Glass-Reinforced Composites of Antifouling Organotin Epoxy Polymers

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Synopsis

The use of a new class of thermoset organotin epoxy polymers as matrix resin for composites has been evaluated. Copolymers of maleic anhydride with hexene-1, decene-1, or styrene were partially esterified with tributyltin, and the residual carboxyl groups were crosslinked with glycidyl methacrylate when preparing glass fabric-reinforced composites. Glass composites were also prepared from DGEBA cured by tributyltin 3,5-diaminobenzoate. The tensile, flexural, and impact strengths of the composite specimens warrant their use in structural applications requiring antifouling protection.

INTRODUCTION

Marine fouling is the term used to describe the growth of marine organisms, such as barnacles, on submerged surfaces in the ocean. Besides increasing fuel consumption, fouling also causes damage to protective coatings of ships and accelerates corrosion. Antifouling paints containing toxic components, such as compounds of copper, arsenic, and tin, provide protection against fouling.[1] Toxicologic studies of organotin compounds have lead to the conclusion that the trialkyltin derivatives are the most toxic to marine organisms.[2,3] Among these, the optimum balance between high toxicity against marine organisms and tolerable toxicity against mammals is shown by the tributyltin compounds which have, therefore, been used widely as toxic additives in marine antifouling paints.[4]

In such formulations, however, reasonably long-range protection is obtained only by incorporation of large amounts of the toxic additive which results in overkill in the earlier stages. In order to overcome this deficiency, polymers have been synthesized which contain the organotin group, particularly tributyltin carboxyl groups, chemically bonded to the polymer chain.[4–6] The controlled release of the chemically linked organotin groups is expected to provide long-term protection against fouling.[7,8] Polymers of tributyltin acrylate (TBTA) and tributyltin methacrylate (TBTMA) are examples of such organotin polymers.[6] Their poor film-forming properties prompted the preparation and evaluation of copolymers of TBTA and TBTMA with other vinyl monomers for improved antifouling coatings.[9–12]

In contrast to the linear polymers employed in these studies, previous work in our laboratories has emphasized the study of crosslinked structures containing tributyltin groups for controlled release of organotin. Initially, thermoset, or-

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ganotin epoxy systems were chosen for investigation because of the desirable bulk properties and adhesive characteristics of epoxy polymers. This research, described in detail elsewhere,[5,13-15] has developed many routes for synthesis of epoxy network polymers and other crosslinked structures.[16,17] These polymers have performed successfully as antifouling coatings during many months of exposure to marine fouling environments.[18,19] The effects of chemical structure upon mechanical properties[13] have been investigated. The crosslinked polymers have been shown to be effective against *Pseudomonas nigrifaciens* (marine bacterium), *Sarcina lutea* (soil bacterium), and *Glomerella cingulata* (soil fungus), and the controlling effect of the nature of crosslinks and degree of crosslinking on release of the toxic groups has also been determined in our earlier work.[20]

The purpose of this report is to present the results of development of glass reinforced composites based on the new organotin epoxy polymers. Such composites would be of value in structural applications in marine environments. For example, pilings, boats, or buoys could be fabricated from these composites. With the organotin biocide incorporated through the thickness of the outer structural element, better and longer protection against fouling might be expected than from thin coatings.

EXPERIMENTAL

Preparation of Composites Using DGEBA Cured with Tributyltin 3,5-Diaminobenzoate

Glass fabric (J. P. Stevens and Co., Inc., style 1581/50, S920 finish), weighing approximately 300 g, was coated with a mixture of 95 g (0.50 equivalent) of epoxy resin (DGEBA, CIBA 6004) and 55.1 g (0.50 equivalent) of tributyltin 3,5-diaminobenzoate (TBT-DABA), which was synthesized as described elsewhere.[14,15] Four 9 × 12-in. plies were used for tensile specimens, and 28 each 6 × 6-in. plies were used for flexural and impact samples. They were placed in a 100°C oven for 33 min, pressed at 150°C (200 psi) for 40 min, and postcured for 2 hr at 100°C. Samples were cut, machined, and tested in accordance with ASTM standards D256-73 (impact), D638-72 (tensile), and D790-71 (flexural). The warp and fill directions were the same in each ply of the multiply laminate specimens. The fill direction was parallel and the warp perpendicular to the length of the specimen in all cases.

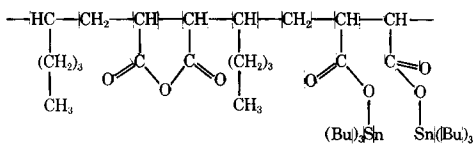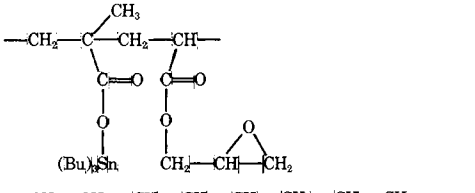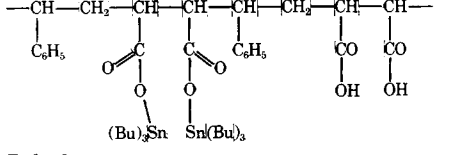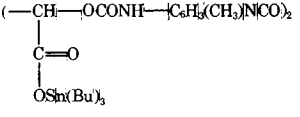### Preparation of 40% Tributyltin Ester of 1-Decenemaleic Anhydride Copolymer (PA 10)
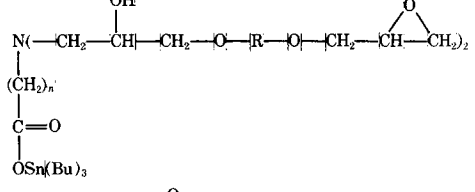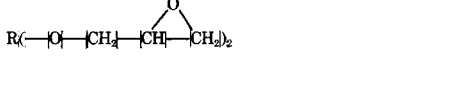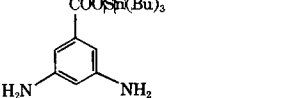
Seventy-five grams (0.315 equivalent anhydride) of PA 10 (Gulf) was dissolved in 300 ml dry ethyl acetate in a 2-liter flask fitted with a water trap and reflux condenser. The solution was brought to reflux, and 75.05 g of previously distilled TBTO was added dropwise from an additional funnel. The solution was refluxed for 1 hr following the addition and cooled and most of the solvent was removed using a rotary evaporator. The remainder of solvent can be removed by vacuum oven, but it was expedient to calculate the amount of residual solvent by mass balance and, from that, compute the anhydride equivalent of the syrup. This syrup was used to prepare composites.

Preparation of a Composite Using 40% Tributyltin Ester of PA 10

Sixty grams of 40% TBT/PA 10 (0.0756 equivalent of anhydride) was dissolved in 100 ml acetone, and 21.47 g glycidyl methacrylate (0.1512 equivalent of epoxide) was added. Two hundred and ten grams (nine 9 × 12-in. plies) of glass fabric (J. P. Stevens, style 1581/50, S920 finish) was coated with this mixture, and the acetone was removed by placing the plies in a 60–70°C vacuum oven for 20 min. Four plies were stacked and pressed to obtain tensile specimens. The remaining five were cut to 3 × 6 in. and the 30 plies pressed for flexural specimens. The panels were pressed at 200 psi, 150°C for 10 min, and postcured for 2 hr at 150°C. Preparation of specimens and testing were conducted in accordance with ASTM standards listed already.

The preparation of the tributyltin ester and composites from hexene–maleic anhydride copolymer (PA 6) and styrene–maleic anhydride copolymer (SMA 1000A, ARCO) was conducted following the procedure described above for PA 10.

TABLE I
Tributyltin Structural Units Employed in Synthesis of Crosslinked Polymers

Prepolymer/monomer structural unit	Crosslinking agent	References
	cycloaliphatic epoxides, DGEBA, glycidyl methacrylate	13
	amines, anhydrides, etc.	17, 20
	aziridines	16, 21
Polyols		16, 21
	DETA, MPDA, etc.	14, 15
		14, 15

RESULTS AND DISCUSSION

Different types of crosslinked organotin polymers synthesized in the course of our research are presented in Table I. Among these, a large group is based on the copolymers of maleic anhydride partially esterified by tributyltin. The residual free carboxyl groups of these prepolymers are then crosslinked through diepoxides, aziridines, or glycidyl methacrylate. In another class, the tributyltin group is attached to crosslinking agents carrying amino or isocyanate functional groups which can react with epoxides or polyols to produce epoxy or polyurethane networks, respectively. In the present research, both these routes have been utilized in forming epoxy matrix resins for composites.

The tributyltin ester of 3,5-diaminobenzoic acid (TBT-DABA) differs from metaphenylenediamine (MPDA) by the additional presence of the organotin carboxylate group, but both of them carry the necessary amine functional groups required to cure epoxides. The bulk properties of DGEBA cured by TBT-DABA are compared in Table II with those obtained when MPDA is used as a curing agent.[14,15] It is, thus, possible to observe changes caused solely by inclusion of TBT carboxylate via the amine curing agent of the epoxy network. The results in Table II show that the mechanical properties of the TBT-modified network are good in spite of about 10–20% reduction in strength and moduli from those of the MPDA-cured polymer. This observation is reinforced by the results shown in Table III for fiber glass composites prepared from DGEBA cured by TBT-DABA. The tensile, flexural, and impact strengths are comparable to those reported in literature[22] for MPDA-cured epoxy composites (included in Table III).

In the case of composites based on the partial tributyltin esters of polyanhydrides, the prepolymers were crosslinked with glycidyl methacrylate following the method devised by Heilman[22] for polyanhydrides. The network is formed

$$CH_2{=}C{-}COOCH_2{-}CH{-}CH_2$$
$$\qquad\quad \overset{\displaystyle CH_3}{\diagup} \qquad\qquad \overset{\displaystyle O}{\diagup\diagdown}$$
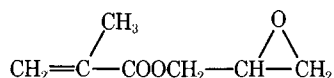
by the reaction of glycidyl groups with anhydride functional groups on the prepolymer with simultaneous addition polymerization occurring through the vinyl double bonds of the monomer. The results presented in Table IV were obtained for composites of three types of polyanhydrides, styrene–maleic anhydride (SMA 1000A), hexene–maleic anhydride (PA 6), and decene–maleic anhydride (PA 10), each esterified 40% with tributyltin. For comparison, the values obtained with unesterified PA 6 are also included. A decrease in modulus and flexural

TABLE II
Mechanical Properties of DGEBA Cured by Metaphenylenediamine (MPDA) or Tributyltin
3,5-Diaminobenzoate (TBT-DABA)

Curing agent	Tensile strength, Mpa (psi)	Flexural		Izod impact strength, J/m
		Strength, MPa (psi)	Modulus, MPa (psi)	
TBT-DABA	63.9 ± 4.8	106 ± 3.2	2,700 ± 250	9.1 ± 0.4
	(9,270 ± 690)	(15,400 ± 500)	(392,000 ± 36,000)	
MPDA	82.9 ± 7.5	123 ± 3.4	3,090 ± 93	10.7 ± 0.7
	(12,000 ± 1,100)	(17,800 ± 500)	(449,000 ± 13,000)	

TABLE III
Tensile, Flexural, and Impact Properties of TBT-Modified and Unmodified Glass–Epoxy Composites[a,b]

Matrix curing agent	Fiber, wt %	Tensile strength, MPa (ksi)	Flexural Strength, MPa (ksi)	Flexural Modulus, MPa (ksi)	Impact strength, kJ/m² Std. notched	Unnotched
TBT-DABA[a]	68[a]	319 ±11 (46.3 ± 1.5)				
TBT-DABA[a]	80[a]		561 + 20 (81.3 ± 2.9)	32,100 ± 1,600 (4,650 ± 230)	88.9 ± 2.7	125 ± 8.1
TBT-DABA[a]	83[a]		498 ± 11 (72.2 ± 1.6)	31,800 ± 1,200 (4,610 ± 180)	95.3 ± 2.0	128 ±13
MPDA[b]	72[b]	345 – 400 (50.0 – 58.0)	545 – 614 (79.0 – 89.0)	24,800 – 26,900 (3,600 – 3,900)	63 – 79	

a This work.
b Data from ref. 22, p. **22**–21.

TABLE IV
Tensile and Flexural Properties of TBT-Modified and Unmodified Polyanhydride-Based Composites[a]

| | Tensile | | | Flexural | | |
Polyanhydride	Fiber, wt %	Strength, MPa (ksi)	Modulus, MPa (ksi)	Fiber, wt %	Strength, MPa (ksi)	Modulus MPa (ksi)
PA 6	78	318 ± 30 (46.1 ± 4.4)	30,300 ± 8,300 (4,390 ± 1,200)	79	386 ± 21 (56.0 ± 3.1)	26,600 ± 1,600 (3,860 ± 230)
PA 6/40% TBTE	82	357 ± 9.0 (51.7 ± 1.3)	23,600 ± 2,700 (3,420 ± 390)	81	290 ± 16 (42.0 ± 2.3)	25,900 ± 1,700 (3,750 ± 250)
PA 10/40% TBTE	79	308 ± 20 (44.6 ± 3.0)	25,600 ± 1,200 (3,710 ± 184)	82	184 ± 9.8 (26.8 ± 1.4)	20,900 ± 1,000 (3,030 ± 150)
SMA 1000A/40% TBTE	77	282 ± 10 (40.8 ± 1.5)	20,300 ± 65 (2,940 ± 9.4)	84	204 ± 8.4 (29.6 ± 1.2)	24,200 ± 630 (3,500 ± 92)

a Crosslinked by glycidyl methacrylate.

strength with comparable or slightly better tensile strength is noticed for 40% TBTE/PA 6. The presence of the longer, flexibilizing eight-carbon side chain in the decene–maleic anhydride copolymer PA 10 is reflected in the much-reduced flexural modulus for the composites prepared from this system. The tensile strength is seen to be the lowest for styrene–maleic anhydride copolymer composites. Considering that the molecular weight of the base prepolymer is only 1600 in this case, a considerable potential for improved properties is seen to exist with this copolymer.

The observed value of 56,000 psi for the flexural strength of the PA 6 composite is significantly lower than 71,000 psi, which is reported by Heilman.[23] This is probably caused by the use of acetone as solvent in formulating the composite matrix resin in our experiments. The solvent was necessary to dissolve the partial TBT ester of PA 6, which could not be dissolved in the crosslinking monomer (glycidyl methacrylate). Since the solvent was used with the esters, it was used also in obtaining strength values for comparison with unesterified PA 6.

It should be noted that the strength values for the polyanhydride-based composites compare quite well with those for epoxy fiber glass composites shown in Table III. Although the strength and stiffness of the different polyanhydride-based systems were similar, the mode of failure was quite different. Tensile and flexural specimens of PA 10 and SMA 1000A showed considerable delamination during testing, which was much less noticeable with PA 6.

While GMA has been used to obtain the detailed results reported here, as mentioned earlier and indicated in Table I, cycloaliphatic epoxides can also be utilized effectively as crosslinking agents for TBT esters of polyanhydrides.[13,24] Thus, with stannous octoate as the catalyst and an anhydride:epoxide ratio of 1:12, composites were prepared from 40% TBT-SMA 1000A and diepoxides bis(3,4-epoxy-6-methylcyclohexyl) adipate and 3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexane carboxylate (Union Carbide ERL 4289 and ERL 4221, respectively). Preliminary tests have yielded values of about 42,000 psi for tensile strength at 72% fiber content for these systems.

The tributyltin polymers, by themselves and when impregnated in wood, have provided long-term protection against marine fouling and decay under conditions similar to those of actual use.[18,25] It should be interesting to observe how the composites prepared from them behave in an ocean environment with regard to both structural integrity and antifouling efficiency. Specimens are presently undergoing long-term exposure at ocean test sites.

SUMMARY AND CONCLUSIONS

Tributyltin-modified polymers have been successfully used as matrix resins for fiber glass composite panels. The tributyltin group can be introduced either via polyanhydride prepolymers or via polyaminofunctional curing agents, and composites can be prepared from them using conventional techniques. Strength and stiffness properties comparable to those obtained for unmodified DGEBA composites can be obtained for the TBT-modified composites, thus warranting their use in structural applications. Based on their mechanical and antifouling performance characteristics, these composites should offer an alternative to coating in small-scale structural applications.

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