

Chemistry and Properties of Crosslinked Polymers

edited by

SANTOKH S. LABANA

Engineering and Research Staff
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Preface

This book describes chemistry, structure property relationship, and methods of characterization of crosslinked polymers. It should be of interest to scientists engaged in research or graduate studies in polymer science.

Crosslinked polymers are an important class of materials used in fiber reinforced plastics, thermosetting molding compounds, elastomers, coatings, adhesives, ion exchange resins, and many other applications. Although the use of these materials has grown rapidly, the understanding of the relationship of structure or chemical nature and properties has not progressed very well, mostly because of the difficulties in the characterization of the network structure and morphology. It is difficult to measure accurately such features as crosslink density, entanglement points, dangling chains, and unattached chains. Hypotheses about the formation of morphological structure during crosslinking remain unproven. This volume contains several papers that attempt to deduce information on network structure from theoretical considerations and several more that describe experimental techniques to study network structure.

Interpenetrating polymer networks have been receiving considerable attention in recent years because of the versatility available in their syntheses and the range of morphological and mechanical properties obtainable. A review on the subject, suggestions for nomenclature, and details on a number of interpenetrating polymer networks are included.

Other papers describe crosslinked polymers for high temperature applications, a novel class of polyurethanes, new crosslinking agents, and the influence of crosslinking agents on thermal and mechanical properties.

I take pleasure in acknowledging Ford Motor Company and Dr. S. Gratch for their support of and interest in this project. I also wish to express my appreciation to Anne Oslanci for her secretarial assistance. My sincere thanks to the authors who put in a great deal of effort to make this book possible. Finally, I thank the Division of Organic Coatings and Plastics Chemistry, American Chemical Society for sponsoring the symposium.

PROPERTIES OF ORGANOTIN POLYESTERS CROSSLINKED BY CYCLOALIPHATIC EPOXIDES

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Washington State University

A new synthesis of thermoset antifouling polymer systems was achieved by the crosslinking reaction of cycloaliphatic epoxides with the free carboxyl groups present on a base polymer partially esterified with tributyltin oxide. The network structure was varied, and the average separation, length and type of epoxy crosslinks were altered by changing the degree of esterification of the base polymer, the structure and proportion of epoxy monomer, and the type of catalyst. Concurrent changes in measured strength, fracture toughness and dynamic mechanical behavior of the polymer systems have been correlated with the structural variables employed. Results presented here pertain mainly to systems based on styrene-maleic anhydride copolymer crosslinked by cycloaliphatic epoxides. Toughening by carboxyl terminated liquid elastomers has also been studied and the improvement in fracture toughness related to the average particle size of the dispersed elastomer phase which was in turn controlled by elastomer content, A:E ratio, and tributyltin content. The formation of domains in the matrix with independent glass transitions was followed by observing variations in loss moduli which also reflected the structural effects of bulky tributyltin groups and different epoxy monomers. The highest degrees of crosslinking were found with uranyl nitrate catalyst.

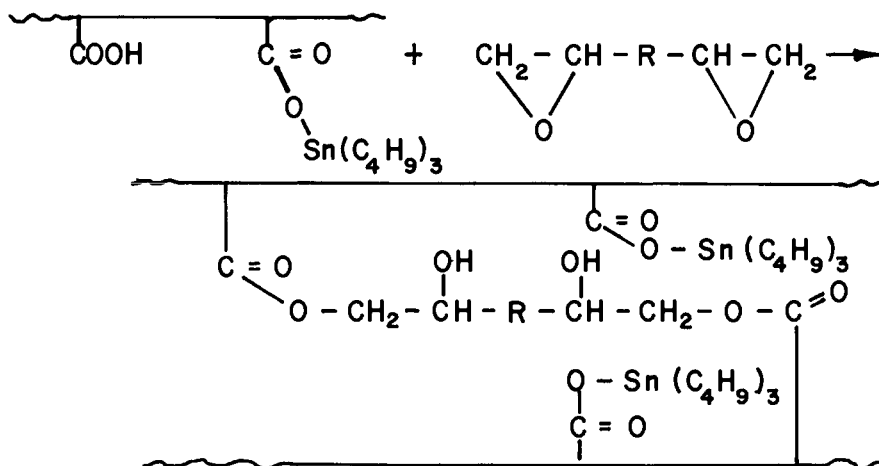
I. INTRODUCTION

Tributyltin compounds are known to be toxic to marine organisms and have been incorporated as toxic additives in marine biocidal paints (1-3). The polymerization and copolymerization with other vinyl monomers of tributyltin and tripropyltin acrylates to form antifouling polymers has been reported (4,5). Recent research in our laboratories has involved chemical anchoring of toxic trialkyltin groups to ther-

most polymers in a new approach to the synthesis of polymer compositions that might be suitable for application as antifouling coatings (6,7). The objective of the investigation reported here was to study the structure-property relationships in antifouling organotin epoxy polymers.

A. Synthesis of Crosslinked Organotin Epoxy Polymers

The synthetic scheme adopted for the preparation of the polymers involves the partial esterification, with tributyltin oxide, of polymers containing carboxylic acid or anhydride groups as the first step. The free carboxyl function of the partial tin ester is then reacted with epoxy monomers to form crosslinked polymer systems as shown below for the simplest crosslinking reaction.



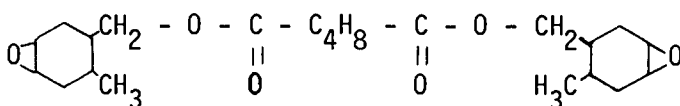
The properties of the network structure obtained thus can be varied over a wide range by changing the chemical structure of the base polymer as well as that of the crosslinking epoxy monomer. The tin content of the polymer is altered by controlling the degree of esterification of the base polymer, which also varies the crosslink density obtained in the second step. Greater esterification with tributyltin oxide will lead to fewer available carboxyl groups for crosslinking, and, consequently, to larger separation between points of crosslinking on the base polymer. Promotion of homopolymerization at high epoxy to anhydride ratios will have the general effect of extending the lengths of epoxy crosslinks. This can be achieved

by appropriate choice of catalysts for the curing reaction.

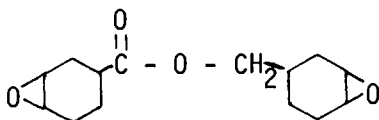
Results are reported here mainly for thermoset systems obtained by the reaction of tributyltin esters of a 1:1 styrene-maleic anhydride copolymer (SMA-1000A) with three cycloaliphatic epoxides, namely bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate (ERL 4289), 3,4-epoxycyclohexylmethyl-(3,4-epoxy) cyclohexane carboxylate (ERL 4221) and [2-(3,4-epoxy) cyclohexyl-5,5-spiro (3,4 epoxy)-cyclohexane-*m*-dioxane] (ERL 4234).

II. EXPERIMENTAL

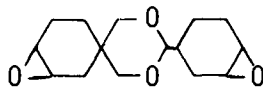
The molecular weight of poly(styrene-*co*-maleic anhydride), SMA 1000A of ARCO Chemical Co., was in the range 1600-1800. Other 1:1 copolymers used as base polymer were poly(methyl vinyl ether-*co*-maleic anhydride), AN 139, poly(methyl vinyl ether-*co*-maleic acid), AT 795 (both of General Aniline and Film Corporation) and Gulf polyanhydrides PA-6 and PA-10 which are copolymers of maleic anhydride respectively with hexene-1 and decene-1. Epoxy monomers ERL 4289, ERL 4221, ERL 4234, whose structures are indicated below, and ERL 4206 (vinylcyclohexene dioxide) were obtained from Union Carbide.



ERL 4289



ERL 4221



ERL 4234

The tributyltin esters were prepared by refluxing the base polymer with the stoichiometric amount of tributyltin oxide (M&T Chemicals) in benzene for 12 hours (8), recovered from solution by vacuum evaporation of the solvent benzene, and dried *in vacuo* at 80-90°C for 24 hours. The tin content was estimated by acid oxidation and incineration to tin oxide (9); the values confirmed the degree of esterification

achieved. The esters of SMA 1000A were soluble in the liquid epoxy monomers; in other cases a small amount of solvent, xylene, was used to prepare the prepolymer-epoxide mixture which was cured, after the addition of a suitable catalyst, in silicone molds at 140°C for 24 hours to prepare impact and tensile test specimens. Benzyl dimethyl amine (BDMA), dimethylaniline (DMA), stannous octoate and uranyl nitrate were the various catalysts employed. A Tinius-Olsen Plastic Impact Tester was used for measuring Izod impact strengths of notched specimens (2.50"x0.50"x0.25", notch radius 0.25 mm). Dog-bone specimens with a gauge length of 2.25" were tested at 0.02 cm/min in an Instron tensile testing machine. Thin pieces were sawed off from impact-tested specimens and thinned down further on emery paper, solvent extracted and dried for use in dynamic mechanical tests in a Rheovibron DDV IIC viscoelastometer.

The effect of added liquid elastomer, carboxyl-terminated butadiene-nitrile copolymer (CTBN), on the strength and fracture properties of the network polymers was studied using HYCAR 1300X8 of B.F. Goodrich Chemical Company, having a molecular weight of 3,200 and an acrylonitrile content of 18%. Thin ($\approx 1000\text{\AA}$) films were microtomed from the bottom remnant of impact test pieces, stained in 4% osmium tetroxide solution and examined by transmission electron microscopy.

III. RESULTS AND DISCUSSION

As was indicated earlier, the variety of prepolymers that could be utilized is an essential merit of the synthetic scheme adopted here. Accordingly a number of maleic anhydride copolymers detailed in the experimental section were screened in preliminary tests and found to produce thermoset systems readily. However, the styrene-maleic anhydride copolymer systems were chosen first for detailed study as the most tractable for arriving at structure-property relationships.

A. Catalyst Efficiency and Structure of Cured Polymer

The curing of 40 TBTE-SMA 1000A and ERL 4206 was carried out at various temperatures using different catalysts, and percent extractables were evaluated at various time intervals of the curing cycle. The efficiency of the various catalysts and curing conditions in producing crosslinked structures was evaluated mainly by such solvent extraction using methyl ethyl ketone to determine the soluble fractions. The extrac-

table portion was a minimum at an epoxy to anhydride ratio of 2 using the basic catalyst BDMA which indicated that the carboxyl-epoxide esterification reaction was the main crosslinking reaction under these conditions. This is illustrated in Figure I with results obtained when the curing reaction was conducted at 95°C for 24 hours.

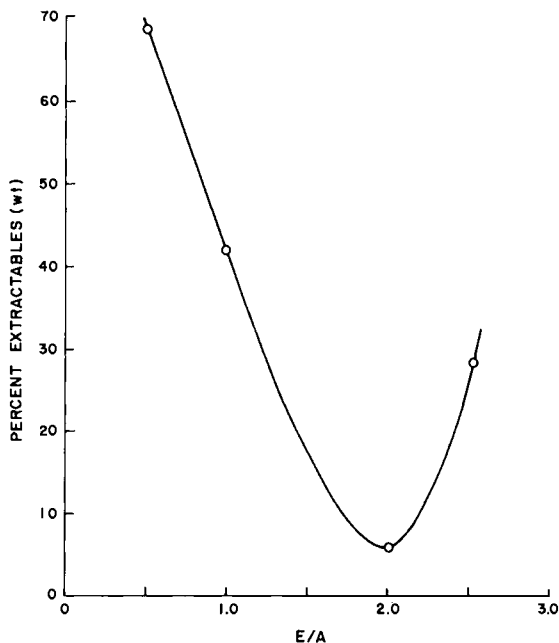


Fig. 1. The variation of percent extractables as a function of E:A ratio for 40 TBTE-SMA 1000A-ERL 4206 using 0.5% (wt) BDMA.

On the other hand, using stannous octoate catalyst, the extractable fraction progressively decreased with epoxide to anhydride ratios up to 4, as shown in Figure 2. It was found in later experiments that even larger amounts of epoxide monomer could be incorporated in the polymerizing systems.

Thus the best thermosetting systems with cycloaliphatic epoxides were obtained by using acid catalysts. In these systems with acid catalysts, it is apparent that considerable homopolymerization of the diepoxide leading to the formation of polyether links must be occurring in addition to crosslinking by ester formation. The initial reaction under acid con-

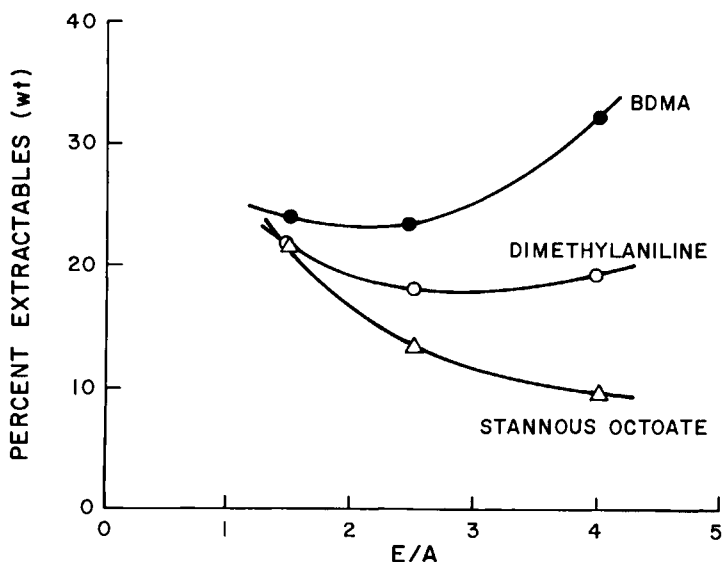


Fig. 2. The variation of percent extractables as a function of E:A for 40 TBTE-SMA 1000A-ERL 4206 cured at 110°C for 20 hours using BDMA, dimethyl aniline, and stannous octoate as catalysts at one weight percent.

ditions is one of esterification by the epoxy of the carboxylic acid groups formed from the anhydride on the base polymer. As a result of this reaction, a hydroxyl group is formed which is capable of further reaction with epoxide monomer in the presence of the acid catalyst. The hydroxyl group which is thus regenerated can initiate the addition of more epoxide monomers to form a homopolymer chain; and, since the soluble fraction is very low, 10% or less, the homopolymerization is probably initiated on the crosslinks to form multiple and branched epoxide crosslinks. This deduction is confirmed by the fact that the neat diepoxide monomer, ERL 4289, in the absence of any carboxyl containing base polymer, could be homopolymerized with stannous octoate catalyst to yield crosslinked polymers with less than 15% extractable fraction. A much more striking observation was that, with uranyl nitrate catalyst, a crosslinked homopolymer was obtained with no extractable fraction. Using stannous octoate or uranyl nitrate, therefore, long sequences of epoxy monomer are efficiently incorporated in the crosslinks of the network structure. Except where otherwise indicated, all results reported below

were obtained with stannous octoate catalyst (0.5%). The curing temperature was held in the range 135-140°C which was found to be optimum.

B. Tensile Strength

It is pertinent to note here that in polycarboxyl-epoxy thermoset polymers based on terpolymers of methacrylic acid, methacrylonitrile and methyl methacrylate using N,N-dimethyl benzylamine as catalyst, optimum values of mechanical properties were recorded by Fellers and Golovoy at carboxyl to epoxy ratios close to one, the stoichiometry required for cross-linking by carboxyl-epoxy esterification (10). In contrast, in the stannous octoate catalysed systems based on the 40% tin ester of styrene-maleic anhydride copolymer (SMA) and ERL 4289, the tensile strength and elongation to break increased progressively with the epoxide:anhydride ratio (Fig. 3).

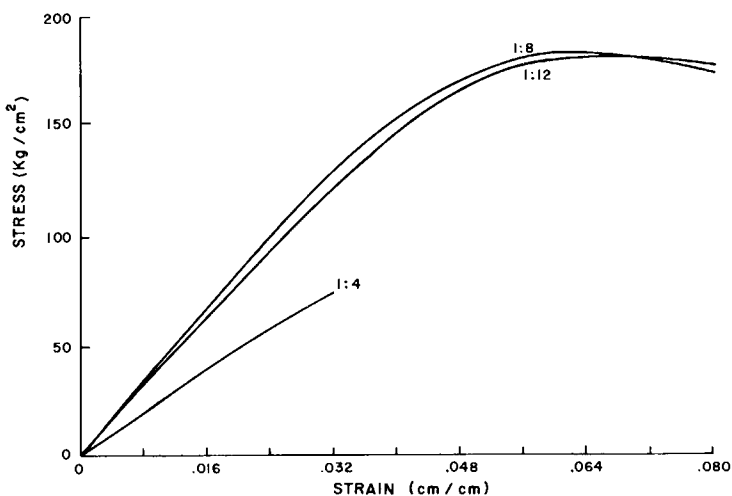


Fig. 3. Stress-strain curves for SMA 40% ester/ERL 4289 polymers formed at indicated A:E ratios.

Similar observations were made in polymers prepared from the 60% ester of SMA and ERL 4289. The position at which the ultimate tensile strength was obtained shifted to a higher E/A ratio with increased esterification of the polymer. This result should be expected because a greater epoxy content is required to compensate for increased distance between cross-links. However, the increase in tin esterification of the

prepolymer from 40% to 60% decreased the strength of the cured polymer considerably. In the case of ERL 4221, the strength showed a slight initial decrease with increasing E/A ratio. The results are summarized in Table I.

TABLE I
Tensile Strengths and Moduli of Cured Products of SMA 1000A

<i>SMA Ester</i>	<i>Epoxide</i>	<i>A:E Ratio</i>	<i>Strength MPa</i>	<i>Modulus MPa</i>
40%	ERL 4289	1:4	7.38	276
		1:8	18.6	441
		1:12	17.8	400
60%	ERL 4289	1:8	1.76	53.8
		1:12	5.58	103
		1:16	5.93	89.6
40%	ERL 4221	1:4	15.4	538
		1:8	11.3	634
		1:12	11.9	689

It can be seen that modulus values show trends similar to those of strength with 40% and 60% esters of SMA and ERL 4289. The initial increase in modulus can be explained on the basis of greater stiffness of the epoxy polymer as compared to the base polymer. As the E/A ratio is increased, the network probably becomes less constrained because of the longer homopolymer chains. In the case of ERL 4221, which is a more rigid and shorter epoxy monomer than ERL 4289, a steady though smaller increase in modulus was observed in the range of E/A ratios studied. These results are also shown in Table I.

C. Impact Strength

Impact strengths were also determined as a function of the amount and type of epoxy polymer which controlled the chemical structure and length of crosslinks, the extent of

esterification of the prepolymer which changed the distance between crosslink points, and the content of liquid elastomer CTBN in the polymerizing system.

The three epoxy monomers in order of decreasing flexibility are ERL 4289, ERL 4221 and ERL 4234. As expected from this, cured products with ERL 4289 showed higher impact strengths than those with ERL 4221 which in turn showed higher impact strengths as compared to compositions with ERL 4234.

With ERL 4289, increasing the content and length of epoxide crosslinks by increasing the E/A ratio gave increasingly higher values of impact strengths in the case of 40%, 60% and 80% esters (Table 2). Increased esterification of the base

TABLE 2
Impact Strengths of Thermoset Polymers

<i>SMA Ester</i>	<i>Epoxide</i>	<i>A:E</i>	<i>Impact Strength</i> <i>J/cm²</i>
40%	ERL 4289	1:4	0.057
		1:8	0.088
		1:12	0.108
60%	ERL 4289	1:4	0.050
		1:12	0.063
80%	ERL 4289	1:30	0.104
		1:50	0.168
40%	ERL 4221	1:4	0.025
		1:8	0.030
		1:12	0.033

prepolymer showed a tendency to decrease strength values. These observations are consistent with the higher strength of the epoxy polymer compared to the base polyester.

In comparison with ERL 4289 systems, cured products with ERL 4221 showed much lower impact strengths because of the

rigidity of their structure. Further, an increase in E/A ratio caused no significant change in impact strength. These results are also included in Table 2. With ERL 4234, an extremely rigid epoxy monomer, impact strength values were even lower. This reduced the reliability of measurements considerably. As in the case of ERL 4221, increase in E/A ratio did not change impact strengths.

The toughness of the polymer systems was also evident in the appearance of the fracture surfaces of the specimens under the scanning electron microscope, as shown in Figure 4(a) for a thermoset incorporating ERL 4289 at A:E of 1:12 and in 4(b) for one incorporating ERL 4221, also at the same A:E ratio. Considerable deformation of the matrix surface is seen in the former while the latter reveals a brittle fracture surface.

The effect of increasing E/A ratios in increasing impact strength is maintained in the presence of added liquid elastomer (CTBN), as illustrated in Figure 5. Toughening of the matrix was achieved by the addition of CTBN which was found to separate out as particles 1-20 μ in diameter (Figure 6) and caused increases of the order of 300% in regions of high E/A ratios and CTBN contents with ERL 4289. Much less improvement was observed with ERL 4221.

TABLE 3

Variation of Elastomer Particle Size and Impact Strength with CTBN Content at Constant A:E ratios

<i>SMA Ester</i>	<i>Epoxyde</i>	<i>A:E</i>	<i>CTBN Content</i>	<i>Particle Size μ</i>	<i>Impact Strength J/cm^2</i>
40%	ERL 4289	1:4	4	2.7	0.059
		1:4	8	3.3	0.107
		1:12	4	0.3	0.130
		1:12	8	1.2	0.241
60%	ERL 4289	1:12	4	5.5	0.170
		1:12	8	10.0	0.180
40%	ERL 4221	1:12	4	0.2	0.030
		1:12	8	2.0	0.107

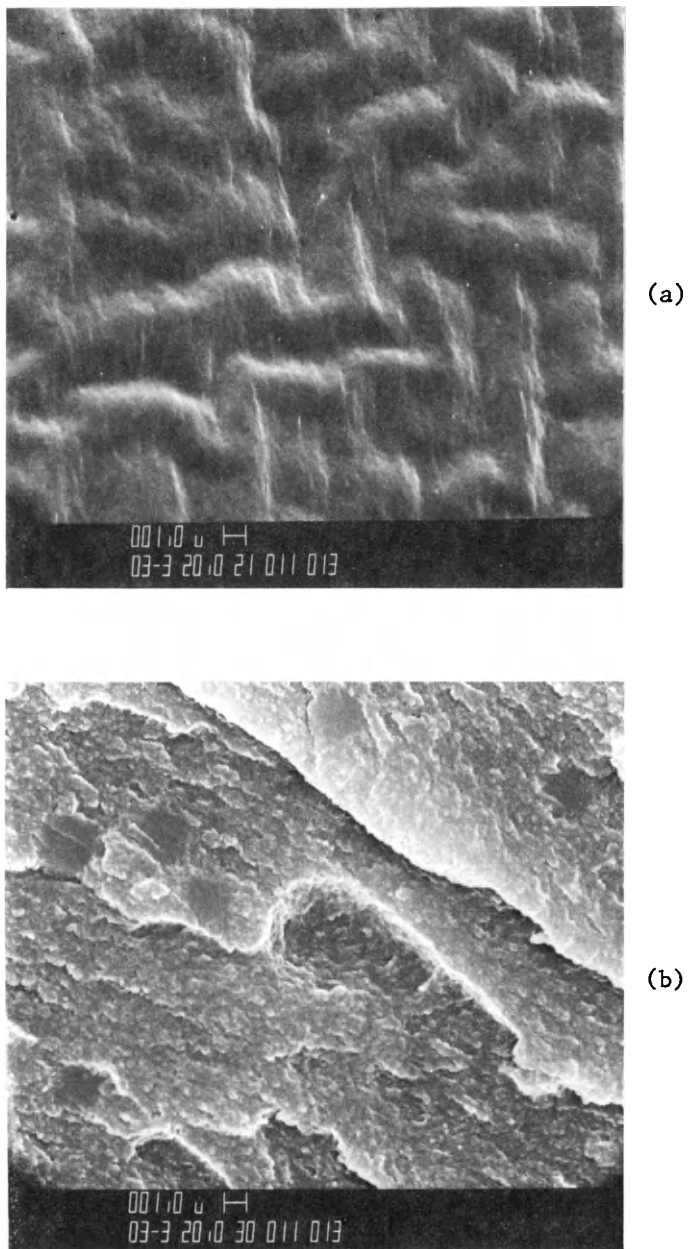


Fig. 4. Fracture surface of crosslinked polymers of (a) ERL 4289 and (b) ERL 4221 at A:E = 1:12, both using SMA 40% tin ester as prepolymer (3000X).

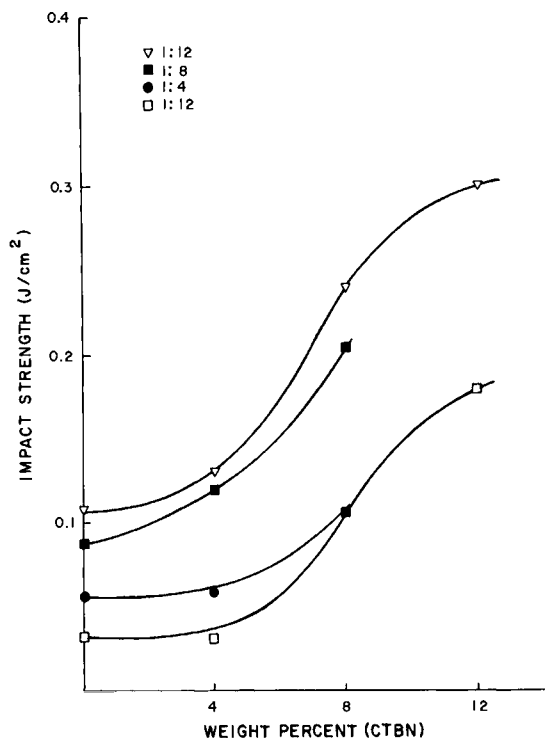


Fig. 5. Increase in impact strength with CTBN content at various A:E ratios for SMA 40% tin ester crosslinked by ERL 4289 (∇ , \blacksquare , \bullet) and by ERL 4221 (\square).

The improvements in impact strength seem to be associated with an increase in size of the rubber particles with increasing CTBN content at the same A:E ratio, as revealed in electron micrographs of microtomed sections (Table 3). The average particle size was also increased considerably for polymers with higher degree of esterification by tributyltin as is shown in the same table.

D. Dynamic Mechanical Measurements

The dynamic mechanical responses of the organotin-epoxy polymer systems were measured in the Rheovibron at 110 Hz from room temperature to about 240°C. Both $T < T_g$ and T_g transitions were observed for the crosslinked polymers as shown in the plots of loss moduli in Figure 7 for 40% ester-ERL 4289 sys-

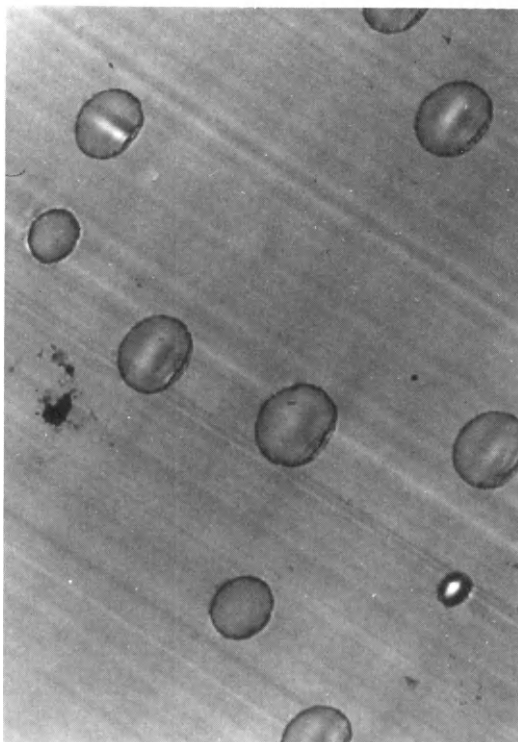


Fig. 6. 40 TBTE - SMA 1000 A - ERL 4289 with 8% CTBN (A:E = 1:4); average size of particles = 3.3 μ ($\approx 3000 X$).

tems at various A:E ratios. Since the $T < T_g$ transition involves only a small group of 4 or 5 atoms (11) it is seen to be relatively insensitive to the crosslink density of the network structure and is unchanged by A:E ratios in the range 1:4 to 1:12. On the other hand, the main glass transition which occurs as closely spaced double peaks for this system, is increased progressively from 75 to 90°C by increasing epoxy content; the shift seems to be caused both by the increasing proportion of the epoxy polymer which is stiffer than the base polyester and also by the concurrent formation of multiple crosslinks. The evidence for the formation of such multiple crosslinks under acidic catalysts was discussed earlier. The observation of the double glass transition would indicate the presence of two separate domains each with a characteristic T_g of its own.

The closely spaced double transitions are not discern-

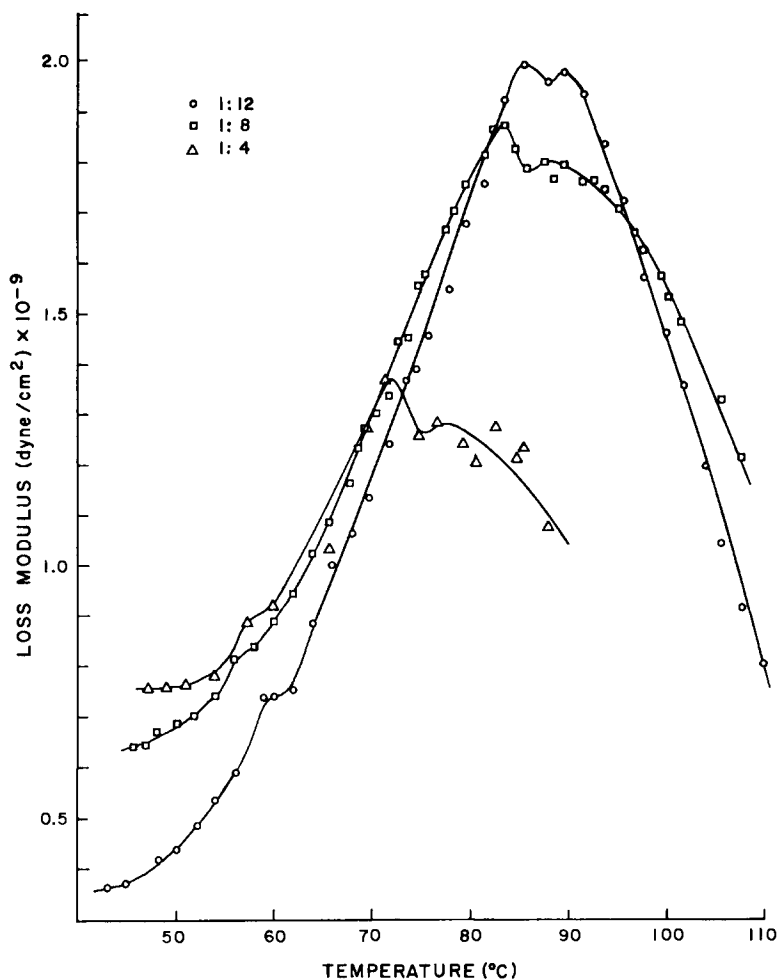


Fig. 7. Loss modulus versus temperature plots for SMA 40% tin ester/ERL 4289 at the indicated ratios of A:E.

ible and seem to have merged in systems based on 60 TBTE - SMA 1000 A - ERL 4289 (Figure 8); but they did tend to become discernible with the 80% ester where the peaks were much broader. The stiffening effect of the bulky tributyltin groups would seem to be the cause of the increase in T_g observed for ERL 4289 systems based on the 60% ester (Table 4). The same phenomenon is observed in systems incorporating ERL 4221; a higher degree of esterification in the base polymer