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Polymers for Controlled Release of Organotin Toxin

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ABSTRACT

An extensive investigation of organotin polymers capable of simultaneously providing long-term fouling resistance and useful engineering properties is discussed. New synthetic routes have been developed for organotin epoxy polymers utilizing (i) the crosslinking reaction of diepoxides with the free carboxyl groups present on a base polymer partially esterified with tributyltin oxide (TBTO), (ii) the polymerization of TBT acrylate and TBT methacrylate with vinyl monomers carrying functional groups capable of crosslinking, and (iii) simultaneous vinyl polymerization and epoxide crosslinking reactions. Flexible polymers curing under ambient conditions have also been developed (iv) by first preparing epoxy-terminated prepolymers by reacting TBT esters of ω-amino acids with diepoxides, and then crosslinking with diethylenetriamine. Room-temperature-curable organotin polymers developed also include (v) urethanes, (vi) aziridines and (vii) polyesters. Finally, (viii) an ablating polymer is developed by copolymerizing methyl methacrylate with TBT methacrylate.

The network structure is varied, and the average separation, length and type of crosslinks or pendant organotin groups are altered by appropriate changes in monomers and synthetic routes. Resultant changes in measured strength, fracture toughness and dynamic mechanical behavior of the polymer systems have been correlated with the structural variables employed.

The structure and reactivity of TBT carboxylate group have come under careful investigation. The bioactive species released from

these polymers has been identified as tributyltin chloride by spectroscopic and chromatographic techniques. The release rate of tin has been determined in the laboratory, and the results fitted to mathematical models corresponding to the bulk abiotic bond cleavage.

An important aspect of organotin compounds that has drawn close attention in recent years is their biological effects which have led to their widespread application in biocidal compositions [1]. Investigations in this area have clearly shown the potential of organotin polymers for use as antifouling coatings. In this context, not only the synthesis and characterization of organotin polymers, but also the understanding of the mechanism of release of organotin toxin from the polymers assume importance. Current research leading to the progressive understanding of structure-property relationships, including the biocidal properties of organotin polymers, is therefore stressed in this review.

Antifouling Coatings

Fouling, i.e., the growth of marine organisms on submerged surfaces, is one of the worst problems in marine environments; and prevention of fouling is next in importance only to corrosion prevention in the protection of ships' bottoms [2]. Fouling of the ship hull leads to a large increase in frictional resistance which, in turn, results in a wastage of fuel. Fouling causes an unpredictable distortion in signals from immersed acoustic and electronic navigational devices. In many cases, the fouling organisms also destroy the anticorrosion coating on marine equipment, leading to serious corrosion damage to such surfaces.

While many techniques have been tried in the prevention of fouling such as ultraviolet irradiation [3], ultrasonic vibration [4] or covering by non-sticky silicone rubber coatings [5], up to now, the use of antifouling paints has been the only economically and technically feasible protection against fouling [2,3]. Antifouling paints, whose mechanism of action is the leaching of toxicants, are attractive because of easy application and maintenance. Their main drawback is the mechanism of action itself; it is based on the release of bioactive materials. Whereas the antifouling action is needed mainly when the ship is in port, the important fouling organisms being denizens of the sea shore, a very high percentage of bioactive material is released when the ship is moving, due to the turbulent conditions around it.

Antifouling Toxicants

Until now, the most important antifouling poison has been cuprous oxide [6-8]. The critical leaching rate, i.e., the rate required to keep off all fouling, is 10 $\mu g/cm^2/day$ for copper [9]. The poison loss rate by the $\sqrt{t}$ relation is the main problem of antifouling coatings. If the amount of poison needed were compared with that used, it would be no more than 20%; thus the efficiency of antifouling paints is very low. On the other hand, the loss due to fouling is so high that it is worthwhile wasting about 90% of the poison if the remainder serves to prevent fouling [2]. Researchers have always been looking for more active poisons [6-8,10] which are effective against the whole spectrum of foulants, because copper is somewhat deficient in its action against algal fouling.

Organoarsenic compounds are very effective; but they are a problem to apply because they irritate the eyes and nasal membranes. Tributyllead and triphenyllead compounds have similar toxicity against fouling organisms as organotin compounds, but their toxic hazards on application are greater. Tributyltin and triphenyltin radicals are very effective against all types of fouling and have been widely used. They are toxic to man, but they are not a hazard to him if some simple precautions are taken [11]. Unlike organoarsenic, organolead and organomercury compounds, organotin compounds easily degrade to nontoxic compounds in the environment. Among the other advantages claimed for the use of organotin toxins in antifouling coatings is the absence of corrosion problem, which always occurs with conventional paints containing cuprous oxide [6].

Extensive toxicological evaluations of organotin compounds have led to the conclusion that the trialkyltin derivatives are the most effective toxins against marine organisms [12]. A comparison of the toxicity of a homologous series of trialkyltin compounds has indicated that the tributyltin derivatives represent the optimum balance between high toxicity against marine organisms and tolerance toward mammals [6]. Field tests have given the best fouling resistance when the tributyltin group is easily hydrolyzable [13]. Detailed investigations by Aldridge [14] and Selwyn [15], of the influence of organotin compounds on mitochondrial functions, support these observations. On the basis of these considerations, tributyltin carboxylate has been the structural feature of choice in our syntheses of polymers for potential use in antifouling compositions.

Improving Antifouling Coatings

The practical possibilities to extend the effective lifetime of antifouling coatings are to increase the film thickness, use more effective bioactive materials, or to control the leaching rate of bioactive substances.

Increasing film thickness is simple, but this does not change the $\sqrt{t}$ dependence of leaching rate. As the rate of release of poison has to be much higher in the initial stages, the accompanying perils like wastage and environmental hazard are aggravated.

The use of stronger poisons, an approach which involves lower leaching rates, is a good approach to the solution of the short-life time problem. But they will also be more toxic to people, and this is the main limitation of this technique.

Several methods have been tried for controlling the release rate. One of them is the use of a special top coat of water-insoluble hydrophilic acrylic resin [16]. A more recent approach designed to solve the excessive leaching problem is the development of organometallic polymers [17], in which biocidal organometallic groups are chemically attached to their backbones. Among these, organotin polymers are likely to have more practical application than the other organometallic polymers. It has been shown that the organometallic polymer is optimally effective against fouling organisms when the organic radical of the organometallic groups is either propyl or butyl [6]. Also, studies of the biocidal action of organometallic compounds have shown that no one of such compounds has effective action against all the sliming bacteria [17].

Therefore, by chemically attaching the organometallic group to a polymer backbone, two goals are aimed. First, and most important, it is possible to reduce the leaching rate in order to achieve longer antifouling protection as a result of the chemical bond between the bioactive group and the polymer. Second, by incorporating two or more organometallic groups into a resin, a broadening of its biocidal action is achieved. Due to the good film characteristics generally exhibited by acrylics, the first polymers prepared were poly(tributyltin acrylate) and poly(tributyltin methacrylate) [6]. However, the film properties, mechanical properties (impact resistance, hardness, adhesion, flexibility), weatherability, and resistance to heat and thermal shock of the organotin acrylate homopolymers are not good enough for application in durable coatings.

Organotin Epoxide Polymers

It is in this context that we undertook the synthesis and characterization of thermoset polymers as a novel approach to improve the film-forming properties and biocidal activity. The synthetic scheme adopted for the preparation of the polymers involves the partial esterification, with tributyltin oxide (TBTO), of linear base polymers containing carboxylic acid or anhydride groups as the first step. The free carboxylic acid or anhydride groups of the prepolymers are then cured with diepoxides [18].

The properties of the network structure obtained thus have been varied over a wide range by changing the chemical structure of the base polymer as well as that of the crosslinking epoxy monomer. The tin content of the polymer is altered by controlling the degree of esterification of the base polymer, which also varies the crosslink density obtained in the second step. Greater esterification with TBTO leads to fewer available carboxyl groups for crosslinking and, consequently, to larger separation between points of crosslinking on the prepolymer. Promotion of homopolymerization at high epoxy-to-anhydride ratios will have the general effect of extending the lengths of epoxy crosslinks; this has been achieved by appropriate choice of catalysts for the curing reaction [18]. When tertiary amines such as dimethylaniline are employed, esterification is the predominant reaction with the epoxide; under these conditions, the maximum amount of epoxide incorporated in the matrix is limited by the stoichiometry of one epoxide to one carboxylic acid unit. On the other hand, when homopolymerization of the epoxide is facilitated by the presence of stannous octoate or uranyl nitrate, the proportion of epoxide units reacting with each carboxyl function is increased over a higher range, with attendant improvements in matrix strength and toughness.

The base polymers employed include poly(styrene-*co*-maleic anhydride) [SMA-1000A, ARCO], poly(methyl vinyl ether-*co*-maleic anhydride) [AN 139, General Aniline & Film], poly(methyl vinyl ether-*co*-maleic acid) [AT 795, General Aniline & Film], poly(1-hexene-*co*-maleic anhydride) [PA-6, Gulf] and poly(1-decene-*co*-maleic anhydride) [PA-10, Gulf]. The diepoxides used include bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate [ERL 4289, Union Carbide], 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate [ERL 4221, Union Carbide], 4-vinylcyclohexane dioxide [ERL 4206, Union Carbide], 2-(3,4-epoxy)cyclohexyl-5,5-spiro(3,4-epoxy)cyclohexane-*m*-dioxane [ERL 4234, Union Carbide] and diglycidyl ether of bisphenol-A [EPON 828, Shell]. Uranyl nitrate, stannous octoate, dimethylaniline, 4-dimethylaminomethylphenol and 2,4,6-tris(dimethylaminomethyl)phenol are some of the catalysts employed [18,19].

The degree of esterification of base polymers, the structure of the epoxy monomers, and the type of catalyst used have thus been varied in these synthetic schemes to effect changes in the average separation between TBT groups and the length of the epoxy crosslinks. Resultant changes in measured strength, fracture toughness and dynamic mechanical behavior of the polymer systems have been correlated with the structural variables employed. Toughening by carboxyl-terminated liquid elastomers has also been studied, and the improvement in fracture toughness correlated with the average particle size of the dispersed elastomer phase. Of the various catalysts studied, uranyl nitrate has caused the highest degree of crosslinking. The formation of domains in the matrix with independent glass transitions is indicated by variations in loss moduli; these also reflect the structural effects of the bulky TBT groups and of the different epoxy monomers [18].

Many variations of this scheme have been investigated, including one which provided for simultaneous vinyl polymerization and carboxyl-epoxide reactions [19]. Compositions of several of these organotin-epoxy coatings, the method of preparing specimens for antifouling tests in marine environments and procedures for determining antifouling performance have been reported [19,20]. Fouling resistance upto 40 months has already been observed. The results show that duration of fouling resistance is not as much dependent on the concentration of tin as it is on matrix characteristics [21].

Controlled Release

Performance tests in marine environments reveal that the resistance to fouling is influenced by matrix characteristics [21]. Parallel tests in the laboratory indicate that only a very small fraction of the available tin is released during the service life of the coating [22]. It is thus reasonable to infer that fouling commences when the rate of release falls below the critical rate, and not because of the complete depletion of tin in these systems. Matrix hydrophilicity and permeability seem to be the factors determining the duration of fouling resistance.

Antifouling performance of these organotin carboxylate polymers indicate that their mode of action corresponds to the bulk abiotic bond cleavage model [13]. We have carefully considered all the controlling factors, viz.,

(1) diffusion of water (and possibly chloride) into the polymer matrix from sea water;
(2) hydrolysis of tributyltin carboxylates to produce TBTO (or TBTCl);
(3) diffusion, from the matrix to the surface, of the mobile species (TBTO or TBTCl) produced;
(4) phase transfer of the organotin species;
(5) its migration across the boundary layer; and
(6) possible mechanical loss of the tributyltin species from the surface.

NMR studies have revealed that the TBT group undergoes fast chemical exchange, and hence a hydrolytic equilibrium is rapidly established between TBT carboxylates and TBTO [23]. Laboratory determination of the release rate, under laminar flow conditions, shows that the phase transfer and migration across the boundary layer are also relatively fast [22]. Thus we have come to the conclusion that diffusion, from the matrix to the surface, of the mobile tributyltin species produced, is the factor controlling the rate of release in epoxy systems.

As the mobile species produced diffuses out, the hydrolysis is expected to proceed at a concentration-dependent rate. The model developed by Godbee and Joy for predicting the leachability of radionuclides from cementitious grouts [24] closely represents this situation. Based on their equations, the rate of release of tin (in g/cm^2/sec) from the surface should be:

$$dq/dt = C_m D^{0.5} K^{0.5} [\mathrm{erf}(K^{0.5} t^{0.5}) + \frac{\exp(-Kt)}{(\pi Kt)^{0.5}}] \qquad (1)$$

where C_m is the concentration of the mobile species in g/cm^3,
D is the effective diffusivity in the matrix in cm^2/sec,
K is the concentration-dependent hydrolysis rate in sec^{-1}, and
t is the time in sec.

The most salient feature of this model is that when Kt becomes large, $\mathrm{erf}(Kt)^{0.5}$ approaches unity, and the rate becomes independent of time. This zero order rate is the coveted characteristic of controlled release systems. However, we have not been able to realize this ideal behavior in the epoxy systems. This may partly be due to the tight matrix in these epoxy systems.

The epoxy compositions discussed so far are highly crosslinked [18] and have glass transition temperatures around 140°C. Their free volumes and segmental mobilities are very low. It is known that these factors decrease the diffusivity (D) in the matrix [25]. Further, the magnitude of decrease is greater the larger the diffusing molecule [25]; TBTO is a relatively large molecule.

Equation (1) predicts greater rate of release when C_m is higher; the concentration of the mobile species is expected to be higher in hydrophilic matrices.

Crosslinking of Organotin Copolymers

Since it has become apparent that matrix hydrophilicity and permeability are the factors determining controlled release from organotin carboxylate polymers, a new scheme for obtaining thermoset plastics that permits closer control of crosslinking sites is pursued. An optimum balance between film properties and biocidal action is expected by the incorporation into the polymer, by means of copolymerization, of epoxy (or hydroxyl) groups and subsequent crosslinking [26].

Organotin monomers are obtained by esterification of acrylic acid and methacrylic acid with TBTO. These monomers are copolymerized with glycidyl acrylate and glycidyl methacrylate (which contain epoxy groups) and with N-methylolacrylamide (that carries a hydroxyl group). The monomer reactivity ratios of the six pairs are determined, and the experimental values used to derive information on the distribution of the units of a particular monomer in the copolymer chain. Thus, a suitable copolymer containing either the blocks of organotin monomer units, or randomly distributed units of either monomer can be selected as desired. Varying crosslink density and rigidity are achieved with crosslinking agents like aliphatic and aromatic amines and also with catalysts like uranyl nitrate [26]. The copolymers from the organotin monomers and N-methylolacrylamide may be crosslinked with diisocyanates to produce polyurethane coatings.

Information on biotoxicity is obtained by studying the inhibition of marine and soil bacteria and of a soil fungus [26]. The nature and degree of crosslinking have a significant effect on the size of the inhibition zone; the tighter the crosslinked network, the smaller is the inhibition zone.

Flexible Epoxy Plastics

The extremely low diffusivity of tributyltin species in the polymer matrix is partly due to the tightness of these epoxy matrices [22]. Past systems have only considered TBT carboxylate group linked directly to the backbone of the polymer. Therefore, by varying the length of the sidechain holding the TBT moiety, greater mobility of the TBT group is to be expected. To accomplish this, diglycidyl ether of bisphenol-A (DGEBA) is first modified by reacting with TBT esters of ω-amino acids; the resulting prepolymers are then cured with diethylenetriamine (DETA) at room temperature. A lower T_g is actually observed as this chain is extended, which means lower activation energy for this motion. The decrease in matrix constraints allowing this motion may also result in decreased resistance to the diffusion of TBTO. The synthesis and characterization of these systems have been the next steps in pursuing the idealized controlled release from epoxy systems [27,28].

TBT esters of glycine, 4-aminobutanoic acid, 6-aminohexanoic acid and 11-aminoundecanoic acid are first synthesized. The prepolymer is then prepared by dissolving EPON 828 (Shell DGEBA) in a benzene solution of the TBT ester, followed by removal of the solvent. Epoxide assay shows the prepolymers to have epoxide equivalents ranging from 344 to 370 (Table 1). The ratio of TBT ester to DGEBA is adjusted to give a consistent number of pendant groups of TBT moiety per gram of the cured resin (Table 1). The prepolymers are mixed with DETA and cured at room temperature [27,28].

The loading of tin in the final cured polymer is nominally 5% (w/w). This value varies since it is the number of pendant organotin chains which is kept constant (Table 1). The small variation in the density of pendants is due to the slight homopolymerization of the epoxide during drying, which changes the amount of DETA required for curing; the variation is not great [27,28].

It is expected that the addition of the TBT esters would have a plasticizing effect; previous work [18] with TBT esters gives precedence for this. In fact, there is a large variation in the plasticizing effect as the chain is lengthened (Table 2). The glass transition varies from 92°C with TBT glycinate to 68°C with

TABLE 1. Epoxy Equivalents and Pendant-chain Concentrations.

Polymer	Epoxy Equiv. of Prepolymer, g/equiv.	Moles of Pendant Chains per Gram of Polymer
TBT Glycinate/DGEBA/DETA	365	5.1×10^{-4}
TBT 4-Aminobutanoate/DGEBA/DETA	344	4.9×10^{-4}
TBT 6-Aminohexanoate/DGEBA/DETA	345	5.0×10^{-4}
TBT 11-Aminoundecanoate/DGEBA/DETA	370	5.0×10^{-4}

TABLE 2. Tensile, Flexural and Glass Transition Values for the Modified Epoxy Polymers.

	Tensile, Kg/cm^2		Flexural, Kg/cm^2		
Polymer*	E	S	E	S	T_g, °C
GLY/DGEBA/DETA	33,368	288	25,170	879	(50) 92
BUT/DGEBA/DETA	39,302	626	33,663	1090	(55) 90
HEX/DGEBA/DETA	30,000	619	27,497	893	(54) 80
UND/DGEBA/DETA	-- ---	---	-- ---	---	(55) 68

*GLY = TBT glycinate; BUT = TBT 4-aminobutanoate;
HEX = TBT 6-aminohexanoate; UND = TBT 11-aminoundecanoate.

TBT 11-aminoundecanoate. The reduction in strength and modulus is also apparent, except in the case of glycinate which has a value lower than expected [27,28],

Room-Temperature-Curable Organotin Polymers

There exists a need for more methods of preparing antifouling coatings that can be cured at room temperature than the one described above. Our results on the incorporation of organotin groups into room-temperature-cured urethanes, aziridines and polyesters have been reported [21,29]. Urethanes and polyesters are also attractive from the point of view of their greater hydrophilicity and segmental mobility. There is evidence in the literature to believe that vinyl and urethane polymers would release organotin species at a greater rate [10].

Urethanes. TBT ester of tartaric acid is first synthesized from TBTO and tartaric acid. TBT tartrate (a dihydroxy monomer) is then reacted with excess tolylene-2,4-diisocyanate (TDI) to produce the NCO-terminated prepolymers. The prepolymers are cured added to the reaction mixture toward the end. Gel time can be controlled, by controlling the addition of the accelerators. The mixtures cure at room temperature to hard, nontacky solids [29].

Ablating Organotin Polymers [30]

As pointed out earlier, the coveted characteristic of controlled release systems is the zero order delivery of the active agent. It is acknowledged that reservoir devices, especially when membrane encapsulated, are capable of steady-state release. Erodible devices of proper geometry can also approach a constant rate of delivery. Matrix devices, however, are generally expected to show $\sqrt{t}$ relation in the release profile. We have shown [31] that a time-independent rate of release of organotin is possible from polymer monoliths in which trialkyltin carboxylate groups are chemically attached to the polymer network; this prediction has yet to be realized.

As mentioned earlier, NMR studies prove that the TBT group undergoes fast chemical exchange [23,22]. As a consequence, even the interfacial reaction between TBT carboxylates and sodium chloride is very fast [23,22]. Thus, if poly(methyl methacrylate-*co*-TBT methacrylate) is used as a coating in marine environments, TBT chloride would be readily released from the surface for antifouling action. As the hydrolysis proceeds, the hydrolyzed groups become hydrophilic and the polymer molecules at the surface would erode. Fresh surface would be exposed, and antifouling performance would not be controlled by diffusion process.

It is known that a rate of release of 0.5 μg Sn/cm^2/day is sufficient protection against barnacles [32]. 5 μg Sn/cm^2/day would be sufficient protection against any form of fouling, in any environment. A release rate of 5 μg/cm^2/day can be expected if the rate of ablation is about 3 x 10^{-10} cm/sec and if the copolymer containing 20% tin is used. If the coating thickness is 1 mm, it may be expected to provide protection for about 11 years.

by crosslinking with castor oil (a trihydroxy compound). The approach guaranteed the completion of the reaction between TBT tartrate and TDI, ensuring the complete incorporation of the organotin moiety into the crosslinked structure. The cured polymers are flexible; they are characterized [29].

A noteworthy feature of this scheme is the fast reaction, even at room temperature, between isocyanate and hydroxyls in the presence of TBT carboxylates. Trialkyltin groups can, in fact, be expected to catalyze the urethane reaction; the isocyanate group can coordinate with tin, getting more polarized and exposing the isocyanate carbon for nucleophilic attack by the hydroxyl oxygen.

Aziridines. Poly(styrene-*co*maleic acid) is prepared from commercially available poly(styrene-*co*-maleic anhydride), and then partially esterified by reacting with TBTO. The free acid groups of these partial esters are found to react with a polyfunctional aziridine [XAMA-2, Cordova], curing to a nontacky solid at room temperature; the cured plastics are characterized. Because of the low molecular weight of the base polymer used [SMA-1000A, ARCO], a significant fraction of the prepolymer molecules does not become incorporated in the network structure when the degree of esterification is high, and the sol fraction becomes consequently large. However, heavy loading of tin in the crosslinked polymer is possible in the aziridine-cured systems; with base polymers of higher molecular weight and different compositions, it should be possible to extend the range of modifications of the network structure even further.

Polyesters. Organotin vinyl monomers, such as TBT acrylate and TBT methacrylate, are mixed with unsaturated polyesters [WEP-661 of Ashland, P-43 of Rohm & Haas] and cured with a free-radical initiator. Benzoyl peroxide or methyl ethyl ketone peroxide is capable of curing the mixture, with the aid of dimethylaniline and /or cobalt naphthenate. However, the organotin group is found to interfere with the activity of cobalt naphthenate. Hence, if cobalt naphthenate is to be used as an accelerator, it should be

A detailed study of the copolymerization of methyl methacrylate and TBT methacrylate has revealed that they form an ideal copolymer system [30,33]. In contrast to the poor film properties of poly(TBT methacrylate) and poly(TBT acrylate), poly(methyl methacrylate-*co*-TBT methacrylate) is found to have excellent film characteristics, even when the tin loading is as high as 25%. The films are clear, with non-sticky surface; they have good adhesion to metals [30].

It has to be pointed out here that special precautions are required in the determination of the monomer reactivity ratios, because of the chemical exchange existing in TBT carboxylates [22]. Thus they are readily hydrolyzable, and unless anhydrous solvents are used in the polymerization of trialkyltin carboxylate monomers, erroneous values of r_1 and r_2 might result.

Organotin Polymers in Wood Preservation

Since some adverse effects of conventional preservatives like pentachlorophenol, creosote, copper, chromium and arsenic have given rise to misgivings about their continued use in the long-term protection of wood against biodegradation, we have undertaken the *in situ* copolymerization of organotin monomers in wood. Trialkyltin has a broad spectrum of activity; the impregnation technique minimizes the environmental hazards and also improves other properties of wood at the same time [34].

Vinyl monomers like maleic anhydride or glycidyl methacrylate are copolymerized *in situ* with TBT methacrylate in grand fir wood. Wood samples are first impregnated with a solution of the monomers and catalysts, and then heated to initiate the reaction. In addition to the vinyl polymerization, grafting of the polymer to wood also proceeds by the reaction between the hydroxyls of wood and the functional groups (epoxide or anhydride) in the polymer [34].

Specimens containing varying amounts of polymers are prepared and tested. The macrodistribution of the polymer in the treated wood is determined by scanning electron microscopy. The microdistribution is determined by microprobe analysis for tin atoms; a significant amount of the polymer is located in the cell wall.

In the longitudinal as well as in the transverse direction, the ultimate flexural strength, flexural modulus of elasticity and impact strength of treated wood increase significantly, compared to those of untreated wood. The swelling and water absorption of treated wood are substantially less than those for untreated wood in all cases. The resistance to degradation is established by exposing specimens of treated wood to brown-rot, white-rot and soft-rot fungi, as well as to a marine bacterium [34].

Summary and Conclusions

An extensive investigation of organotin polymers capable of simultaneously providing long-term fouling resistance and useful engineering properties is discussed. New synthetic routes have been developed for organotin epoxy polymers utilizing (i) the crosslinking reaction of diepoxides with the free carboxyl groups present on a base polymer partially esterified with TBTO, (ii) the polymerization of TBT acrylate and TBT methacrylate with vinyl monomers carrying functional groups capable of crosslinking and (iii) simultaneous vinyl polymerization and epoxy crosslinking reactions. Flexible polymers curing under ambient conditions have also been developed (iv) by first preparing epoxy-terminated prepolymers by reacting TBT esters of ω-amino acids with diepoxides, and then crosslinking with amine curing agents. Room-temperature-curable organotin polymers developed also include (v) urethanes, (vi) aziridines and (vii) polyesters. Finally, (viii) an ablating polymer is developed by copolymerizing methyl methacrylate with TBT methacrylate.

The network structure is varied, and the average separation, length and type of crosslinks or pendant organotin groups are altered by appropriate changes in monomers and synthetic routes. Resultant changes in measured strength, fracture toughness and dynamic mechanical behavior of the polymer systems have been correlated with the structural variables employed. Many of the compositions show prolonged fouling resistance in marine environments; some have excellent composite properties in fiberglass laminate composites [35,28].

The structure and reactivity of TBT carboxylate groups have come under careful investigation. The bioactive species released from these polymers has been identified as tributyltin chloride by spectroscopic and chromatographic techniques [23]; Aldridge [14] and Selwyn [15] have already shown that TBT chloride deranges the mitochondrial functions. The release rate of tin has been determined in the laboratory, and the results fitted to mathematical models corresponding to bulk abiotic bond cleavage [22]. The attainment of zero order release of organotin toxin from polymers can be expected to be realized with further detailed studies of the modification of polymer properties and of the mechanism of transport of the organotin species in the polymer matrix.

In conclusion, reference must be made to various other types of organotin polymers reported in recent years [36] whose biochemical activity and biocidal properties are under various stages of investigation and confirmation. Particularly noteworthy among these are the novel classes of organotin polymers, incorporating tin atoms in the backbone of the polymer chain, which have been synthesized by Carraher and coworkers [37-46] and many of which would prove to have diverse and interesting applications.

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