

Unsaturated Polyester Resin Modified with Poly(organosiloxanes). II. Acoustic Emission Study on Glass-Fiber-Reinforced Resin

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ABSTRACT: This work aims to study the adhesion of an isophthalic acid based unsaturated polyester resin chemically modified by grafting copolymerization of a poly(organosiloxane) to the glass fiber. The failure mode of the single-edge notched tensile specimen, cut from pressed plates containing 50 wt % of nontreated and silane-treated milled glass fiber, was studied by acoustic emission (AE) technique. It was found that the aforementioned resin modification enhanced the adhesion between the fiber and the resin. This was suggested by a shift in the AE amplitude and energy toward higher values. On the other hand, the matrix modification had no significant effect if glass fiber with suitable unsaturated polyester resin (UP) sizing was incorporated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3280–3289, 2001

Key words: unsaturated polyester resin; poly(organosiloxane); acoustic emission

INTRODUCTION

Unsaturated polyester resin (UP) is used in a large field of applications, especially as a reinforced plastic because of its good mechanical properties and low price. However, in some structural applications, its low-impact resistance limits its use. The toughening of the resin^{1,2} may circumvent this problem if suitable modifiers can provide a good adhesion between the UP resin and the fillers or reinforcements³ at the same time. However, improvement in the impact resistance may be accompanied by adverse effects on some others properties such as stiffness and tensile strength.⁴

Apart from this fact, the miscibility between resin and modifier is limited in most cases and can induce the phase separation. Several studies^{5,6} proposed the resin modification with adducts or oligomers, which are chemically incorporated in the resin as flexible segments. In this way, the mean entanglement molecular weight between the crosslinks is increased and yields an inherent toughness improvement.⁷ In the case of composites, the low adhesion between the matrix and the reinforcements hinders an effective stress transfer from the matrix toward the reinforcement phases and leads to a premature fracture on the weak interface. Adhesion promoters such as silane-coupling agents are normally used to improve the adhesion between UP and fillers and reinforcements.⁷

In this work, UP resin was modified with a poly(organosiloxane) to create flexible segments

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Table I Compositions of the Tested Samples

Sample	APTS (wt %)	APTS : GMA (molar ratio)	APTS : Siloxane (molar ratio)	APTS : H ₂ O (molar ratio)	Total Weight of Additives (wt %) ^a
UP1	0	—	—	—	—
UP2	2.5	1 : 1	1 : 1	1 : 3	7.23
UP3	2.5	1 : 1	1 : 3	1 : 3	12.25
UP4	2.5	1 : 2	1 : 3	1 : 6	14.47

^a In relation to the pure resin.

within the crosslinked structure and, thus, improve the toughness of the resin.⁸ Further, it was anticipated that the poly(organosiloxane) could also enhance the adhesion between the UP matrix and the glass fiber (GF) reinforcement. The acoustic emission (AE) technique was adopted to study this effect.

EXPERIMENTAL

Isophthalic resin (RESAPOL 10-169) in a 38 wt % styrene solution containing cobalt-II octoate (0.5 wt %) as accelerator (supplied by Resana SA, Brazil) was used in this work. Methyl ethyl ketone peroxide was used as initiator in 1 wt %.

The modifiers used were glycidyl methacrylate (GMA), 1,3-aminopropyl-triethoxysilane (APTS), both supplied by Aldrich, and 1,1,3,3-tetramethyl-1,3-diethoxydisiloxane as extender, supplied by Hüls. GMA was incorporated in the resin by radical copolymerization. The epoxy group of GMA is able to react with the amine group of the APTS as well as with the acid and hydroxyl groups of polyester resin. The incorporation of a chain extender allows network density by polycondensation. Water was added to the mixture containing the modifiers to guarantee the hydrolysis and condensation of the silane and siloxane during the cure. A more detailed description of the possible reaction is given in our previous work.⁸

Cure of the reinforced samples containing 50 wt % fibers took place in steel molds. After impregnating the fibers with the resin, the material was kept under pressure (1 MPa) for 1 min at 70°C. Then it was cooled to room temperature in the matched die mold and kept for 24 h. Postcuring occurred at 65°C for 24 h and then dried in vacuum at 75°C for 2 h. Samples measuring 80 × 20 × 3 mm were cut from molded sheets. These

rectangular specimens were notched 5 mm deep to act as a starter crack in the single-edge notched tensile loaded specimens (SEN-T). The compositions of the modified resin are listed in Table I.

As reinforcement, two types of glass fibers were added in the modified resin. A milled E-glass free from surface treatment (12- μ m average diameter and 70- μ m average nominal length) and a milled E-glass with silane-based coupling (12- μ m average diameter and 130- μ m average nominal length) were supplied by PPG Industries Ltd.

To avoid the segregation of the fibers, a thixotropy enhancer based in fumed silica (code number 210, 120-x; R & G GmbH Faserverbundwerkstoffe) and a wetting and dispersing additive (BYK[®], W980; Byk Chemie) were used. An air-release agent was also used to minimize the entrapped air (BYK[®]-A555; Byk Chemie).

The SEN-T specimens were subjected to tensile loading at the crosshead speed of 0.2 mm/min at room temperature in a Zwick 1445 machine. During the tests, the AE events were collected by a broad frequency piezoelectric transducer and stored in a Defektophone NEZ 220 analyzer (Central Research Institute for Physics, Budapest, Hungary). The AE parameters monitored were the number of the events, AE amplitudes, energy, and the ringdown counts. The fracture mode of the specimens was analyzed by scanning electronic microscopy (SEM), using Jeol 5400 equipment. Samples were gold-sputtered before SEM analysis.

RESULTS AND DISCUSSION

Effect of the Resin Composition on the Adhesion Between Resin and Filler

The modified and unmodified polyester resins were used to prepare composites containing non-

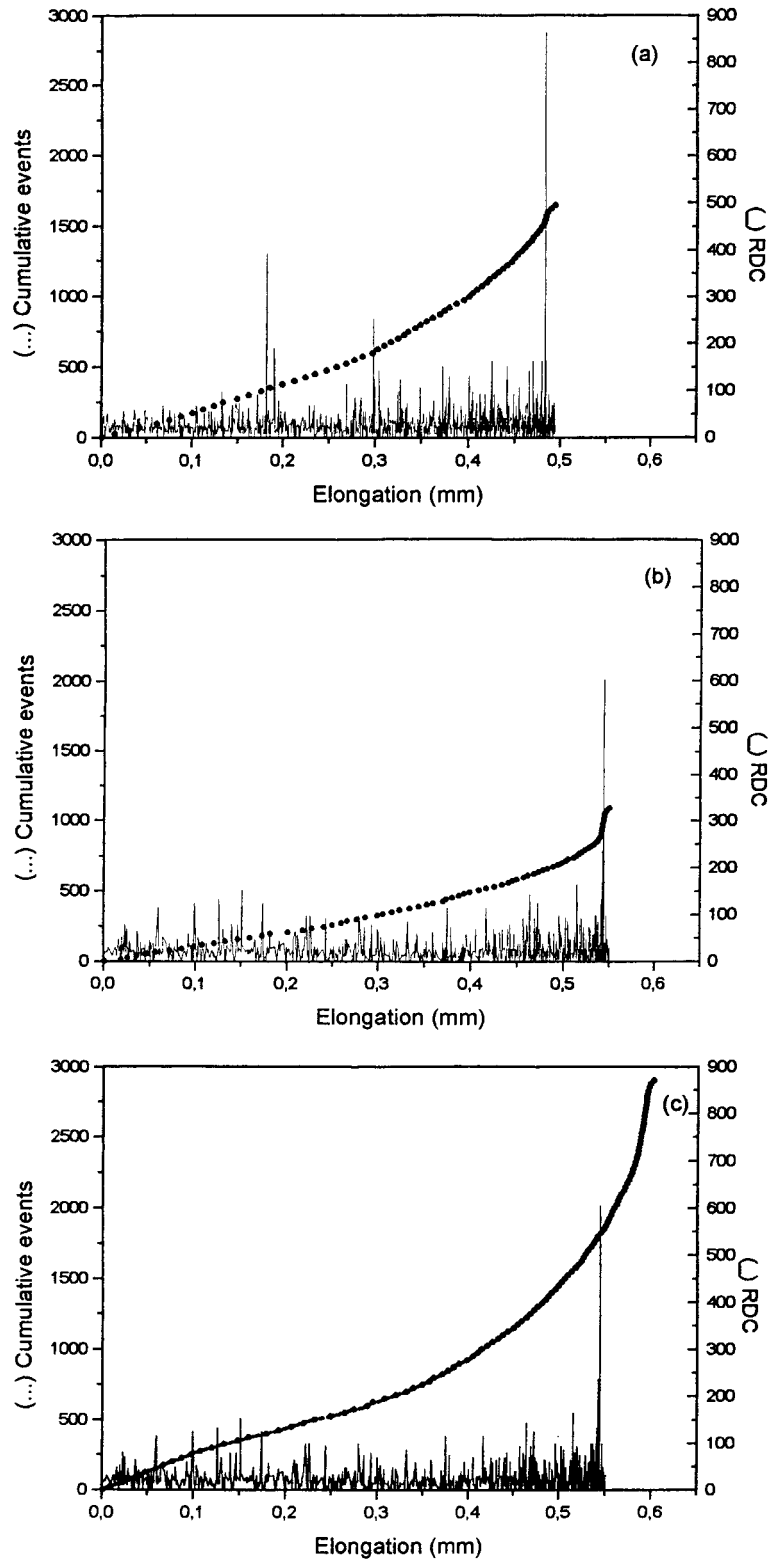
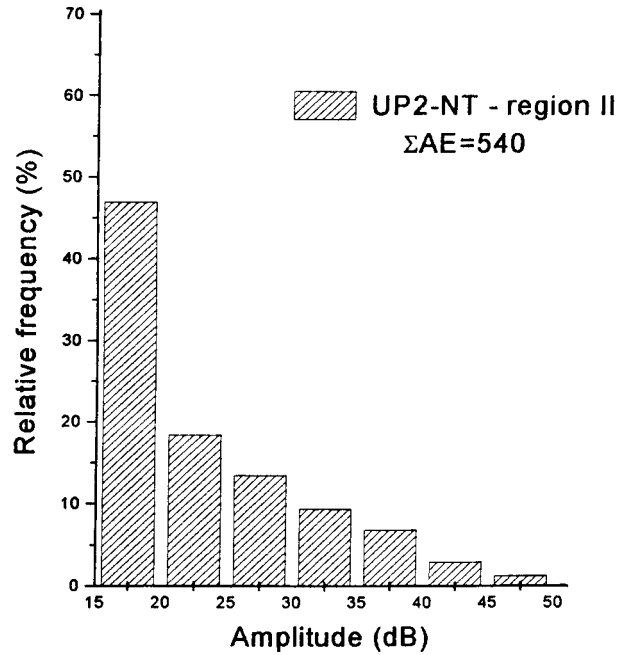
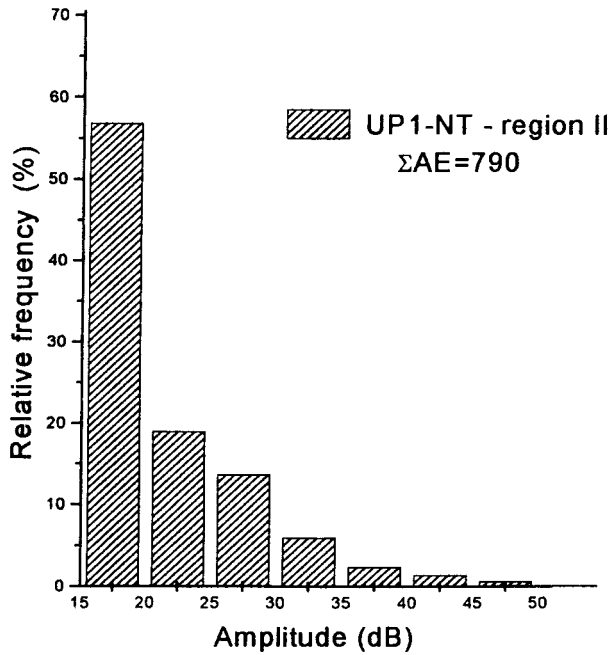
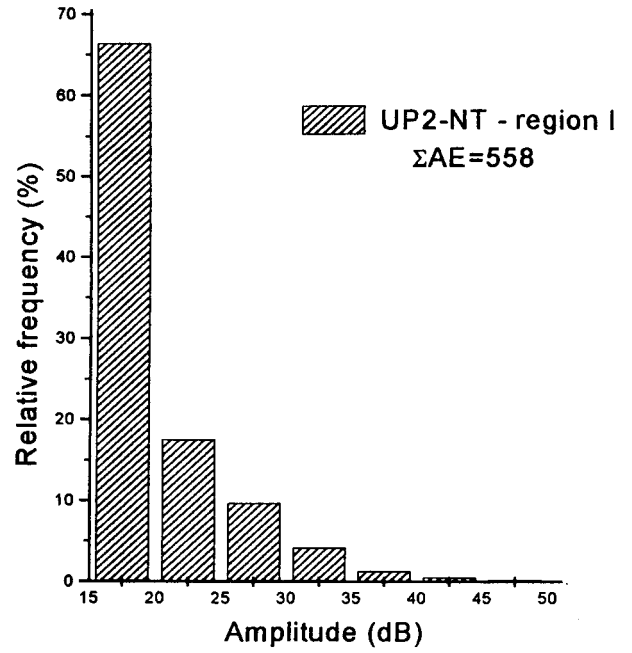
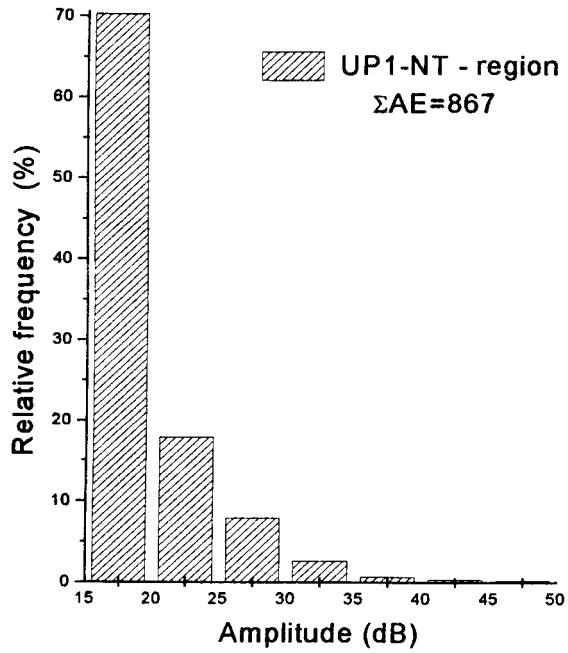


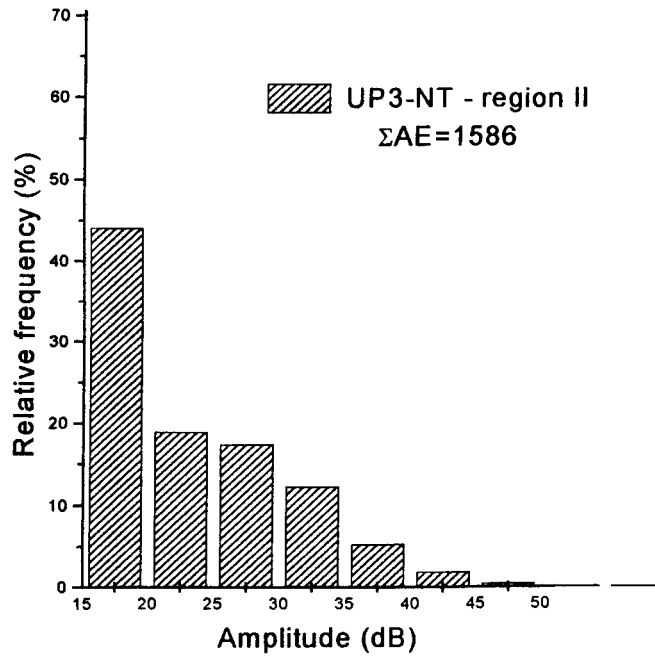
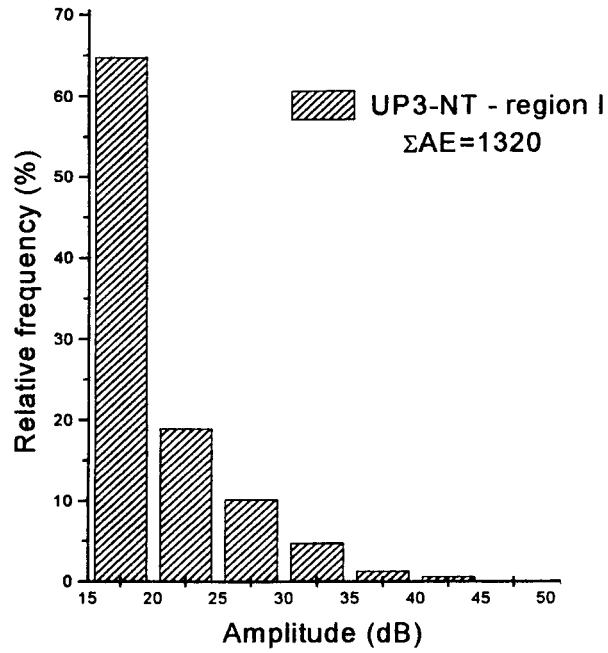
Figure 1 Cumulative events and ringdown counts as a function of the elongation of polyester resin filled with nontreated glass fiber: (a) UP1-NT; (b) UP2-NT; (c) UP3-NT.



(a)

(b)

Figure 2 Amplitude distribution for modified resin filled with nontreated glass fiber: (a) UP1; (b) UP2; (c) UP3.



(c)

Figure 2 (continued from previous page)

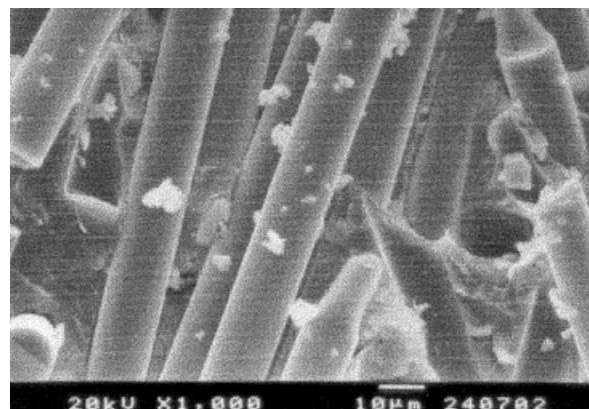
treated (NT) milled glass fiber that is in the compositions UP1, UP2, and UP3 (Table I).

Figure 1 shows the curves of the cumulative events and the ringdown counts (RDC) as a function of the elongation for the unmodified resin (UP1) and for the composites UP2 and UP3.

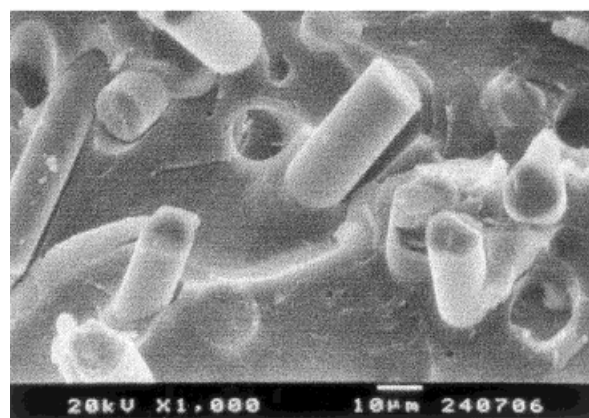
Comparing the curves in the Figure 1(b) and (c), related to the UP2 and UP3 composites, respectively, one can recognize that the chain extension or the flexibility effect of the poly(organosiloxane) as the ultimate elongation was shifted to higher values as compared to neat resin UP1 [Fig. 1(a)]. On the other hand, the RDC seems to be insensitive to the matrix formulation. Based on the cumulative sum of the events, the best fiber/matrix adhesion is achieved in the UP2 sample. This conclusion is drawn from the fact that the number of event changes adversely with the adhesive bond nature and/or intensity.⁹ It was reported that fiber/matrix adhesion is best reflected in chopped fiber-reinforced polymeric composites when the AE amplitude or energy is considered.¹⁰ Further, a partition of the AE loading (I, from zero up to 80% of the maximum load; II, from 80% up to the maximum load) may be very useful to distinguish between the relative amount and the several types of individual failure events (fiber debonding, pull-out, and fracture).

According to literature data,^{10,11} it is possible to assign given ranges of the AE amplitude or energy to individual failure types. Supposedly AE amplitudes in the range between 15 to 25 dB are due to the matrix cracking; 25 to 40 dB are caused by debonding of the fibers (interfacial failure), and from 40 to 60 dB, the likely pull-out of the fibers is behind. Above this value, fiber fracture could occur if the fiber length were longer than the critical one. Recall that in our case the length of the fibers was definitely below the critical value.

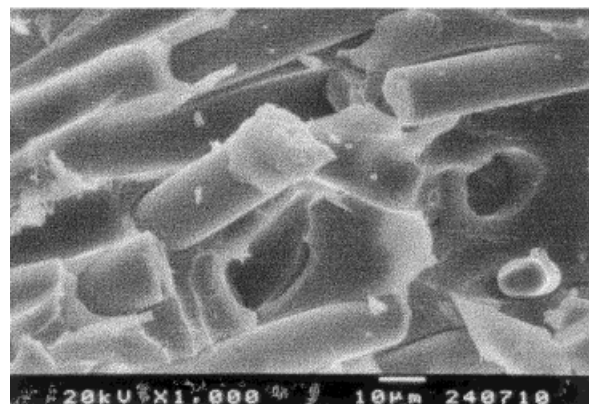
Comparing the AE amplitude distributions in the loading ranges I and II for the resin formulations UP1, UP2, and UP3 (Fig. 2), one can conclude that the resin modification has resulted in a better fiber/matrix adhesion because the cover curves of the AE amplitude histograms moved toward higher values. This was associated with some change in the shape or the cover curve. Figure 2(b) suggests that the UP2 composition has the highest adhesion to fibers. Does the failure mode reflect this scenario? The pull-out length of the fibers is highest for UP1-NT [Fig. 3(a)] and smallest for UP2-NT [Fig. 3(b)]. As the



(a)



(b)



(c)

Figure 3 Micrographs of samples reinforced with 50 wt % untreated milled fiber: (a) UP1; (b) UP2; (c) UP3.

pull-out length changes adversariously with the bond intensity, this may be a direct result of the above speculation with respect to the AE amplitude distribution. Note that by increasing the

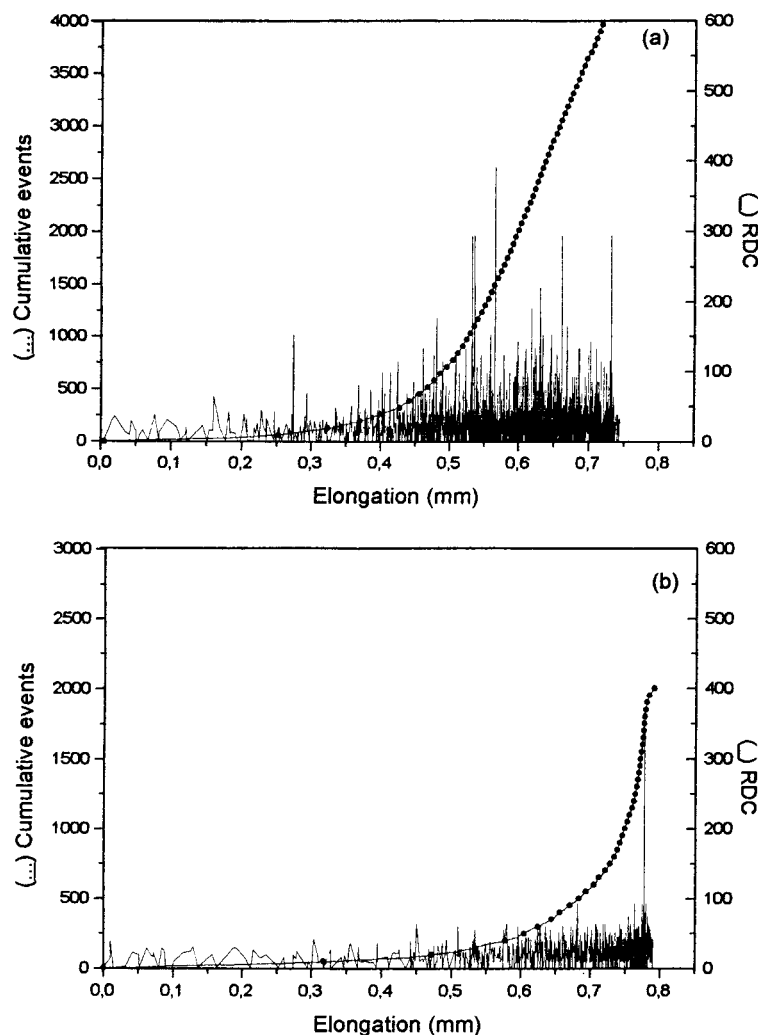


Figure 4 Cumulative events and ringdown counts as a function of the elongation for modified polyester resin filled with (a) nontreated glass fiber (UP4-NT) and (b) silane-treated glass fiber (UP4-ST).

amount of the poly(organosiloxane) in the UP, the matrix became very ductile, showing a matrix phase around the fibers [Fig. 3(c)].

Effects of Fibers Sizing on Adhesion

The effect of fibers sizing was studied for composite UP4, in which the NT and silane-treated (ST) fibers were incorporated. This composite presents a larger amount of GMA, which can favor the incorporation of larger amounts of APTS to the polyester matrix. For this reason, more water is added to the system to guarantee the hydrolysis (Table I).

In Figure 4, cumulative events and the ringdown count for samples filled with NT and ST

glass fiber are presented. The fact that the knick point of the cumulative events is shifted toward higher elongation suggests an improvement in the fiber/matrix adhesion when ST glass fiber was used. It is supposed that the smaller RDC and its small deviation in the case of UP4-ST reflect that the pull-out is less superimposed than to debonding events. This corroborates once more an improvement in the bonding between GF and UP resin. However, this finding is less clearly reflected in the AE amplitude and in the energy histograms of UP4-NT and ST, as shown in Figures 5 and 6, respectively.

The analysis of the fracture surface or the SENT specimens shows slight enhance in the

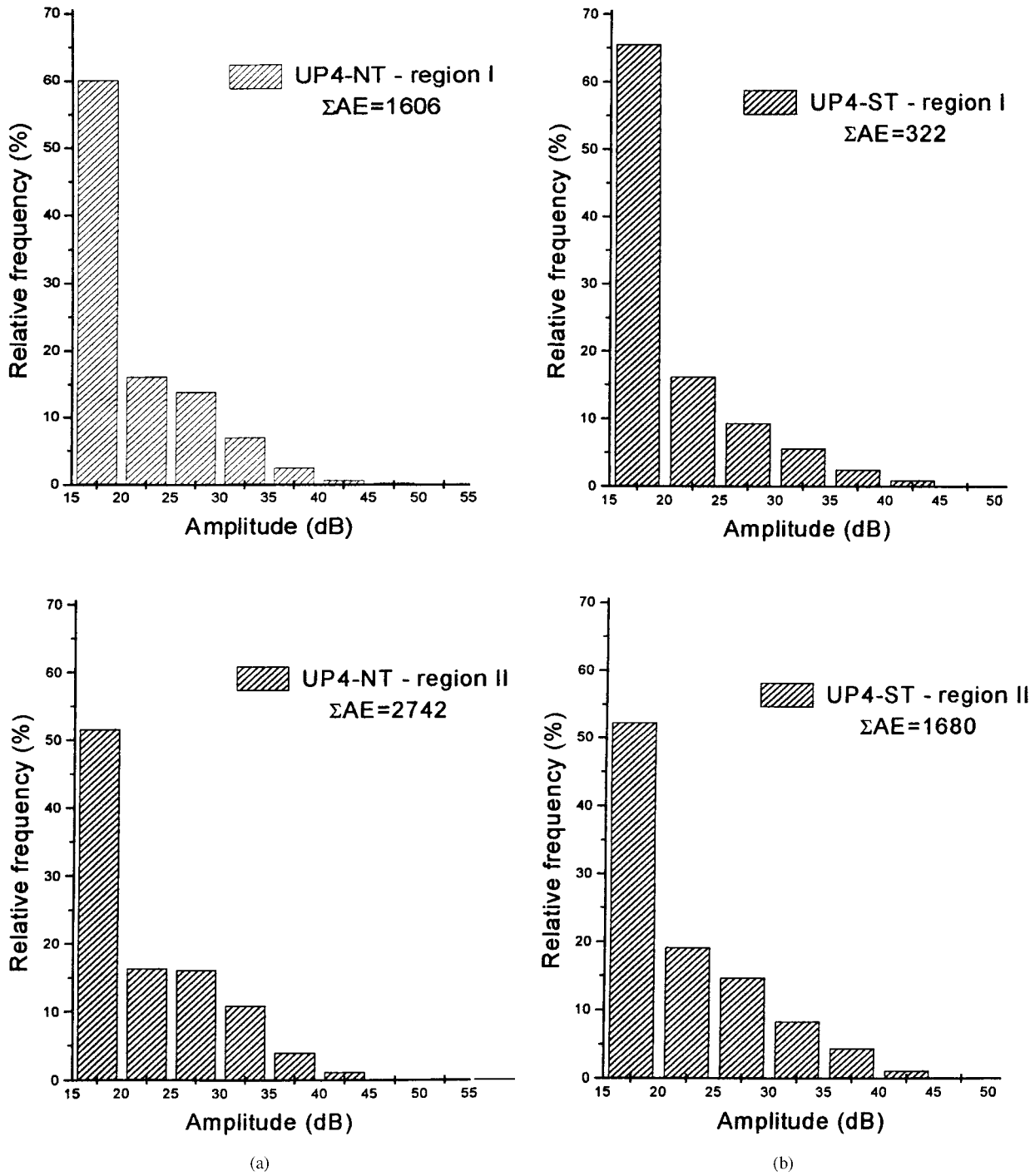


Figure 5 Amplitude distribution for modified resin filled with (a) nontreated glass fiber and (b) silane-treated glass fiber.

adhesion, when the sample is filled with treated glass fiber (Fig. 7). In this case, one can observe both debonding and pull-out events but the sample also presents some localized points where fiber adheres more to the matrix.

CONCLUSION

Based on the study performed on the failure mode of the UP resin modified with poly(organosiloxane) and filled with glass fiber by means of the

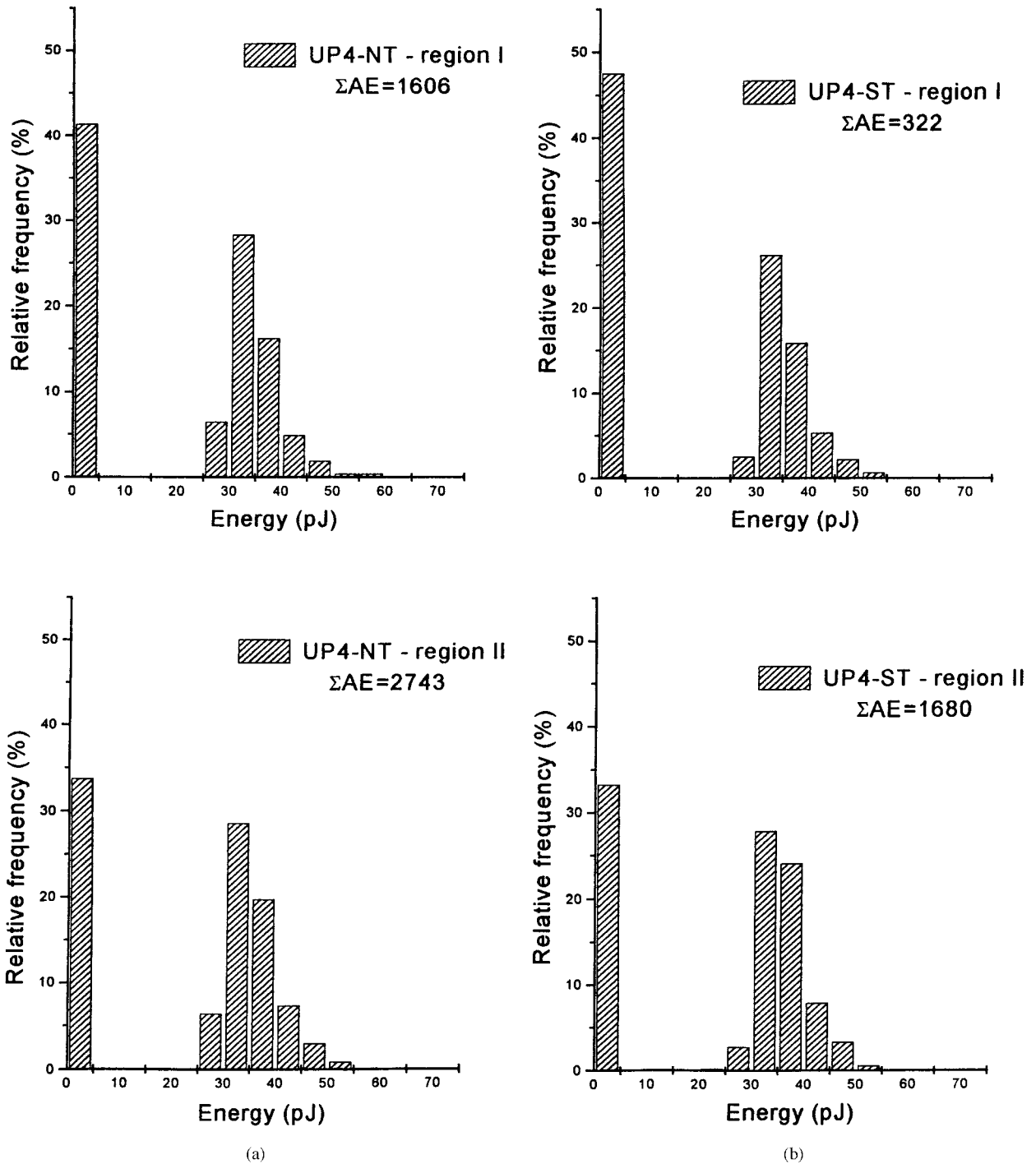
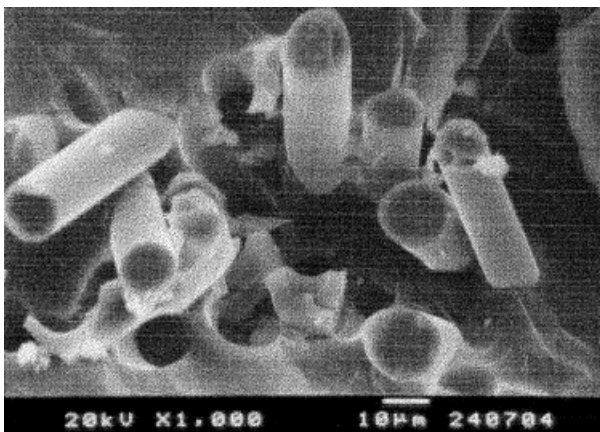


Figure 6 Energy distribution for modified resin filled with (a) nontreated glass fiber and (b) silane-treated glass fiber.

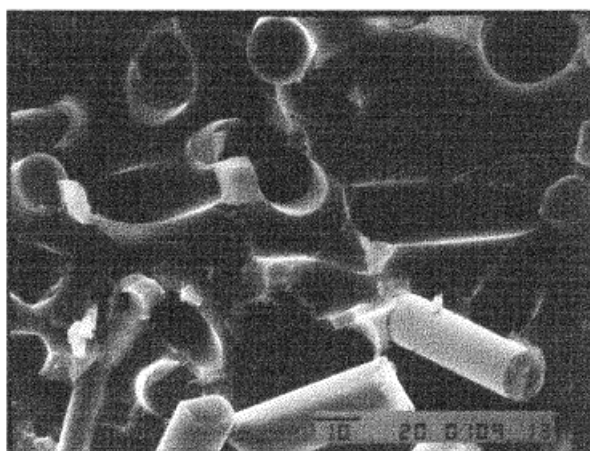
acoustic emission technique, the following conclusions can be drawn:

- The chemical modification of the resin enhances the fiber/matrix adhesion when NT

glass fibers are used. However, the adhesion is even better if a fiber with UP suitable sizing is adopted, which shows that in this system the pull-out events are less superimposed than in the debonding ones. By these



(a)



(b)

Figure 7 Micrographs of UP4 samples reinforced with 50 wt % glass fibers: (a) untreated glass fiber and (b) silane-treated glass fiber.

results we can conclude that the modification of the UP resin enhances the adhesion between matrix and fiber, but does not eliminate the use of sized glass fibers in UP composites;

- The AE proved to be a useful tool to study the changes in the failure mode, which was caused by the matrix modification.

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