

# Vinyl Ester Resin Modified with Silicone-Based Additives.

## I. Mechanical Properties

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Received 15 June 2004; accepted 26 April 2005

DOI 10.1002/app.22770

Published online 9 December 2005 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Silicone-based additives have been used as fire retardants for thermoplastics and present the advantages of improving the processing and impact resistance of the polymers. In this study, we used three different silicone-based additives as modifiers of a vinyl ester resin. The additives were fine powders made up of about 50 wt % polydimethylsiloxane and 50 wt % silica. The differences among them were the functional groups inserted in the polymer chains and the size and size distribution of the particles. The additives were dispersed in resin containing 35 wt % styrene. To cure the mixture, a conventional catalyst and initiator were used, and the reaction was carried out in three ways, which differed in the curing temperature, post-curing temperature, time, and addition of dimethylaniline (DMA) as a promoter of the polyaddition reaction. Dynamic

mechanical analysis showed that the phase behavior of the resulting composites depended strongly on the curing conditions. The flexural modulus of composites containing 5 wt % additive was lower than that for the cured resin. The impact resistance of the composites also depended on the curing conditions but not on the composition or size of the particle of the additive. The fracture morphologies of specimens subjected to impact resistance tests were different for samples cured in the presence or in the absence of DMA, which suggested that it influenced the mechanism of network formation. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2279–2287, 2006

**Key words:** additives; mechanical properties; silicones; thermosets

### INTRODUCTION

Vinyl ester resins (VERs) are widely used thermosetting materials because of their low cost and good combination of properties, including chemical resistance and, especially, mechanical and thermal properties.<sup>1–3</sup>

VERs are addition products of an epoxy resin and an unsaturated carboxylic acid such as acrylic or methacrylic acid. There are a great number of possible products depending on both the resin and the acid used, but the most used is that based on bisphenol A epoxy resin, as it exhibits easy handling properties and good resistance to most chemical agents and has suitable mechanical and thermal properties.<sup>1,4–8</sup>

In general, the vinyl ester prepolymer is dissolved in a reactive solvent, such as styrene, the functions of which are to decrease the viscosity, which makes its application easier, and to react with the methacrylic groups of the prepolymer, which results in thermosetting.

The polymerization goes through a free-radical polyaddition mechanism with methylethyl ketone peroxide (MEKP) as an initiator and a cobalt II octanoate solution (CoOc) as promoter or accelerator, which also acts as an initiator to increase free-radical production.<sup>4,9–12</sup>

VERs are brittle in nature, and therefore, to improve their fracture resistance and to reduce overall production costs, they are usually blended or reacted with different additives and modifiers, which generally form a second disperse phase.<sup>13</sup> Fillers are added to the thermosetting polymeric matrix for one or more of the following reasons: to reduce costs, to increase stiffness, to reduce mold shrinkage, to control viscosity, and to produce a smoother surface.<sup>14</sup>

Reinforcements and fillers can influence the curing of thermosetting resins, and the performance of the fabricated composites depends strongly on the preparation and formulation of the molding compounds.<sup>15</sup> Although fillers increase the modulus of composites, they tend to reduce its strength impact.<sup>14</sup>

It is generally believed that the filler particle/matrix interface is the weakest part of the material, and the performance of materials is strongly related to these interfacial properties.<sup>16</sup> The interfacial adhesion between the filler particle and the matrix has been considered an important factor for determining the mechanical properties of the final material. These prop-

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Contract grant sponsor: Fundação de Amparo à Pesquisa do Estado de São Paulo; contract grant number: 98/13016-0.

erties can, therefore, give indirect information about interfacial behavior.<sup>14,17</sup> If the interfacial adhesion is weak, stress transfer between the matrix and additive is reduced, which makes the material fragile.<sup>18</sup>

Dow Corning, Ltd., entered the market for fire-safe products by developing silicone fire additives with the major goal of improving the fire safety of plastics. Other goals were to minimize the loss of mechanical properties, such as impact resistance and the tensile strength and modulus, and to promote other benefits of silicone fire additives.<sup>19</sup>

The effect of a siloxane powder as a processing aid in polypropylene has been demonstrated by extrusion torque. Polypropylene, when compounded with typical fire retardants, is very difficult to process. Because of the high filler content and nonlubricating nature of the additives, high torque and machine wear are problems during processing. With the addition of 1 wt % methacrylic-functional silicone powder, extrusion torque was reduced over 50% in the fire-retardant system. Siloxane-modified polypropylene also exhibited improved mechanical properties. The addition of 1 wt % of the same siloxane powder increased the impact strength by approximately 100% over the fire-retardant system, which restored mechanical properties lost from the use of the fire-retardant additives.<sup>20</sup>

The effect of silicone powder as a processing aid in poly(phenylene oxide) (PPO) has also been demonstrated by dynamic mechanical analysis. PPO is very difficult to process by conventional methods in the molten state and, for commercial applications, is blended with high-impact polystyrene to give a processable resin. If high-impact polystyrene is replaced with as little as 1 wt % epoxy-functional silicone powder, PPO can then be processed easily, and its mechanical properties, fire resistance, and thermal stability can be improved. Also, impact strength is improved at 10 to 15 wt % of the silicone-based additives.<sup>21,22</sup>

Attempts at using silicone-based additives not functionalized with epoxy groups have resulted in a poorer dispersion of the powder in PPO. A better dispersion of additive functionalized with epoxy groups has been believed to result from epoxy reactivity with the phenol groups of the PPO.<sup>21</sup>

The aim of this study was the modification of thermosetting VER with additives based on silicone. This article describes the preparation of composites with different silicone-based additives and their dynamic mechanical and stress-strain properties and morphology.

The silicone additives used in this study were supplied by Dow Corning in powder form. They were a combination of ultra-high-molar-mass polydimethylsiloxane and fumed silica filler. The particle size of the additives was between 6 and 600  $\mu\text{m}$  (average = 90  $\mu\text{m}$ ).<sup>20-23</sup> These powders can be further modified by the attachment of organoreactive sites, such as epoxy

and methacrylic functional groups, to enhance the compatibility of the powders with various organic resins.<sup>20,23</sup>

The siloxane powders, when compounded into an organic resin with mixing equipment, can break into smaller sizes. The additives have the capability of improving the processability and mechanical properties and show synergistic behavior with conventional flame-retardant additives.<sup>23</sup> Silicone additives containing silica present many acidic silanol sites that can form a network during the combustion process, which act as a thermal barrier and prevent feedback to the substrate.

## EXPERIMENTAL

### Materials

The commercial materials used in this study are summarized in Table I.

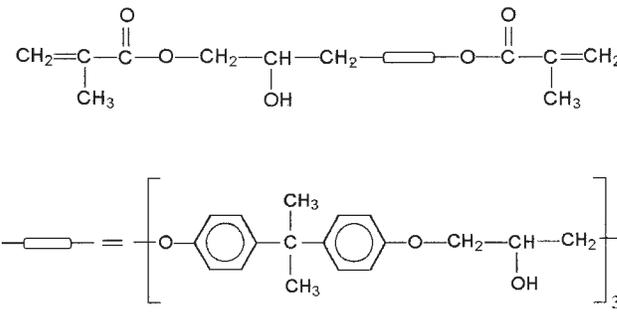
The resin used was a VER (Resapol 10-500) based on bisphenol A epoxy resin containing 35 wt % styrene monomer. The resin was supplied by Reichold S/A (São Paulo, Brazil) as a yellow liquid. Silicone-based additives were supplied by Dow Corning (Hortolândia, Brazil) in powder form. The reactive groups shown in Table I represent the chemical groups additionally inserted into the additives, which presented hydroxyl groups, vinyl groups, and other groups.<sup>21</sup> The resin, reagents, and additives were used as received.

The curing of the resin was conducted at room temperature with MEKP as the catalyst and CoOc and *N,N*-dimethylaniline (DMA) as promoters.

### Sample preparation

Three different additives were used to modify the resin (Table I). For this purpose, 5 wt % additive was dispersed in the resin with a mechanical stirrer at 2300 rpm for 4 h. Reaction curing was conducted with two different curing systems. In one, 0.5 wt % CoOc was added. In the other, 0.5 wt % CoOc and 0.05 wt % DMA were added to the dispersion. All the resulting mixtures were stirred at 2300 rpm for 15 min; then, the stirring rate was decreased to approximately 140 rpm, and the mixture was maintained in an ultrasonic bath at room temperature for 30 min for degassing. MEKP (1.0 wt %) was added to the mixture, and it was stirred for 15 min. The mixture was quickly transferred to appropriate polytetrafluoroethylene molds and cured by two different methods. In the first one, the samples were cured at 25°C for 24 h and postcured at 65°C for 48 h. In the second one, the samples were cured at 25°C for 24 h and postcured at 130°C for 4 h *in vacuo*. Table II summarizes these cure conditions.

TABLE I  
Characteristics of the Vinyl Ester Resin and Silicone-Based Additives

Material	Code	Composition	Reactive groups
Vinyl ester resin	VER		Hydroxyl, epoxy, acrylic, and vinyl
Additive 4-7105	05	Poly(dimethyl- <i>co</i> -methylvinylsiloxane) with terminating hydroxyl groups and fumed silica	Hydroxyl and vinyl
Additive 4-7081	81	Poly(dimethyl- <i>co</i> -methylvinylsiloxane) with terminating vinyl groups, poly(dimethyl- <i>co</i> -methyl- <i>co</i> -methylvinyl phenylsiloxane), and fumed silica	Hydroxyl and vinyl
Additive 4-7051	51	Poly(dimethyl- <i>co</i> -methylvinylsiloxane) with terminating vinyl groups and fumed silica	Hydroxyl, vinyl, and epoxy

### Characterization

The additives were characterized by granulometry to determine grain size and distribution. The determination was carried out with a set of 7 sieves for additives 51 and 81 and 13 sieves for additive 05.

The  $^{29}\text{Si}$ -NMR spectra of the additives were obtained in the solid state at room temperature. The analysis were performed on a Bruker AC-300 spectrometer (300 MHz, Rheinstetten, Germany) with a cross-polarization/magic-angle spinning probe (MAS). The experimental conditions were as follows: observed center =  $^{29}\text{Si}$ , frequency = 99.3 MHz, spectral window = 74,980 Hz, acquisition time = 0.067 s, pulse =  $45^\circ$  (5.7  $\mu\text{s}$ ), interval between pulses = 600 s, transient numbers > 128, rotor = 5 mm ( $\text{Si}_3\text{N}_4$ ), rotation rate = 7000 Hz, and reference = Kaolin (peak at  $-91.16$  ppm).

The modified VERs were characterized by dynamical mechanical analysis. The tests were carried out with a DMTA V dynamic mechanical analysis instrument (Rheometric Scientific, Piscataway, NJ) operating in the temperature scan mode and of the single-point bending geometry type. Samples with dimen-

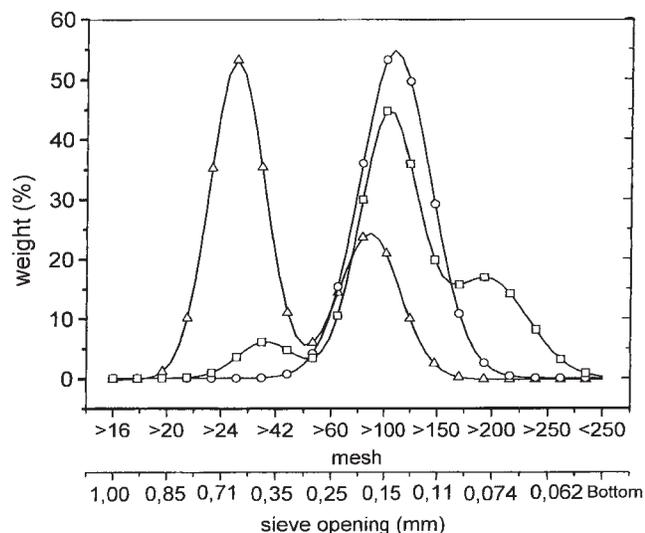
sions of  $30 \times 10 \times 3$  mm were clamped into the clamping frame of the dynamic mechanical thermal analyzer with a torque driver to tighten the clamp bar nuts to a torque of 20 cN m. The measurement conditions included a temperature range from  $-150$  to  $300^\circ\text{C}$ , a heating rate of  $2^\circ\text{C}/\text{min}$ , a frequency of 1 Hz, and an oscillatory strain amplitude of 0.2 mm.

The unnotched Izod impact strength was measured following ASTM D 256-79 specifications with samples with dimensions of  $62 \times 124 \times 3$  mm in an EMIC AIC apparatus (São José dos Pinhais, Brazil). The flexural properties were determined according to NBR 7447 specifications in an EMIC DL 2000 universal testing machine (São José dos Pinhais, Brazil). The sample dimensions were  $60 \times 10 \times 4$  mm, the span between the two supports was 43 mm, and the crosshead speed was 2 mm/min.

The fractures of the samples obtained from the impact strength tests were examined by scanning electron microscopy (SEM) in a Jeol-T300 microscope (Middleton, WI) operating at 20 kV. All of the specimens were coated with a thin layer of gold and carbon to eliminate charging effects.

TABLE II  
Compositions and Curing Conditions of the Composites

Method	A	B	C
Curing temperature time	25°C and 24 h	×	×
Postcuring temperature and time	65°C and 48 h	×	—
	130°C and 4 h	—	×
Curing system	0.5 wt % CoOc	×	×
	1 wt % MEKP	×	×
	0.05 wt % DMA	—	×



**Figure 1** Particle size distributions obtained from curve adjustment with the Gaussian function: additives ( $\square$ ) 51, ( $\circ$ ) 81, and ( $\triangle$ ) 05.

## RESULTS AND DISCUSSION

### Characterization of the silicone-based additives

Granulometry was used to determine the particle size distributions of the additives because the size of the additives influences the final morphology and, consequently, the mechanical properties of materials modified with them. Figure 1 shows the particle size distributions obtained from curve adjustment with the Gaussian function.

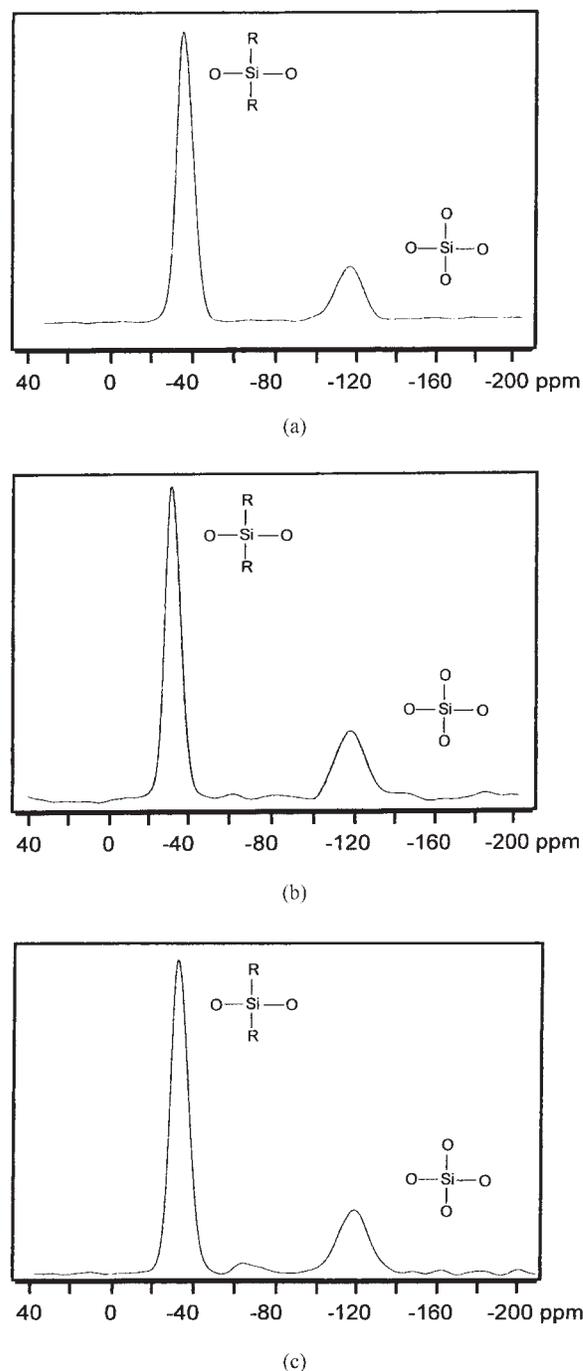
Additive 05 showed a bimodal size distribution with a major fraction in the range of 0.250 to 0.850 mm and a minor fraction between 0.074 and 0.250 mm. Additive 51 showed a trimodal distribution with the major fraction between 0.074 and 0.250 mm. Additive 81 showed particles with diameters between 0.074 and 0.250 mm.

The overall composition of the additives was determined by  $^{29}\text{Si}$ -MAS-NMR. This technique allows the elucidation of the molecular structures of material containing silicon according the number of oxygen atoms linked to it, as shown in Table III.<sup>24</sup>

$^{29}\text{Si}$ -MAS-NMR allowed semiquantitative analysis of the composition of the silicone-based additives,

**TABLE III**  
Composition of the Silicone-Based Additives

Unit	Number of oxygen atoms linked to silicon	Additive 51 (mol %)	Additive 81 (mol %)	Additive 05 (mol %)
M	1	0	0	0
D	2 ( $\text{R}_2\text{SiO}_2$ )	53	49	45
T	3	0	0	0
Q	4 ( $\text{SiO}_4$ )	47	51	55



**Figure 2**  $^{29}\text{Si}$  MAS-NMR spectra of the additives (a) 51, (b) 81, and (c) 05.

through the integration of the signals of the spectra shown in Figure 2. Table III shows the compositions expressed in terms of molar fractions of D and Q. From these results, it was concluded that the additives were constituted of about 50 wt % polydimethylsiloxane chains and 50% silica. Others components declared by the supplier (Table I) could not be determined by this technique, probably due to their low concentrations. It was expected that the additives should exhibit elastomeric characteristics.

## Modified VER

VER contains styrene as a reactive diluent. When the silicone-based additives are dispersed in a resin, styrene can swell in elastomeric phase and react during curing with vinyl groups present in the elastomeric chains (see Table I). Reactions between additives and resin components are desired and can result in better interfacial adhesion.

The curing of unsaturated polyester resins and VER is very well described in the literature.<sup>3,4,9,11,15</sup> The curing reaction involves styrene homopolymerization, styrene–resin reactions, and resin–resin reactions, which results in a very complex network. As reaction conversion increases, the miscibility of the complex mixture decreases, which leads to phase separation, which is very dependent on the curing mechanism and curing kinetics. Therefore, the physical and mechanical properties of this type of thermosetting are imposed by the chemical composition and curing conditions.<sup>25,26</sup>

In this study, dynamic mechanical analysis was used to evaluate the influence of the silicone-based additives and the curing conditions on the extent of the reaction and on the extent of phase segregation.

Figure 3 shows the storage modulus ( $E'$ ) curves for VER containing, or not containing, additives based on silicone and cured in the absence of DMA and postcured at 65°C (method A) or 130°C (method C) and samples cured in the presence of DMA and postcured at 130°C (method B). DMA was used as the curing promoter in method B, and its function was to accelerate the curing. However, there is good evidence from kinetic studies of VER curing that DMA interacts with silicone-based additives, changing the mechanism of the curing kinetics.<sup>27</sup>

The profile of the  $E'$  curves of the cured resin and cured modified resins were similar and showed a decrease in modulus around 100°C attributed to the  $\alpha$  relaxation or glass transition of VER.<sup>28</sup> In the rubbery region above 150°C, all of the samples showed an increase in  $E'$  as the temperature increased because of residual curing reactions during heating. The samples did not undergo thermal degradation or thermal oxidation up to 300°C, as concluded from thermogravimetry.<sup>27</sup>

Figure 4 shows the  $E'$  at 250°C for all of the materials studied. The modulus in the rubbery region was influenced by the additives, the curing systems, and the curing conditions, which indicated that these factors determined the degree of phase separation and the extent of curing. For example, for additives 81 and 05, curing in the presence of DMA at 130°C (method B) resulted in materials with higher modulus. Curing method C was not efficient in promoting complete curing. The curing temperature was high, but the time

for curing was probably not long enough to promote a high extent of curing.

A slight drop in  $E'$  was observed at temperatures around -100°C, which was attributed to the glass transition of polydimethylsiloxane and to a secondary  $\beta$  relaxation of polystyrene segments.

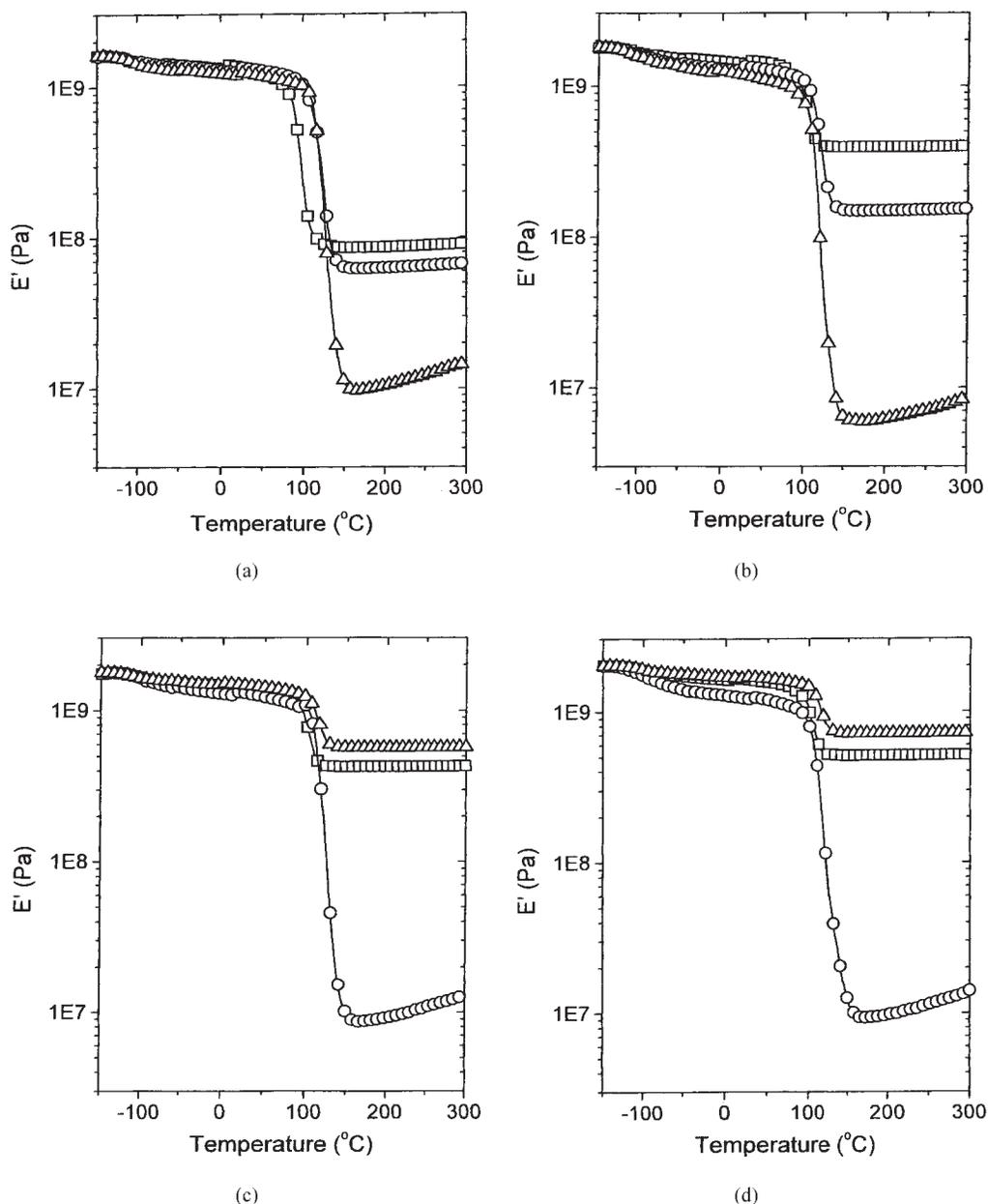
A glassy polymer exhibits relaxations as glass transition and secondary relaxations. Structural relaxation in the glass-transition ( $\alpha$ -relaxation) region results from molecular segments of the polymer backbone chain. In contrast, the secondary ( $\beta$ ) relaxations, which occur at lower temperatures, are generally believed to involve much more localized molecular motions. These relaxations show characteristic behaviors, which are quite distinct from that of the main glass transition and lead to many interesting mechanical properties.<sup>26</sup>

Dynamic mechanical analysis, in particular the loss modulus ( $E''$ ) versus temperature curves, allows one to identify and to characterize polymer relaxations. The peaks present in the  $E''$  versus temperature curves are related to relaxation. The peak at higher temperature is attributed to the glass transition of the cured resin, whereas peaks occurring at temperatures lower than the glass-transition temperature ( $T_g$ ) are related to secondary relaxations.<sup>26</sup> The temperatures corresponding to the maxima of the peaks in the  $E''$  curves are assumed to be the glass transition and secondary relaxation temperatures ( $T_\beta$ ).

$E''$  as a function of temperature for the samples are shown in Figure 5. The curves were shifted in relation to each other to facilitate the presentation of the results.

The  $E''$  curves of the analyzed samples were very similar, independent of the additives used. The curves revealed two peaks. The first peak, from -120 to -50°C, was related to  $\beta$  relaxation<sup>29,30</sup> because of some mobility of the phenyl groups from the polystyrene segments. In the same temperature range, relaxations of the polymeric phase of the additives occurred (glass transition and melting of the polydimethylsiloxane chains). The second peak ( $\alpha$  relaxation) was attributed to the glass transition of the cured resin.<sup>26,29,30</sup> The  $\alpha$  relaxation or glass transition appeared centered in the temperature range of 100–120°C. Table IV shows the  $T_g$  and  $T_\beta$  values obtained from the  $E''$  versus temperature curves.

Figure 5(a) shows the influence of the curing temperature on the  $E''$  curves of the cured samples in the absence of DMA. Samples cured at 65°C (method A) exhibited peaks around 100°C attributed to glass transitions of the resin, whereas samples cured at 130°C (method C) presented glass transitions at higher temperatures, which indicated a higher extent of curing in the latter case. In addition, a shoulder was observed after the maximum of the peak when the sample was cured at 65°C. The  $E''$  curves in the region of the glass



**Figure 3**  $E'$  for samples cured with ( $\square$ ) method A, ( $\triangle$ ) method B, and ( $\circ$ ) method C: (a) VER, (b) VER + 5 wt % additive 51, (c) VER + 5 wt % additive 81, and (d) VER + 5 wt % additive 05.

transition for samples cured at 65°C were typical of materials exhibiting incomplete curing. Similar behavior has been observed for modified unsaturated polyester resin and resins containing different amounts of styrene.<sup>25,26</sup> Figure 5(b) shows that the influence of DMA on the  $E''$  curves was lower than that of the curing temperature. This means that temperature influenced the extent of curing more than the promoter DMA.

The curing schedule is very important because when the curing temperature used is lower than the  $T_g$  of the resin, additional reactions will take place at higher temperatures. Besides, the crosslinking density

reached for inadequate curing conditions will remain quite distant from the maximum, and so the thermal and other physical and mechanical properties will be lower than those corresponding to the thermosetting system cured under optimum conditions.<sup>31</sup>

The broadening of the glass transition is determined by the relaxation modes and time. The broadening of the glass transition is associated with the development of microenvironments with different compositions and crosslinking densities.<sup>25,26</sup> These microenvironments are formed during resin curing as a consequence of the drop in the miscibility with the growth of the molecular chains.<sup>26</sup> The glass transitions of the

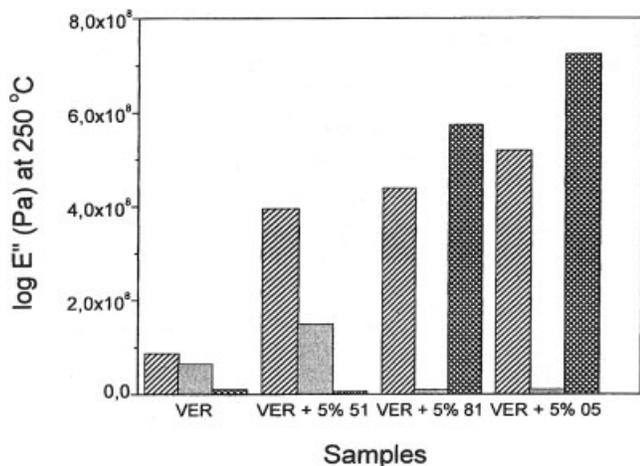


Figure 4 E' values at 250°C for samples prepared by the methods (▨) A, (▩) B, and (□) C.

samples cured by method A were broader than the glass transitions of the samples cured by method B. In this case, the narrowing of the glass transition when the sample was cured in the presence of DMA and postcured at higher temperatures was associated with a higher extent of curing, which diminished the differences among microenvironments, as consequence of the more pronounced curing or a homogeneous distribution of the components.

The mechanical properties of the composites with 5 wt % additive, as determined by tensile tests and impact resistance, are listed in Table V.

The results indicate that the additives improved the impact resistance of the resin cured by method A (in the absence of DMA). On the contrary, samples containing additives cured by method B presented lower impact resistance than the pure resin, which reinforces the hypothesis that DMA influenced the microstructure of the network formed.

In a general way, it was possible to observe that additives influenced the flexural modulus. The flexural modulus at 25°C represented the mechanical resistance of the samples in the glassy state, which was a function of composition, the elastomer contents in the samples, and the adhesion between the elastomeric dispersed phase of additives and the resin. Better adhesion between these phases led to better mechanical energy transfer and dissipation, decreasing the flexural modulus.

Another important result shown in Table V was associated with the elasticity modulus, stress at break, and deflection at break. These values decreased with the addition of additives, which indicated a decrease in the stiffness of the composites.

Examination of the fracture surfaces resulting from impact resistance tests of the modified resin by SEM gave information about how additives and curing conditions affected the fracture of the resin.

Figures 6 and 7 show the fracture surfaces of the neat resin and the composites. The fracture surface of the neat resin and the composites revealed a feather-like morphology, except for the composite with additive 81 obtained by method B, whose morphology was composed of parabolic structures. This confirmed the influence of additives and the curing program on the mechanism of network formation.

The mapping of silicon revealed that the additives were distributed uniformly in the matrix. The dimensions of additive 81 in the matrix (120 μm) were higher than the dimensions of the original additive (15 μm).

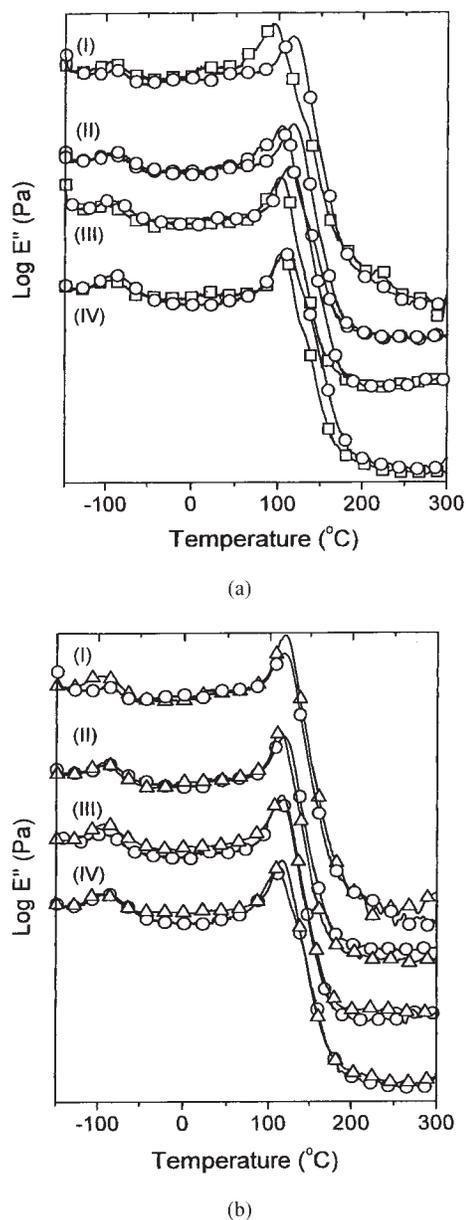


Figure 5 E' curves for (a) samples prepared by methods (□) A and (○) C and (b) samples cured by methods (△) B and (○) C: (I) VER, (II) VER + 5 wt % additive 51, (III) VER + 5 wt % additive 81, and (IV) VER + 5 wt % additive 05.

**TABLE IV**  
 **$T_g$  and  $T_\beta$  Values for the Neat Resin and the Resin Modified with 5 wt % Additives**

Sample	Method	$T_g$ (°C)	$T_\beta$ (°C)
VER		103	-98
VER + 5% 51	A	105	-90
VER + 5% 81		104	-96
VER + 5% 05		104	-92
VER		118	-96
VER + 5% 51	B	112	-93
VER + 5% 81		116	-91
VER + 5% 05		118	-93
VER		118	-89
VER + 5% 51	C	119	-86
VER + 5% 81		113	-90
VER + 5% 05		110	-89

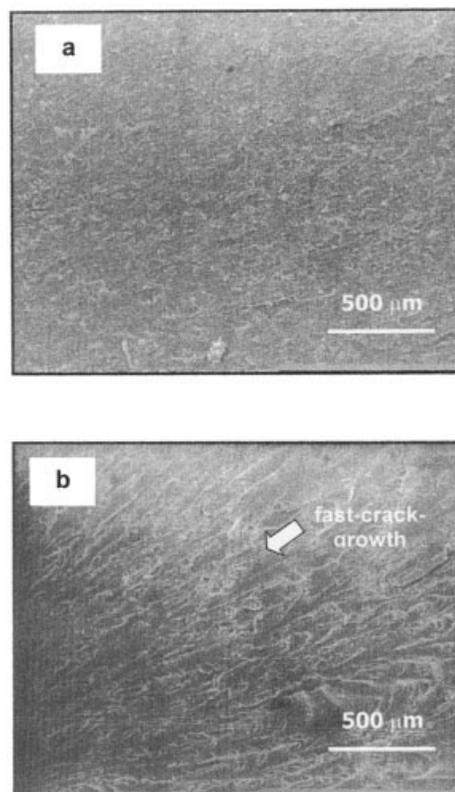
This indicated an agglomeration of the particles of additive 81 or an increase in the particle size due to swelling with styrene during sample preparation.

In the micrographs of the neat and modified resin, two regions were observed: a slow-crack-growth region and a fast-crack-growth region. In the slow-growth region, the crack propagation rate was much smaller, and it was smooth and featureless under low magnification. In the fast-crack-growth region, the crack propagation was unstable and propagated very rapidly.<sup>32</sup>

The fracture morphology is a direct reflection of the energy required for crack propagation, the main crack front velocity ( $V_m$ ) and the secondary crack front velocity ( $V_{sr}$ ). If  $V_m \gg V_{sr}$ , a marking feature is formed. If  $V_m > V_{sr}$ , the primary front will completely enclose it, and an ellipse will result. If both velocities are equal ( $V_m = V_{sr}$ ), a parabolic structure is formed.<sup>32</sup>

## CONCLUSIONS

VER and its composites containing silicone-based additives presented phase behavior, mechanical properties, and fracture morphology dependent on the composition, curing system, and curing conditions. The



**Figure 6** SEM micrographs of neat resin obtained by methods (a) A and (b) B.

composition, size, and size distribution of the particles of the additives had no influence on the properties of the composites.

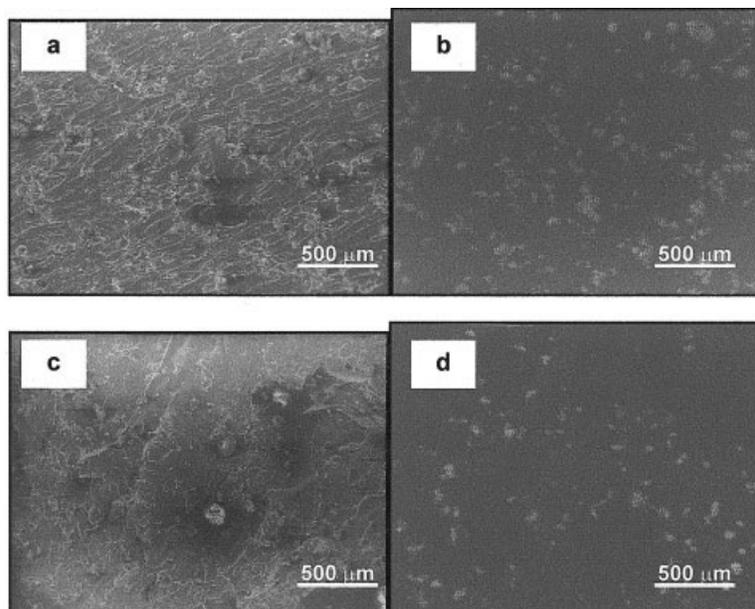
Despite the elastomeric characteristics of the additives, the impact resistance of the composites was not improved.

The morphology of the fractures and the mechanical behavior of the resin and composites suggested the formation of networks with different microstructures when curing was conducted in the presence of DMA.

The authors thank Reichold S/A and Dow Corning for supplying the materials used in this work.

**TABLE V**  
**Mechanical Properties of the Composites**

Sample	Method	Impact strength (J/m)	Flexural modulus (MPa)	Elasticity modulus (MPa)	Stress at break (MPa)	Deflection at break (%)
VER		32 ± 2	2967 ± 33	3031 ± 42	133 ± 5	31 ± 2
VER + 5% 51	A	36 ± 3	2555 ± 35	2645 ± 35	73 ± 4	19 ± 1
VER + 5% 81		41 ± 1	2673 ± 116	2155 ± 130	77 ± 4	19 ± 1
VER + 5% 05		42 ± 2	2135 ± 74	2146 ± 79	60 ± 4	21 ± 1
VER		140 ± 7	2603 ± 107	2818 ± 237	409 ± 111	32 ± 5
VER + 5% 51	B	62 ± 3	2451 ± 78	2566 ± 174	116 ± 14	19 ± 1
VER + 5% 81		71 ± 3	2609 ± 56	2712 ± 123	135 ± 22	19 ± 2
VER + 5% 05		121 ± 4	2390 ± 75	2484 ± 194	135 ± 32	20 ± 3



**Figure 7** (a) SEM micrographs and (b) Energy Dispersive Spectroscopy (EDS) of modified resin containing 5 wt % additive 81 cured by method A and (c) SEM micrographs and (d) EDS of modified resin containing 5 wt % additive 81 cured by method B.

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