

# The Role of Additives in the Manufacture of Sheets of Unsaturated Polyester and Postconsumer Unsaturated Polyester/Glass Fiber Composites: Mechanical and Dynamic Mechanical Properties

A. G. Pedroso,<sup>1</sup> D. S. Rosa,<sup>2</sup> T. D. Z. Atvars<sup>1</sup>

<sup>1</sup>Instituto de Química, UNICAMP, Caixa Postal 6154, Campinas, 13083-970, SP, Brazil

<sup>2</sup>Centro de Ciências Exatas e Tecnológicas da USF, Rua Alexandre Rodrigues Barbosa 45, Itatiba, SP, 13.251-900, Brazil

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**ABSTRACT:** The storage of postconsumer glass fiber reinforced unsaturated polyester composite impacts negatively on the environment because of the long lifetime and the volume/amount ratio of residuals, which are important aspects to be considered. Two types of additives were employed as an attempt to improve the mechanical properties of sheets manufactured with ground postconsumer glass fiber reinforced orthophthalic unsaturated polyester resin composite and virgin orthophthalic unsaturated polyester

resin, a silane-coupling agent and an organic dispersant. Flexural and impact tests, and dynamic mechanical analyses, demonstrated that the coupling agent increased the mechanical properties, while the dispersant decreased these properties, compared to material without either additive. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1834–1839, 2004

**Key words:** unsaturated polyester; glass fiber; composites; recycling; mechanical properties

## INTRODUCTION

Unsaturated polyester resins are among the most widely used thermosetting materials in the composites industry. Commercial interest in glass fiber reinforced polyester composites is principally due to their high strength-to-weight ratio and low cost. In Brazil, the public telephone weather protector covers are manufactured, by a laminating process, with a composite made of glass fiber and unsaturated polyester. The storage of covers which no longer can be used impacts negatively on the environment because of the long lifetime and the volume/amount ratio of residuals,<sup>1</sup> both important aspects to be considered. Different from thermoplastics, thermosetting materials are softened, molded, and irreversibly cured at room or higher temperatures. Thus, the material cannot be melted again. As a consequence, the available methodologies for the recycling process of thermosetting artifacts are still limited. In general, these recycling methodologies involve the following: (1) incorporation of ground material in concrete, mortar compositions, and thermoplastics or thermosetting systems; (2) recovering of the raw material via hydrolysis or

glycolysis; (3) chemical recovery via pyrolysis; (4) energy recovery through incineration.<sup>2–9</sup> Most of the scraps are obtained from sheet molding compounds (SMC), ground to different grain sizes and used in bulk molding compounds (BMC) or in thermoplastic compositions.<sup>2–5</sup> The global results show that the ground scraps do not act as reinforcing fillers. Risson et al.<sup>9</sup> studied recycling of polyester/glass fiber laminate scraps. The ground material was used in BMC manufacturing and mechanical tests showed a decrease in their flexural and impact properties.

Several factors contribute to the improvement of the properties of composite materials. Of fundamental importance are the wettability of the reinforcement by the resin and the adhesion of the reinforcement to the matrix, transferring, by shearing stress, the load from one reinforcement to another, throughout the matrix. The more uniform and continuous the impregnation process, the better the properties of the final product. A poor impregnation of the reinforcement will cause the formation of voids, which will impair the resulting material properties.<sup>10</sup> The interface region is the main region responsible for load transfer from the matrix to the filler. An improvement of interface adhesion can be achieved by treating the filler with silane-coupling agents or by adding silane to the composition during mixing.<sup>11</sup> Works from the literature<sup>12–14</sup> show an increase in the mechanical properties of polyester composites when fillers and fibers are treated with silane-coupling agents.

Correspondence to: T. D. Z. Atvars (tatvars@iqm.unicamp.br).

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The present work evaluates the improvement of the mechanical properties of composites made of postconsumer telephone protector covers and unsaturated polyester resin by using a silane-coupling agent or an organic dispersant. The mechanical properties of the resulting sheets were analyzed by using flexural and impact tests and were confirmed by means of dynamic mechanical analyses (DMTA).

## EXPERIMENTAL

### Materials and preparation of the samples

A postconsumer telephone protector cover was supplied by the Fundação Centro de Pesquisas e Desenvolvimento, CPqD (Brazil). A commercial orthophthalic unsaturated polyester resin (room temperature curing), Resapol 10-116, was supplied by Resana S.A. (Brazil). The Busperse 47 dispersant agent was supplied by Buckman Laboratories, Ltda. The silane coupling agent 3-methacryloxypropyltrimethoxysilane, Z 6030, was supplied by Dow Corning (Brazil).

The resin was cured using 1.5% (by weight of resin) of methyl ethyl ketone peroxide (MEK-P) as initiator agent. The resin/MEK-P mixture was cured in  $20 \times 20 \times 0.32$  cm aluminum molds for 30 min at 50°C with a further 30 min at room temperature. Then, it was removed from the mold and submitted to a postcure heating at 60°C for 48 h.

The sheets of ground material/unsaturated polyester resin were prepared according the processing conditions optimized in our previous article,<sup>15</sup> where we established the conditions to produce composite materials with the best mechanical properties values and visual aspects. The sheets were prepared in different proportions, by weight, of ground material/polyester resin and 1.5% of MEK-P by weight of resin. The formulations were mixed for approximately 3 min by using a homemade circular disk mechanical agitator (Cowles type). After the mixing processes, the mixtures were transferred to the  $20 \times 20 \times 0.32$  cm aluminum molds and pressed at 1.5 MPa for 30 min at 50°C. Then, the pressure was released and the sheet was maintained in the mold for 30 min more at room temperature. Then, the sheets were removed from the mold and submitted to postcuring at 60°C for 24 h. In some formulations, we also added different amounts of the dispersant Busperse 47 (by weight of total formulation) to the resin before the mechanical mixing and in others 1% of a silane coupling agent (by weight of ground material) was added to the resin before the mechanical mixing. Other formulations were prepared by using ground material pretreated with silane.

### Characterization and tests

The contents of inorganic materials and the resin of the cover were determined by gravimetry after burning off the polyester matrix at 550°C for 4 h.

Pieces of the cover were ground in a Rone three rotary-blade grinder, model MFA 1302. The grain size distribution analysis of the ground material was performed with a Tyler model Ro-tap agitating sieve, sifting the ground material in standard sieves of 6.3, 4.8, 2.4, 1.2, 0.6, 0.3, and 0.15 mm. The material retained by each sieve was determined by gravimetry.

Part of the ground material was treated with the silane-coupling agent Z-6030, using the following two different protocols: (1) A water solution having 1% w/w of silane was prepared. The ground material was immersed in this solution for 24 h and then dried at 90°C for 24 h. (2) An ethanolic solution having 1% w/w of silane was prepared. The ground material was immersed in this solution for 24 h and then dried at 90°C for 2 h.

Flexural tests were performed by using method I (three-point loading system) according to the ASTM D-790-95-a standard.<sup>16</sup> Sheets of different formulations were cut according to the dimensions specified by the ASTM standard. The borders of specimens were sanded. Flexural tests were performed in an EMIC, model DL-2000, at a rate of 5.0 mm/min. Average and standard deviation values of the flexural strength were determined with five specimens for each formulation.

The impact tests were accomplished according to method A (Izod with notch) established by the ASTM D 256-93-a standard,<sup>17</sup> in a CEAST model Resil 25 equipment. Sheets of different formulations were cut according to the dimensions specified by the ASTM standard. The borders of specimens were sanded. Average and standard deviation values of impact resistance were determined with 10 specimens for each formulation.

Dynamic mechanical properties were measured by employing a DMTA MK III from Rheometric Scientific over the temperature range of 20 to 120°C at 1 Hz frequency. The temperature ramping rate was 2°C/min. The analyses were done on specimens with  $35.0 \times 9.0 \times 3.2$  mm. Average and standard deviation values of the temperatures where  $\tan \delta$  and  $E''$  are maxima were determined with two specimens for each formulation.

## RESULTS AND DISCUSSION

### Grain-size distribution

The inorganic material and the resin contents (% w/w) of the cover obtained by burning off the polyester matrix were 38 and 62%, respectively. Figure 1 shows the grain size distribution for the ground cover. We observed that the ground material presented a grain size predominantly between 2.4 and 4.8 mm. Nevertheless, the volumetric fraction of the grains up to 0.3 mm was relatively high. These are the size

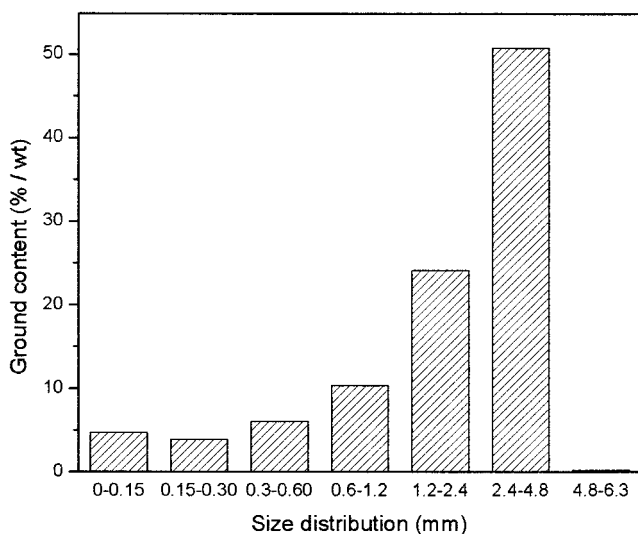


Figure 1 Grain size distribution of the ground material.

characteristics of the ground material to be used in all formulations.

### Mechanical properties

Table I shows flexural strength and impact resistance values obtained for the resin and different formulations, described by different numbers. For example, samples 1 to 3 were prepared with three weight proportions (60, 70, and 80%) of ground material, which was added to the raw polyester resin. For these formulations, we evaluated the effect of the recycled material on the resin properties. Samples 4 to 7 were prepared to evaluate the effect of dispersant on the mechanical properties of two weight proportions of the ground material. Samples 8 and 9 allowed the study of the influence of the silane-coupling agent

directly added to resin; , finally, samples 10 and 11 showed the influence of other silane treatments.

Samples 1 to 3 showed that higher values of the mechanical properties were obtained for ground contents of ~ 60 and 70%. When the amount of resin was larger than 40%, it leaked out of the mold. Therefore, this resin content was the upper limit for all of the other formulations. Despite high standard deviations, we observed a tendency of improvement (on average) of the mechanical properties values in sample 1 (60% ground material) compared with sample 2 (70% ground material). Higher values of the standard deviation are common for composite materials, for which the heterogeneity of the specimens is larger than for monodisperse or isotropic materials. In addition, higher standard deviations are also expected for sheets and specimens prepared by manual processing, which can cause dimensional variations, when compared, for example, with specimens molded by injection. Furthermore, the dispersion of the data obtained in impact tests was greater than in the flexural tests, because the former is more sensitive to test conditions and specimen preparation than the latter. The reason for this higher sensitivity is the complex behavior of crack initiation and propagation mechanisms.

The addition of Busperse dispersant to the mixture decreased the mechanical properties, and this decrease was more relevant for larger amounts of dispersant (4% w/w). The accentuated decrease may be related with the following: (1) improvement of ground material dispersion, which acts as filler, leading to larger ground material/resin contact area; (2) if the solubility of the dispersant in the resin is high, the dispersant may interact more efficiently with small particles of the ground material, because these small particles exhibit large surface area. However, these particles exercise no function of reinforcement. (3) The

TABLE I  
Flexural Strength and Impact Resistance for the Resin and Several Formulations of Resin/Ground Material

Sample	Ground material (% w/w)	Resin (% w/w)	Dispersant (% w/w)	Silane treatment	Silane added to the formulation	Flexural strength (MPa)	Impact resistance (J/m)
Resapol 10-116	—	—	—	—	—	64.5 ± 10.2	10.8 ± 0.8
1	60	40	—	—	—	38.2 ± 3.9	70.2 ± 16.1
2	70	30	—	—	—	31.2 ± 6.1	65.4 ± 12.4
3	80	20	—	—	—	15.7 ± 5.2	49.2 ± 17.2
4	60	40	2	—	—	33.8 ± 2.8	64.5 ± 18.3
5	70	30	—	—	—	29.3 ± 3.0	51.1 ± 8.7
6	60	40	4	—	—	17.2 ± 2.8	49.0 ± 13.0
7	70	30	—	—	—	15.4 ± 0.8	44.4 ± 15.6
8	60	40	—	—	1	43.3 ± 2.1	69.5 ± 15.0
9	70	30	—	—	—	37.2 ± 6.6	63.7 ± 10.8
10	60	40	—	Aqueous solution	—	39.0 ± 2.2	63.0 ± 11.7
11	60	40	—	Alcoholic solution	—	44.7 ± 3.6	63.0 ± 17.5

TABLE II  
Temperature Values, where  $\tan \delta$  and  $E''$  are Maxima, for the Resin  
and Several Formulations of Resin/Ground Material

Sample	Ground material (% w/w)	Resin (% w/w)	Dispersant (% w/w)	Silane treatment	Silane added to the formulation	$T_g$ ( $\tan \delta_{\max}$ ) (°C)	$T_g$ ( $E''_{\max}$ ) (°C)
Resapol 10-116	—	—	—	—	—	93 ± 0	69 ± 3
1	60	40	—	—	—	95 ± 1	79 ± 0
2	70	30	—	—	—	94 ± 0	74 ± 2
4	60	40	2	—	—	90 ± 2	74 ± 1
5	70	30	—	—	—	88 ± 1	69 ± 0
6	60	40	4	—	—	84 ± 2	66 ± 2
7	70	30	—	—	—	85 ± 2	61 ± 3
8	60	40	—	—	1	93 ± 0	76 ± 3
9	70	30	—	—	—	92 ± 1	72 ± 1
10	60	40	—	Aqueous solution	—	95 ± 2	80 ± 3
11	60	40	—	Alcoholic solution	—	96 ± 1	81 ± 1

high solubility of the dispersant should also induce a reduction of the glass transition temperature ( $T_g$ ) of the resin and, consequently, a decrease of material rigidity may be produced.

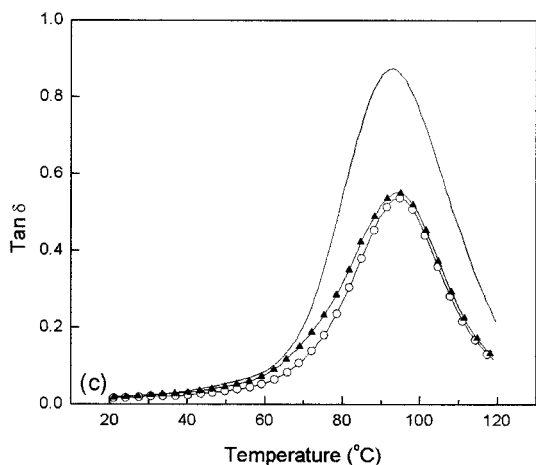
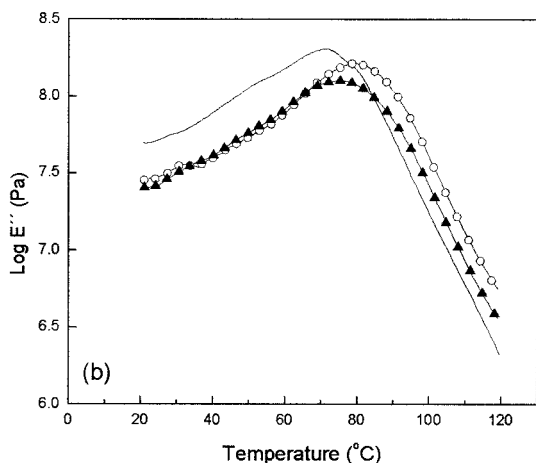
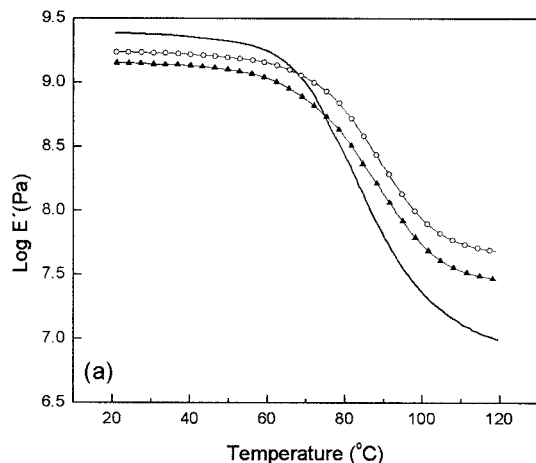
Samples 8 and 9 were prepared by the direct addition of a silane-coupling agent to the resin. As shown in Table I, this agent caused increases of ~ 13 and 19% of the flexural strength for the samples with 60 and 70% of ground material, respectively. Significant modification of the impact resistance was not observed. Silane treatment of the ground material using an alcoholic solution is seen to be more appropriate than treatment with an aqueous solution. There was not a significant increase of the flexural strength when the ground material was treated with an aqueous solution (sample 10) and there was an increase of ~ 17% of the flexural strength when the ground material was treated with an alcoholic solution (sample 11). Impact resistance values of both samples decrease ~ 10%. We suggest that the reason for the larger effectiveness of the alcoholic medium is related to the facility of drying the material after treatment, due to the higher vapor pressure of this solvent. Nevertheless, the mechanical analysis of these samples revealed that the addition of silane-coupling agent did not improve the mechanical properties, as observed in other systems, such as those containing virgin glass fiber.<sup>12-14</sup> One possible reason for these unsuccessful results may be that the silane-coupling agent is more efficient in modifying the glass fiber surface but that it is unable to modify the surface of fibers covered with a residual resin layer.

Based on the dynamic mechanical analysis, the glass transition  $T_g$  values can be defined as the temperature where (1) the loss tangent ( $\tan \delta$ ) is maximum; (2) the loss modulus ( $E''$ ) is maximum; (3) the inflection point at which a significant drop of the storage modulus ( $E'$ )

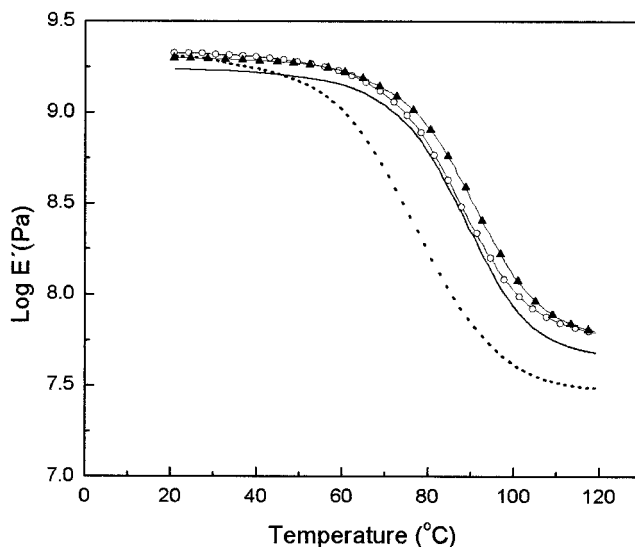
occurs.<sup>18</sup> Table II shows temperature values where  $\tan \delta$  and  $E''$  are maxima, for the raw resin and for several formulations of resin/ground material. Figure 2 shows the plots of  $\text{Log } E' \times T$  (a),  $\text{Log } E'' \times T$  (b), and  $\tan \delta \times T$  (c) for the raw resin and samples containing 60% (w/w) and 70% (w/w) of ground material.

Figure 2(a) shows that the addition of ground material to the resin caused a decrease of  $E'$  for values below  $T_{g'}$ , an increase of  $E'$  for values above  $T_{g'}$ , and a shift toward higher temperatures of the inflection point, at which a significant drop of  $E'$  occurs. Because the inflection point is related to  $T_{g'}$ , this shift implies that there was an increase of  $T_g$ . Furthermore, the difference between glass and rubber moduli is much smaller in the composites than in the matrix. This fact, according to Marcovich et al.,<sup>19</sup> could be attributed to the combination of the hydrodynamic effects of the particles embedded in a viscoelastic medium and to the mechanical restraint introduced by the filler at high concentrations, which reduced the mobility and deformability of the matrix. The increase of  $T_g$  is confirmed by  $E''$  maximum peaks, as shown in Figure 2(b) and given in Table II. Figure 2(c) and Table II show that the temperatures corresponding to the  $\tan \delta$  maximum peak did not show significant changes when the ground material was added to the resin. Because of the relatively broad  $T_g$  temperature range of thermosets, it would be inappropriate to choose the temperature corresponding to the  $\tan \delta$  peak as the  $T_g$  value, where the polymer is already in a soft rubbery state, showing a very low storage modulus. For purposes of engineering applications, as the  $T_g$  is not a specific temperature, one should consider that  $T_g$  extends from the inflection point of the  $E'$  curve to the  $\tan \delta$  peak temperature.<sup>20</sup> According to ASTM D 4065-94,<sup>21</sup> the recommended standard for reporting  $T_g$  is the temperature corresponding to the  $E''$  peak. Data in Table II





**Figure 2** (a)  $\text{Log } E' \times T$ , (b)  $\text{Log } E'' \times T$  and (c)  $\tan \delta \times T$  plots for the resin (—) and samples containing 60% w/w (—○—, sample 1) and 70% w/w (—▲—, sample 2) of ground material.



**Figure 3**  $\text{Log } E' \times T$  for the some formulations containing 60% of ground material (—; sample 1), 60% ground material/4% Busperse (—, sample 6), 60% ground material/1% silane (—○—, sample 8), and 60% ground treated with alcoholic silane (—▲—, sample 11).

also demonstrate that the addition of dispersant (samples 2 and 6) decreased  $T_g$  values, indicating, as suggested before, that the resin was plasticized by this additive.

Figure 2(c) shows that the  $\tan \delta$  peak decreased when ground material was added to resin. A possible explanation for this result is that the height of the main  $\tan \delta$  peak was a relative measure of the amount of material involved with the glass transition.<sup>19</sup>

Although the  $T_g$  value was not changed when ground material was added to the resin (sample 1), this value changed when dispersant was added (sample 6). We are assuming again that this additive acts as a plasticizer of the resin, interfering with the mechanical properties of the composite obtained.

Figure 3 shows that when silane was directly added to resin and the ground material was previously treated with silane (samples 8 and 11), there was an increase of  $E'$  and a shift toward higher temperatures of the inflection point at which a significant drop in  $E'$  occurs, indicating that there was an improvement in interfacial interaction. These results corroborate the values obtained in the flexural tests.

## CONCLUSION

Sheets manufactured with postconsumer public telephone weather protector covers and unsaturated polyester resin presented greater toughness and lower flexural strength compared to the pure resin. These mechanical properties may be improved by processing methods.

The use of dispersant altered the interactions between the resin polymer chains and the composite interfacial interactions, causing a decrease in the mechanical properties of the composites.

Ground material treated with silane and silane blended into the material increased flexural strength of the composite and an increase of the ground material/resin interfacial interaction was obtained.

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