

# Unsaturated Polyester Resin Modified with Poly(organosiloxanes). I. Preparation, Dynamic Mechanical Properties, and Impact Resistance

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**ABSTRACT:** Unsaturated polyester resins (UP) display a wide range of applications depending on the proper choice of raw materials and cure conditions. However, some applications are limited to their low-impact resistance, which can be enhanced by the incorporation of modifiers that increase the flexibility of the network. This work aims to incorporate flexible poly(organosiloxane) segments in the UP network as a graft copolymer, as a way of minimizing the low adhesion between the resin and the modifier and enhance its flexibility. Because polyester and poly(organosiloxanes) are immiscible mixtures, the grafting copolymerization during the cure can promote compatibilization between both polymers. Hence, glycidyl methacrylate (GMA) is added to the resin network by radical reaction, as well as 1,3-aminopropyltriethoxysilane (APTS), amino groups of which react with GMA. The addition of a siloxane (1,1,3,3-tetramethyl-1,3-diethoxydisiloxane) allows the poly(organosiloxane) network to grow and the addition of water guarantees the hydrolysis and polycondensation during the cure. In this way it is possible to increase its flexibility. The grafting copolymerization is evaluated by dynamic mechanical analysis and the impact resistance of pure and modified polyester resins is evaluated by the Izod test. The grafting of a flexible segment in the UP chains enhances the impact resistance of the polyester resin at low-modifier concentration. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3272–3279, 2001

**Key words:** unsaturated polyester; poly(organosiloxane); impact resistance; dynamic mechanical analysis

## INTRODUCTION

Unsaturated polyester (UP) resins find a large field of applications, especially as a reinforced plastic, because of their good mechanical properties and low price. The proper choice of glycols, alcohols, and comonomer, as well as the conditions of cure, provide different characteristics and properties to the resin. Acrylic monomers, for example, can be used to improve the weathering resistance of the resin. However, the most com-

mon system uses styrene as a comonomer because of its low cost and good compatibility with the resin. Styrene also acts as a solvent to the resin.

The addition of fillers and fibers (usually glass fiber) allows the resin to be processed by different manufacturing techniques, such as sheet-molding compounds (SMC), bulk-molding compounds (BMC), resin-transfer molding, pultrusion,<sup>1</sup> and the conventional methods of resin casting, hand lay-up, and spray.<sup>2</sup> The use of polyester resin in some structural applications is, however, limited in its low-impact resistance. This problem may be solved by increasing the toughening of UP resins, but it is not easy to obtain this characteristic because of the difficulty of finding out modifiers miscible or compatible with the resin<sup>3</sup> or fillers

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with good adhesion to it.<sup>4</sup> In addition to this, the improvement in the impact resistance can lead to an adverse effect on some other properties such as tensile strength. Several studies<sup>5,6</sup> proposed resin modification with adducts or oligomers, which can be incorporated to the resin as flexible segments. These segments would grant more toughening and, consequently, impact resistance to the resin.

This work aims to incorporate flexible polysiloxane segments in the UP resin in a way of promoting network flexibility. However, its low-solubility parameter and low-surface tension lead to immiscibility and incompatibility.<sup>7</sup> For this reason, blends of these compounds are immiscible with low adhesion between the different phases. Therefore, it is proposed that the formation of a graft copolymer during the cure, which can minimize the low miscibility between resin and the modifier, can promote the compatibilization between the polymers. Different from the studied systems<sup>5,6</sup> where oligomers or adducts are introduced to the resin network, we tried to introduce a reactive group in the polyester chain using a similar procedure to the reactive mixture of rubbers and thermoplastics performed in extruders and mixers.<sup>8</sup> Glycidyl methacrylate (GMA) is incorporated into polyester chain by radical polymerization, whereas the oxirane group reacts with specific groups of a silane compound. The hydrolysis of the silane allows the incorporation of siloxane segments resulting in a graft of the poly(organosiloxane) in the polyester chain.

A commercial orthophthalic resin is modified in different conditions and compositions as a way of evaluating the influence of each compound and the cure conditions on the dynamic mechanical properties of the resin. The best compositions are also compared with samples prepared with isophthalic resin. Besides, impact resistance tests are performed to investigate the toughening of the UP resins.

## EXPERIMENTAL

### Materials and Methods

Orthophthalic resin (RESAPOL 10-230) and isophthalic resin (RESAPOL 10-169), supplied by Resana SA (Mogi das Cruzes, SP, Brazil), were used in this work. They are preaccelerated by the cobalt octoate (0.5 wt %). Methyl ethyl ketone peroxide was used as an initiator (1 wt %).

GMA, 1,3-aminopropyltriethoxysilane (APTS), supplied by Aldrich, and 1,1,3,3-tetramethyl-1,3-

**Table I** Methods of Cure

Method	Cure	Postcure	Drying
A	25°C/24h	65°C/5 h	Vacuum at 75°C/3 h
B	25°C/24h	65°C/5 h	Vacuum at 130°C/2 h
C	25°C/24h	65°C/24 h	Vacuum at 75°C/3 h

diethoxydisiloxane (chain extender), supplied by Hüls, were used as modifiers for the UP resins.

To establish the influence of each modifier and the method of cure on the phase behavior of the modified UP resins and the influence of the water as a promoter of hydrolysis of the silane, samples of orthophthalic resin were prepared as follows and were characterized using dynamic mechanical analysis (DMA). Some compositions of isophthalic resin were investigated too.

### Methods of Cure

Samples of orthophthalic resins were modified with GMA (5 wt %) and submitted to the three methods of cure described in Table I to investigate the occurrence of phase separation or the volatilization of residual monomers. The mixture of the resin and the methacrylate was made for 24 h at room temperature under magnetic stir and the cure took place in cylindrical molds of high-density polyethylene (HDPE).

### Influence of Each Modifier

Samples of orthophthalic resins were modified with GMA, APTS, a combination of GMA and APTS, and with the three modifiers, as described in Table II. All mixtures were stirred for 24 h at room temperature under magnetic stir and cured in molds of HDPE according to method A (see Table I).

### Effect of Water in the Hydrolysis

Modified polyester resins were prepared in the presence and absence of water to evaluate the influence of the silane hydrolysis on the formation of poly(organosiloxane) network. Water was added in stoichiometric amounts in relation to the APTS (molar ratio, APTS : water = 1 : 3). First, GMA and APTS were mixed with the resin for about 2 h. The water is only added after this time in a way to avoid premature hydrolysis of the silane. We noted that the mixture gets opaque when water is added at the same time as the other additives. When water is added after a pre-

**Table II Orthophthalic Resins Modified with GMA, APTS, and Chain Extender Cured by Method A**

Sample	APTS (wt %)	GMA (wt %)	APTS : GMA <sup>a</sup>	APTS : Extender <sup>a</sup>	Total of Additives (wt %) <sup>b</sup>	T <sub>g</sub> (°C)
0A	—	—	—	—	—	74, 100 (s)
1A	—	5	—	—	5	79 (l)
2A	—	10	—	—	10	84 (s), 91
3A	—	15	—	—	15	74, 106 (s)
4A	5	—	—	—	5	58 (l)
5A	10	—	—	—	10	46
6A	15	—	—	—	15	36
7A	10	—	1 : 1	—	16.4	40 (l), 68 (s)
8A	10	—	1 : 0.5	—	13.2	40 (l)
9A	10	—	1 : 0.5	1 : 0.5	18.2	20 (s), 31

<sup>a</sup> Molar ratio.<sup>b</sup> In relation to the unmodified resin weight.

(l) large peak; (s) shoulder.

vious mixture of additives, it gets translucent at the beginning and then transparent as the cure occurs. The total time of mixture was 24 h.

The composition of the resins modified with APTS and GMA in the presence or not of water is described in Table III. The mixtures were poured into the HDPE molds and cured by methods A and C (Table I).

#### *Influence of the Chain Extender*

The compositions of the orthophthalic resin modified with APTS, GMA, and different amounts of chain extender are listed in Table IV. The mixture conditions were the same as the last experiment and the samples were cured by method C (Table I).

#### *Chemical Composition of the UP Resins*

After the earlier tests, the dynamic mechanical behavior of ortho and isophthalic resins modified with GMA, APTS, water, and chain extender in

two compositions were evaluated. The sample preparation followed the procedure previously described. Method C was chosen as the best method of cure and was used in this final analysis. Compositions are presented in Table V.

#### **Characterization**

##### *Dynamic Mechanical Tests*

The modified polyester resins were characterized by dynamic mechanical analysis. The tests were carried out in the DMA 938 (TA Instruments). Pure and modified orthophthalic resins of 2 mm diameter and 20 mm length were heated at 5°C/min in a range of -150 to +150°C, under oscillatory deformation amplitude of 0.2 mm and frequency of 1 Hz.

##### *Impact Resistance Tests*

The tests followed the Cantilever Beam (Izod type) test (ASTM D256-79) in a TMI testing ma-

**Table III Orthophthalic Resins Modified with GMA and APTS in the Presence and Absence of Water Cured by Different Methods**

Sample	Method of Cure	APTS (wt %)	APTS : GMA <sup>a</sup>	APTS : Water <sup>a</sup>	Total Weight of Additives (wt %) <sup>b</sup>	T <sub>g</sub> (°C)
1B	A	—	—	—	—	75
2B	C	—	—	—	—	82
3B	A	5	1 : 1	1 : 0	8.2	62
4B	A	5	1 : 1	1 : 3	9.4	56
5B	C	5	1 : 1	1 : 0	8.2	62, 85
6B	C	5	1 : 1	1 : 3	9.4	64

<sup>a</sup> Molar ratio.<sup>b</sup> In relation to the unmodified resin weight.

**Table IV Orthophthalic Resins Modified by GMA, APTS and Variable Amount of Chain Extender Cured by Method C**

Sample	APTS (wt %)	APTS : GMA <sup>a</sup>	APTS : Extender <sup>a</sup>	APTS : Water <sup>b</sup>	Total Weight of Additives (wt %) <sup>b</sup>	$T_g$ (°C)
1C = 6B	5	1 : 1	1 : 0	1 : 3	9.4	64
2C	5	1 : 1	1 : 1	1 : 3	14.5	31.5 (s), 56 (s)
3C	5	1 : 1	1 : 3	1 : 3	24.5	61 (s)

<sup>a</sup> Molar ratio.<sup>b</sup> In relation to the unmodified resin weight.

(s) shoulder.

chine. At least 12 samples of each composition were tested. The sample dimensions were  $62 \times 12.4 \times 3$  mm.

## RESULTS AND DISCUSSION

### Proposed Structure of the Modified UP Resins

GMA can be incorporated into the polyester chain by radical reaction. Its epoxy group is able to react by nucleophilic addition of the amine group of the APTS. Water is added to the mixture in a way to guarantee the hydrolysis of the silane groups of the APTS to silanols. The incorporation of a chain extender allows the network to grow by polycondensation of these silanol groups.

The scheme of the reactions of the graft copolymerization is shown in Figure 1.

### Characterization of the Modified UP Resins

The logarithmic curves of the loss modulus as a function of temperature ( $\log E'' \times T$ ) for the modified samples as described in Table II are illustrated in Figure 2. All curves are shifted in relation to each other to facilitate the presentation of

the results. The glass transition temperature ( $T_g$ ) is related to the maximum of the curve peaks and its values are also presented in Table II.

The addition of GMA to the orthophthalic resin shifts the glass transition to a higher temperature [Fig. 2(a)] because of the incorporation of rigid methacrylate segments to the resin network. In contrast, the addition of APTS to the orthophthalic resin caused a decrease in the  $T_g$  [Fig. 2(b)] because of the silane plasticization effect.

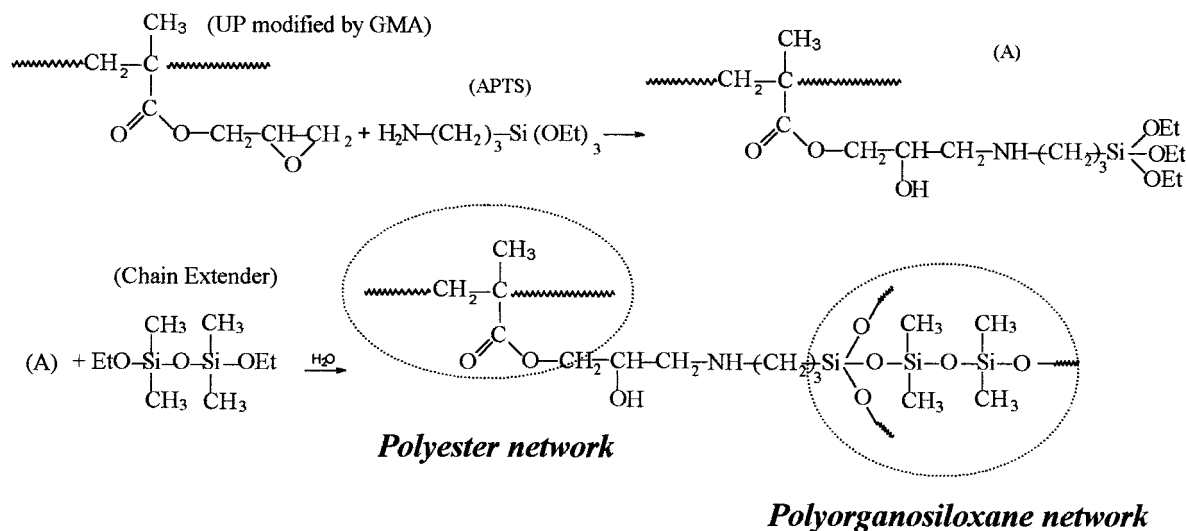
However, when the resin is modified with a combination of APTS and GMA, the  $T_g$  values shift to lower temperatures [Fig. 2(c)] as compared with the mixture without GMA [Fig. 2(b)], indicating a more pronounced plasticization effect of the silane segments over the rigidity of the GMA. This effect is attributed to the grafting of silane segments in the polyester chains. In this case the silane branches act as a spacer among the UP chains, changing the free volume and consequently improving the flexibility of the network. The phase segregation as well as the evaporation during cure and postcure of samples containing only APTS is not discarded and may explain a lower plasticization as compared to the samples containing GMA and APTS. In the UP

**Table V Composition of the Modified Ortho and Isophthalic Resin Cured by Method C**

Sample	APTS (wt %)	APTS : GMA : Extender (molar ratio)	Total Weight of Additives (wt %) <sup>a</sup>	$T_g$ (°C)	Impact Resistance (J/m)
1D <sub>a</sub>	0	—	0	82	15.1 ± 1.7
2D <sub>a</sub>	2.5	1 : 1 : 1	7.23	66	17.5 ± 1.8
3D <sub>a</sub>	5.0	1 : 1 : 1	14.46	55	15.1 ± 1.9
1D <sub>b</sub>	0	—	0	98	13.3 ± 1.5
2D <sub>b</sub>	2.5	1 : 1 : 1	7.23	84	14.9 ± 1.7
3D <sub>b</sub>	5.0	1 : 1 : 1	14.46	71	13.3 ± 1.1

<sup>a</sup> In relation to the unmodified resin weight.

(a) orthophthalic. (b) isophthalic.



**Figure 1** Schematic representation of the proposed modification of UP resins.

resin modified with GMA and APTS, APTS hangs in the UP chains and the extension of the phase segregation and evaporation must be limited.

The addition of the chain extender to the resin modified with GMA and APTS decreases the  $T_g$  values [Fig. 2(d)] more pronouncedly because of the increase of the network flexibility.

The UP resins modified with 5% GMA were cured by different methods (Table I) in a way to find out the best cure conditions. The dynamic mechanical behavior of the samples were analyzed and the respective  $\log E'' \times T$  curves are shown in Figure 3.

The difference between method A and method C is the time of postcure (5 and 24 h, respectively). By the  $\log E'' \times T$  curves, it can be observed that the sample postcured for a longer time presents a broadening of the peak related to the glass transition of polyester phase, probably as a consequence of the larger cure conversion.

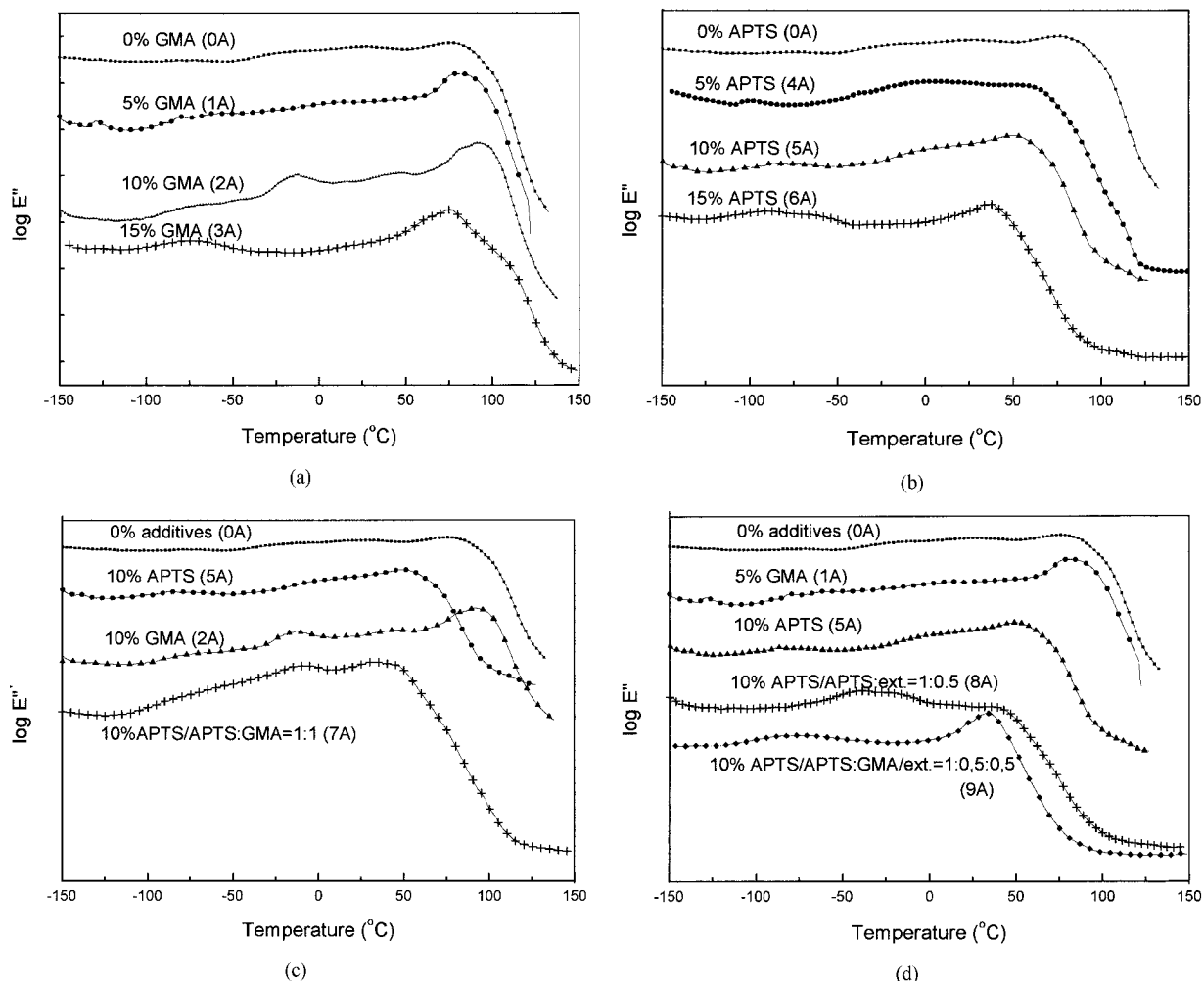
In method B, the drying temperature is increased to optimize the conversion and to remove some volatile substances. Comparing methods A and B, the sample cured by the latter also presents a broadening of the glass transition of the UP resin and it can be also observed at 125°C. This behavior is a consequence of a broad distribution of the relaxations times attributed to microheterogeneities. These microheterogeneities represent fluctuations of the composition and crosslink densities through the materials and may reflect a larger cure conversion. Therefore, methods B and C are more appropriate from the viewpoint of conversion. Besides, the conditions of cure are milder in method C, with lower drying

temperatures, and the surface finishing of the modified resin is also the best. The good results in the system containing water and cured by method C (described below) reinforce the advantages of this method over the others.

The addition of water must guarantee the hydrolysis of the silane group of APTS, which will favor the polycondensation with the chain extender and consequently the formation of poly(organosiloxane) chains. Figure 4 points out the loss modulus curves of samples modified with GMA and APTS and cured in the presence or absence of water by methods A and C, as described in Table III. The  $T_g$  decreases for samples cured by method A when water is added. In the method C, the samples presented no significant change in the  $T_g$  (Table III).

For the mixture cured by method A [Fig. 4(a)], the addition of water shifts the glass transition to lower temperatures as compared with the modified and unmodified resins in the absence of water. In addition, the transitions at lower temperatures (secondary relaxations and transitions related to other phases) also change in intensity and position. However, this change is more pronounced for the resin cured without water as can be seen in the range from -50 to +50°C. Samples cured by method C, either in the presence of water or not, showed a similar behavior as method A below -50°C, but the transition between -50 and +50°C is more intense in samples containing water and cured by method C [compared in Fig. 4(c)]. The larger intensity of the secondary relaxation in the range of -50 to 50°C implies a larger capacity of energy conversion in this temperature





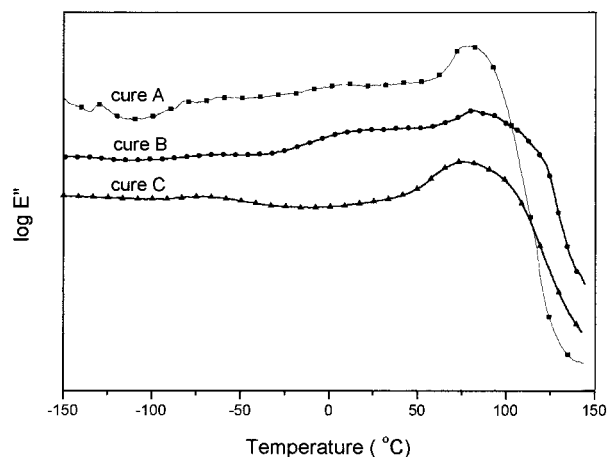
**Figure 2** Loss modulus versus temperature of pure and modified orthophthalic resin as a function of (a) GMA concentration; (b) silane concentration; (c) GMA and silane concentration; (d) resin modified with all the additives in variable amounts.

range, which clearly shows the importance of the cure conditions.

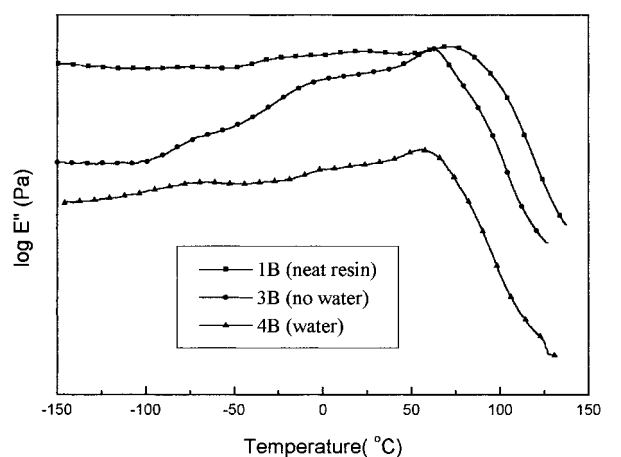
Method C was chosen for sample preparation in the next steps due to its advantages to other methods.

The addition of a chain extender (siloxane) will allow an increase of the polysiloxane chain in the polyester network. The influence of the siloxane on the dynamic mechanical properties were previously analyzed in samples without water and cured by method A. The compositions of the orthophthalic resin modified with GMA, APTS, and water and different amounts of siloxane are shown in the Table IV and the  $\log E'' \times T$  curves in Figure 5.

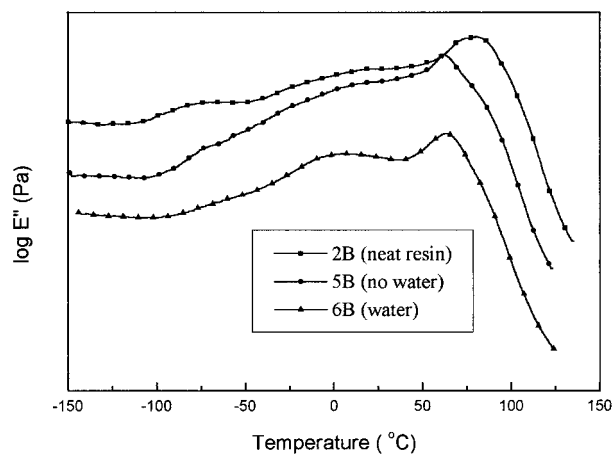
The chain extender promotes an increase in the intensity of the transitions between  $-100$  and  $-50^\circ\text{C}$ , which is not clearly perceivable in sample 6B (without extender), and these transitions be-



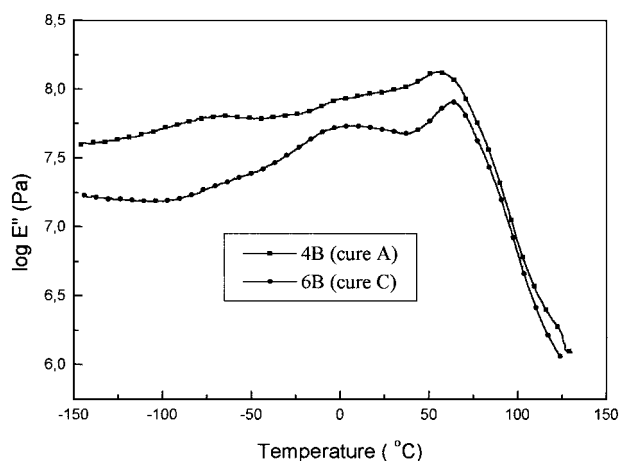
**Figure 3** Orthophthalic resin modified with 5% of GMA and cured by different methods.



(a)

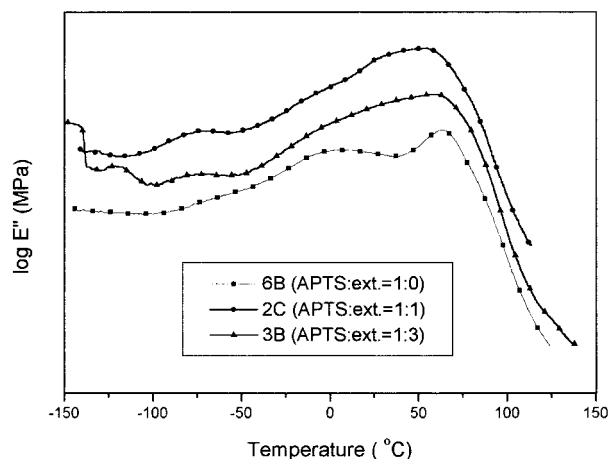


(b)



(c)

**Figure 4** Influence of water on the loss modulus for samples of orthophthalic resin modified with GMA and APTS and cured by methods A and C, according to the Table III.



**Figure 5** Loss modulus curves for orthophthalic resin modified with GMA, APTS, water, and a variable amount of chain extender.

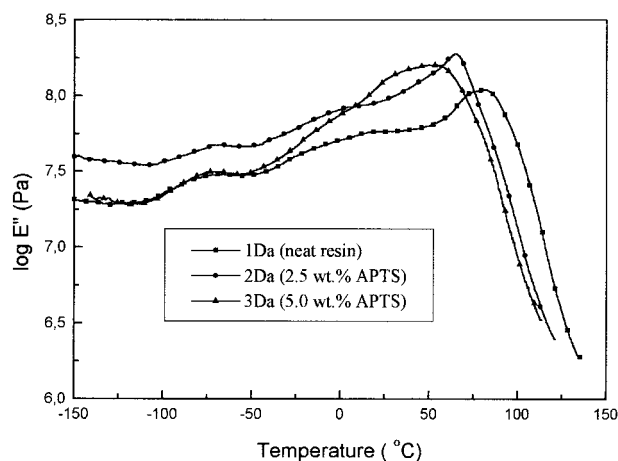
come broader as a consequence of a flexible phase formation, a poly(organosiloxane) phase. Therefore, an increase in the amount of chain extender can lead to the formation of an elastomeric phase, which is a positive indication of impact resistance enhancement and decreasing shrinkage.

Finally, the dynamic mechanical behavior of the ortho and isophthalic resins modified with APTS, GMA, chain extender, and water and cured by method C is shown in Figure 6. Both resins presented a decrease of  $T_g$  of the polyester phase as a function of the modifier amount (see Table V for compositions and  $T_g$  values). The addition of the resins contributes to the network flexibility but larger quantities of additives promote phase separation that is indicated by the broadening of the loss modulus peak, especially in the samples of orthophthalic resin [Fig. 6(a)].

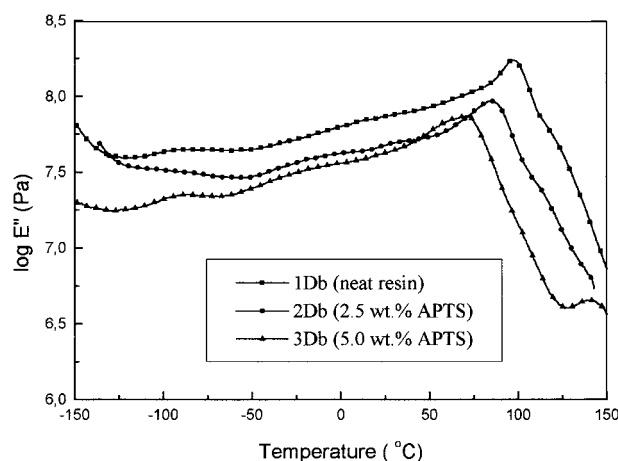
The ortho resin presents a broader glass transition in comparison to the isophthalic resin, and this characteristic is preserved when the modifiers are added to the resin. This fact indicates a similar behavior of modified ortho and isophthalic resins.

### Impact Resistance

The impact resistance results presented in Table V pointed out that small amounts of additives improved the impact resistance (about 12%), whereas the larger amounts cause no changes. The small amount of modifiers can increase the network flexibility because of the incorporation of dangling flexible polysiloxane segments, shown in the DMA analysis as a decrease of  $T_g$  values. However, the modifiers can induce a phase separation. The low adhesion between the resin and



(a)



(b)

**Figure 6** Loss modulus curves for unmodified and modified samples (APTS : GMA : extender : water = 1 : 1 : 1 : 3): (a) orthophthalic resin; (b) isophthalic resin.

the poly(organosiloxane) phase is a possible factor responsible for the impact resistance properties. The phase separation hypothesis is confirmed by DMA analysis (see the broadening of the loss modulus in Fig. 5). At small concentrations, the poly(organosiloxane) chains can be grafted and dispersed in the resin. In this case, the resins become flexible.

## CONCLUSION

By means of the dynamic mechanical analysis, we can conclude that APTS is incorporated to the

resin by reaction of its amino group with GMA, generating a graft copolymer, which has its flexibility improved by the addition of a chain extender. The addition of water in the mixture containing GMA and APTS favors the hydrolysis of the silane and induces the formation of microdomains with lower flexibility. However, the hydrolysis of the silane promotes the polycondensation of the siloxane and allows the increase of the poly(organosiloxane) chains.

The cure conditions (temperature and time) determine the conversion degree and the extension of the phase segregation. As a consequence, the macroscopic properties of the resin are also determined.

The impact resistance tests presented a good performance to systems containing a lower amount of additives. However ortho and isophthalic resins containing a larger amount of modifiers showed no changes in impact resistance values because of the phase separation.

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