

Evaluation of the Mechanical Properties of Sisal–Polyester Composites as a Function of the Polyester Matrix Formulation

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ABSTRACT: In this work a comparative study on the impact and tensile properties of polyester/sisal fiber reinforced composites was undertaken. The polyester matrix was used bare and modified with: (1) a silane coupling agent; (2) a flame retardant system; and (3) a blend of the silane agent and the flame retardant system. The experimental results show that the flame retardant acts as a particulate reinforcement to the polyester matrix and the silane coupling agent acts as a plasticizer. The simultaneous addition of these two compounds to the polyester resin tended to decrease the performance of the composites. The results obtained show that strength or toughness could be tailored,

and although none of the composites manufactured with the modified polyester matrices showed a significant improvement on the fiber–matrix interface strength, a better compromise between impact and tensile properties was obtained with the silane modified matrix. The critical fiber volume fraction was also evaluated and shown to be less than 10% for the sisal–polyester composite investigated here. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1209–1217, 2004

Key words: sisal fibers; mechanical properties; modified polyester resins; silane treatment

INTRODUCTION

Natural fiber reinforced polymer composites are being largely studied worldwide. Lignocellulosic fibers are biodegradable and renewable resources with a strong ecological appeal for their use. New technologies for the production of natural fiber reinforced composites, or the adaptation of the existing ones, are of great interest for many tropical or subtropical countries, like Brazil, where there exists a great biodiversity and large areas dedicated to plantations.

Nowadays, natural fibers like jute and sisal, as well as other lignocellulosic fibers not so extensively cultivated, which are used for baskets, carpets, and decorative artifacts, are gaining new perspectives of employment in composite materials.^{1,2} Besides their already mentioned biodegradable aspect, the advantages of natural fibers over their synthetic counterparts include their lower cost, toxicity, and abrasiveness. This last aspect is especially relevant during the manufacture of natural fiber composites as it causes less wear and deterioration of machine parts.

Sisal fiber (*Agave sisalana* Perrine) is largely produced in Brazil. Around 90% of the Brazilian production is exported as fibers, tows, and manufactured products, and 60% of this amount is directed to the baler-twine industry. By-products of the sisal fiber industry are transformed in waxes, alcohol, plastics, and fertilizers. Therefore, in many aspects, the development of new products and materials from sisal fibers are more attractive than from many other natural fibers in this country.

One of the main problems associated with the use of sisal and other lignocellulosic fibers as reinforcement in polymers is the very weak interface that is commonly developed between these fibers and most of the polymers used as matrices.^{3–5} Better interfaces can, however, be obtained by modifying the fibers by physical or chemical treatments.^{4–8} Another way to increase the fiber to matrix interaction and/or compatibility is to modify the matrix. The introduction of reactive sites with higher chemical affinity toward the fibers, an increase in matrix toughness, or even a reduction in resin viscosity to promote fiber impregnation or wetting are among the ways employed to improve the fiber–matrix interface.^{9,10}

In this work the mechanical properties of polyester–sisal reinforced composites were determined as a function of matrix modification. Different compounds

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(silane coupling agent, flame retardant system, and a combination of the two) were added to the polyester matrix to promote its compatibility with sisal fibers and the effect of each modification on the mechanical properties of the unreinforced polyester and sisal composites was evaluated.

EXPERIMENTAL

An orthophthalic insaturated polyester resin with an additional 10% v/v of styrene monomer, added as a solvent, was cured with 0.3% v/v methylethyl ketone as catalyst and was used as the reference matrix.

Sisal fiber was used as the reinforcement. The fiber mat, with the mold's cavity dimensions, was weighted to obtain composites with 10% v/v fiber. This low-volume fraction was used to compare the results obtained in this work with those reported previously.¹¹

The flame retardant system employed consisted of a mixture of decabromo diphenyl oxide and antimony trioxide with a 3:1 (Br:Sb) molar ratio. This mixture was stirred with the polyester resin to obtain a homogeneous blend. The weight fraction of flame retardant was kept constant at 7.5%. This value was experimentally determined as a concentration capable of providing a good compromise of properties for the system under investigation.¹²

In this work, the 3-methacryloxypropyl-trimethoxysilane, which is normally used as a coupling agent, was blended with the polyester resin. The silane (1% v/v) was added to the polyester and the system was stirred at 50 rpm for 5 min before the catalyst was added. The system was stirred for another 2 min and poured over the fibers.

The composites were manufactured by compression molding. The preweighted mats were placed inside the cavity of the mold, and the resin formulation was poured over the fiber mat. Proper impregnation was achieved with the aid of a metal roll-on. The assembly was then closed with 8 ton force. Curing took place at room temperature. Demolding took place after 3 h and the composite was allowed to rest for 28 days before mechanical testing. Composites having polyester, silane modified polyester, flame retardant modified polyester, and a combination of silane and flame retardant modified polyester were used as matrices. Table I shows the complete set of matrix formulations and composites investigated.

Tensile tests were performed according to ASTM D 3039 standards on a Lloyd LR-10 kN apparatus and with a test speed of 1 mm/min. The specimens were pretensioned with a force of 1 kgf to guarantee a perfect alignment of the specimens between the grips of the test machine.

Izod impact testing was conducted at room temperature on a Ceast Resil 5.5 J equipment operating with 2J pendulum, according with ASTM D 256 standard,

TABLE I
Materials Analyzed

Material	Specification
P	Bare polyester matrix
M	Blended polyester-silane matrix
R	Blended polyester-flame retardant matrix
RM	Blended polyester-silane and flame retardant matrix
SP	Bare polyester-sisal fiber composite
SM	Polyester / silane matrix-sisal fiber composite
SR	Polyester / flame retardant matrix-sisal fiber composite
SRM	Polyester / silane / flame retardant matrix-sisal fiber composite

on unnotched specimens. An average result of 10 specimens was reported for both mechanical tests.

The effect of the matrix modification on the thermal decomposition of the composites was investigated by thermogravimetric analysis. A Mettler 851 thermobalance was calibrated over all heating rates, using a gas purge, and samples of about 10 mg were used. The samples were then heated in the temperature range of 30–1000°C, with a heating rate of 10°C min⁻¹, under nitrogen flow of 120 cm³ min⁻¹.

The fracture surface of the materials was analyzed by scanning electron microscopy on a Zeiss DSM 960 microscope, operating with secondary or backscattered electrons imaging with a beam voltage of 15–20 kV. The surface of the specimens was previously sputtered with a conductive layer of gold-palladium.

RESULTS AND DISCUSSION

Unreinforced resin blends

The effect of matrix modification by the silane coupling agent, flame retardant system, and the combination of the two on the tensile properties of the polyester resin under investigation is shown in Figure 1. The results indicate that scarcely any variation on Young's modulus was observed with the flame retardant system (R) addition (Fig. 1a). A slight modulus decrease with respect to the matrix was observed with the combined addition of silane coupling agent and the flame retardant system (RM), whereas a very compliant system was obtained with the silane modified matrix (M). The tensile strength (Fig. 1b) and the maximum strain (Fig. 1c) were also shown to vary with matrix modification. A better overall performance was depicted by the flame retardant system modified resin (R) because its tensile strength was higher and its deformation comparable to that of the unmodified matrix.

Flame retardants usually behave as inert fillers, i.e., their addition to polymer matrices, tend slight increase the modulus and decrease the tensile strength

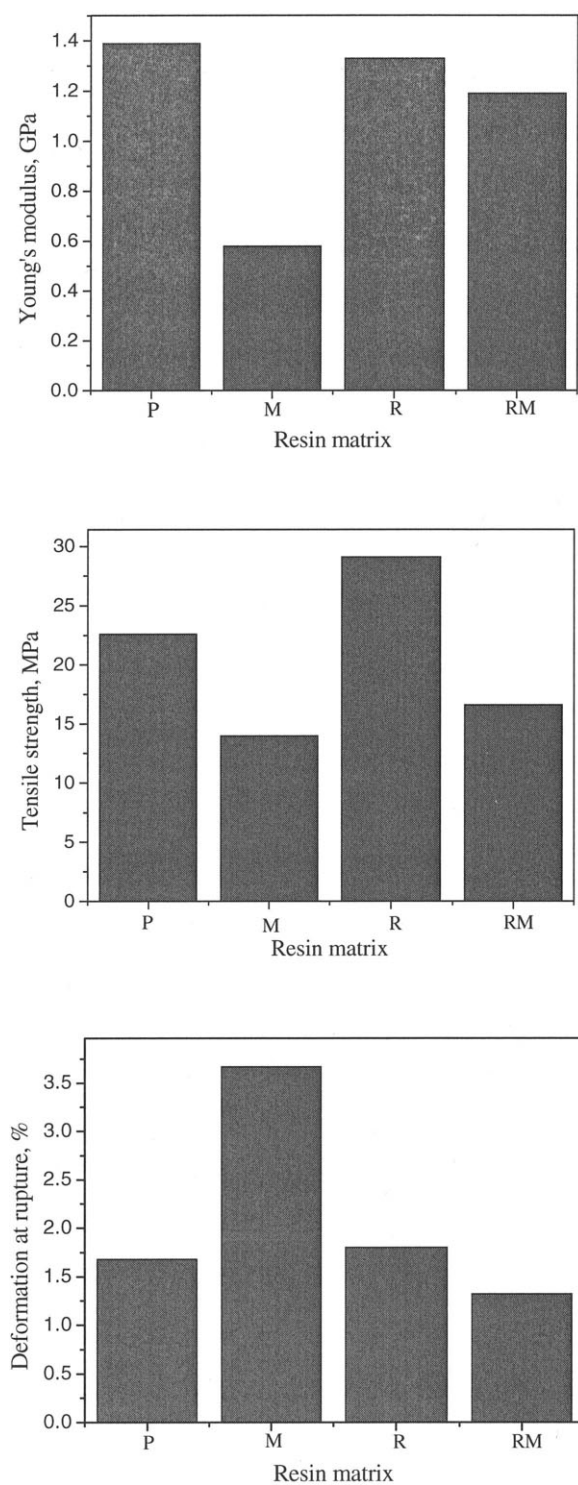


Figure 1 Effect of matrix modification on the mechanical properties of the polyester resin. (a) Young's modulus; (b) tensile strength; (c) maximum strain. P, unmodified polyester; R, flame retardant system; RM, silane coupling agent + flame retardant; M, silane.

and elongation at break. The results illustrated in Figure 1b show the flame retardant system used to act as a particulate reinforcement for the polyester matrix

here analyzed. In fact, SEM analysis showed that a very uniform distribution of the particles of the flame retardant was achieved (Figure 2).

Figures 1b and c showed that a systematic decrease of the tensile properties was observed for the matrix modified by the simultaneous addition of silane and flame retardant system, which is taken as an indication that the silane coupling agent renders the matrix more compliant loosening its interaction with the flame retardant system. The silane modified matrix showed the lowest tensile strength (Fig. 1b) and the highest deformation capacity (Fig. 1c) of all systems investigated. This behavior can be attributed to plasticization of the resin by silane addition and is also held responsible for the lower values obtained for the tensile modulus (Fig. 1a). Similar behavior was reported when an excess of silane was used on an epoxy-hollow glass microspheres composite.¹³ In fact, the fracture surface of the silane modified polyester employed in this work shows clear topographic aspects of an enhanced deformation capacity. Figure 3 shows that an incipient banding of crazes was developed at the fracture surface. Crazing is a main toughening mechanism of thermoplastic polymers,¹⁴ but its occurrence on crosslinked polymers has experimental evidences,¹⁵⁻¹⁷ and its presence is attributed to network heterogeneity.¹⁷

Table II shows the results obtained for Izod impact tests. The experimental values agree well with the data obtained on the tensile tests. The flame retardant system modified polyester showed the lowest impact strength among the modified matrices investigated. This result was to be expected since this matrix exhib-

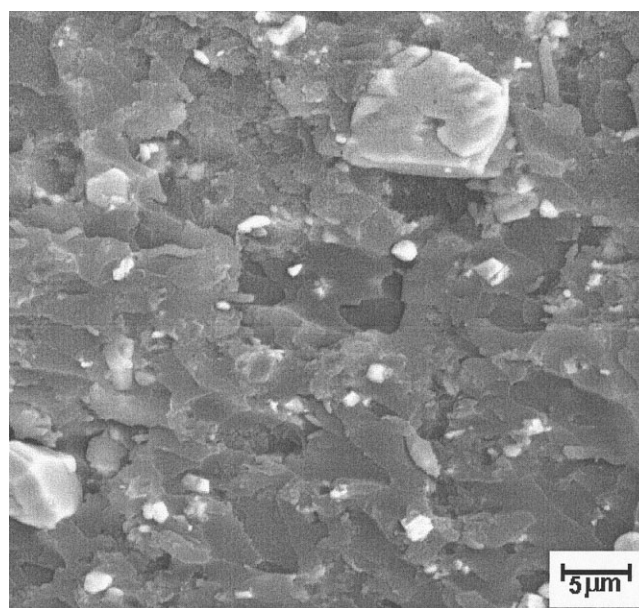
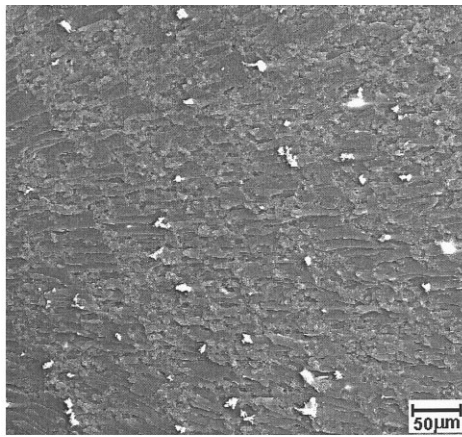
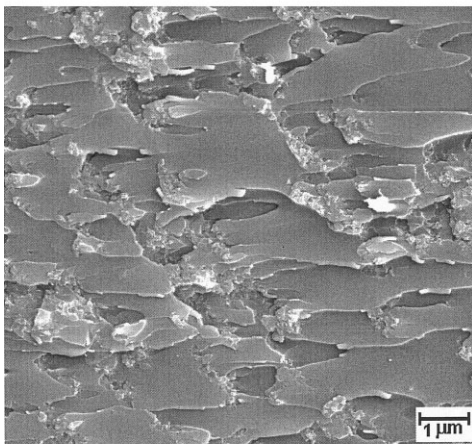


Figure 2 SEM analysis depicting the uniform distribution of the flame retardant compound on the fracture surface of the R modified polyester matrix.



(a)



(b)

Figure 3 Fracture surface of the silane modified polyester matrix showing: (a) incipient banding of crazes and (b) detail of the craze-like banding.

ited the highest tensile strength without any significant reduction on elongation at break. The same arguments can be used to explain the behavior of the combined silane/flame retardant system modified matrix, which showed a decrease on impact strength, which would be expected from the tensile data obtained. This shows that, in fact, the mixture of these two compounds is not synergistic. Instead, it is deleterious to the mechanical performance of the unrein-

TABLE II
Experimental Results of the Impact Tests: Unreinforced Matrix Formulations

Material	Impact energy (J/m)
P	87 ± 36
M	102 ± 35
R	48 ± 15
RM	65 ± 18

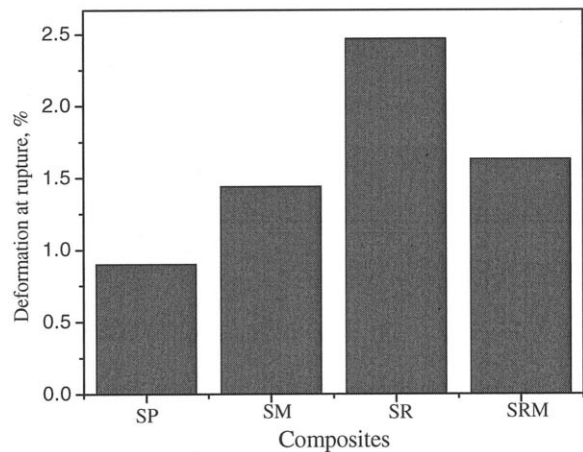
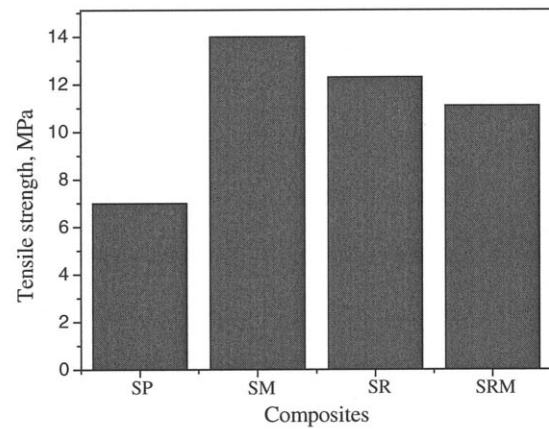
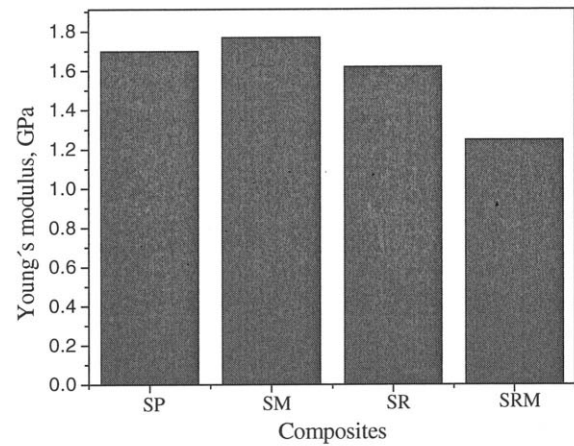
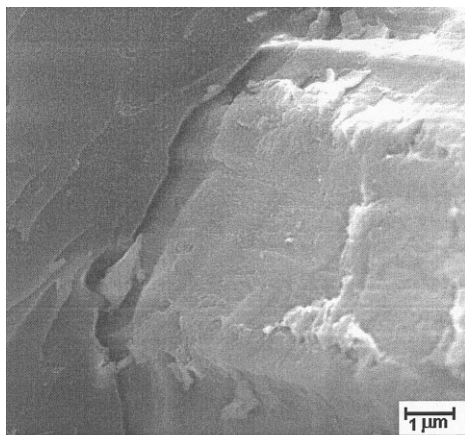
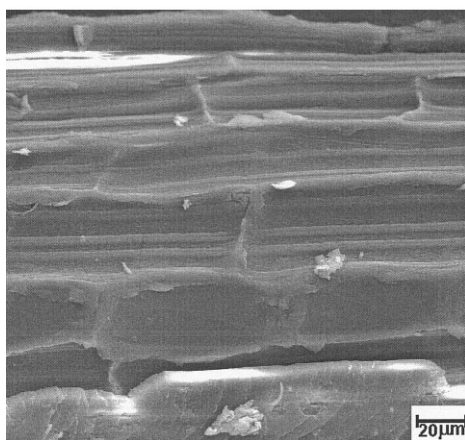


Figure 4 Variation of the tensile behavior of the sisal reinforced composites, as a function of the matrix modification. (a) Young's modulus; (b) tensile strength; (c) maximum strain. Labels are as given in the legend to Figure 1.

forced polyester matrix. On the other hand, the significant increase in toughness showed by the silane modified polyester is associated with a plasticizing effect caused by the silane compound.



(a)



(b)

Figure 5 Aspects of the fiber/matrix interface. (a) Broken interface, characteristic of low strength interfaces; (b) Pulled-out fiber surface, without signs of deformation.

Composites

The tensile behavior of the sisal reinforced composites investigated is illustrated in Figure 4. The results show sisal addition to increase (~20%) Young's modulus of the unmodified polyester (SP) and of the flame retardant system (SR) modified composites in comparison with their respective matrices. This behavior was expected, since sisal fibers have higher Young's modulus than both the unmodified and the flame retardant modified matrices. The uniform increase in modulus values for these two composites is in accordance with the fact that the volume fraction of fibers in both composites was equivalent and that the modulus of both resins is nearly the same (Fig. 1a). Fiber addition to the silane modified matrix (SM) caused a marked increase on its tensile modulus. This behavior is thought to be due to an enhancement on fiber/matrix adhesion, caused by the incorporation of the silane coupling agent. Although the general procedure ado-

pted with lignocellulosic fiber reinforced polymer composites is to chemically modify the fiber rather than the matrix, in principle this procedure can be employed. Indeed, a similar behavior, i.e., an increase in fiber/matrix compatibility, was observed for polyester/jute composites whose matrix was chemically modified with urethane and isocyanate prepolymers.¹⁸ There was no increase in tensile modulus with fiber incorporation for the combined silane + flame retardant modified matrix (SRM). This behavior is thought to indicate that, for this matrix formulation, no effective stress transfer is occurring from the matrix to the fibers and is associated with the data obtained for the unreinforced resin formulation where the mixture of these two compounds was shown to decrease the mechanical properties of the blended polyester matrix.

Figure 4b shows that, except for the silane modified matrix composite, sisal fiber incorporation caused a reduction in tensile strength. A 69% decrease on tensile strength and a 46% decrease on elongation at break were observed with sisal addition for the polyester-sisal composites. A weak fiber-matrix interface was expected for this composite, since no fiber treatment or matrix modification was performed.³ The weak interface and the low fiber volume fraction employed are held responsible for the low mechanical properties and premature failure of that composite. Figure 5 shows that, indeed, no strong fiber-matrix interface interaction was observed. Figure 5 evinces the usual aspect of open interfaces (Fig. 5a) and undeformed pulled out fibers (Fig. 5b), common to the fracture surface of composites with low interfacial strength.^{3,19}

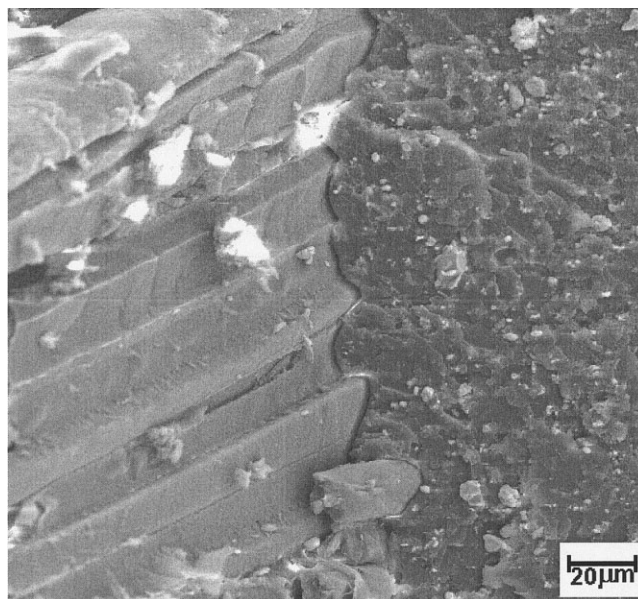
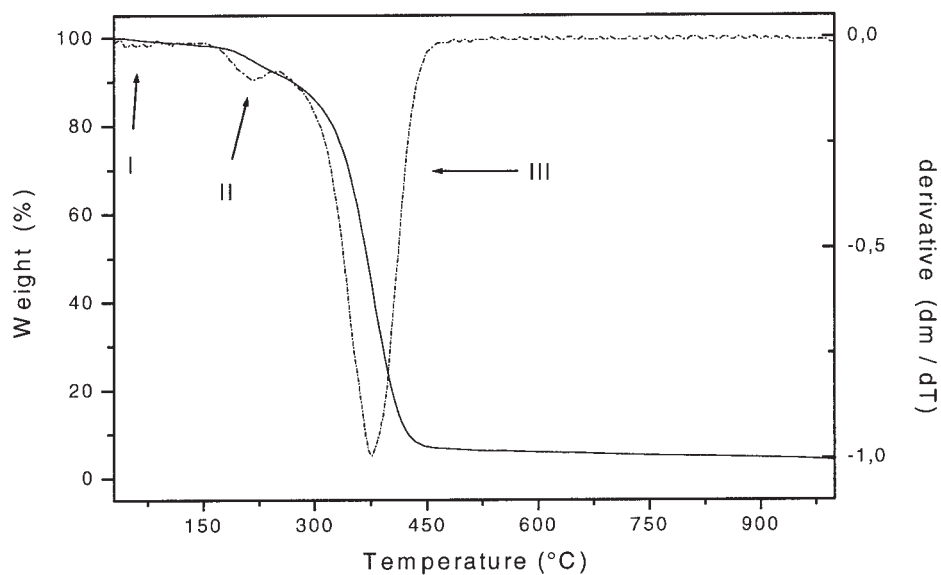
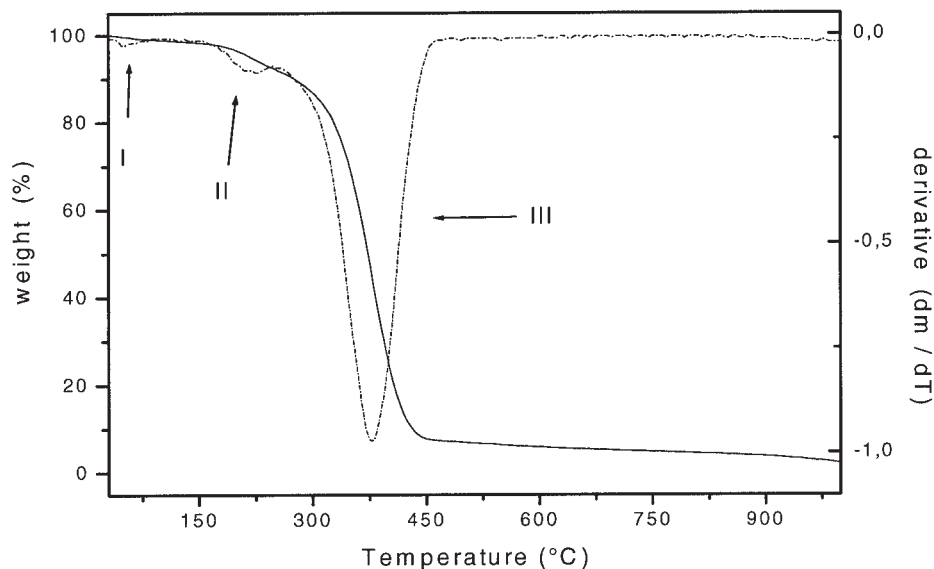


Figure 6 Common aspects of the fiber/matrix interface observed for all modified matrix composites: open interface and undeformed fibers.



(a)

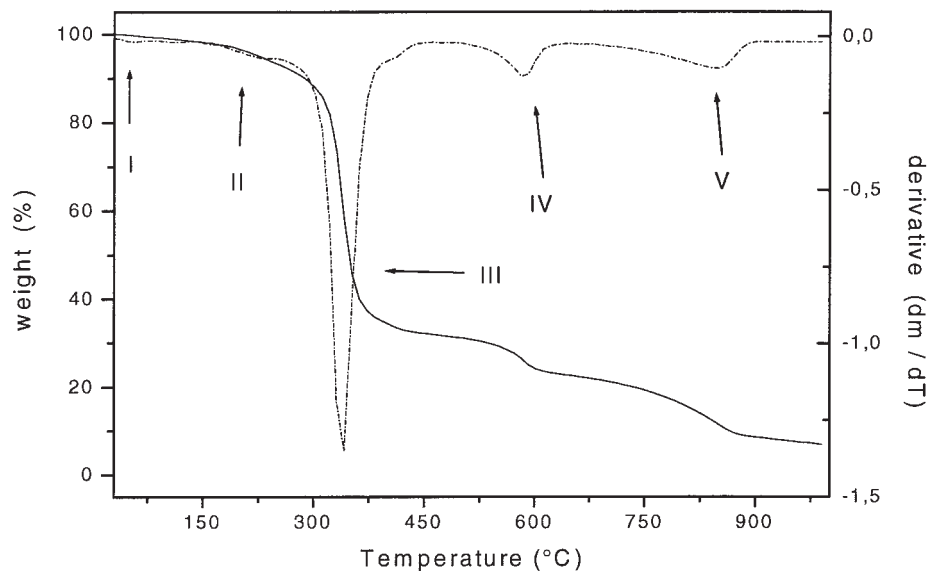


(b)

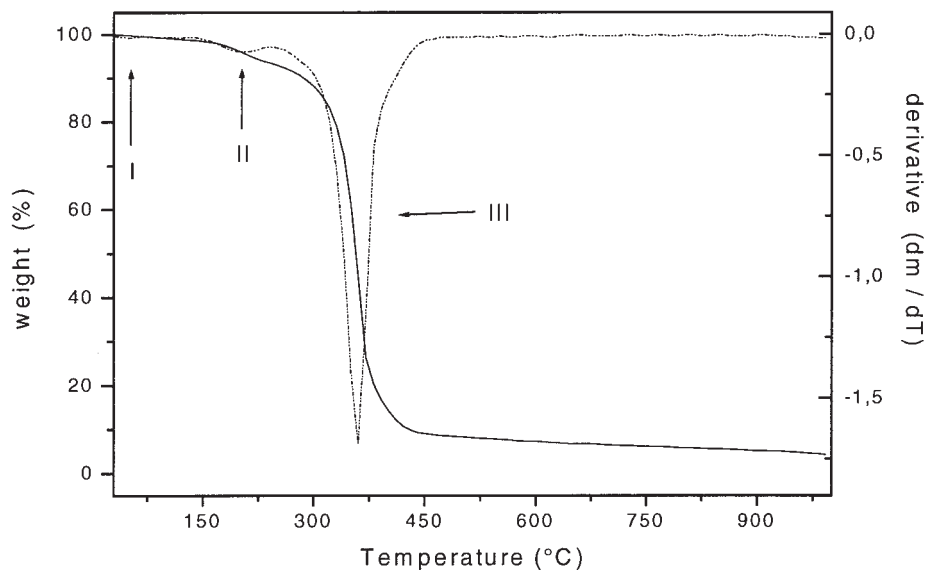
Figure 7 Thermal analysis of the sisal fiber reinforced composites. (a) SP; (b) SM; (c) SR; (d) SRM. (S stands for sisal fiber; P, unmodified polyester; R, flame retardant system; RM, silane coupling agent + flame retardant; M, silane).

The results obtained for the composites manufactured with the modified matrices show that, if weak interfaces are obtained, tensile strength is not the only relevant property to be looked for. The data show that matrix toughness is an important property to be considered as it can delay crack propagation. Therefore,

the composite manufactured with the silane modified matrix, which displayed higher deformation at break (Fig. 1c), was the sole composite in which a significant reduction on tensile strength was not observed with sisal fiber incorporation ($\Delta\sigma = -3.5\%$). It is thought that the silane coupling agent promotes interfacial



(c)



(d)

Figure 7. (Continued from the previous page)

adhesion for this system as the loss in tensile strength of the SRM composite ($\Delta\sigma = -33.7\%$), was also lower than that of the silane free SR composite ($\Delta\sigma = -58.0\%$). SEM analysis of the fracture surfaces of these two composites, however, did not show any noticeable fiber-matrix interface differences for the silane modified and unmodified composites. Open interfaces and undeformed fibers are the common aspects observed for all modified matrix composites, as illustrated in Figure 6.

To verify the interaction between the silane and the flame retardant system, as well as to exploit the possibility that phase separation, which is held responsible for the lower mechanical performance of this system, is occurring, the composites were analyzed by thermogravimetry. Figure 7 shows the results obtained. The SP composite (Fig. 7a) shows two low-temperature regions of weight loss that can be attributed to humidity (I) and volatiles from the matrix (II). The main degradation of this composite occurs be-

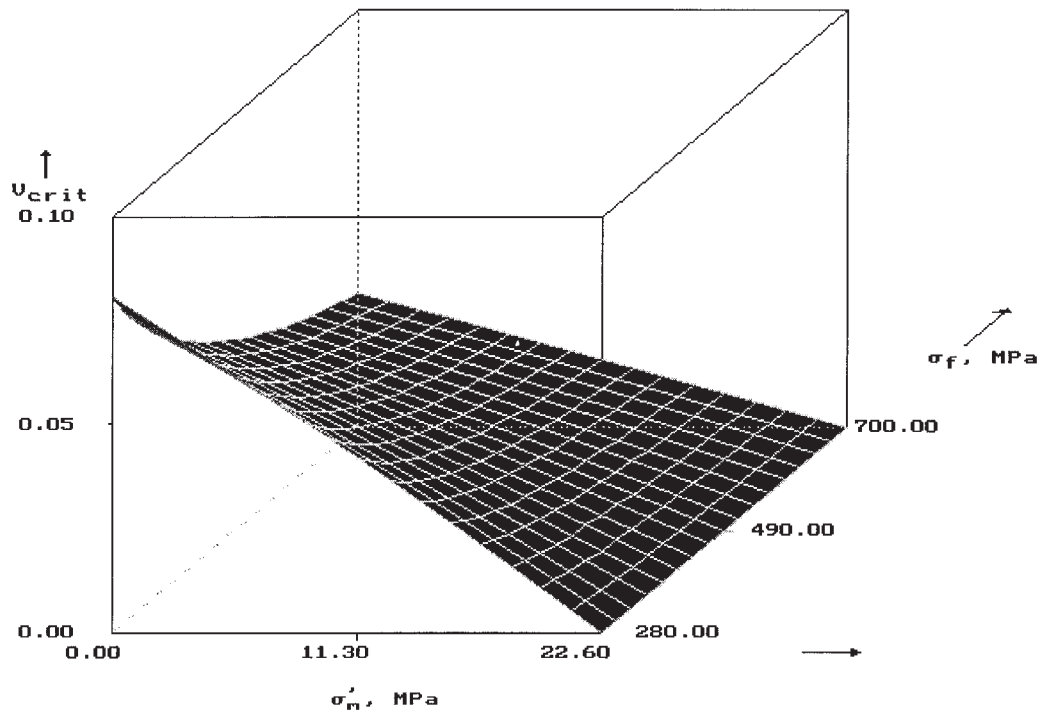


Figure 8 Variation of the critical volume fraction of fibers, V_{crit} , as a function of σ'_m and σ_f .

tween 252 and 494°C (III), where as much as 85% of the material degrades. The char residue at 900°C was 4.7%. Silane addition to the matrix did not bring any relevant modification on the thermal degradation behavior of the SM composites, as shown in Figure 7b. The same three degradation steps are observed, with virtually the same behavior of the main degradation event with respect to the onset temperature (258°C), range of degradation (252–498°C), weight loss (85.1%), and char residue (3.7%). This result indicates the silane coupling agent to be homogeneously distributed on the polyester matrix and also indicates that no phase separation occurred.

Figure 7c shows that the flame retardant system addition to the matrix produced strong modifications on the thermal behavior of SR composites. Two high-temperature events (IV; V) follow the two original low-temperature weight losses and the main degradation peak of the unmodified polyester–sisal composite (see Fig. 7a). These peaks are associated with the decomposition of the flame retardant system,¹² and their presence shows the flame retardant to keep its own decomposition characteristics after it has been mixed with the polyester matrix. Figure 7d shows the thermal behavior of the SRM composite, which is almost identical to those observed for the SP and SM composites and is strikingly different from that observed for the SR composites. The sole difference observed for the degradation profile of the SRM composite was the final degradation temperature, which was increased to 513°C. The thermal behavior of this composite seems

to point out to a strong silane–flame retardant system interaction, which is deleterious to both the thermal degradation behavior and the reinforcing effect observed with the flame retardant modified matrix. Further tests are needed to fully comprehend the interactions between these two compounds (flame retardant–silane agent).

When low fiber volume fractions are used, the question of whether this volume fraction is above or below a critical threshold that really enables the increase of the tensile properties of the composites always arises. In other words, one must determine whether the lack of reinforcement observed (Fig. 4a) is a consequence of the presence of weak interfaces or if the low fiber volume fraction employed is below its critical value. To answer this question the critical volume fraction was estimated using the following well-known equation, from the micromechanical approach of composites:²⁰

$$V_{crit} = \frac{\sigma_m - \sigma'_m}{\sigma_f - \sigma'_m} \quad (1)$$

where σ_m is the tensile strength of the matrix, σ'_m is the stress at the matrix at the failure strain of the fiber, and σ_f is the tensile strength of the reinforcing fiber. Figure 8 shows a plot of the variation of V_{crit} with σ'_m and σ_f for the SP composite. One can see that V_{crit} falls below 10%, even with the large bounds used for both σ'_m and σ_f . Therefore, the lack of reinforcement observed, re-

TABLE III
Experimental Results of the Impact Tests: Composites

Material	Impact energy (J/m)	Δ^a (%)
SP	328 ± 65	277
SM	313 ± 83	207
SR	214 ± 45	345
SRM	237 ± 28	265

^a Variation of the impact strength in relationship to the unreinforced resins; see Table II.

ported in Table II, when the sisal fiber were incorporated to the matrices probably results from weak interfaces.

The bounds used to model Eq. (1) were $0 < \sigma'_m < 22.6$ MPa and $280 \leq \sigma_f \leq 700$ MPa. Specifically for sisal fibers, large bound values for tensile properties must be used, as there is a great variation on the values reported in the literature.^{4-6,21-23} The proper value for the tensile stress supported by the matrix at the fiber failure strain should, in fact, fall above ≈ 15 MPa, but even if the analysis of σ'_m is restricted to $15 < \sigma'_m < 24$ MPa, the value of V_{crit} would remain below 10%, as shown in Figure 8.

The presence of a weak interface on all composites can also be inferred by the impact testing results. As shown in Table III, a marked increase of the impact strength was obtained even with the low fiber volume fraction employed. This behavior can be attributed to crack branching and deflection at low strength interfaces. This mechanism is, in fact, a powerful way to absorb energy.²⁴ The large scatter in the data presented in Table III, which is rather common on impact testing, does not allow one to unequivocally state whether silane addition to the polyester matrix really promoted an increase on fiber-matrix interfacial strength. However, the lower increases observed for the impact strength of the composites with silane modified matrices (viz. SM and SRM) are thought to result from better, if small, fiber-matrix interfacial strength.

CONCLUSION

Mechanical, SEM, and TG analysis performed on the several systems investigated indicate that: (a) the flame retardant system (decabrom diphenil oxide/antimony trioxide) acted as a particulate reinforcing filler for the unsaturated polyester matrix; (b) silane coupling agent addition increased matrix and composite toughness, i.e., the silane agent acted as a plasticizer to the matrix; (c) craze formation on the fracture surface of the silane modified polyester matrix indicates that the structure of the matrix was strongly modified and that an effective toughening mechanism was introduced; (d) none of the resin mod-

ifications employed was able to significantly increase sisal-polyester interfacial adhesion. Nevertheless, the silane modified matrix showed the best overall mechanical performance, i.e., the best compromise among Young's modulus, tensile strength, deformation at break and impact strength; (e) an estimate of the critical volume fraction, V_{crit} , for effective fiber reinforcement, indicates that for the polyester-sisal composites under study, $V_{crit} < 10\%$; (f) thermogravimetric analysis showed that the simultaneous addition of silane and flame retardant system to the matrix was deleterious to the thermal stability of the composites (SR and SRM) even so both of these composites achieved the same (V0) classification on flammability tests (UL-94V).¹²

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