double bonds during emulsion polymer synthesis, is to first carry out a synthesis providing a latex particle with acid, epoxy, or carbodiimide functionality, which is followed by reaction with an epoxy or acid functional compound, respectively, which contains a double bond.

An air drying and air curable latex coating with unsaturated resin particles dispersed in the water phase, which are combined with an emulsion of a drier salt, have been described (28).

The coating compositions are formed by first preparing a latex with carboxyl or 1,2-epoxide functionality. After the formation of the latex, a portion of the reactive carboxyl or 1,2-epoxide functionality is reacted with, e.g., glycidyl acrylate. The emulsion of a drier salt is then added after the post reaction. Drier salts, such as cobalt naphthenate, are used to facilitate the air curing of the residual acrylate moiety.

Acrylic dispersion polymers have been described that contain pendent methacrylate double bonds (29). Glycidyl methacrylate is reacted with carboxylic acid-containing polymers in solution.

Then, the solvent is removed under reduced pressure and replaced by a polymerizable monomer. The polymer solutions are neutralized with ammonia, diethanolamine, or triethyl amine, and then dispersed into water to form an emulsion.

The emulsion may contain conventional initiators such as dibenzoyl peroxide or azobisisobutyronitrile. For photocuring, photosensitizers such as benzoin or benzoin methyl ether have been proposed.

Another approach is to react the carboxylic acid-containing latex particles with carbodiimide methacrylates to produce latex particles with pendent methacrylate moieties (30).

Emulsion particles can also be prepared from allyl methacrylate, ethyl acrylate, and methyl methacrylate produced acetone insoluble films when they are baked at 150°C for 30 min.

Amino-containing waterborne particles can be prepared by reacting propylene imine with carboxylic acid-containing latexes (31). The amino functionalized latexes are then subsequently reacted at 25–60°C with acetoacetoxyethyl methacrylate. Ambient and thermal cure studies resulted in clear films with a significant increase in solvent resistance, gel fraction, and crosslink density.

The preparation of waterborne allyl-containing core/shell particles has been described in much detail (32). Stable waterborne polymer compositions have been developed, which are stabilized against gelling. The composition has a glass transition temperature of greater than 0°C.

The compositions contain an acetoacetoxy-type functional polymer, a poly(alkylene imine), and a nonionic surfactant with a hydrophilic-lipophilic balance of at least of 17.5. These waterborne polymer compositions are particularly useful in a variety of adhesive formulations such as pressure sensitive adhesives or laminating adhesives.

3.4.4 UV-Curable Latex Coating

An aqueous coating composition has been described that is opaque, UV-curable and mar or scratch resistant (33, 34).

The coating composition includes a UV-curable film-forming resin component, a mar or scratch resistant additive, water, and a thixotropic or pseudoplastic anti-settling agent such as an amine salt of a synthetic wax, a microcrystalline cellulose compound, or a urea urethane compound.

The coating composition can be applied to a substrate by spraying and cured with UV radiation to form a highly mar and scratch resistant coating. Further, the cured coating has excellent leveling and reduces surface defects such as orange peel.

Also, an excellent storage stability is shown for a period of at least 180 *d*. The compositions have a relatively low volatile organic content without sacrificing the balance of properties desired for a dry coating. These coating compositions are waterborne, and include about 40–70% water.

The film-forming component of the composition contains a UV-curable water-dispersible or latex polymer. Water-dispersible polymers have a nonionic or anionic functionality on the polymer, which render them water-dispersible.

Suitable UV-curable polymers are poly(urethane)s, epoxy resins, poly(amide)s, chlorinated polyolefins, or acrylic resins.

An acetoacetyl functionality may be incorporated into the UV-curable polymer through the use of comonomers shown in Table 3.1.

Basically, any polymerizable hydroxy functional or other active hydrogen-containing monomer can be converted into the corresponding acetoacetyl functional monomer by the reaction with diketene (35).

Table 3.1 Monomers with acetoacetyl functionality (34).

Monomer
Acetoacetoxyethyl acrylate
Acetoacetoxypropyl methacrylate
Allyl acetoacetate
Acetoacetoxybutyl methacrylate
2,3-Di(acetoacetoxy)propyl methacrylate
2-(Acetoacetoxy)ethyl methacrylate
tert-Butyl acetoacetate
Diketene

For example, an acetoacetyl functional latex polymer can be prepared through chain-growth polymerization, using 2-(acetoacetoxy)ethylmethacrylate and styrene. The latex polymers should be stabilized by surfactants. Examples of suitable surfactants are shown in Table 3.2.

The latex polymer may also be stabilized with an alkali-soluble polymer. Alkali-soluble polymers can be prepared by making a polymer with acrylic or methacrylic acid and solubilizing the polymer by addition of ammonia or another base.

A water soluble free radical initiator is typically used in the chain growth polymerization of a latex polymer together with a reducing agent. Suitable water soluble free radical initiators and reducing agents are shown in Table 3.3.

Besides latex polymers, other water-dispersible polymers can be used such as polyesters and poly(urethane)s (PUs). For example, a water-dispersible polyester can be prepared by the reaction of polybasic acids with polyols, which results in a polymer with an excess hydroxyl functionality. The resulting polyester can be further reacted with *tert*-butyl acetoacetate or diketene to incorporate a acetoacetyl functionality onto the polymer, and with a suitable anhydride such as trimellitic anhydride to render the polyester acid functional. Suitable water soluble free radical initiators and reducing agents are shown in Table 3.4. Acids and alcohols are also shown in Figures 3.2 and 3.3.

Mar or scratch resistant additives are macrocrystalline or single crystal mineral abrasives, including metal oxides such as aluminum

Table 3.2 Surfactants for latex polymers (34).

Nonionic emulsifiers
tert-Octylphenoxyethylpoly(39)-ethoxyethanol
Dodecyloxypoly(10)ethoxyethanol
Nonylphenoxyethyl-poly(40)ethoxyethanol
Polyethylene glycol 2000 monooleate
Ethoxylated castor oil
Fluorinated alkyl esters and alkoxylates
Polyoxyethylene (20) sorbitan monolaurate
Sucrose monococoate
Di(2-butyl)phenoxypoly(20)ethoxyethanol
Hydroxyethylcellulosepolybutyl acrylate graft copolymer
Dimethyl silicone polyalkylene oxide graft copolymer
Poly(ethylene oxide)poly(butyl acrylate) block copolymer
Block copolymers of propylene oxide and ethylene oxide
Ethoxylated 2,4,7,9-tetramethyl-5-decyne-4,7-diol
N-Polyoxyethylene(20)lauramide
N-Lauryl-*N*-polyoxyethylene(3)amine
Poly(10)ethylene glycol dodecyl thioether
Ionic emulsifiers
Sodium lauryl sulfate
Sodium dodecylbenzenesulfonate
Potassium stearate
Sodium dioctyl sulfosuccinate
Sodium dodecyldiphenyloxide disulfonate
Nonylphenoxyethylpoly(1)ethoxyethyl sulfate ammonium salt
Sodium styrene sulfonate
Sodium dodecyl allyl sulfosuccinate
Linseed oil fatty acid
Salts of phosphate esters of ethoxylated nonylphenol
Sodium octoxynol-3-sulfonate
Sodium cocoyl sarcocinate
Sodium 1-alkoxy-2-hydroxypropyl sulfonate
Sodium α-olefin (C14-C16) sulfonate
Sulfates of hydroxyalkanols
Tetrasodium *N*-(1,2-dicarboxy ethyl)-*N*-octadecylsulfosuccinamate
Disodium *N*-octadecylsulfosuccinamate
Disodium alkylamido polyethoxy sulfosuccinate

Table 3.3 Water soluble free radical initiators and reducing agents (34).

Initiator	Reducing agent
Hydrogen peroxide	Alkali metal metabisulfite
tert-Butyl peroxide	Hydrosulfite
Sodium persulfate	Hyposulfite
Potassium persulfate	Sodium formaldehyde sulfoxylate
Lithium persulfate	Ascorbic acid
Ammonium persulfate	Isoascorbic acid

Table 3.4 Acids and alcohols for polyesters (34).

Acid or anhydride	Alcohol
Adipic acid	Ethylene glycol
Azelaic acid	Propanediol
Fumaric acid	Butanediol
Glutaric acid	2-Ethyl-1,3-propanediol
Hexahydrophthalic acid	2-Methylpropanediol
Hexahydrophthalic anhydride	2-Butyl-2-ethylpropanediol
Isophthalic acid	2-Ethyl-1,3-hexanediol
Maleic acid	1,3 Neopentyl glycol
Maleic anhydride	2,2-Dimethyl-1,3-pentanediol
Phthalic acid	1,6 Hexanediol
Phthalic anhydride	1,2-Cyclohexanediol
Pyromellitic acid	Bisphenol A
Sebacic acid	1,2-Bis(hydroxymethyl)cyclohexane
Succinic acid	Bis(4-hydroxycyclohexyl)methane
Succinic anhydride	Diethylene glycol
Terephthalic acid	Triethylene glycol
Tetrahydrophthalic acid	Dipropylene glycol
Tetrahydrophthalic anhydride	1,2,4-Butanetriol
Trimellitic acid	1,2,6-Hexanetriol
Trimellitic anhydride	Trimethylolethane
	Trimethylolpropane
	Glycerol
	Pentaerythritol
	Dipentaerythritol
	Mannitol
	Sorbitol

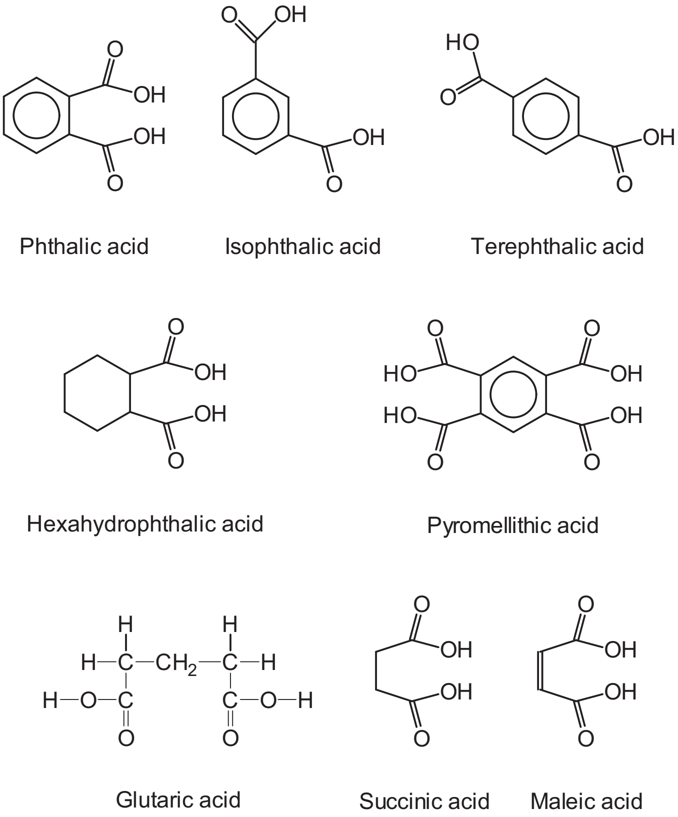


Figure 3.2 Diacids.

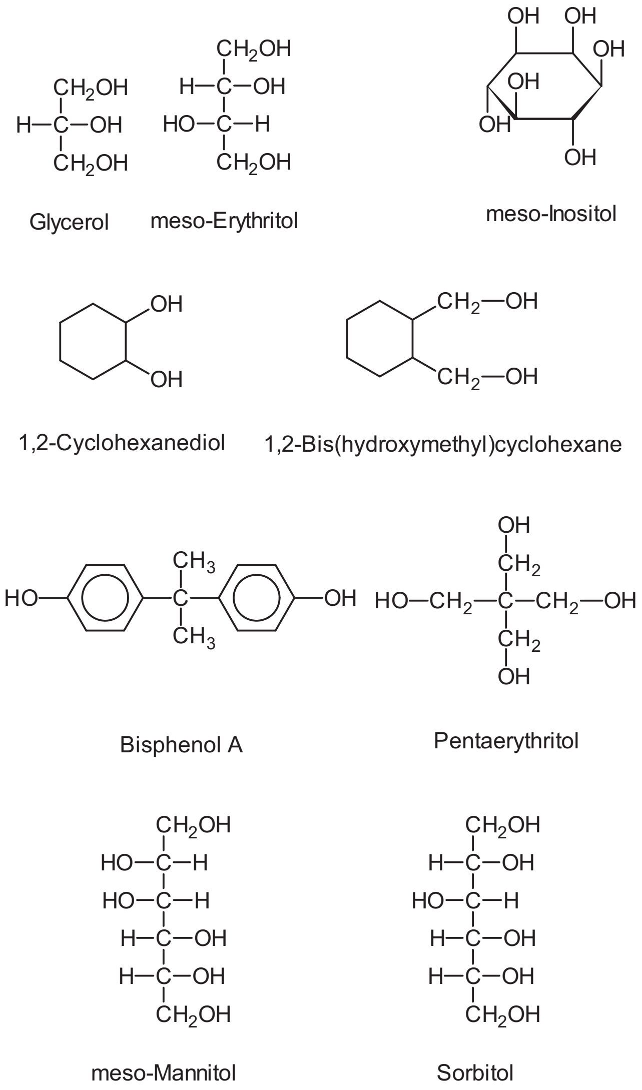


Figure 3.3 Polyols.

oxide, inorganic nonmetal oxides such as silica oxides, calcium oxides, or boron oxides, ground glass particles and beads, and ceramic particles and beads.

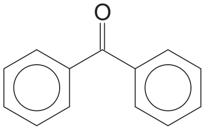
As curable moieties, ethylenically unsaturated compounds are added, such as acrylate or methacrylate ester monomers. Also, allyl ether monomers or vinyl ether monomers have been proposed. The ethylenically unsaturated compounds may be used in various combinations and may also provide a crosslinkable diluent function, e.g., ethylene glycol divinyl ether.

Preferred photoinitiators are summarized in Table 3.5 and some are shown in Figure 3.4. Synergists for photoinitiators are shown in Figure 3.5

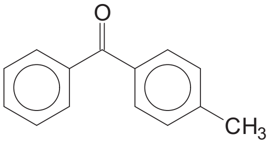
Table 3.5 Photoinitiators and photoinitiator synergists (34).

Photoinitiator
Benzophenone
4-Methylbenzophenone
Benzoyl benzoate
2,2-Dimethoxy-2-phenylacetophenone
α,α-Diethoxyacetophenone
Hydroxycyclo-hexylphenylketone
2-Hydroxy-2-methyl-1-phenylpropan-1-one
Bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide
2-Hydroxy-2-methyl-1-phenylpropan-1-one
2-Hydroxy-2-methyl-1-phenylpropan-1-one
2,4,6-Trimethylbenzoyl-diphenylphosphine oxide
Synergist
Methyl diethanol amine
Triethanol amine
Amylparadimethylaminobenzoate
2-*n*-Butoxyethyl-4-(dimethylamino)benzoate
2-(Dimethylamino)ethylbenzoate
Ethyl-4-(dimethylamino)benzoate
2-Ethylhexyl-4-(dimethylamino)benzoate

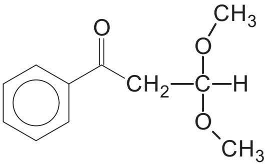
Preferred compositions include a free radical initiator that is a hydrogen abstraction-type photoinitiator such as benzophenone or 4-methylbenzophenone. Such compositions are at least partially curable by ultraviolet light. An exemplary composition is shown in



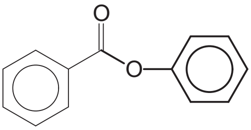
Benzophenone



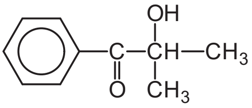
4-Methylbenzophenone



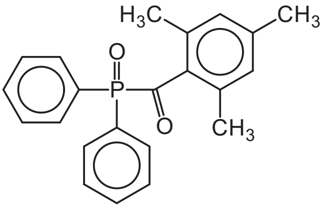
2,2-Dimethoxy-2-phenylacetophenone



Benzoyl benzoate



2-Hydroxy-2-methyl-1-phenylpropan-1-one

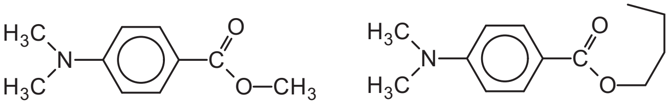


2,4,6-Trimethylbenzoyldiphenylphosphine oxide

Figure 3.4 Photoinitiators.

Methyl diethanol amine

Triethanol amine



Methyl 4-dimethylaminobenzoate

Amyl 4-dimethylaminobenzoate

Figure 3.5 Synergists for photoinitiators.

Table 3.6.

The coating compositions can be applied using techniques such as (34):

- Spray coating,
- Brush coating,
- Curtain coating, or
- Direct or differential roll coating applications.

Alternatively, the surface to be coated can be impregnated with the coating composition by immersion in a bath that contains the coating composition (34).

3.4.5 Poly(urethane)s

A major change in coatings technology was caused by the restrictions on volatile organic compounds (VOCs) in coatings. These government regulations combined with performance advantages were the key to the success of WPUs. The production and chemistry of waterborne one-component PUs and reactive two-component systems have been discussed (36).

WPUs are used mainly for coatings, but also for composites and nanocomposites. Water-dispersable paints can be produced from

Table 3.6 UV-curable polyester coating (34).

Compound Remark	Amount/[$g\,l^{-1}$]
Styrene Acrylic Emulsion	263.64
WB UV PUD/Acrylic/PU copolymer dispersion	149.4
Trifunctional acrylic monomer	90
Surfynol 104-A/Flow and defoaming agent	8.88
ANTI-SAG/Anti-settling agent	89.28
Acrysol RM-2020/Thickener	23.16
Disperbyk 190/Surfactant and dispersing aid	22.32
Byk-025/Surfactant	2.4
Spw 1000/Al_2O_3	36
Syloid 7000/Silica flatting agent	8.16
Michem emulsion 32535/Wax	49.8
Ceraflour 928/Wax	10.8
Dehydran 1293/Defoamer	2.4
Irgacure 819DW/Photoinitiator	12.72
Irgacure 500/Photoinitiator	14.04
Dynol 607/Surfactant	4.44
Pigment	100.2
Solvent	24.84
Water	223.8
Total	1136.4

a polyester polyol, e.g., isophorone diisocyanate and carboxylic monomers, such as dimethylol propionic acid and tartaric acid (37). Phosphorus-containing flame retardant water-dispersed PU coatings have been synthesized by incorporating a phosphorus compound into the PU main chain (38).

Bis(4-aminophenyl)phenylphosphine oxide can be synthesized from bis(4-nitrophenyl)phenylphosphine oxide by the reduction of the nitro groups (39). The synthesis is shown in Figure 3.6.

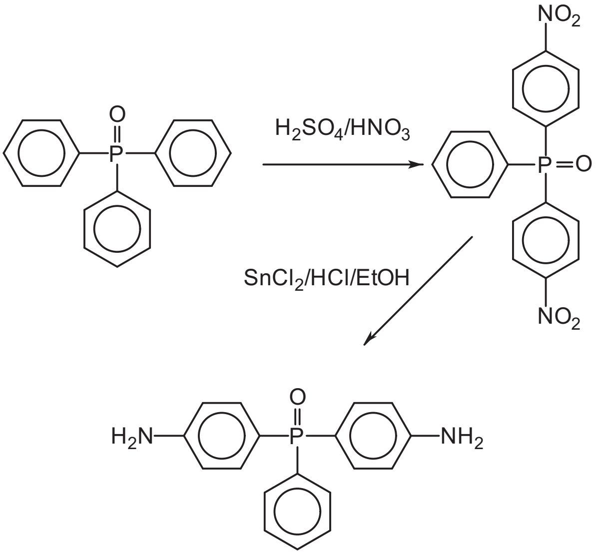


Figure 3.6 Synthesis of bis(4-aminophenyl)phenylphosphine oxide (39).

The stability of WPUs is shown in Table 3.7. As can be seen in

Table 3.7 Stability of waterborne poly(urethane)s (36).

Dispersion type		
	Ionic	Nonionic
Freezing	Unstable	Stable
Temperature above 70°C	Stable	Unstable
Addition of electrolytes	Unstable	Stable
Strong shear forces	Partly stable	Stable

Table 3.7, nonionic dispersions perform better with respect to the addition of electrolytes, freezing, and strong shear forces.

In contrast, they are sensitive to heat. Thus, PU dispersions with both ionic and nonionic emulsifiers built into the same polymer are the best choice in order to produce stable dispersions. Further, a low content of hydrophilic moieties in films results in a lower sensitivity to water (36).

The stability of waterborne dispersions can be improved by a continuous process of preparation (40). The addition of acetone has a large effect on the particle diameter (41). Several methods of preparation are common, such as the (36):

1. Acetone process,
2. Prepolymer mixing process,
3. Melt dispersion process, and
4. Ketamine-ketazine process.

In the acetone process, the chain extension of a hydrophilic isocyanate prepolymer with diamines is performed in acetone to get poly(urethane) poly(urea) compounds. By the addition of water and the removal of the acetone solvent a purely waterborne dispersion of small particle size is eventually formed. The aqueous dispersion can be formed either by precipitation of the hydrophobic segments or by phase inversion of an intermediately generated inverse emulsion.

In the prepolymer mixing process a hydrophilically modified prepolymer with free isocyanate groups is mixed with water. Then, the chain extension with amines is done.

The melt dispersion process uses a ionically modified isocyanate terminated prepolymer which is reacted with urea or ammonia to form a capped oligomer with terminal biuret groups. A chain extension can be done by methylation of the biuret groups with formaldehyde.

In the ketamine-ketazine process, an isocyanate prepolymer is blended with a blocked amine, i.e., a ketamine or hydrazine, and dispersed in the aqueous phase (36).

Waterborne anionomeric PU-ureas can be synthesized from dimethylol-terminated perfluoropolyethers, isophorone diisocyanate, dimethylol propionic acid, and ethylene diamine. These materials can be obtained as stable aqueous dispersions. Isophorone diisocyanate is shown in Figure 3.7

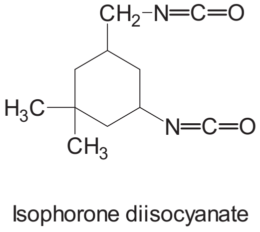


Figure 3.7 Isophorone diisocyanate.

The surface properties and the chemical resistance have been estimated by the measurement of the contact angles and spot tests using various solvents. The surface hydrophobicity is not affected by the composition. However, the water sorption behavior is sensitive to the content of the carboxyl groups in the polymer (42).

Another type of WPU urea anionomers consists of isophorone diisocyanate, poly(tetramethylene ether) glycol, dimethylol butanoic acid, and hydrazine monohydrate. Ethylene diamine, 1,4-butane diamine are chain extenders. The pendent carboxylic groups can be neutralized by ammonia hydroxyde, copper hydroxyde, or triethylamine (43).

Table 3.8 summarizes some composites made from WPU materials. Such composite materials can be prepared by blending of carboxymethyl konjac glucomannan with a WPU .

Table 3.8 Composites from waterborne poly(urethane)s.

Second Compound	Reference
Starch	(44)
Carboxymethyl konjac glucomannan	(45)
Casein	(46)
Carboxymethyl chitin	(47,48)
Soy flour	(49)

For example, a blended sheet with 80% carboxymethyl konjac glucomannan exhibits a good miscibility and higher tensile strength of 89.1 MPa than that of both of the individual materials, i.e., WPU sheets and carboxymethyl konjac glucomannan sheets with 56.4 MPa.

With an increase of carboxymethyl konjac glucomannan content, the tensile strength, Young's modulus, and thermal stability increased significantly, attributed to intermolecular hydrogen bonding between carboxymethyl konjac glucomannan and WPU (45).

Waterborne poly(urethane) and casein have been prepared by blending at 90°C for 30 min, and then crosslinking with ethanedial. Water resistance of the materials proved to be quite good (46).

A WPU aqueous dispersion could be synthesized from castor oil (50). This was blended with thermoplastic starch to get a biodegradable polymer with improved physical properties. The effect of the PU content on the morphology, miscibility and physical properties of the resulting blends was elucidated.

It was confirmed that the blends exhibit a higher miscibility when the PU content is lower than 15%. This occurs due to the hydrogen bonding interaction between urethane groups and the hydroxyl groups on the starch. A phase separation occurs in blends with a content of PU of more than 15%. The PU also plays an important role in improving the surface- and bulk-hydrophobicity and the water resistance of the blends (50).

Also, WPU was prepared from a rapeseed oil-based polyol, and then used to modify a glycerol plasticized starch (51). This modified polymer overcomes the intrinsic drawbacks of starch materials such as poor mechanical properties and water sensitivity. Blend films could be prepared by casting aqueous dispersions of gelatinized starch and PU. Glycerol plasticized starch can mix with rapeseed oil-based WPU on the molecular level at low contents of PU.

3.4.5.1 *Aqueous Poly(urethane)*

There are many variables in the preparation of aqueous PU dispersions. Chemical and compositional variables, such as carboxylic acid concentration, concentration of the polymer, the degree of preneutralization and post-neutralization of the carboxylic acids and chain extension, all impact the solution properties such as particle size and viscosity.

Another issue is the method by which the dispersion is prepared. In industrial processes, mainly the prepolymer mixing process and the acetone process are used.

The impact of the chemical variables on a given PU dispersion formulation prepared by the acetone process has been evaluated (52). The changes in the concentration of the carboxylic acid moiety, the degree of pre-neutralization and post-neutralization, and the chain extension were shown to have impacts on dispersion solution properties. An increased ionic concentration, and degree of pre-neutralization results in a lower particle size and a higher viscosity. An increased degree of chain extension led resulted in a larger particle size and lower viscosity.

The increased post-neutralization increases both particle size and viscosity. Further, an increased concentration of the polymer increases the viscosity without any change in the particle size (52).

Aqueous PU dispersions were prepared using 4–10% of polyhedral oligomeric silsesquioxane (POSS) by a homogeneous solution polymerization method in acetone followed by a solvent exchange with water (53). The use of acetone as the initial polymerization solvent allows the facile incorporation of both diamino and dihydroxy functional POSS monomers in a homogeneous reaction environment.

After the addition of water and the removal of the acetone, stable dispersions with unimodal particle sizes could be obtained. The incorporation of the POSS monomers does not have a significant effect on the properties of the dispersions.

However, the physical properties of the isolated polymers display significant changes. A notable increase in the storage modulus, glass transition temperature, complex viscosity, and surface hydrophobicity has been observed. These changes have been attributed due to the incorporation of POSS residues into the PU hard segment domains (53).

The preparation of one-component thermally curable aqueous poly(urethane) coating compositions has been detailed (54). The compositions contain a polyol resin, an aminoplast resin, and a polycarbonate-poly(urethane) resin.

It as been shown that the addition of a nonfunctional polycarbonate-poly(urethane) resin can improve the flexibility and toughness of the coatings. Further, addition of the nonfunctional polycarbonate-poly(urethane) resin does not have a negative affect on the adhesion (54).

A series of WPUs were synthesized by a pre-polymer process from isophorone diisocyanate, 1,6-hexamethylene diisocyanate and polycarbonatediol with varying molecular weight and composition (55). The effect of polycarbonatediols on the performance of the emulsion was studied by the apparent viscosity, particle size distribution and Zeta potential analysis.

WPU dispersions with a mean particle size of 50–70 nm showed an excellent storage stability. It was found that the mean particle size, thermal stability, crystallinity, low temperature flexibility, mechanical properties and hydrophobicity increased with the molecular weight of the polycarbonate diols. In contrast, the particle distribution decreased.

Copolycarbonate-based WPU showed a higher crystallinity of the hard segments, thermal stability and wettability than the homopolycarbonate-based compounds (55).

Composites consisting of commercial WPU and silica were prepared by in-situ synthesis, i.e., the sol-gel method, and compared to those prepared by the addition of commercial silica, i.e., the blending method (56). It was observed that the composites containing commercial silica displayed a higher mechanical resistance, but a better adhesion was obtained with the in-situ method.

3.4.5.2 Nanoclays

WPU/poly(methyl methacrylate) (PMMA) hybrid materials could be reinforced with exfoliated organoclays (57). The size of the particles in the emulsion increased when the contents of PMMA or organoclay was increased. X-ray measurements showed an effective exfoliation of the silicate layer in the polymer matrix.

A series of siloxane modified waterborne UV-curable poly(urethane) and its nanocomposites were synthesized using a diol with side-chain triethoxysilane derived from 2-hydroxyethyl acrylate, 3-aminopropyltrimethoxysilane and aqueous colloidal silica (58). The effects of the components on its colloidal, physicochemical and surface properties were studied.

It was found that the incorporation of 2-hydroxyethyl acrylate and 3-aminopropyltrimethoxysilane enhanced the Young's modulus, the tensile strength, the surface hydrophobicity, and the water resistance of the WPU films.

The introduction of silica nanoparticles further improved the modulus, tensile strength and water resistance of the films without damaging its surface hydrophobicity and transparency, due to the homogeneous dispersion of silica clusters in the WPU matrix (58).

3.4.5.3 Antibacterial Coatings

Because of the progress of nanotechnology in the past years, the fabrication of nanoscaled inorganic oxide or metallic particles has become possible (59). A small amount of metallic silver or silver ion is sufficient to kill bacteria by destroying a bacterial protein. Therefore, metallic silver and silver ions have been applied as antibacterial material.

A polymer emulsion can be prepared by blending a nanoscaled inorganic metal with the polymer that can be subsequently coated onto a variety of substrates to form thin films. The resulting film exhibits antibacterial properties even when only a small amount of nanoscaled inorganic metal or metal oxide is used.

A problem arises in that the particles can barely be uniformly dispersed in an organic polymer emulsion. The nanoscaled particles tend to flocculate together. To solve these problems, several approaches have been typically used (59):

1. Surface-modifying the nanoscaled particles, so that the particles can be dispersed in the organic polymer more easily,
2. Mixing the nanoscaled particles with a dispersing agent in advance, and then blending the mixture thus obtained with polymer, in which the dispersing agent is used as a medium, and
3. Blending the nanoscaled particles with a polymer having the property of a dispersing agent, so that the nanoscaled particles can be dispersed uniformly in the polymer by utilizing the polymer chain to separate the nanoscaled particles.

However, the approaches mentioned above have many drawbacks. For example, because the nanoscaled silver particles have to be synthesized first, and then modified and dispersed in the polymer, the manufacturing process becomes complicated and time-consuming.

Also, because the modifier or the dispersing agent may be adsorbed on the surface of the blended nanoscaled silver particles, the properties of the blended nanoscaled silver particles are less effective and the mechanical and thermal properties of the blended polymer may also be affected.

When the modifier is adsorbed on their surface, the effective weight of the surface-modified nanoscaled silver particles cannot be easily measured. In addition, the modified nanoscaled silver ion particles or nanoscaled silver particles with dispersing agent still cannot be completely uniformly dispersed. Importantly at present the sizes of commercially available nanoscaled silver particles are uneven in size.

A one-pot process has been developed for synthesizing silver-containing WPU in which a silver ion-containing solution is directly added into a WPU emulsion through the one-pot method. In this way, a stable silver-containing WPU emulsion could be produced (59).

A silver nitrate solution is added to WPU emulsion by stirring. The resulting solution shows a light brown color without aggregation or precipitation phenomenon, exhibiting that the stability of the silver-containing WPU emulsion is excellent.

It is known that a conventional WPU emulsion without the addition of silver nitrate solution shows a milky color. Due to the presence of hydrophilic groups in WPU, the resultant product is presented in emulsion form when WPU is dispersed in water. In addition, the WPU micelles can hardly aggregate together due to the surface electric charges. Therefore, the silver nitrate solution and WPU emulsion can be mixed well.

The silver ions in the silver nitrate solution tend to be attracted by the WPU's surface electric charges provided by the functional groups therein. Therefore, silver particles can be dispersed uniformly in the WPU emulsion when the silver ions are reduced to metallic silver.

The silver-containing WPU emulsion can stand for a long time, without the WPU micelles aggregating or precipitating. The silver particles in the emulsion have uniform size and can be well dispersed in the emulsion.

A uniform transparent thin film with a straw-yellow color can be obtained by coating the silver-containing WPU emulsion on a surface of a substrate at room temperature and then drying or dehydrating the coated substrate. A film formed by coating and drying the emulsion has a good transparency, thermal property and mechanical strength compared to a pristine product prepared by a conventional method.

The emulsion was evaluated under standard JIS Z 2801 method (60). The JIS Z 2801 and ISO 22196 standard test methods are used to evaluate the efficacy of antibacterial plastics, metals, and ceramics (60, 61).

The amount of *Staphylococcus aureus* apparently decreases on the surface of the PU film formed by the silver-containing WPU emulsion in which the amount of silver nitrate is 0.01% of WPU (59).

3.4.5.4 Electrochemical Cell

An electrochemical cell was built from poly(*p*-phenylene vinylene) as light-emitting material and lithium ion conducting WPU ionomer as solid electrolyte (62). The PU was prepared from a poly-(ethylene glycol), α,α'-dimethylol propionic acid and isophorone diisocyanate.

3.4.5.5 Zinc oxide Nanowhiskers

A WPU flowerlike ZnO nanowhiskers composite with different ZnO content up to 4% was synthesized via an in-situ copolymerization process (63). The ZnO consisting of uniform nanorods has been prepared using a hydrothermal method.

In order to disperse and to incorporate ZnO into the WPU matrix, the ZnO was modified with γ-aminopropyltriethoxysilane. The morphology of ZnO in WPU matrix was elucidated by a scanning electron microscope (SEM) technique.

The mechanical strength, thermal stability, as well as the water swelling of the composites were found to be strongly influenced by the ZnO content. An appropriate amount of ZnO with a good dispersion in the WPU matrix significantly improves the performance of such composites (63).

The mechanical properties are enhanced with an increase of the ZnO content up to 1% and above this content the mechanical properties decline. Also, the water resistance of the composites is remarkably enhanced due to ZnO. On the other hand, the thermal degradation temperatures of the composites with low content of ZnO decrease significantly.

The antibacterial activity of the WPU/ZnO composite films against *Escherichia coli* and *Staphylococcus aureus* increase with the increasing ZnO content. The best antibacterial activity was obtained using an amount of 4% ZnO (63).

3.4.5.6 Starch Nanocrystals

New nanocomposites of WPU as a matrix were prepared by filling a low loading of starch nanocrystals as the nanophase (64). The resultant starch nanocrystal/WPU nanocomposites show a significant enhancement in strength, elongation and Young's modulus. Obviously, the starch nanocrystals effect a simultaneous reinforcing and toughening.

With an increase of the loading of the starch nanocrystal, the self-aggregation of starch nanocrystals causes a size expansion of the nano phase, thus the mechanical performance decreases.

Also, it was verified that the chemical grafting onto the starch nanocrystal surface does not enhance the strength and elongation. Obviously, the chemical grafting inhibits the formation of a physical interaction and the network density in the nanocomposites increases (64).

In a subsequent study, starch nanocrystals with a distinct platelet-like structure similar to an exfoliated layered silicate were incorporated into WPU matrix at high loading levels (65). Previously, the starch nanocrystal loading level was restricted to lower than 8% because a self-aggregation of the starch nanocrystals resulted in its sedimentation during the process of preparation.

Subsequently, a good dispersion of the starch nanocrystal nanophase in the nanocomposites was observed, even when the starch nanocrystal loading level reached 30%.

A starch nanocrystal loading level of 10% showed the maximum tensile strength of 31.1 MPa and an enhanced Young's modulus, 35.7-fold over those of neat WPU (65).

When the starch nanocrystal loading level increased, the self-aggregation of the starch nanocrystals resulted in a decrease in strength. The rigidity of starch nanocrystal supported an increase in Young's modulus, which was highest in nanocomposites containing 30% starch nanocrystals. Thus, high performance WPU-based green bionanocomposites could be established (65).

The surface of starch nanocrystals could be functionalized by grafting with poly(caprolactone) (PCL) chains using a microwave ring-opening polymerization (66). Then, the modified natural nanoparticles were compounded into a PCL-based WPU as the matrix material. Here also, as before, a simultaneous enhancement of tensile strength and elongation at break was observed and similar other situations as described above.

3.4.5.7 Plasticized Starch Compositions

Biodegradable blends have been prepared from plasticized starch and poly(ε-caprolactone)-based WPU by casting and evaporation (67).

The blends show a good miscibility when the WPU content is lower than 20% due to the hydrogen bonding interactions between the carboxyl, carbonyl, and urethane groups of the WPU and the hydroxyl groups of starch. A phase separation occurred with an increase of WPU content.

The tensile strength of the blend containing 10% of WPU increased from 2.93 to 3.89 MPa. Also, the water uptake of the blends decreases because of the presence of WPU in the plasticized starch matrix. Therefore, the WPU plays an important role in improving the mechanical properties and water resistance of the starch-based material (67).

3.4.5.8 Organoclay Nanocomposites

Clay/WPU nanocomposites were synthesized from PU and an organoclay (68). The clay was organically modified using a swelling agent, i.e., 1,12-diaminododecane.

The characterization with Fourier transform infrared spectroscopy (FTIR) revealed that the addition of the clay does not affect the synthesis process of the WPU itself. X-ray diffraction and transmission electron microscopy experiments indicated that the clay retains a layer structure in the clay/WPU nanocomposite.

The molecular weight decreases with increasing content of clay. Thermogravimetry (TG) results revealed that the addition of the clay increased the temperature of thermal degradation by some 15°C (68).

3.4.5.9 Self-Curable Waterborne Hybrid Poly(urethane)s

Room temperature self-curable silanized WPUs were synthesized using the acetone process (69). As curing agent covalently linked 3-aminopropyltriethoxysilane was used. FTIR confirmed the incorporation of this curing agent.

There is an increase in particle size due to the effect of the (3-aminopropyl)triethoxysilane. This is more pronounced at higher concentrations due to the condensation of the alkoxysilane groups. The presence of silanol groups on the particle surface was demonstrated by ζ-potential measurements.

All the samples could be cured at room temperature. The extent of curing was dependent on the concentration of (3-aminopropyl)-triethoxysilane and the curing temperature (69).

3.4.5.10 Soy Protein Plastics Plasticized with Waterborne Poly(urethane)

A soy protein isolate plastics was prepared by using a WPU as plasticizer (70). The WPU was prepared via the emulsion extending chain method. Then the WPU was mixed with the soy protein in an aqueous dispersion (70). The mixture was cast, cured, pickled and hot-pressed to eventually form the protein isolate plastics plasticized with WPU.

The characterization experiments revealed that the compositions have good mechanical properties, good water resistance, optical transmittance and thermal stability. This arises because of the good miscibility and strong interactions between the WPU and the protein isolate (70).

3.4.5.11 Crosslinked Poly(urethane) Dispersions

The stringent environmental regulations have endowed dispersible coatings with excellent property profiles in industrial applications. In this aspect, aqueous PU dispersions are of special interest (71).

The synthesis of hydroxylated polyester-based PU polyols has been reported. These compounds contain internal carboxyl group with different diisocyanates. The PU polyols were partly acetoacetylated with ethyl acetoacetate to incorporate a β-ketoester in the PU polyol backbone. The PU dispersions were crosslinked with hexamethoxy methyl melamine (71).

3.4.5.12 Hyperbranched Poly(urethane) Dispersions

Waterborne hyperbranched PU acrylates for UV-curable aqueous dispersions have been prepared (72). These are based on hydroxy-functionalized hyperbranched aliphatic polyesters.

The effects of the overall composition, including acidic and acrylate groups, and functionality of hyperbranched polyester, were studied in terms of particle size, rheology, and photopolymerization kinetics. Also, the mechanical and thermal properties were assessed.

The average particle sizes of the aqueous dispersions were 43–134 nm, as found by laser light scattering. The stability and the particle size are dependent on the amount of carboxylic acid groups, degree of neutralization, and the molecular structure.

The dispersions belong to pseudoplastic fluid types. The shear thinning behavior of waterborne hyperbranched PUs is more pronounced for the lower generation of hyperbranched polyester.

TG experiments using the cured films indicated a good thermal stability with no appreciable weight loss until 200°C. An increase in the hard segment content provoked an increase in the thermal degradation temperature (72).

3.4.5.13 Imide Modified Poly(urethane)s

Imide groups have been introduced in the hard segment of UV-cured PU dispersions by extending the $-N{=}C{=}O$ terminated prepolymers with pyromellitic dianhydride (73). The soft segments were prepared from poly(tetramethylene ether) glycol 4,4′-methylene dicyclohexyl diisocyanate, hexamethylene diisocyanate, and 7,12-dimethylbenzanthracene.

It was found that the imide hard segment resulted in remarkably high mechanical properties as well as thermal stability in comparison to conventional urethane hard segments. These results were interpreted in terms of the partial mixing of soft segments and the imide hard segments (73).

3.4.5.14 Effects of Crosslinking

Films from WPU and carboxymethylated guar gum with contents of 20–80% were prepared by solution casting (74). These materials were crosslinked with $\mathrm{CaCl_2}$. The effect of the content of carboxymethylated guar gum on the miscibility, morphology and physical properties of the blend films was investigated by FTIR, SEM, density measurements, differential scanning calorimetry, TG, water sensitivity measurements, solvent-swelling, and tensile tests.

The results of these tests indicate that the uncrosslinked films exhibit a good miscibility when the content of carboxymethylated guar gum is lower than 60%, whereas a typical *sea-island* structure occurs when the carboxymethylated guar gum content further increases.

After crosslinking with Ca^{2+} ions, the blend films form a relatively dense architecture, which results in a better miscibility, higher storage modulus, and thermal stability.

Also, the crosslinked films exhibit a better tensile strength of 11.6–56.5 MPa and solvent-resistance than the non-crosslinked films over the entire range of composition. A model that describes the configuration of Ca^{2+} chelating structure has been proposed (74).

3.4.5.15 Self-Crosslinking Waterborne Poly(urethane)s

A specific crosslinking agent for PU has been developed (75). *N*-[(1,1-Dimethyl-2-acetyl)ethyl]-β-dihydroxy ethylamino propanamide (DDP) was synthesized by a Michael reaction using diethanolamine and diacetone acrylamide.

DDP is a dihydroxyl-containing compound with a ketone moiety, which crosslinks during the film formation through a reaction between ketone of DDP and the hydrazide in water soluble dihydrazide compound that is added in the course of the preparation of the WPU.

The optimal molar ratio of diethanolamine and diacetone acrylamide used for the Michael reaction was determined by gas chromatography to be 1.05. Highest yields of 80% were obtained with this ratio when the reaction was carried out at 90°C at 12 *h* reaction time using acetonitrile as solvent.

The experimental conditions for the separation of DDP from the reaction mixture were predetermined first through thin-layer chromatography. The DDP separation was done by column chromatography. A DDP with a purity of 97% could be obtained. The structure of DDP was fully characterized by infrared and nuclear magnetic resonance spectroscopy.

PU latexes with DDP and post-added dihydrazide were prepared, and polymer film properties compared with DDP-free latex film. The tensile strengths increased with a decrease in elongation in the crosslinked polymers. Also, a higher performance in water and solvent adsorption was found (75).

3.4.5.16 Compositions without N-Methyl pyrrolidone

Many poly(urethane) dispersions contain *N*-methyl-2-pyrrolidone (NMP) because it is often a required component in the polymerization process. In fact, NMP has been the solvent of choice for the widely used prepolymer mixing process for the synthesis of aqueous PU dispersions. This particular solvent reduces the prepolymer viscosity during the production steps to enable smooth handling and dispersing of the prepolymer. NMP also supports the coalescence of the dispersion particles when the dispersion is applied to a substrate, and thereby facilitates film formation.

Unfortunately, various studies have suggested that NMP may be a fetotoxin. Recent studies on NMP have resulted in labeling NMP as a toxic substance (76). Formulations containing at least 5% NMP have to be labeled as being irritant and toxic.

Therfore, a worldwide effort in the paint industry has been made to eliminate NMP from coating formulations.

Alternative production processes have been developed to make aqueous Poly(urethane) dispersions without NMP. A process for forming a waterborne composite PU/acrylic polymer dispersion without the use of *N*-methyl pyrrolidone has been described (77). This process comprises:

1. Introducing a reaction mixture to an organic solvent medium, the reaction mixture comprising:
   (a) A polyisocyanate,
   (b) A polyol, and
   (c) A reactant containing both hydroxyl and carboxylic acid functional groups, wherein the organic solvent medium is essentially free of *N*-methylpyrrolidone and comprises an alkyl carbonate,
2. Allowing the reaction mixture to polymerize and yield a poly(urethane) polymer in the organic solvent medium, the poly(urethane) polymer having terminal isocyanate functional groups and pendant acid functional groups,
3. Adding a monoamine to the organic solvent medium to neutralize pendant acid functional groups on the poly(urethane) polymer,
4. Adding one or more ethylenically unsaturated monomers to the organic solvent medium,
5. Inverting the organic solvent medium containing the poly(urethane) polymer and ethylenically unsaturated monomers into an aqueous medium containing one or more polyamines to form an aqueous dispersion,
6. Adding a free radical polymerization initiator to the aqueous dispersion,
7. Holding the aqueous dispersion at a temperature and for a time sufficient to polymerize the ethylenically unsaturated monomers and yield a waterborne composite poly(urethane)/acrylic polymer dispersion, and
8. Heating the aqueous dispersion to a temperature and for a time sufficient to hydrolyze the alkyl carbonate.

An example that demonstrates the synthesis of a dispersion using NMP as a solvent is shown in Table 3.9. However, it has been demonstrated that all the NMP used in Table 3.9 can be replaced by propylene carbonate (77).

Table 3.9 Synthesis of a dispersion (77).

Feed	Ingredient	Parts per weight
1.	*N*-Methyl pyrrolidone	69.8
	Poly (1,6-hexanediol adipate)(FORMEZ® 66-561)	134.9
2.	Methoxy poly(ethylene glycol)	34.0
	Dimethyl propionic acid	23.6
3.	*N*-Methyl pyrrolidone	5.3
	Isophorone diisocyanate	99.8
4.	Dibutyltin dilaurate	0.27
	N-Methyl pyrrolidone	2.6
5.	Methyl methacrylate	110.6
	Butyl acrylate	76.4
	Ethylene glycol dimethacrylate	7.8
6.	Dimethyl ethanol amine	15.7
7.	Deionized water	1339.3
	Diethylene triamine	12.8
8.	Ammonium persulfate	0.7
	Deionized water	7.2

3.4.5.17 Waterborne Poly(urethane) Wood Coatings

Water-based coatings applied on wood are increasingly used for the respect of environmental legislation. The advantages of the reduced impact on the user and the environment have been progressively associated to a high level of quality of coatings, that are comparable to solvent-based coatings (78).

One of the requirements of coatings for furniture and interiors is the wide variety of aesthetic finishes and the ability to maintain a long-term appearance, color stability, and gloss stability.

The durability of WPU coatings with different aesthetic properties has been elucidated. Samples were artificially weathered by UV exposure. Color and gloss measurements were done to evaluate possible aesthetic changes. FTIR was used to determine a chemical degradation of the polymers. The falling abrasive test has been used to simulate the coating abrasion (78).

The results indicated differences between transparent and pigmented coatings and the influence of initial surface roughness and gloss properties (78).

3.4.5.18 Eco-friendly Functional Floor Plates

Three types of nonmetallic mineral particles, calcium carbonate, titanium oxide, and loess, were incorporated into WPU acrylate in order to improve the surface properties of ecofriendly floor tiles (79).

Several properties of the WPU acrylate containing nonmetallic mineral materials were measured using FTIR, dynamic mechanical thermal analysis, swelling tests, and contact angle measurements.

When the molecular weight between the crosslinks is decreased by the variation of the molecular weight of the polyol, the modulus and glass transition temperature of the WPU acrylate film increase, because of an increase in the crosslinking density.

The resistance properties, such as swelling and the contact angle against water, can be enhanced by the addition of the mineral particles. This arises because of an increased hydrophobic nature of the polymer matrix (79).

3.4.5.19 Biocompatible Elastomer of Waterborne Poly(urethane)

Biocompatible WPU based on castor oil and poly(ethylene glycol) (PEG) filled with low level loadings of *Eucalyptus globulus* cellulose nanocrystals was prepared (80).

The cellulose nanocrystals could be obtained by sulfuric hydrolysis and consisted of rod-like crystals with an average length of 518.0 ± 183.4 nm and an average diameter of 21.7 ± 13.0 nm.

The nanocomposites with low level loadings of cellulose nanocrystals showed a significant enhancement in the tensile strength from 5.43 to 12.22 MPa and Young's modulus from 1.16 to 4.83 MPa. It has been shown by SEM that the cellulose nanocrystals were well dispersed in the WPU matrix.

Further, the cellulose nanocrystals favored the microphase separation of the hard segments and the soft segments of the WPU. This causes shifts of the glass transition temperature and the melting temperature to higher temperatures (80).

3.4.5.20 Shape-Memory Polymers

Shape-memory polymers are a class of smart materials that offer a mechanical action that is triggered by an external stimulus (81). Shape-memory polymers feature a large strain elastic response and extensibility, but temporary shapes can be stored through network chain immobilization by vitrification, crystallization or some other mechanisms.

For example, a complex three-dimensional shape-memory polymer shape can be compacted into a slender form by a cycle of heating to a rubbery state, elastically deforming this rubbery state, cooling to immobilize the network chains, and unloading. Later, the application of heat, light, or solvent exposure can trigger a return to the equilibrium shape through network chain mobilization.

In terms of the macromolecular architecture, shape-memory polymers are responsive polymers that contain crosslinked network polymer backbones, where the polymer backbones between the crosslinking junctions are crystallizable or glassy and can behave as a switching segment (81).

Shape-memory polymers can be fixed into a deformed temporary shape and later recover to a permanent shape memorized by the crosslinked network structure upon a stimulus, that is most commonly heat. Generally, shape-memory polymers are stiff materials at the shape-fixed state due to the primary mechanism of shape fixing, i.e., crystallization or vitrification of their network polymer backbones. Thus, a large force can be generated during the shape recovery.

Although shape-memory polymers and waterborne polymer coatings are known as such, their combination is a new concept. Shape-memory polymers have three main components along their backbone, including a (81):

1. Switching segment for shape fixing,
2. Ionically charged group for water dispersion, and
3. Crosslinkable group for shape-memory.

Examples of waterborne shape-memory polymers have been prepared that when applied to fibers, such as hair, from an aqueous solution impart shape-memory to the hair. Also, batches of waterborne shape-memory polymers have been synthesized and are proven to work.

The waterborne shape-memory polymers can be added as a coating to the fibrous substrate for improved performance under wet or dry conditions, and have other enhanced performance characteristics. For example, a fibrous substrate can have coated thereon a waterborne shape-memory polymer that facilitates imparting a shape-memory effect that can serve to cause a texture change upon wetting, so that after wetting a fibrous structure, such as a paper towel, it can have a three-dimensional texture for better cleaning performance.

Possible industrial and medical applications for waterborne shape-memory polymers are temperature sensors and actuators as bulk materials, as well as a self-repairable coating where a scratch can be healed simply by heat (81).

A water-triggered shape change or actuation may find use in household products that dispense material upon contact with water, medical products that dispense a drug or other material upon contact with body fluids, or industrial products that cause a desired shape change upon exposure to water as an autonomous control system that protects devices or materials from water without need for a complex water sensor and control electronics.

Also, photo-curable waterborne shape-memory polymers have been developed. The switching segment has a phase transition temperature like the melting temperature or the glass transition temperature above room temperature in the range of 40–80°C. Materials for switching segments are shown in Table 3.10.

Table 3.10 Materials for switching segments (81).

Semicrystalline materials	
Poly(ε-caprolactone)	Poly(δ-valerolactone)
Poly(γ-hydroxybutyrate)	Poly(β-hydroxybutyrate)
Poly(β-hydroxypropionate)	Poly(β-hydroxyoctaonate)
Poly(*L*-lactide)	Poly(D-lactide)
Poly(glycolide)	Poly(tetramethylene succinate)
Poly(trimethylene succinate)	Poly(ethylene succinate)
Poly(tetramethylene adipate)	Poly(trimethylene adipate)
Poly(ethylene adipate)	Poly(tetramethylene sebacate)
Poly(trimethylene sebacate)	Poly(ethylene sebacate)
Poly(ethylene oxide)	Poly(oxymethylene)
Amorphous materials	
Poly(*D*,*L*-lactide)	Poly(vinyl acetate)
Poly(methyl methacrylate)	Poly(methyl acrylate)
Atactic poly(styrene)	

The semicrystalline and amorphous switching segments from Table 3.10 should be functionalized at the chain ends to get incorporated into the shape-memory polymer chain. Suitable functional groups at the chain ends of the switching segment are hydroxyl, carboxyl, amino, mercapto, and vinyl groups.

The crosslinking by means of the crosslinkable unit can be done by either chemical or physical crosslinking. Chemical crosslinking should occur in the bulk state and can be a photo-induced or heat-induced cycloaddition reaction, a Menschutkin reaction, or a Huisgen cycloaddition reaction.

Physical crosslinking can be achieved by hydrogen bonding, ionic association, and crystallization. Among these physical crosslinking methods, crystallization is considered to be the most stable crosslinking in a broad temperature range below the melting temperature. On the other hand, when the crystallization of the crosslinkable unit is selected as the physical crosslinking reaction, the melting transition temperature should be higher than that of the switching segment.

The chargeable unit includes cationically and anionically chargeable groups. Chargeable groups are summarized in Table 3.11.

Table 3.11 Chargeable groups (81).

Anionically chargeable groups	
2,2-Bis(hydroxymethyl)propionic acid	2,3-Dihydroxy-1-propanesulfonic acid
β-Glycerophosphoric acid	
Cationically chargeable groups	
2-Amino-1,3-propanedithiol	1,6-Heptadien-4-amine
Bis(2-sulfanylethyl)amine	Diallylamine
Methyldiallylamine	*N*,*N*-Bis(2-mercaptoethyl)methylamine
N-Methyldiethanolamine	*N*-Methyldipropanolamine

Examples of compositions are shown in Table 3.12. The synthesis methods of the compounds listed in Table 3.12 have been detailed (81).

Table 3.12 Examples of compositions (81).

Compound	Function
Thermoplastic PUs synthesized from PCL diol	Switching segment
2-Ethyl-2-Cinnamoyloxymethyl-1,3-propanediol	Crosslinkable unit
N-Methyldiethanolamine	Chargeable unit
1,6-Hexanediisocyanate with tin catalyst dibutyltin dilaurate	Catalyst

3.4.6 Acrylic Coatings

A one-component, ambient curable waterborne coating composition based on acrylic materials has been described (82). The self-crosslinking water-based acrylic latex was made using the components and amounts listed in Tables 3.13 and 3.14 according to the following procedure.

Preparation 3–1: Charge No. 1 was added to a 5 l, 4-necked flask equipped with a motor driven stainless steel stir blade, a water-cooled condenser, a nitrogen inlet, and a heating mantle with a thermometer connected through a temperature feedback control device. The contents of the flask were heated to 80°C and held at that temperature for about 10 min for temperature stabilization. During this hold, Charge No. 3 was premixed and added to the flask over 5 min was added. Then 1/6 of monomer premixed Charge No. 2 over 30 min and held at 80°C for 15 min. Charge No. 5 was then added into remaining Charge No. 2 premix and mixed for about 15 min. Charge No. 2 remainder was added over 150 min and premixed Charge No. 4 was added over 210 min. Charge No. 6 was used as a rinse for Charge No. 2. After the completion of Charge No. 4, the reaction was held for 30 min at 80°C. The batch was cooled to 50–60°C and premixed Charge No. 7 was added at 50-60°C and then held for 5 min. Charge No. 8 premix was then added over 5 min and held for 30 min. After 30 min, the contents of the flask were cooled to room temperature, Charge No. 9 and No. 10 were added, and held 30 min at room temperature. Charge No. 11 was then added at room temperature and held for 15 min. The latex pH was adjusted to 8–9 using dimethylethanolamine. A sample of the acrylic latex was placed in a 50°C hot room for 28 d, and the resin remained as emulsion.

The resulting emulsion has a solids content of 42% measured for 1 h at 110°C, a density of 1.04 $g\,cm^{-3}$, and a pH of 9.0. The emulsion

Table 3.13 Components for a water-based acrylic latex (82).

Ingredients	Parts per weight
Charge No. 1	
Distilled water	592.07
Rhodapex AB/201	4.84
Ammonium Carbonate	0.75
DMEA	1.91
Charge No. 2	
Distilled water	215.9
Diacetone Acrylamide	37.62
Adeka Reasoap SR103	1.08
Ammonium Carbonate	0.67
Rhodapex AB/201	9.60
Methacrylic Acid	4.0
Methyl Methacrylate	360.0
Ethyl Hexyl Acrylate	190.0
Styrene	200.0
Charge No. 3	
Distilled water	13.36
Ammonium Peroxydisulfate	0.83
Charge No. 4	
Distilled water	79.96
Ammonium Peroxydisulfate	1.17
Charge No. 5	
Distilled water	25.49
PAM-1004	8.51

Table 3.14 Components for an water-based acrylic latex (82).

Ingredients	Parts per weight
Charge No. 6	
Distilled water	47.95
Charge No. 7	
Distilled water	7.30
tert-Butyl Hydroperoxide (70%)	0.58
Charge No. 8	
Distilled water	27.07
Erythorbic Acid	0.67
Charge No. 9	
Sipon L-22	2.17
Charge No. 10	
Adipic Acid Dihydrazide	19.39
Distilled water	111.9
Charge No. 11	
Acticide	0.42

can be cured in a relatively short period of time to provide films that have good early properties which allow for handling of the coated objects without detrimentally affecting the film appearance and which ultimately cure to films which exhibit excellent hardness, solvent resistance and impact resistance (82).

3.4.7 Epoxy Coatings

Waterborne coatings are dispersions of special formulations of the resins with suitable surfactants. These materials can be applied by electrodeposition techniques. Powders can be applied as coatings by fluidized-bed techniques.

Waterborne epoxy acrylate-butylated melamine formaldehyde coatings and ferrite (Fe_3O_4) dispersed nanocomposite coatings have been developed to effectively replace hazardous solvent-borne polymeric coatings (83).

The Fe_3O_4 nanoparticles in the matrix act as filler, which fill the pinholes, interstitial crosslinked spaces, microcracks, and voids. This increases the strength of the coating materials.

Also, the coatings were found to be effective in restricting the penetration of aggressive ions by forming a strong barrier layer at the metal interface (83).

Thermoset nanocomposites were prepared from a waterborne terpene maleic ester type epoxy resin and cellulose nanowhiskers (84). The curing behavior of the nanocomposites were measured using a rotational rheometer. The storage modulus of these nanocomposites increased with the increase of the content of the cellulose nanowhiskers.

The incorporation of cellulose nanowhiskers into the matrix caused a microphase separation and destroyed the compactness of the matrix. This leads to a small decrease of the glass transition temperatures. The addition of the cellulose nanowhiskers results in an excellent reinforcement effect on the matrix, due to the formation and increase of interfacial interaction by hydrogen bonds (84).

3.4.8 Phenol Resins

Generally, waterborne laminating phenol resins are similar to the solvent-borne types except that they lack an organic solvent and usually have lower molecular weight than their solvent-borne counterparts. Because they have lower molecular weight, they typically have a higher level of free phenol.

3.4.9 Amide Resins

For waterborne polymers, which could be cured at ambient temperature, acetoacetoxyethyl methacrylate containing copolymers have been synthesized (85).

Acetoacetoxyethyl methacrylate is an ambient crosslinking monomer that, when incorporated into architectural coating binders, provides coatings with improved hardness, scrub, stain, and dirt pick-up resistance (86).

Immediately after synthesis, well-cured films could be obtained. However, a decline in the film performance was observed that correlated with the age of the copolymer solution or dispersion (85).

So it was decided to replace the acetoacetoxyethyl methacrylate by an amide type monomer, 3-isopropenyl-α,α'-dimethylbenzyl acetoacetamido, which was synthesized from 3-isopropenyl-α,α'-dimethylbenzyl isocyanate.

This new monomer did not homopolymerize but was found to copolymerize readily with styrene or *n*-butylacrylate. Films from polymers that contained the new monomers showed equal or better properties than films obtained from polymers containing acetoacetoxyethyl methacrylate. It could be confirmed that the new monomer did not hydrolyze over a period of one year at ambient temperature (85).

Waterborne linseed poly(ester amide) clay composites have been prepared by a microwave-assisted route to increase the application of biobased materials like seed oils (87). These composites may serve as prospective candidates in the area of environmentally friendly waterborne protective coatings. They can be safely used up to 290°C.

3.4.10 Poly(carbodiimide)s

Coating compositions in which all of the components are stored together in a single container are desirable in many cases from the standpoint of convenience to the end user (88). Among the properties that such coating compositions should exhibit is storage stability. In other words, the viscosity of the composition should not significantly increase over time to the point in which the composition is no longer suitable for convenient use for depositing a coating.

In many cases, it is desirable to use liquid coating compositions that are borne in water as opposed to organic solvents. This desire stems primarily from environmental concerns with the emission of VOC during the painting process.

Coating compositions were developed, containing (88):

1. Poly(carbodiimide),
2. Ketocarboxylic acid, and
3. A compound with moieties reactive with keto functional groups, such as diamines and polyamines.

A water-based poly(carbodiimide) resin was made using the ingredients listed in Table 3.15.

Table 3.15 Water-based poly(carbodiimide) resin (88).

Compound	Parts
Desmodur® W (methylene-bis-(4-cyclohexyldiisocyanate))	280
Phospholene oxide	4.2
Dibutyltin dilaurate	0.024
Methylisobutylketone	170
Aliphatic polycarbonate diol, PC-1122	259.3
Jeffamine® M1000 (XTJ-506) (polyetheramine)	216.5
Deionized water	1500
Abex® 200 (anionic surfactant)	48.28

3.4.10.1 Compressable Substrates

Many substrates, such as textiles, thermoplastic poly(urethane), ethylene-vinyl acetate foam and leather, have a significant amount of flexibility (89). It is often desirable to coat these substrates with a coating to improve its appearance, water resistance, chemical resistance, scratch resistance, ultraviolet resistance, or durability. It may also be desired to coat or to decorate these substrates to provide an improved appearance, or to apply a pattern. Many coatings that improve these properties are rigid coatings suitable for use only on rigid substrates. When a rigid coating, such as an acrylic coating, is applied to a flexible substrate, the coating will often crack and peel away from the substrate when the substrate is flexed. Accordingly, a flexible coating suitable for use on flexible substrates is desired.

It is often desirable to maintain color uniformity among these various components. However, when the components are made of different types of materials, it can be difficult to provide a uniform visual appearance of the article when the components are assembled.

For example, footwear, such as athletic shoes, often contain different types of materials such as natural leather, synthetic leather, vinyl, fabric, foam, or rubber. A different coating composition is conventionally applied to each type of the substrate.

Also, it is common to incorporate pigments into foam midsoles of shoes in order to impart a color to the midsole. The use of multiple specialized coatings and pigments may result in relatively complex and costly manufacturing processes. Color matching is a process by which the visual characteristics of more than one coating are matched so that two or more coatings give the same or substantially same appearance.

While color-matched components may have substantially the same appearance in some viewing and illumination conditions, they may not maintain the same appearance when the viewing angle is changed, or when the spectral distribution of the light source is changed.

A coating composition capable of coating various different types of substrates of an article of manufacture while eliminating the need to do color matching has been developed. A compressible substrate can be coated with a waterborne coating composition comprising (89):

1. One base neutralized active hydrogen containing film-forming resin, and
2. A water-dispersible carbodiimide crosslinker capable of reacting with the film-forming resin to form a crosslinked film.

Suitable acrylic or methacrylic polymers include copolymers containing carboxylic acid groups and acid groups of sulfur and phosphorus. Acid monomers include acrylic acid, methacrylic acid, maleic acid, fumaric acid, crotonic acid, itaconic acid, 2-sulfo ethyl methacrylate, 2-acrylamido-2-methyl-1-propane sulfonic acid, methacrylamido methyl phosphonic acid, and 2-phosphoethyl methacrylate. The presence of these acid groups facilitates dispersing the acrylic polymer in water in the presence of a base neutralizing compound.

A suitable water-dispersible carbodiimide crosslinker is dicyclohexyl carbodiimide. Also, oligomeric or polymeric carbodiimide crosslinkers can be used (89). Some carbodiimides are commercially available.

3.4.11 Silicones

A method for providing a waterborne, inorganic barrier coating to a polyolefin substrate has been described. The coating of thermoplastic polymer substrates with moisture-resistant barrier coating compositions is used to achieve impermeability to gases such as oxygen, and liquids.

A metallized polymeric film structure has been used to create both an oxygen barrier and a moisture barrier (90). The barrier material consists of crosslinked PVA and the moisture barrier is metallized oriented poly(propylene) or poly(ethylene).

The term *waterborne coatings* refers to coatings that are applied from solutions in which the solvent is primarily water, but may also contain smaller amounts of organic cosolvents.

However, the conventionally used barrier coatings do not accommodate the need in the market for longer shelf life of packaged food. Further, many of these products, e.g., films coated with aluminum, are not microwave-safe, or are not readily disposable, e.g., films coated with poly(vinylidene chloride), and thus fail to satisfy current environmental concerns (91).

A newly developed method targets promoting the wetting of waterborne barrier coating solutions on poly(olefin) substrates and adhesion of resulting inorganic barrier layers to polyolefin substrates by applying a selected primer composition to the substrate before application of the barrier coating solution. The improved adhesion of dried inorganic barrier layers manifests in an improved vapor barrier performance. In particular, the method consists of (91,92):

1. Applying a primer layer containing PVA or poly(*p*-hydroxystyrene) to the poly(olefin) substrate,
2. Allowing the primer layer to dry, and
3. Applying the waterborne coating solution, which eventually forms a dry inorganic barrier layer over the dried primer layer.

The polymeric articles to be coated by the primer and the coating composition may be previously untreated. Usually, the polymeric article, such as a film or bottle, is first plasma treated to improve its wetting by the primer solutions and adhesion of the dried primer layer. Alternatively, the polymeric article may be corona treated by a corona discharge treatment method. Other surface treatments are flame treatment and chemical oxidation, or etching.

The inorganic waterborne coating contains an alkali metal polysilicate, such as sodium polysilicate, potassium polysilicate, or lithium polysilicate. Also, a mixture of two different alkali metal polysilicates can be used. Another barrier coating contains a selected layered silicate, e.g., a delaminated vermiculite dispersed in a solid matrix of an alkali metal polysilicate (91).

3.5 Special Applications

3.5.1 Waterborne Silicone Mold Release Agents

Silicones can be used as mold release agents in the rubber and plastics industries. Molds made from silicone rubber itself are common.

Silicone resins are typically applied to surfaces by dissolving the silicone resin in volatile solvents. The evaporation of the solvent leaves behind the silicone resin in the desired location, e.g., on the surface of the mold for release, or in the cavities and interstices of the port as a sealant. Then, with the application of heat or chemicals, the resin is cured in-situ, forming a hard, polymeric network.

Waterborne silicone release agents are common. An advantage of using water as a carrier is that the presence of water can prevent or delay the silanol condensation of the resin. A catalyst may be added and stored in a water-based composition without inducing immediate curing. Hence, the use of water as a carrier improves the shelf life of the composition.

The most significant difficulty associated with using water as a carrier is that silicone resins are relatively immiscible in water. Water-based silicone resin compositions can be formulated using conventional surfactants. Large amounts of surfactant, however, are usually required, and the dispersion formed may not be very stable. The dispersion can be stabilized with a hydrophobically modified polycarboxylic acid (93).

3.5.2 Stabilizers for Sandy Soil

Waterborne polymer emulsion systems were used for the structural modification of sandy soils (94). Three emulsions were tested, a styrene-acrylic copolymer emulsion, and two vinyl-acrylic, copolymer-based emulsions. The samples were prepared by adding the polymer emulsions to the sand and water.

The performance of the different emulsion systems as sand stabilizers was estimated by the measurement of the hydraulic conductivity and the compressive strength.

The measurements of the hydraulic conductivity were done in a flexible membrane test apparatus. The hydraulic conductivity for the three emulsions decreased at different rates, with an increase in polymer content up to 3%. An additional increase of the polymer content did not introduce a significant decrease in hydraulic conductivity. At 5% content, all the emulsions had essentially the same effect.

The compressive strength and the modulus of elasticity increased at a higher concentration of polymer. SEM revealed that the reduction in the permeability and the improved mechanical properties can be attributed to three dominant structural changes (94):

1. The development of interconnecting ties between the sand particles,
2. The development of adhesion between neighboring sand particles in contact, and
3. The covering of the sand particles with a thin polymer film.

3.5.3 Water, Oil, and Stain Repellency

The use of waterborne fluoropolymer solutions for treating hard surfaces, such as masonry, have been described in order to impart water, oil, and stain repellency.

3.5.4 Protective Coatings for Culturally Significant Objects

Protective coatings are commonly used to protect culturally significant works such as outdoor sculptures and architectural elements (95). The cost of damage due to corrosion is much higher than that of more common coating applications.

Coatings that have both a chemical and a physical intelligence may offer a superior weatherability and can act as better barriers to water absorption than commonly used materials such as waxes and acrylics.

It was found that the use of waterborne resins containing poly(vinylidene fluoride) with nanoclays of laponite significantly improved the performance. This may be a viable option in the protection of materials that are important for cultural heritage (95).

3.5.5 Waterborne Adhesives

Water-based adhesives have been reviewed among other adhesive types in a monograph (96).

Copolymerizing an acrylic acid comonomer is often beneficial for the adhesive properties of waterborne pressure-sensitive adhesives (97).

Poly(acrylic acid) (PAA) has been distributed as a percolating network within a pressure-sensitive adhesive film formed from a polymer colloid. A diblock copolymer composed of PAA and poly(*n*-butyl acrylate) blocks was synthesized using a reversible RAFT polymerization.

This material was adsorbed onto soft acrylic latex particles prior to their film formation. The thin adsorbed shells on the particles can create a percolating network that raises the elastic modulus, creep resistance, and tensile strength of the final film. At pH 10, ionomeric crosslinking occurs and a high tack adhesion is obtained together with a high creep resistance.

Thus, the addition of an amphiphilic PAA and poly(*n*-butyl acrylate) diblock copolymer to a soft latex is a simple method of tailoring the mechanical and adhesive properties of the resulting composite films (97).

3.5.6 Latex

The feasibility of obtaining specialty waterborne adhesives in a continuous stirred-tank reactor was investigated for the possibility of replacing the traditional semi-batch reactors, which are commonly used in their production, with a more efficient system (98).

The key aspects which were focused on were the safety of the process, the kinetic feasibility, and the quality of the products, having as a reference the adhesive performance of the polymers produced in the semi-batch reactors.

Simulations showed that the production of 280 tons per week could be safely carried out even using mean residence times as short as 10 min.

From a kinetic point of view, it was found that under these conditions, reasonably high conversions could be achieved in the reactor, resulting in a high production per unit volume of reactor.

Furthermore, the adhesive properties of the latex were assessed. A much higher shear resistance was found for the latexes produced in the continuous reactor, while peel resistance and tack were found to be very similar regardless of the type of reactor used (98).

3.5.6.1 Ethylene-Vinyl acetate Copolymers

Ethylene-vinyl acetate aqueous emulsion copolymers containing high concentrations of functionalized monomers have been used as waterborne adhesives.

The incorporation of large amounts of functionalized monomer in the growing ethylene-vinyl acetate polymer creates a polar micellar environment that discourages the migration of gaseous ethylene to the micelles. Functionalized monomers are shown in Table 3.16.

The use of water-insoluble comonomers with acrylic acid and the incorporation of 0.5–7% of acrylic acid has been described (99). Additional additives are collected in Table 3.17.

The functionalized ethylene-vinyl acetate polymers can exhibit pH sensitivity, have good emulsion stability, are water soluble or water-dispersible, cast clear and form tough films, and can redisperse readily in water after drying.

These functionalized ethylene-vinyl acetate aqueous emulsion copolymers have applications as adhesives, thickeners, alkali-sol-

Table 3.16 Functionalized monomers (100).

Compound
2-Hydroxy-2-sulfinicacetic acid
Styrene sulfonic acid
2-Acrylamido-2-methylpropane sulfonic acid
Sodium vinyl sulfonate
Styrene phosphoric acid
Sodium vinyl phosphonate,
Acrylic acid
N-Methylol acrylamide

uble polymers, redispersible adhesives, graft copolymers, crosslinkable polymers, binders, hair care polymers, nonwoven fabric adhesives, protective topcoats, floor polishes, temporary printing binders, adhesive binders, skin creams, sunscreens, temporary decorative paints, marine coatings, repulpable paper coatings, nonwoven fabric binders, glass fiber sizers, erodible coatings, antiperspirant films, and thermoset replacements (100).

3.5.6.2 Terpene Resins

Pressure-sensitive adhesives are used for adhesive tapes and labels. The substrates include paper, poly(vinyl chloride), polyester, poly(propylene), or cellophane (101).

Pressure-sensitive adhesives can be prepared via hot melts, solvents, and waterborne systems. In solvent-containing systems, formulations with a high content of solid material are possible, requiring a minimum solvent recovery. Mixtures of polyterpene resins with different molecular weights can be used to establish the desired adhesive properties.

For waterborne applied systems, the structural polymer and the tackifying resin must be supplied as dispersion. No solvent recovery system is necessary. For waterborne systems, the manufacture via rosin esters is easier than the emulsification of polyterpene resins. For carboxylated styrene butadiene rubber, pure polyterpenes are suitable. For neoprene and acrylic rubbers, terpene phenol polymers are used.

Table 3.17 Additives (100).

Plasticizers	Plasticizers
Acetyl tributyl citrate	Butyl benzyl phthalate
Butyl phthalyl butyl glycolate	Dibutyl phthalate
Dibutyl sebacate	Diethyl phthalate
Diethylene glycol dibenzoate	Dipropylene glycol
Dipropylene glycol dibenzoate,	Ethyl phthalyl ethyl glycolate
Ethyl-*p*-toluene sulfonamide	Hexylene glycol
Methyl phthalyl ethyl glycolate	Tributoxyethyl phthalate
Tackifiers	Tackifiers
Coumarone-indene	Gum rosin
Hydrocarbon resins	Hydrogenated rosin
Rosin esters	Tall oil rosins
Terpene resins	Wood rosin
Thickeners	Thickeners
Ethoxylated poly(urethane)s	Aliginates
Bentonite	Casein
Fumed silica	Guar gum
Gum tragacanth	Hydroxyethylcellulose
Locust bean gum	Methylcellulose
Polyacrylic acid salts	Polyvinyl alcohol
Sodium carboxymethyl cellulose	Starches
Fillers	Fillers
Bentonites	Calcium carbonate
Calcium silicate	Clay
Mica	Nutshell flours
Silica	Talc
Uncooked starches	Wood flour
Humectants	Humectants
Calcium chloride	Diethylene glycol
Glycerine	Hexylene glycol
Propylene glycol	Magnesium chloride
Sodium nitrate	Sorbitol
Sucrose	Urea

3.5.7 Wet Labeling

Waterborne adhesives are known as adhesives for a wet labeling process. Such adhesives will be applied on one side of a label and thereafter the label will be glued to the container. For processing reasons the bottles are already filled with their content when the label is applied. In many cases the content is cooled. As a consequence, the bottle will have a cooled outside surface below the temperature of the environment. As the surface of the bottle is cooled, water vapor from the surrounding environment will condense on the surface. On such a surface the labels will be bonded in a high-speed labeling process. A problem that may arise in practice is poor adhesion on this wet surface directly after labeling.

A waterborne adhesive based on acrylic polymers has been developed which may be applied in a high-speed application process as labeling adhesive to containers which have a humid surface of condensed water. The initial bonds strength on the surface will be high. No failure due to the wet surface will occur, the label will remain in place, and a good adhesion will be seen. Additionally, after the use cycle of the container the label will be removed from the surface by washing the adhesive with water or an alkaline solution.

One component of the adhesive is an acrylate or methacrylate copolymer as backbone. A dispersion of the copolymer can be prepared by emulsion polymerization. Monomers are summarized in Table 3.18.

Table 3.18 Monomers for adhesives (102).

Hydrophobic type	Hydrophilic type
Acrylic acid alkylesters	Acrylamide
Methacrylic acid alkylesters	Methacrylamide
Styrene	Hydroxyethyl acrylate
α-Methyl styrene	Hydroxyethyl methacrylate
Vinyl toluene	Hydroxypropyl methacrylate
Acrylonitrile	Hydroxyethyl acrylamide
Vinyl chloride	*N*-Vinyl pyrrolidone
Ethene	Methacrylic acid glycol ester
Butadiene	
Isoprene	

Such monomers may be used alone or as mixture. Such monomers will enhance the polarity of the polymer and improve the water sensitivity (102).

Preferably the copolymer may contain 40–80% hydrophobic monomers, 10–50% hydrophilic monomers, and 2–20% ionic group-containing monomers.

As additional component, the adhesive composition may contain components to modify rheological properties of the adhesive. Such polymers can be selected from starch, dextrin, cellulose or proteins. The starch is selected from non-jellified commercially available starches, e.g., rice, wheat, corn, potato, tapioca, or pea starch.

Also, modified starch can be used, such as degraded, oxidized or grafted starch, starch ethers or starch esters. Preferably nonionic starch ethers are used, e.g., hydroxypropyl or hydroxyethyl starch or carboxy-methyl starch.

Alternatively, dextrin can be used. Dextrins are manufactured as degradation products from starch, e.g., enzymatically degraded starch like maltodextrin. Also, it is possible to add protein polymers, for example, casein, as further component.

In addition, the adhesive contains a component for regulating the viscosity. Such component is selected from water soluble low-molecular weight liquefiers like urea, thiourea, guanidine, dicyandiamide, or their derivatives.

Further, the composition should contain superabsorbent polymers (SAPs). SAP polymers have been described in the literature (103). These polymers have the capacity to include high amounts of water in their polymer chains without dissolving totally in water. Water-swellable polymers that form either a chemical or ionic network or have a high molecular weight with dipole binding are SAPs.

The polymers can form a network. For example, the polymer chains are chemically crosslinked or at least are partially crosslinked. Another type of polymer contains a large extent of ionic bonds or hydrogen bonds. This different polarity may form a network by ionic bonding. Another type of polymer is a high molecular weight polymer with more then 500 kD, which may form a linear or branched structure. Such polymer chains can be entangled or form a high dipole interaction, and will show a high capacity of swelling with water. Special types of SAPs are acrylic acid polymers or crosslinked starches.

The adhesive may also contain a tackifying resin. The tackifying resin provides additional tackiness and improves the compatibility of the other adhesive components. The resin is preferably selected from rosin and derivatives thereof. As adhesion promotors, silanes can be added. Examples are shown in Table 3.19.

Table 3.19 Adhesion promotors (102).

Compound
3-Glycidoxy-propyltrialkoxysilan
3-Acryloxypropyltrialkoxysilan
3-Aminopropyltrialkoxysilan
1-Aminoalkyltrialkoxysilan
α-Methacryloxymethyltrialkoxysilane
Vinyltrialkoxysilane
N-Aminoethyl-3-aminopropyl-methyldialkoxysilane
Phenylaminopropyltrialkoxysilane
Aminoalkyltrialkoxydisilane
i-Butylmethoxysilane
N(2-Aminoethyl)-3-aminopropyltrialkoxysilane
Methacryloxymethyl-triethoxysilane

The viscosity of the adhesive should be adjusted between 30,000 to 150,000 $mPa\,s$ at 25°C. For plastic surfaces a viscosity range from 10,000 to 100,000 $mPa\,s$ should be adjusted. The waterborne adhesive is stable and can be stored for a longer time. The solid content can reach from 30 to 65% (102).

3.5.8 Aqueous Polymeric Dispersions

Aqueous polymeric dispersions have been described (104). These compositions are composed of a hydrophilic macromonomer, a hydrophobic polymer and a bridging monomer. The hydrophilic macromonomer and the hydrophobic polymer are grafted to one another in the presence of the bridging monomer.

The hydrophobic polymer represents the bulk of the composition and may act as the binder material in a coating. The polymeric composition should contain 55–90% of the hydrophobic polymer, 1–10% of the hydrophilic macromonomer, and 7–40% of the bridging monomer. The manufacturing proceeds through the following steps (104):

1. Adding the hydrophilic macromonomer to the hydrophobic polymer under agitation and heating,
2. Adding the bridging monomer and a free radical initiator,
3. Optionally adding a solvent,
4. Neutralizing the polymer composition, and
5. Adding water to the polymeric composition and mixing to obtain a secondary emulsion.

Also, alternative procedures have been suggested (104). For example, the preparation of a hydrophobic alkyd polymer has been described as follows (104):

Preparation 3–2: A four-necked reaction flask equipped with a condenser, agitator, heating mantle, addition funnel, thermocouple attached to a control box, and a primed Dean-Stark trap with methyl isobutyl ketone, was charged with 28.5 parts of Pamolyn®-200 (an unsaturated fatty acid available from Hercules Pinova Products, having 77% linoleic acid and 22% oleic acid content), 28.5 parts of tall oil fatty acid, 22.4 parts of trimethylol propane, 20.2 parts of isophthalic acid, 0.4 parts maleic anhydride, 0.05 parts of Fascat® 4350 (Butyl tin catalyst available from Arkema Inc.) and 2 parts methyl isobutyl ketone, and heated under 0.014 $m^3 hr^{-1}$ nitrogen flow to 165°C. At 165°C, water starts to distill azeotropically. The reaction temperature was increased to 230°C and maintained at such temperature until an acid value of less than 8 was attained. The Dean-Stark trap was drained and the nitrogen flow was increased to 0.057 $m^3 hr^{-1}$ to remove as much of the azeotropic methyl isobutyl ketone as possible. The alkyd was cooled to 150°C and filtered.

The preparation of a hydrophilic macromonomer runs as follows (104):

Preparation 3–3: A four-neck reaction flask equipped as in preparation 3–2 was charged with 0.5 parts of methyl methacrylate, 6 parts of methoxy polyethyleneglycol methacrylate, 5 parts of α-methylstyrene dimer and 13 parts of propylene glycol methyl ether and heated under a 0.006 $m^3 hr^{-1}$ flow of nitrogen to 127°C. A monomer mixture of 4.5 parts of methyl methacrylate, 54 parts of methoxy polyethyleneglycol methacrylate, and 2.8 parts of *tert*-butyl peroctoate was then added over 4 h via addition funnel. The temperature was increased to 132–135°C throughout the monomer addition. A second monomer mixture composed of 5 parts methyl methacrylate, 25 parts lauryl methacrylate, 1.2 parts *tert*-butyl peroctoate and 3 parts glycol ether was added over 2 h maintaining the temperature at 132–135°C range. Heating was continued for an additional 1 h

at 132°C. The hydrophilic macromonomer thus obtained was cooled and filtered.

Finally, the copolymerization of hydrophilic macromonomer and bridging monomers has been described (104):

Preparation 3–4: To a reaction vessel similar to that described in preparation 3–2, 26.7 parts of ethylene glycol butyl ether and 46.1 parts of the hydrophilic macromonomer of preparation 3–3 were added. The reaction content was heated to 132°C and a mixture of 21.9 parts of styrene, 18.75 parts of butyl acrylate, 9.4 parts of methyl methacrylate, 12.5 parts of methacrylic acid, and 1.5 parts of *tert*-butyl peroxy-3,5,5-trimethylhexanoate was added over a 4 h period while maintaining the temperature at 132°C. The reaction contents were held at 132°C additionally for 1 h. Another 0.2 parts of *tert*-butyl peroxy-3,5,5-trimethylhexanoate and 0.3 parts of ethylene glycol butyl ether were added while holding the reaction at 132°C. The resultant acrylic copolymer had 62% solids, a viscosity of 21 $mPa\,s$, and an acid value of 77.

3.5.9 Waterborne Soft-Feeling Coatings

Soft-feeling coatings provide desirable aesthetic and tactile characteristics for a variety of applications, in particular for articles that are touched by their consumers (105). Automotive manufacturers have used soft-feeling coatings on instrument panels, armrests, and horn buttons to give hard, glossy plastic components a velvety smooth matte finish. Other consumer products, such as notebook computers and cellular phones, also use soft-feeling coatings to enhance the look and finish of the products and give the appearance of a high-quality product.

Typical soft-feeling coating compositions use a two-component solvent-based paint. While this two-component coating has desirable features, the content of VOCs is high, in the order of 500–600 $g\,l^{-1}$. Increasingly stringent environmental regulations have forced coating manufacturers to use other solvent systems with lower levels of VOCs. In addition, two-component soft coatings often result in different gloss levels due to varying ambient humidity and different rates of solvent evaporation on different areas of the coated article. Due to these problems, some manufacturers have experienced difficulties in producing uniformly finished parts.

One-component waterborne soft-feel coatings have been developed as an alternative to solvent-based coatings. These coatings have considerably less VOCs, in the order of 200–250 $g\,l^{-1}$.

However, they are generally regarded as not as soft as the two-component solvent-based coatings. In addition, one-component waterborne coatings exhibit poor chemical resistance and weatherability.

Two-component waterborne soft-feel coating systems have been developed to overcome the shortcomings of the one-component system. A two-component waterborne system has been described (106–108). However, such two-component waterborne systems provide about one-half the level of gloss provided by the two-component solvent-based system.

Accordingly, such waterborne coatings are not suitable when a high gloss, soft feeling coating is desired (105). In addition, these coatings display inadequate wetting and flow characteristics when applied to substrates, which, in turn, result in surface defects. To combat these defects, additives such as flow modifiers are included to enhance the flow and level attributes of the composition.

Flow modifiers are used primarily to reduce or eliminate surface defects such as craters, fisheyes, pinholes, and orange peel. They also aid in pigment dispersion, help facilitate air release, improve substrate wetting, and promote flow and leveling. Flow modifiers are typically used at 0.25–0.5% in liquid coatings and at 0.5–1.5% in powder coatings.

It has been found that an alcohol alkoxylate surfactant added to a waterborne coating composition provides improved flow characteristics during application of the composition to a substrate. In addition, the alcohol alkoxylate surfactant aids in leveling the composition on the substrate as it is applied, and results in enhanced gloss and soft feel when the composition is dry (105).

In particular, a waterborne two-component topcoat for industrial application based on a water-soluble hydroxy-functional acrylic-poly(urethane) has been prepared using the components shown in Table 3.20.

The POLY-TERGENT® S405LF surfactant is a linear alcohol alkoxylate known chemically as poly(oxyethylene/oxypropylene)-monohexyl ether, monooctyl ether, or monodecyl ether. The surfactant has a synergistic effect on the coating in the wet state to

Table 3.20 Waterborne two-component topcoat (105).

	Part A	
Type	Component	Parts
Solvent	Water	25
Solvent	*N*-Methylpyrrolidone	1
Solubilizer	Diacetone alcohol	9
Pigment	Titanium Dioxide	15
Filler	Calcium Carbonate	7
Pigment	Talc	2
	Part B	
Type	Component	Parts
Solvent	Water	25
Antimicrobial	Dabco T1402 dibutyltin	0.02
Surfactant	POLYTERGENT® S405LF	0.28
Acrylic-poly(urethane) resin	ACPU-1	70.27
Solubilizer	Propylene glycol methyl ether acetate	10.23

minimize the formation of microfoam. In addition, increased gloss results from improved air release and low foam.

3.5.10 Waterborne Polymeric Photoinitiators

The use of water soluble or waterborne polysilane photoinitiators meets the demand for environmentally friendly photopolymerization applications (109).

A waterborne polysilane photoinitiator polysilane-*co*-poly(polyethyleneglycol acrylate) could be prepared by the efficient photodecomposition of poly(methylphenylsilane) in the presence of an acrylate functionalized PEG.

The polymer could be easily dispersed in water to form micelles with a size of 46 nm as measured by dynamic light scattering. The kinetic data of the photopolymerization indicated that the conversion of acrylamide reached 80% and 100% after 40 s and 110 s irradiation, respectively (109).

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4

Water-Resistant Polymers

Water-resistant polymers are desired for a wide variety of uses, mostly for outdor and marine applications. Here, the issues and materials concerning water-resistant polymers are summarized.

4.1 Coatings

4.1.1 Polyolefin Coatings

Exterior parts of motorcars made of resins instead of metals or glass are widely used in practice, for example, as bumpers, door mirror covers, moldings and spoilers (1,2).

Polyolefin-based materials are now used in a larger amount than urethane resins for economical reasons. In addition, the polyolefin resins are excellent in their chemical resistance, water resistance and moldability.

When such a polyolefin resin material is used, it is under more restrictions than metal coatings. Since the polyolefin resins have a low polarity, the resultant coating has a poor adhesion. Another disadvantage of the polyolefin resin material is that since its thermal resistance is low, the coating must be heat-dried at a temperature of below 140°C.

The polyolefin resin molding can be pretreated by a flame treatment, corona discharge, plasma treatment, or treatment with chromium sulfate. Then, the top coating is done.

The surface of the polyolefin resin molding can be cleaned with a solvent such as trichloroethane. Then the surface is coated with a primer having a high adhesion and the top-coating is conducted. However, a satisfactory adhesion is not always obtained by these methods and, in addition, these methods have problems in that they are complicated because of the large number of steps and high costs, since a specified expensive primer is used.

For improving these techniques, a method for improving the adhesion to the polyolefin resin molding by using a coating composition containing a chlorinated polyolefin resin has been proposed. Various coating compositions were proposed. These include (2):

- Coating compositions containing a mixture of a chlorinated polyolefin resin and acrylic resin,
- Coating compositions comprising a copolymer of a chlorinated polyolefin resin and acrylic monomer, and a polyester prepolymer combined with an isocyanate compound,
- Coating compositions comprising a combination of a copolymer of chlorinated polyolefin resin/acrylic monomer/chlorinated polydiene, with an isocyanate compound, and
- Coating compositions prepared by incorporating a hardener such as an isocyanate prepolymer or melamine resin into a mixture of a chlorinated polyolefin resin and an acrylic resin or into a product obtained by grafting an acrylic monomer onto a chlorinated polyolefin.

However, such coating compositions exhibit undesirable properties, such as phase separation, gloss, or adhesion. Also, the isocyanate may cause problems, as isocyanates are highly toxic.

Thus, although various improved coating compositions have been proposed, they are not yet sufficient for use in a field wherein a particularly high durability is strictly required, such as the field of coating compositions for bumpers of motorcars. Therefore, they are used in only limited fields.

A coating composition has been developed that can better handle the properties and is safe, capable of being cured at a low temperature and also able to provide a coating with excellent water resistance, solvent resistance and adhesion to the polyolefin resin moldings has been developed (2).

A grafted chlorinated polyolefin resin is used. The chlorinated polyolefin can be obtained by chlorinating a polyolefin itself or a polyolefin modified by introducing a carboxyl group, acid anhydride group or hydroxyl group. The polyolefins include, for example, poly(ethylene), poly(propylene), ethylene/propylene copolymers, and poly(butadiene).

The grafted resin can be obtained by grafting a vinyl monomer onto a chlorinated polyolefin. The graft part should have a hydroxyl group at a position of 8–13 atoms distant from the main chain of the vinyl polymer grafted onto the chlorinated polyolefin. When the carbon chain derived from the alcohol residue in the vinyl monomer has less than 6 atoms, the water resistance is poor. In contrast, when it exceeds 18, the coating film becomes too soft to obtain excellent water resistance and solvent resistance.

The vinyl monomers include, hydroxyl group-containing alkyl (meth)acrylates such as 13-hydroxytridecyl acrylate and 14-hydroxytetradecyl acrylate and the corresponding methacrylate compounds. On the other hand, 2-hydroxyethyl methacrylate, 3-hydroxypropyl acrylate, 2-hydroxypropyl acrylate, or 4-hydroxybutyl acrylate reacted with a lactone can be used.

These monomers can be reacted again with a lactone in order to further elongate the distance between the vinyl group and the hydroxyl group. The lactones include, for example, ε-caprolactone, β-propiolactone, δ-valerolactone and γ-butyrolactone. These lactones are very useful for controlling the position of the hydroxyl group.

The grafted chlorinated polyolefin resin should have an acid value of 5–30 mg KOH g^{-1}, the graft part should have a calculated glass transition temperature of -20–30°C. When the acid value is below 5 mg KOH g^{-1}, the crosslinking reactivity is apt to be easily reduced to make the crosslinking insufficient and, therefore, reduces the gasoline resistance and weather resistance. On the contrary, when the acid value is above 50 mg KOH g^{-1} and the storability and water resistance are apt to be easily reduced (2).

In addition, the composition contains a methylol melamine resin, a complete alkoxy group-containing melamine resin, or an imino group-containing melamine resin. The melamine resin is produced by the polymerization of an addition product of melamine and formaldehyde, followed by the modification with an alcohol. Melamine is shown in Figure 4.1

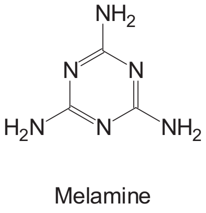


Figure 4.1 Melamine.

In addition, the composition contains acidic curing catalysts, anti-settling agents, dispersing agents, defoaming agents, ultraviolet absorbers, light stabilizers, thinners, and coloring pigments.

Preferred strongly acidic catalysts are aromatic sulfonic acids and acid esters. In particular, dodecylbenzenesulfonic acid and dinonylnaphthalenedisulfonic acid are preferred, since they are effective in improving the water resistance of the coating film. Examples of such compositions have been detailed (2).

The water resistance of the final coatings have been measured as follows: Test pieces are immersed in warm water at a temperature of 40°C for 240 h and then taken out. The condition of the coating surface is observed and the adhesion test is conducted. Those having no change in the condition of the coating pass the test (2).

4.1.2 *Adherent Coatings*

A water-resistant polymer with adhesive behavior has been reported that has long-term antimicrobial activity under diverse conditions (3).

To obtain a highly adhesive polymer with prolonged antimicrobial activities and a catechol moiety, 2-chloro-3′,4′-dihydroxyacetophenone has been quaternized onto poly(dimethylaminoethyl methacrylate). 2-Chloro-3′,4′-dihydroxyacetophenone is shown in Figure 4.2. In order to extend the antimicrobial effects, the polymer was additionally quaternized with 1-bromododecane.

Poly(dimethylaminoethyl methacrylate)-terminated with a hydroxyl group at one end was prepared by chain transfer polymerization. 2-Mercaptoethanol was used as chain transfer agent. The method of preparation has been detailed (4).

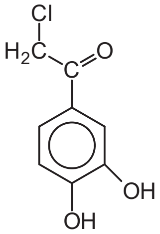


Figure 4.2 2-Chloro-3′,4′-dihydroxyacetophenone.

Coated substrates with this composition showed remarkable bacterial killing efficiency against both Gram-positive *Staphylococcus aureus* and the Gram-negative *Escherichia coli* after an incubation time of 24 h.

Also, the remarkable antimicrobial activity in an aqueous medium at 60°C for up to 60 d indicates the strong adhesiveness of the compositions on the substrate (3).

4.1.3 Wire Coatings

Thermoplastic dicyclopentadiene (DCPD) ring-opening polymers can be used for wire coating materials and for plate lenses (5, 6). The wire coating materials are excellent in flexing resistance and flexibility. The wires can be used for high-voltage power cables and high frequency cables.

Thermoplastic DCPD ring-opening polymers can be obtained by subjecting DCPD or DCPD derivatives to a suitable solvent in the presence of a ring-opening polymerization catalyst such as a metathesis catalyst. Preferred monomers are dicyclopentadiene, 8-methyltetracyclo-[4.4.0.12.8.17.10]-dodeca-3-ene, and 8-ethyl-tetracyclo[4.4.1_2,5.1_7,10.0]-dodeca-3-ene.

The basic principles of ring-opening polymerization have been described (7, 8). A range of metathesis catalysts have been used to prepare polymers from dicyclopentadiene and their 7,8-dihydro derivatives. With endo-dicyclopentadiene, the catalyst $\mathrm{RuC_3} \times 3\mathrm{H_2O}$ produced a high-*cis* polymer. This anomalous result has been explained to be due to a steric effect at the catalyst site caused by endo-dicyclopentadiene that is also acting as a permanent ligand because of its unique potential to chelate in a bidentate fashion (7).

Hydrogenation products can be obtained by hydrogenating the C=C bonds in the main chains and the polycyclic rings of the polymers. The conversion by hydrogenation results in an improvement of heat resistance, weathering resistance, light resistance, solvent resistance, chemical resistance, and water resistance.

By using the hydrogenation products of the DCPD polymers, wire coating materials can be obtained that are excellent in elongation and impact strength (5).

4.2 Biodegradable Resins

Poly(lactic acid)s (PLAs) can be produced from agricultural products and are thus free from the problem of resource depletion. L-lactic acid has been used as the raw material. It can be produced by fermentation in large quantities and at low cost. However, PLAs have the drawback of being rigid, brittle and inflexible because of their high crystallinity and rigid molecular structure. Therefore, PLAs as such are not suitable for applications that require flexibility, such as films and packaging (9).

A biodegradable ester resin composition has been described for use as a plasticizer for biodegradable aliphatic polyester resins. The biodegradable aliphatic polyester resin is poly(butylene succinate), poly(butylene succinate adipate) or a mixture from these polyesters, including PLA. Mixed alcohol ester plasticizers preferably used are summarized in Table 4.1.

Table 4.1 Mixed alcohol ester plasticizers (9).

Ester compound
Methyl diglycol butyldiglycol adipate
Benzyl butyldiglycol adipate
Benzyl methyl diglycol adipate
Ethoxycarbonyl methyldibutyl citrate

When single alcohol esters, such as bis(methyl diglycol) adipate and dibenzyl adipate, are used as plasticizers, no satisfactory properties in both non-bleeding and water resistance were observed.

Further, the test pieces had a high tensile modulus and low elongation, demonstrating a poor plasticizing effect.

In contrast, the test pieces in which methyl diglycol butyldiglycol adipate or benzyl butyldiglycol adipate, respectively, were used as the mixed alcohol ester plasticizer, were excellent in both nonbleeding properties and water resistance. Further, these test pieces had a little tensile modulus and large elongation, demonstrating an excellent plasticizing effect.

The compositions can be used in films, sheets, and molded articles that require flexibility. The composition has excellent water resistance and can be molded into an article from which the plasticizer is difficult to bleed out to the surface (9).

4.3 Water-Based Printing Inks

The majority of aqueous inks have advantages such as high transparency and high color density, since a water-soluble dye, which is dissolved in a molecular state, is used in such compositions (10). However, because such dye is water soluble, the aqueous inks suffer from disadvantages such as poor water resistance and a tendency to bleed when printing on paper, thus significantly deteriorating print quality, and poor light fastness.

In a glossy plain paper, the moisture in a printing ink is rapidly absorbed in base paper as a substrate through the glossy layer and then the ink receiving layer (11). Accordingly, water resistance is not significantly important, because there is no likelihood that the glossy layer may hold the moisture for a long time.

On the other hand, in photo-like paper, the substrate does not have water absorbability, and the amount of ink per unit area is increased, if multicolor printing is performed to obtain a fine image. As a result, the glossy layer or the glossy layer/ink receiving layer may contain a large amount of moisture immediately after printing. Thus, high water resistance is required for the recording layer.

A poly(vinyl alcohol) (PVA)-based resin becomes tacky by absorbing moisture. Accordingly, in the case where a glossy layer containing a PVA-based resin as a binder, or a recording layer serving as an ink receiving layer is formed on a surface of recording media, the recording media are likely to adhere to each other (11).

In PVA-based resins, water resistance can be imparted by crosslinking with a boron compound. Orthoboric acid, metaboric acid, and paraboric acid may be used. Also, borates such as sodium salts, potassium salts, and ammonium salts can be used. The inkjet recording medium has satisfactory photo-like gloss by containing the PVA resin with a 1,2-diol unit on a side chain (11).

In recent years, there has been an increasing demand for inkjet recording methods in which an aqueous inkjet recording ink is applied to a recording medium (12). The recording medium is then irradiated with active energy rays, as well as an active energy ray curable ink used in this recording method.

A technique has been proposed for improving the scratch resistance and water resistance of an image using an aqueous active energy ray curable inkjet recording ink composition. The composition contains a poly(urethane) (PU) compound with a double bond. This moiety is curable by irradiation.

Aqueous compositions that contain a wax have been proposed (12). Since the specific gravity of the wax is generally lighter than that of water, the wax accumulates preferentially on the outer surface side with respect to a recording medium compared to other components in the composition.

So, the physical contact of oxygen introduced into the recording medium from the air can be prevented, and the kinetics of the photoinduced radical reaction is less disturbed. As a result, the radically polymerizable compound can form a stronger film and can improve the water resistance and scratch resistance to a greater degree.

The wax also enhances the lubrication. Therefore, the scratch resistance of the image can be improved by adding the wax (12).

Vegetable waxes suitable for use are carnauba wax, Japan wax, Ouricury wax, and Espar wax. Animal waxes are beeswax, insect wax and shellac wax. Also, petroleum waxes and mineral waxes, such as montan wax, ozokerite, and ceresin can be used. Synthetic waxes are hydrocarbon waxes such as poly(ethylene) (PE) wax and poly(propylene) (PP) wax (12).

The water resistance was assessed as follows: The images were used to evaluate the water resistance of each recorded article. A 0.2 *ml* water droplet was dropped on the image of the recorded article, and the image that formed in a region of the recorded article where the water droplet had been dropped was rubbed with silbon paper after left to stand for 1 min. Thereafter, the condition of the coating film formed on the recording medium was visually observed to make an evaluation. The evaluation criteria of the water resistance are as follows (12):

1. No image scrape is observed in the region rubbed with silbon paper,
2. An image scrape is slightly observed in the region rubbed with silbon paper,
3. An image scrape is observed in the region rubbed with silbon paper,
4. An image scrape caused in the region rubbed with silbon paper is marked.

Inkjet recording inks using fine particle dispersions and using 1,2-hexane diol as the ink solvent have been shown to be excellent in their printing performance, free from dependency on kind of paper and excellent in water resistance, high-degree rubbing resistance, light fastness, and ozone resistance (10).

The fine particles are an oil-soluble dye with an oxidation potential higher than 1.0 V and a polymer containing both hydrophobic and hydrophilic moieties. Examples of the dispersable monomers for the copolymers used are listed in Table 4.2.

The average particle size of the fine particles should be 3–200 nm. The particle size distribution is not particularly limited and may be a broad particle distribution or a monodisperse particle size distribution. The particle size and the particle size distribution can be regulated by means of centrifugation or filtration (10). Methods of preparation of dispersion have been detailed. These consist of preparing a latex of the dispersable polymer and impregnating the latex with the oil-soluble dye, and a co-emulsification dispersion method.

4.4 Reinforcing Fibers

It is common to use reinforcing fibers in order to increase the strength or durability of various rubber products such as rubber tires or rubber belts (13). The fibers are coated with a coating film

Table 4.2 Monomers for dispersable copolymers (10).

Monomers		Mass ratio
n-Butyl acrylate	*tert*-Butyl acrylamide	50:50
n-Hexyl methacrylate	*tert*-Butyl acrylamide	50:50
Isobutyl acrylate	*tert*-butyl Acrylamide	70:30
n-Butyl acrylate	Glycidyl methacrylate	70:30
n-Hexyl methacrylate	Glycidyl methacrylate	70:30
n-Butyl acrylate	Glycidyl acrylate	70:30
n-Butyl acrylate	2-Hydroxyethyl acrylate	70:30
n-Butyl acrylate	2-Hydroxyethyl methacrylate	50:50
n-Butyl acrylate	*tert*-Butyl acrylamide	70:30
n-Butyl acrylate	*tert*-Butyl acrylamide	80:20
n-Butyl acrylate	*tert*-Butyl acrylamide	90:10
n-Butyl acrylate	*tert*-Butyl acrylamide	30:70
n-Butyl acrylate	*tert*-Butyl acrylamide	20:80
n-Butyl acrylate	*tert*-Butyl acrylamide	10:90
n-Butyl acrylate	Glycidyl methacrylate	80:20
n-Butyl acrylate	Glycidyl methacrylate	90:10
n-Butyl acrylate	Glycidyl methacrylate	50:50
n-Butyl acrylate	Glycidyl methacrylate	30:70
n-Butyl acrylate	*tert*-Butyl acrylamide	50:50
n-Butyl acrylate	*N*-Isopropyl acrylamide	70:30
n-Butyl acrylate	*N*-Isopropyl acrylamide	50:50

formed by a rubber type treating agent in order to increase the adhesion between the fiber, and a rubber base material in order to increase the durability of the rubber product by protecting the fiber itself.

As such, a rubber type treating agent, a condensate of resorcinol, formaldehyde, and a rubber latex have been used. However, such treating agents may have the problem of not enough water resistance, even when the heat resistance of the reinforcing fiber is sufficiently satisfied.

To solve this problem, fibers coated with a coating film of a rubber latex containing a vinylpyridine/styrene/butadiene terpolymer and a halogen-containing latex has been used together with the conventional condensate of resorcinol and formaldehyde (13).

4.5 Paper Industry Applications

4.5.1 *Ketene Dimers*

The use of ketene dimer based agents in the paper industry to impart sizing or water resistivity to paper products is well known (14).

Ketene dimers used in the paper industry to impart sizing or water resistivity to paper have the general chemical structure shown in Figure 4.3.

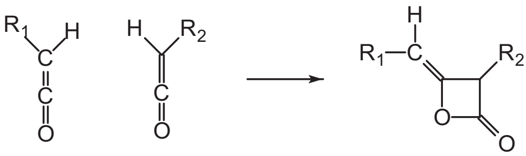


Figure 4.3 Synthesis of ketene dimers.

These sizing agents, when added to the wet end of the paper machine, at the size press, or to the finished product in an off-machine application, impart water resistivity to the paper by decreasing the hydrophilicity of the sheet. The use of these sizing agents in writing paper, liner board, grocery bags and milk cartons is common, as all of these types of paper products require sizing.

These types of sizing agents are known to produce very hard sized material, such as a milk carton. On the other hand, the use of these sizing agents in tissues and towels has been limited, because water resistivity is not desirable in these products.

On the other hand, it has been a goal in the tissue and towel industry to increase rather than to decrease the rate at which the product is wetted and so the total amount of water that the product can absorb (14).

Typically, tissue made without the use of sizing agents shows an absorbency rate test of from about 1 s to about 10 s. Towel made without sizing agents will typically show an absorbency rate of about 1–50 s. When tissue and towel are sized with a ketene dimer sizing agent it can be anticipated that sizing levels, or water resistivity, will substantially increase with absorbency rate tests of as much as 25 s or larger occurring in, for example, tissue. Tissues having improved softness from the use of hydrolyzed ketene dimer agents remain hydrophilic, having a very low resistance to wetting, i.e., they are not sized and thus wet easily.

The water absorbency rate test for such softened sheets are from around 1–4 s, but may be up to about 10 s or more depending on the type of paper, basis weight and other physical characteristics of the sheet. For tissue and towel products water absorbency test results of less than 40 s are believed to show that the sheet is still substantially hydrophilic, and are viewed as low or negligible levels of sizing (14).

4.5.2 Anhydrides for Sizing

A size mixture of a substituted cyclic dicarboxylic acid anhydride and polyoxyalkylene alkyl or alkyl-aryl ether can be used to size paper products. The liquid size mixture is added directly to the paper stock system without prior emulsification (15).

Anhydrides are listed in Table 4.3

These size mixtures are easily emulsifiable with water in the absence of high shearing forces and under normal pressure by merely stirring, passing through a mixing valve or common aspirator or by the usual agitation present in a stock preparation system. The components are premixed without water and then added to the paper stock preparation system at any point during preparation where

Table 4.3 Anhydrides for sizing (15).

Anhydrides
Iso-octadecenyl succinic acid anhydride
n-Hexadecenyl succinic acid anhydride
Dodecenyl succinic acid anhydride
Dodecyl succinic acid anhydride
Decenyl succinic acid anhydride
Octenyl succinic acid anhydride
Triisobutenyl succinic acid anhydride
(1-Octyl-2-decenyl)-succinic acid anhydride
(1-Hexyl-2-octenyl)-succinic acid anhydride

good agitation can be achieved. It has been found that the required agitation is achieved when passing through refiners, pumps, and other operating equipment, thereby producing the emulsion in-situ and excellent sizing properties in the resultant sized web.

An important factor in the effective utilization of the size mixtures is their use in conjunction with materials that are capable of ionizing or dissociating to produce positively charged moieties. These cationic agents have been found useful as a means for aiding the retention of the substituted cyclic dicarboxylic acid anhydride as well as for bringing the latter into close proximity to the pulp fibers.

Such cationic agents are various cationic starch derivatives. Such starch derivatives can be prepared from all types of starches, including corn, tapioca, potato, waxy maize, wheat, and rice. The paper products prepared using the above compositions exhibit an improved water resistance (15).

4.5.3 Epoxidized Soybean Oil

Epoxidized soybean oil-based paper composites could be prepared by fabricating a poly-epoxidized soybean oil on paper (16). Soybean oil contains both saturated fatty acids such as stearic acid, palmitic acid, and unsaturated fatty acids, such as linolenic acid, oleic acid. The double bonds of the unsaturated fatty acids can be epoxidized.

Boron trifluride diethyl etherate was used as catalyst. In this way, the epoxidized soybean oil was polymerized in-situ on the surface of the paper and within the interspaces of the paper cellulose fibers (17,18). The epoxy moieties react with the pending hydroxyl groups on cellulose.

The composites showed a nanostructured wrinkle morphology on the surfaces and were tightly combined with the cellulose fibers of the paper. Further, the composites were thermally stable up to 360°C in nitrogen atmosphere, as shown by differential scanning calorimetry.

The permeability of water vapor is significantly lower than many other biobased polymeric materials. This finding suggests the application of vegetable-based polymers as potential water-resistant materials (16).

4.6 Masonry Products

Masonry products have been widely used in the construction industry. These products include building materials such as cementitious materials, concrete, brick, tile, stone, grout, and others. Driveways, garage flooring, concrete block, brick fronts, fireplaces, fireplace hearths, as well as tiled floor, wall and counter top surfaces are exemplary applications (19).

Masonry surfaces are porous and if they are left unprotected they can deteriorate from exposure to water and become discolored. The penetration of water can cause spalling or lead to discoloration via microbial growth. Tiles and grouts employed in homes may come in contact with various foods and liquids, e.g., fruit juice, coffee, vegetable oil, ketchup, or mustard that can cause discoloration. Motor oils, brake-oils, and transmission fluids can cause discoloration of garage floors.

Therefore, it has been common practice to coat masonry surfaces with materials capable of rendering them resistant to water, oils, and other contaminants.

Coatings for masonry can be generally subdivided into two types, one type being a waterproof coating and another type being a water-repellant coating. A coating of the waterproof type renders the surface completely impervious to both liquid water, water vapor, and other contaminants. On the other hand, a coating of the water-repellent type renders the surface impervious to water in the liquid phase but is permeable to water in the gas phase.

Exemplary materials for making masonry surfaces waterproof are waterproof membranes, such as poly(vinyl chloride), PE, butyl rubber, and sealants such as tar, asphalt, paints, PU, epoxy, or mastics. While these waterproofing agents offer excellent resistance to water penetration and other contaminants, they can alter the appearance of the masonry surface, e.g., they may change the color of the surface or leave it with a shine. Waterproofing treatments can also trap moisture within the masonry surface and promote spalling (19).

Water-repellent treatments for masonry surfaces are done with metal stearates, oils, waxes, acrylates (both polymers and monomers), silicones (solvent-based and emulsion), siliconates, silanes, and fluorochemicals. In contrast to waterproofing coatings, water-repellent coatings, because they are permeable to water vapor, do not trap moisture and, therefore, they can reduce spalling. In addition, most water-repellent coatings do not alter the appearance of a porous masonry.

Some specific chemicals for the treatment of masonry surfaces to make them water-repellent are summarized in Table 4.4.

Table 4.4 Water-repellent chemicals for masonry surfaces.

Chemical	References
Trimethyl silicon chloride and silicon tetrachloride	(20)
Partially condensed Silicone resin	(21)
Alcoholic solutions of alkyltrialkoxysilanes	(22)
Acrylonitrile/butadiene latex	(23)
Aqueous emulsion of a hydrolyzable silane	(24)
Organopolysiloxane resin solutions	(25,26)
Waterborne fluoropolymer solutions	(27,28)
Fluorine-containing phosphate esters	(29)
Ethylene-vinyl acetate copolymer	(19)

Masonry surfaces can be sealed from penetration by water and other contaminants by the use of an aqueous-based emulsion polymerized ethylene-vinyl acetate (EVA) polymer containing crystalline ethylene segments. Because of the ethylene crystallinity, the normally water sensitive EVA polymers now become useful for imparting water repellency and stain resistance to masonry substrates (19).

Additional comonomers can be polymerized into the EVA polymer backbone. Such comonomers include carboxylic acids such as acrylic acid or acrylamide. The polymer is fabricated by the emulsion polymerization.

Chain transfer agents can be used, such as mercaptan derivatives. Dodecylmercaptan is an example of an oil-soluble chain transfer agent. For example, dodecylmercaptan can be dissolved in the vinyl acetate monomer and introduced to the reactor via the monomer delay feed.

One preferred way to enhance the crystalline domain formation of ethylene in the EVA polymer is to delay the addition of the vinyl acetate during the polymerization process so that the unreacted vinyl acetate level present in the reactor is minimal at different stages during the process, i.e., below 5% unreacted free vinyl acetate monomer.

Particularly, it is preferred to stage the addition of vinyl acetate in the polymerization process over an initial period of time. Typically, one completes the addition within 75% of the total polymerization period and generally within 3 h or less. Thus, the copolymerization can take place in one stage where most, but not all, of the ethylene will reside in amorphous regions, and the formation of the majority of crystalline ethylene domains can occur in another stage of the polymerization process (19).

Other ingredients can be incorporated into the formulations to improve properties further. Examples are wax particles or emulsions or silicone to improve the water resistance, UV absorbers to improve weathering and durability, and mildewcides to improve the resistance to mildew and fungus. Other additives traditionally used in coatings to improve application and performance properties, such as surfactants and defoamers, also can be included (19).

EVA polymers have also been described for applications on asbestos cement plates (30). The polymer powders have an excellent storage stability, are easily dispersable in water, and yield plastic mortars of high water resistance and plastering which are free from cracks.

4.7 Medical Uses

4.7.1 *Tissue Engineering*

A scaffold with an extracellular matrix mimic structure based on hyaluronic acid fibers has been prepared via lyophilization (31). Hyaluronic acid is shown in Figure 4.4

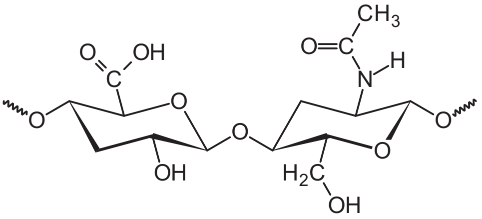


Figure 4.4 Hyaluronic acid.

The diameter of the hyaluronic acid fibers increased and the morphology changed from fiber to sheet-like structure when the concentration of hyaluronic acid solution was increased. To enhance the water resistance, the pure hyaluronic acid fiber membranes were chemically crosslinked by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride.

The in-vitro degradation behavior of the cross-linked hyaluronic acid fiber membranes in both the water and phosphate buffered saline solutions was investigated. The results indicated that the bonding water capacity increased after crosslinking and that crosslinked hyaluronic acid fibers could be used as scaffold in tissue engineering (31).

4.7.2 *Tooth Cleaning*

A simultaneous tooth cleaning and whitening method has been described (32). A light transmitting oxidizing gel is moved to the teeth. Thereafter, a hand-held light-emitting diode light source with a light transmitting lens and a cup forming a chamber with an open end is moved over the teeth. So, the cup distributes the gel while the teeth are exposed to the transmitted light.

This ensures an intimate contact of the teeth with the gel. Also, a more or less constant spacing between the light source and the tooth surfaces is maintained to get optimum results.

A sealant is then applied to the gel-coated teeth, after which a dental prophylaxis is performed by cleaning and scaling the teeth at the gum line, gingival margins, and crevicular spaces while avoiding excessive disruption of the sealant composition. Thus, the simultaneous cleaning and whitening procedure reduces the time of treatment at the dentist in comparison to a separate cleaning and whitening.

Sealant compositions contain water-resistant copolymers and a fluid carrier. The water-resistant polymer should be soluble or dispersible in the fluid carrier.

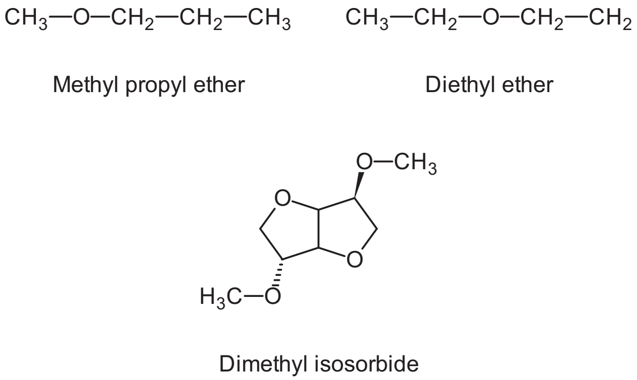
Suitable water-resistant polymers include poly(butyl methacrylate-*co*-(2-dimethylaminoethyl)methacrylate-*co*-methyl methacrylate), poly(ethyl acrylate-*co*-methyl methacrylate-*co*-trimethylammonioethyl methacrylate chloride), ethylcellulose, and esterified or crosslinked poly(methyl vinyl ether-*co*-maleic anhydride) (32).

The fluid carrier may be a volatile solvent that evaporates after contacting the sealant composition with the tooth surface, leaving behind a liquid or solid coating or film. Fluid carriers include water, ethanol, diethyl ether, methyl propyl ether, dimethyl isosorbide, and combinations of these compounds (32). Some fluid carriers are shown in Figure 4.5.

The ingredients that remove the acquired pellicle and open the enamel porosities for better penetration of the oxidizing composition are compounds that have acidic and chelating capabilities.

Useful acidic compounds include both inorganic and organic acids such as phosphoric acid, hydrochloric acid, acetic acid, lactic acid, citric acid, and their salts. Useful calcium chelating compounds include ethylenediamine tetraacetic acid, phytic acid, 1-hydroxyethylidene-1,1′-diphosphonic acid, citric acid, and their salts. These compounds are shown in Figure 4.6.

Preferred oxidation catalysts are chelated of iron and manganese, such as iron catalysts with a tetraamido-*N*-macrocyclic ligand. The synthesis of these compounds have been detailed (33,34).



$CH_3—O—CH_2—CH_2—CH_3$

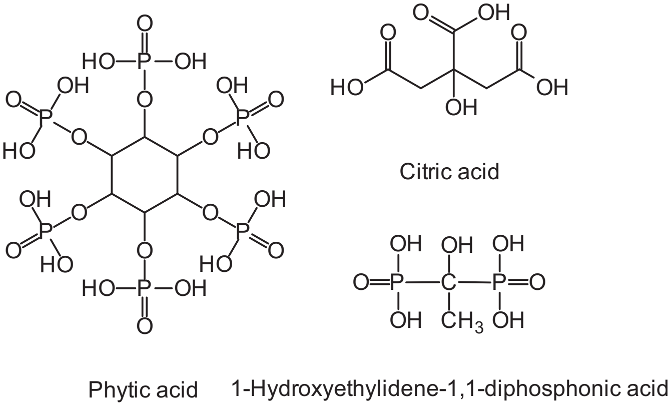
Methyl propyl ether

$CH_3—CH_2—O—CH_2—CH_2$

Diethyl ether

Dimethyl isosorbide

Figure 4.5 Fluid carriers.



Phytic acid

Citric acid

1-Hydroxyethylidene-1,1-diphosphonic acid

Figure 4.6 Calcium chelating compounds.

Also, colorants and pigments to assist in the placement and application of the tooth conditioning composition onto the teeth can be added (32).

4.8 Membranes

4.8.1 Microfiltration Membranes

Conventional materials used for porous membranes include cellulose derivatives, such as cellulose acetate, and polymers such as poly(acrylonitrile) resins, poly(amide) resins, poly(methyl methacrylate) resins, PE resins, poly(carbonate) (PC) resins, among others.

The membranes prepared from these materials are widely employed for ultrafiltration or microfiltration. However, the membranes of these materials are inferior in heat, chemical and boiling water resistance.

Therefore, attention has been paid to aromatic polyether ketones as materials for filtration membranes because of their extreme excellence in heat and chemical resistance.

Separation membranes that contain sulfones of aromatic polyether ketones have been proposed (35). However, these materials are known to swell in water (36). Further, the membranes dissolve and intensely swell in organic solvents, such as acetone, alcohols, tetrahydrofuran, dimethyl formamide, so that their application range is limited.

Processes for preparing porous membranes have been proposed, wherein aromatic polyether ketones are homogeneously dissolved in strong acids to prepare membrane-forming stock solutions, which are formed into desirable shapes and immersed in poor solvents against the polyether ketones for precipitation and coagulation (37, 38). Also, a method of crystallizing the thus obtained membranes has been described (39).

These wet processes are effective for obtaining membranes which are asymmetric in cross section, but the surfaces of these membranes do not have open pores that can be observed with a scanning electron microscope or have tight skin layers which are very low in open pore ratio. For these reasons, the membranes are useful for ultrafiltration but are unusable, for example, for microfiltration because of their low water permeability (40).

A porous crystalline aromatic poly(ether ketone) membrane has been developed, which has excellent heat resistance, chemical resistance, water resistance, water permeability and a balance of water permeability and fractionating characteristics (40).

4.8.2 Biobased Nanofiber Membranes

Protein-based nanofibers have been fabricated without using toxic crosslinking agents (41). Defatted soy flour was purified using an acid-wash process to obtain material with higher protein content, blended with gluten, and then electrospun into nanofibers with the help of PVA. The oxidation of sucrose with hydrogen peroxide was done to get oxidized sugar-containing aldehyde groups (−CHO). This compound is then used as green crosslinking agent. Crosslinking is the most common technique ussed to get an enhanced resistance to water and to improve the physical and mechanical properties.

Scanning electron microscope (SEM) micrographs of the fibers are shown in Figure 4.7. The nanofibers consist of 30% gluten, 25% purified soy flour and 45% PVA. They are both crosslinked by glyoxal and oxidized sucrose.

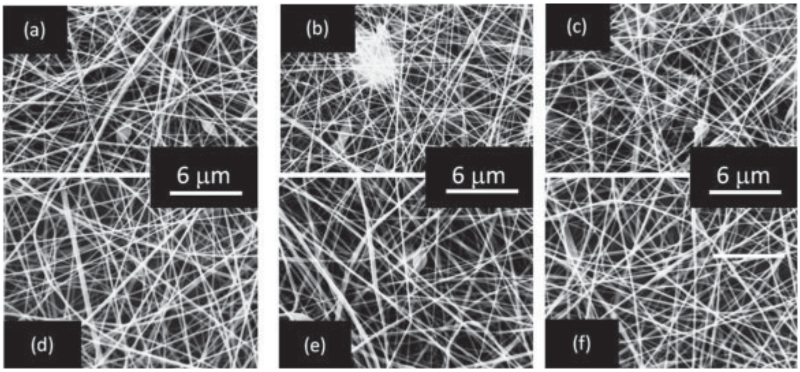


Figure 4.7 SEM micrographs of the fibers (41). (a) 5% glyoxal, (b) 10% glyoxal, (c) 15% glyoxal, (d) 5% oxidized sucrose, (e) 10% oxidized sucrose, (f) 15%oxidized sucrose. Reprinted from (41) with permission from Wiley.

The quality of crosslinking of the thus modified protein-based nanofibers was found to be similar to nanofibers crosslinked with toxic glyoxal. Also, a show of good resistance to water was established.

The nanofibers can be useful in fabricating inexpensive products with very high specific surface area and highly porous structure (41).

For these reasons, the use of such nanofiber-based membranes for filtering fine dust, bacteria, and possibly viruses is promising (42). Such protein-based nanofiber membranes may also be used in combination with other natural resins.

4.9 Personal Care Compositions

Compositions for imparting water resistance and aiding retention of active ingredients in personal care compositions are a basic issue (43, 44). Without them, personal care actives, such as sun care actives, may wash off, wear off, be re-emulsified, or otherwise lose their efficacy.

The problem with conventional water resistance imparting polymers is that they are usually tacky and impart a bad aesthetic feeling to consumers when formulated in sunscreen formulations.

Compositions for personal care use are shown in Table 4.5.

Table 4.5 Compositions for personal care (43).

Monomer	Amount/[%]	Amount/[%]
Allyl methacrylate		0.075
Butyl acrylate	25	20
Ethylhexyl acrylate		40
Methacrylic acid	15	1.5
Methyl methacrylate		38.5
Stearyl methacrylate	31	
Styrene	29	

For the synthesis of the copolymers, a standard emulsion polymerization method is used (44).

The personal care compositions and formulations containing the water-resistant polymers are of four basic compositions (43):

1. Oil dispersions,
2. Oil-in-water emulsions,

3. Water-in-oil emulsions, and
4. Solutions from one or more organic solvents.

Oil dispersions are prepared by dispersing the water-resistant polymers in the oil base with one or more active ingredients. The water resistance polymers can be dispersed in an oil phase or are prepared as an aqueous suspension prior to preparing the final oil-in-water or water-in-oil emulsion. The polymers can be added in either phase at any stage in preparing the composition or formulation.

Personal care formulations are prepared by combining water resistance polymers, an oil base, optionally including an aqueous phase, one or more active ingredients and optional additives, by warming the mixture with slow agitation. The oil-based personal care compositions and formulations include 0.01–10% of the water-resistant polymer based on the total weight of the formulation. Suitable solvents for preparing a solution of the polymer are typically alcohols, such as ethyl alcohol, and volatile silicones such as cyclomethicone.

Additives include fragrances, fillers, dyes, colorants, preservatives, biocides, and antioxidants. Other active ingredients include sunscreening actives, moisturizing actives, cleansing actives, detergent actives, vitamins, folic acid derivatives, exfoliating agents, deodorizing actives, fragrance actives, skin exfoliating actives, topical medicament actives, cosmetic agents, hair conditioners, facial care products, or body washes (43).

4.10 Package Uses

4.10.1 Adhesives for Beverage Labels

Reuseable beverage containers, especially beer bottles, are labeled with product name and consumer information using paper labels applied with an initially wet adhesive (45). After use of the container, the labels are removed in a washing process which is typically performed at 80°C in an aqueous 2% sodium hydroxide solution for several minutes before refilling and relabeling will occur.

Much activity has been undertaken to develop filmic or polymeric labels for reuseable beverage containers similar to those using paper labels because of the enhanced printing and appearance resulting from filmic labels.

However, problems were noted. Even though filmic labels may be resistant to caustic washing solutions, such labels are still prone to label separation or removal due to the effect of the caustic washing solution on the label adhesive.

Only a small number of reusable beverage containers receive direct printing and do not require relabeling when being refilled. However, these are more expensive to produce and have the lowest print quality (45). An acrylic polymer adapted for incorporation in an adhesive formulation that is resistant to aqueous environments has been found. Preferred monomers for the acrylic copolymer are shown in Table 4.6.

Table 4.6 Monomers for water-resistant label compositions (45).

Monomer	Monomer
Octyl acrylate	*n*-Butyl acrylate
Ethyl acrylate	Methyl acrylate
Lauryl methacrylate	Octyl methacrylate
Butyl methacrylate	Ethyl methacrylate
Methyl methacrylate	Vinyl acetate

Preferably, the acrylic copolymer used in the adhesives is formed from a combination of monomers, selected in proportions so that the resulting polymer has a glass transition temperature of −70 to −10°C.

Also a label assembly has been developed, adapted for reuse, which is resistant to aqueous environments. The label assembly is a layer of an acrylic pressure-sensitive adhesive that is disposed on a polymeric film.

As base material for the labels, biaxially oriented PP, PE, polyesters, poly(styrene), and PC can be used. Biaxially oriented PP is a preferred material (45).

4.11 Grouting Compositions

Tile installation involves the grouting of tile with a water-based cementitious grout, which is typically prepared by mixing a cementitious powder with water immediately prior to the application of the grout (46). Mixing of the cementitious powder with water is typically messy, and the success of the grouting application is highly dependent upon using the correct proportions of cementitious powder and water, and the proper amount of mixing and slaking time.

Slaking involves allowing the mixture to rest before a final mixing so that the water can thoroughly penetrate and chemically combine with the cementitious powder and other elements, e.g., dyes, pigments, binders, and solids. This causes the powder to become wetted and to better develop.

Getting an acceptable color uniformity with the grouts is problematic, since cementitious grouts are prone to efflorescence. Further, cementitious grouts commonly have a poor stain resistance and must be treated with topical sealers to resist staining (46).

Premixed grouts are typically more convenient to use than cementitious grouts, since they come ready to use. Thus, the application time can be reduced with wetting, mixing, and slaking steps eliminated. Premixed grouts are especially beneficial for color consistency and stain resistance. However, conventional premixed grouts do not harden as fast as cementitious grouts, and often require many days to cure properly.

Common tile grout compositions are water-based epoxy grout compositions, waterborne PU vinyl-based polymers, and organosilicon compounds. Moisture resistance is a key performance attribute of tile grouts, so that they can be used in showers, tub surrounds, kitchens and other areas with intermittent or continual wetness. Another key performance attribute of tile grouts is cleanability.

A premixed composition that contains a latex resin, a silicone emulsion, and a silane has been developed that shows quick curing and is water-resistant (46).

The latex polymer is a copolymer of styrene and butylacrylate. The silicone emulsion contains poly(methylethoxy siloxane) and alkylalkoxy silane such as octyl triethoxy silane (46).

A good staining resistance was observed against coffee, coke, red wine, soy sauce, ketchup, mustard, and vegetable oil (47).

4.11.1 Alginates

An alginate polymer has been used to prevent dyes from leaching out of colorimetric oxygen indicator films, which enable the customers to observe the presence of oxygen in the package in a simple manner (48). The oxygen indicator film does not leach when in contact with water.

UV-activated visual oxygen indicator films were fabricated using thionine, glycerol, TiO_2, and zein as a redox dye. Further, a sacrificial electron donor, UV-absorbing semiconducting photocatalyst, and an encapsulation polymer are used.

Thionine, is a strongly staining metachromatic dye that is widely used for biological staining (49). The compound is shown in Figure 4.8.

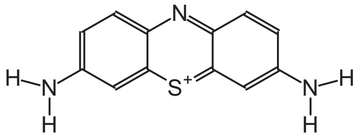


Figure 4.8 Thionine.

When this zein-coated film is immersed in water for 24 h, a dye leakage of 80.8% is observed. However, the introduction of alginate into an amount of 1.25% as a coating agent considerably diminishes the dye leaching to only 5.8%. This arises because the ion-binding ability of alginate can prevent the ionic dye from leaching into water (48).

The percentage of the remaining thionine in the zein-based and the alginate-based oxygen indicator films after dip coating is shown in Figure 4.9.

4.11.2 Dopamine

Mussels can attach themselves to nearly all types of hard surfaces in wet environments. Such attractive adhesive ability of mussels is

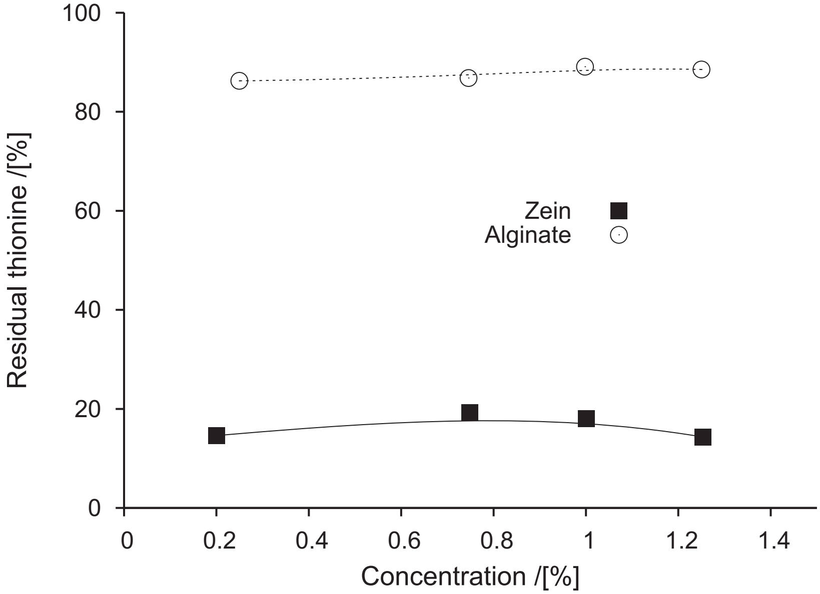


Figure 4.9 Percentage of the remaining thionine (48).

believed to rely on the amino acid composition of proteins found near the plaque-substrate interface (50). Dopamine has been identified as a simplified mimic of mussel proteins, which are rich in 3,4-dihydroxy-l-phenylalanine and lysine, because it contains both catechol and amine functional groups. Dopamine is also addressed as 3,4-dihydroxyphenethylamine and is shown in Figure 4.10.

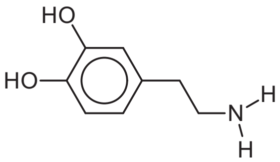


Figure 4.10 Dopamine.

This bioinspired adhesive has been used to tackle a dye leaching problem of colorimetric oxygen indicator films, which are widely used to verify the absence of oxygen inside a package of oxygen-sensitive materials. Simple immersion of packaging films into a dopamine solution results in the deposition of poly(dopamine).

This decreases the water contact angle of the films from 105° to 65°. The poly(dopamine) coating can reduce the thionine leakage of an UV-activated oxygen indicator film.

The film is then resistant to dye leaching. It looses its color by 5 *min* UV-B irradiation and the color returns in the presence of oxygen (50).

4.12 Xerogels

PVA silica hybrids with a considerably reduced solubility in water have been synthesized (51). These hybrid xerogels can be fabricated by a sol-gel processing of a mixture of PVA and the acid-catalyzed silica precursor tetraethoxysilane.

The effects of varying ratios of PVA and the silica precursor on the surface structure, thermal properties, crystallinity, and solubility of the hybrids have been assessed.

In contrast to the highly water soluble nature of PVA, all the hybrids displayed a considerably reduced solubility in water. This anomalous behavior of the PVA in the hybrids can be explained by the unavailability of its pendant hydroxyl groups. Such water-resistant PVA silica hybrids may find applications in various technologies requiring biocompatible systems, which are stable in an aqueous environment (51).

Macroscopic examination indicates that almost all the xerogels exhibit a semitransparent nature. The degree of transparency was found to increase with increasing polymer content of the hybrid. The semitransparent nature of the hybrids can be explained by the acid-catalyzed sol-gel process, which causes a faster hydrolysis resulting in the formation of an open polymeric structure that does not contribute to light scattering. SEM micrographs of silica and polymer silica hybrid xerogels are shown in Figure 4.11.

It is apparent from the images that the morphology varies from an interconnected mesoporous structure to a granular structure in the samples, depending on their composition. Even a low polymer content makes significant changes to the morphology. The microstructure becomes more uniform with increasing polymer content.

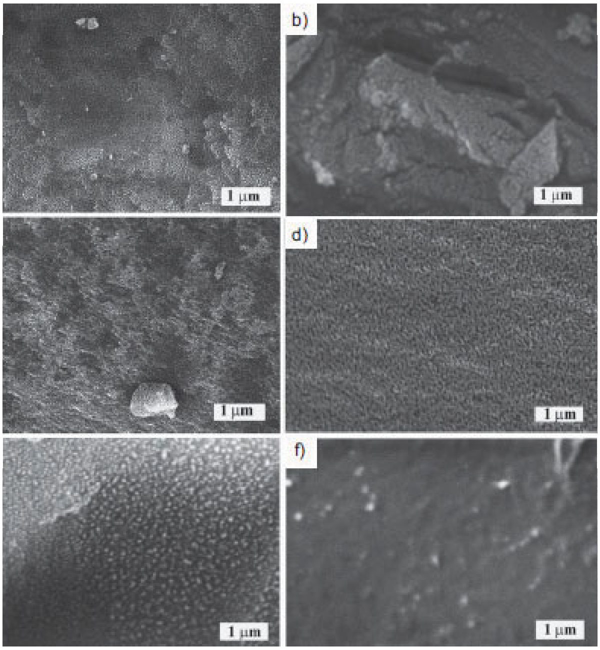


Figure 4.11 SEM micrographs of the xerogels (51). Tetraethoxysilane/PVA solutions at mass ratios of (a) silica only, (b) mass ratio 4:1, (c) mass ratio 3:2, (d) mass ratio 1:1, (e) mass ratio 2:3, (f) mass ratio 1:4. Reprinted from (51) with permission from Wiley.

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Acronyms

ATRP
  Atom transfer radical polymerization, 104
DCPD
  Dicyclopentadiene, 177
DDP
  N-[(1,1-Dimethyl-2-acetyl)ethyl]-β-dihydroxy ethylamino propanamide, 137
DMSO
  Dimethyl sulfoxide, 27
DOC
  Dissolved organic carbon, 2
EVA
  Ethylene-vinyl acetate, 187
FTIR
  Fourier transform infrared spectroscopy, 135
NMP
  N-Methyl-2-pyrrolidone, 138
PA
  Poly(amide), 74
PAA
  Poly(acrylic acid), 155
PAO
  Poly-α-olefin, 95
PC
  Poly(carbonate), 192
PCL
  Poly(caprolactone), 134
PE
  Poly(ethylene), 84, 180
PEG
  Poly(ethylene glycol), 67, 141
PET
  Poly(ethylene terephthalate), 107

PHB
  Poly(3-hydroxybutyrate), 25
PI
  Poly(imide), 61
PLA
  Poly(lactic acid), 178
PMMA
  Poly(methyl methacrylate), 129
POSS
  Polyhedral oligomeric silsesquioxane, 128
PP
  Poly(propylene), 180
PU
  Poly(urethane), 115, 180
PVA
  Poly(vinyl alcohol), 107, 179
QCM-D
  Quartz crystal microbalance dissipation, 7
RAFT
  Reversible addition-fragmentation chain transfer, 106
ROC
  Reduced organic carbon, 2
SAG
  Self-assembled microgel, 2
SAP
  Superabsorbent polymer, 160
SEM
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TBN
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TG
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UHMWPE
  Ultra-high molecular weight poly(ethylene), 84
UP
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VOC
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WBM
  Water-based drilling mud, 95
WPU
  Waterborne poly(urethane), 106

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