Composites from Sawdust and Unsaturated Polyester

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SYNOPSIS

Wood is an inexpensive filler that reduces the overall cost of polymer composites, with loss in some properties (e.g., ultimate strength, elongation, and water sorption often suffer with the addition of fillers) and a gain in others (e.g., Young modulus increment, reduced weight with respect to inorganic fillers, reduced wear of the processing equipment). Sawdust of *Eucaliptus saligna* or calcium carbonate have been used as reinforcing fillers of an unsaturated polyester matrix. The ultimate strength, elongation, and modulus are presented as a function of the filler concentration and surface treatment. The dynamic mechanical properties were used to determine the influence of the moisture content on the performance of the final material. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Fillers are added to polymer matrices in order to improve thermal and mechanical properties. There are, however, some adverse effects, for example, toughness and ultimate elongation of polymers often suffer with the addition of fillers. A practical interest in this subject has arisen mainly because of economies originated from the addition of mineral (inorganic) fillers to known polymers, increasingly to enlarge their potential and actual applications. There is also a good potential for the use of natural fibers/particles as reinforcing fillers in polymeric materials. The main advantage of these fibers are their low cost (especially in developing tropical countries where they are abundant), low density, and resistance to breakage during processing.[1]

The use of sawdust as a reinforcement for unsaturated polyester resins has been limited compared to mineral glass fibers or calcium carbonate. The main drawbacks of wood particles are their relative low degradation temperature and their hygroscopicity, which weaken their adhesion with hydrophobic polymers. However, wood fibers show very good mechanical properties (tensile strength between 0.5 and 1.5 GPa and Young's moduli between 10 and 80

GPa).[2] Moreover, compared to inorganic fillers, organic materials impart added benefits such as weight reduction, a highly reduced wear of the processing machinery, and a relative reactive surface.[3]

One difficulty encountered during the incorporation of these particles into a polymeric matrix (except for phenolics or urea-formaldehyde matrices) is the hydrogen bonding, which tends to hold the cellulose fibrils together. The polar nature of wood-based fillers adversely affects the dispersion of such polar materials in a nonpolar matrix.[4] A number of attempts have been made to improve the adhesion of cellulosic fillers to the polymer matrix by modifying the surface of the fiber or the matrix. The incorporation of various additives/coupling agents in these systems helps to promote the adhesion at the polymer–filler interface, improves the degree of filler dispersion, increases the fiber loading in the polymer, and improves the processability and moldability.

Chemical modification of the surface of organic fibers with different silane coupling agents and isocyanate has been reported by Raj et al.[4,5] Clemons et al.[6] modified milled aspen fibers with maleic anhydride, carrying out the reaction in a vessel with refluxing xylene for different times.

Composites of maleic anhydride-modified polypropylene with wood and cellulose fibers were prepared by Takasae and Shiraishi[7] and Felix and Gatenholm,[8] respectively. Maldas and Kokta[9] reported

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the preparation of wood fiber-filled polystyrene with maleic anhydride (coupling agent) incorporated during the kneading process. Young et al.[10] produced biobased composites from esterified aspen fibers with either a thermosetting (phenol-formaldehyde) or thermoplastic (polypropylene) matrix material.

Many studies have been published concerning the properties and processing conditions of thermoplastics with wood fibers/particles, but there is not much literature available on the reinforcing of thermosetting polymers with those fillers. These fillers should reduce the tendency of the resin to crack during cure and reduce resin shrinkage.[11] The current study deals with the evaluation of the mechanical properties of composite materials of unsaturated polyester filled with sawdust. In order to improve compatibility between reinforcement and matrix, the filler surface was modified with maleic anhydride under mild reaction conditions (no catalyst, low reaction temperature). The modifier was selected because of its ability to react with the polar wood surface through its acid group and with the matrix through its insaturation.

EXPERIMENTAL

Materials

The matrix was a solid unsaturated polyester (UPE) based on bisphenol A-fumarate (RQ 426, Perlinac S. A., Argentina), that was crosslinked with styrene in a 60 : 40 proportion with the resin. The initiator was benzoyl peroxide (Lucidol 0.75, Akzo Chemical S. A.), 1.5% wt. with respect to the total reaction mixture.

Sawdust from *Eucaliptus saligna* (Entre Rios, Argentina) was used in this work. Particles greater than mesh 40 were rejected.[12] The major fraction of the particles (about 76%) was between 0.2 and 0.37 mm; less than 7% of the distribution have sizes smaller than 0.1 mm.

Sawdust was dried and part of it was treated with maleic anhydride. In this case, sawdust was immersed in a solution of maleic anhydride (0.12M) in acetone. The mixture was refluxed for 7 h. This procedure assures a complete saturation of the filler surface with the modifier.[13] The effectiveness of the treatment was determined by measuring the hygroscopicity of the particles and by diffuse reflectance spectroscopy (DRIFT). The first technique indicated that the material was more hydrophobic after treatment, while second allowed determination that esterification took place. These results are detailed in

a previous publication[13] and can be summarized by saying that the carbonyl vibrations due to the maleic anhydride (1845 and 1780 cm^{-1}) disappear after reaction, while two peaks appear corresponding to ester and acid carbonyls (1704 and 1730 cm^{-1}).

Treated sawdust was finally acconditionated in two different ways: (1) they were washed up to three times in distilled water to eliminate excess of reactants and then dried at 60°C in an oven up to constant weight, (2) they were dried directly after treatment without any further washing.

Calcium carbonate-filled composites were also prepared for comparison (Blancolit 792, CAMUATI, Argentina, particle range between 2 and 20 μm).

Different composite materials were prepared: (1) composites where the sawdust was incorporated without treatment (SC), (2) composites where the sawdust was treated with maleic anhydride with no further washing (MSC), and (3) composites where the sawdust was treated with maleic anhydride and then washed in water (WMSC).

In all cases the concentration by weight of the fillers will be indicated between brackets, for example, SC(40) indicates a composite made with untreated sawdust in a 40 : 60 (filler : matrix) proportion.

Compounding and Molding

Filler and resin were mixed in a Brabender type mixer (volume capacity 50 cm^3) for about 1 h. The paste was filled in a metal mold (145 mm of diameter and about 3 mm of thickness), which was left open during 2 h at 50°C for degassing. Then, the mold was closed and the temperature was increased to 80°C. The reaction was carried out under a pressure of 3.8 MPa, selected according to Maldas et al.,[14] during 1.5 h. After that time, it was postcured in an oven for 2 h at 150°C.

Samples of neat resin and calcium carbonate-filled composites were obtained by pouring the mixture into a two-glass plate mold of 2.4 mm thickness. Degassing was performed for one day at room temperature, followed by the same curing cycle mentioned above.

Mechanical Properties Testing

Three-Point Bending Test

The mechanical test (three-point bending) was carried at room temperature at a crosshead speed of 1 mm/min in a Shimadzu Autograph S-500-C Universal testing machine. The sawdust composites
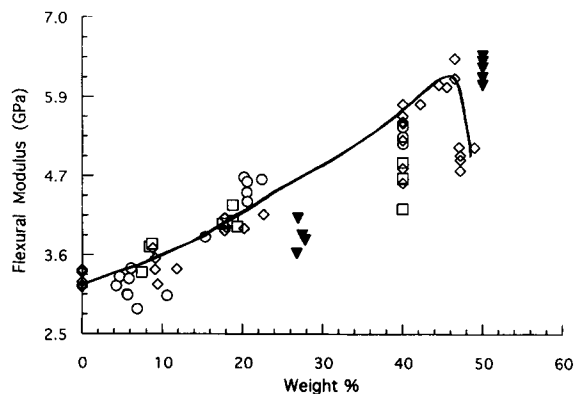
Figure 1   Flexural modulus as a function of the filler content. ◇ SC, □ MSC, ○ WMSC, ▼ calcium carbonate.

were cut to dimensions of 12×3 mm^2; the calcium carbonate composites and neat resin samples were cut to dimensions of 12×2.4 mm^2 (procedure A, ASTM D 790-86).

Dynamic Mechanical Test

A Perkin–Elmer dynamic mechanical analyzer (DMA7) was used in these experiments to obtain the dynamic flexural storage modulus (E'), and loss tangent (tan δ) of the samples. The tests were carried out using the temperature scan mode, three-point bending fixtures with a specimen platform of 15 mm length and a dynamic and static stresses of 3×10^5 and 5×10^5 Pa, respectively. The frequency of the forced oscillations was fixed in 1 Hz. All specimens for dynamical mechanical analysis were cut to $20 \times 3 \times 2$ mm^3, approximately, and the dimensions were measured up to 0.01 mm.

RESULTS AND DISCUSSION

Three-Point Bending Tests

The stress–strain response was linear up to the point of rupture for both matrix and composites. Thus, the maximum stress (stress in the outer layer at midspan, σ_u) was selected in order to compare the different materials.

Figure 1 shows the bending modulus (E_b) of the composites made from wood particles and calcium carbonate as a function of the filler content. The continue curve shows the behavior of the composites made with untreated sawdust. The elastic bending modulus shows a maximum at about 40% sawdust and then decreases. This could be explained by uncompleted wetting of the particles, because a monotonous increment of the modulus with filler con-

tent would be expected otherwise. This explanation is confirmed by nude eye observation of the composites obtained at larger filler contents. On the contrary, the carbonate particles were well wetted for the whole concentration range studied. This can be expected, because for the same weight load the volumetric fraction of the inorganic particles is always smaller than that of the organic ones.

The moduli of the filled composites are higher than that of the neat polymer resin as expected, although there is no significant differences between the moduli of sawdust or calcium carbonate composites. Compared to the inorganic filler, the organic one imparts an additional benefit: a weight reduction. Figure 2 shows the specific flexural modulus for the same samples presented in Figure 1. It is interesting to note, that when the specific properties are compared, the mechanical behavior of sawdust composites can be considered rather satisfactory.

Figure 3 shows the ultimate stress of the different materials. All the composites present a σ_u smaller than that of the unloaded matrix. Stress data for all samples are rather dispersed, and there is no significant difference between them. However, there is a slight increment with filler content for all the composites tested.

The elongation of the composites decreases compared with that of the original polymer (Fig. 4) and continues to decrease with the increase of the filler content in the samples.

To improve the stress transfer between wood fibers and polymer, an interphase region was created by forming covalent bonds between the —OH group of the wood and the —COOH group of the maleic anhydride, which was confirmed in a previous work.[13] In this way, maleic anhydride develops an interphase area between sawdust and polymer ma-
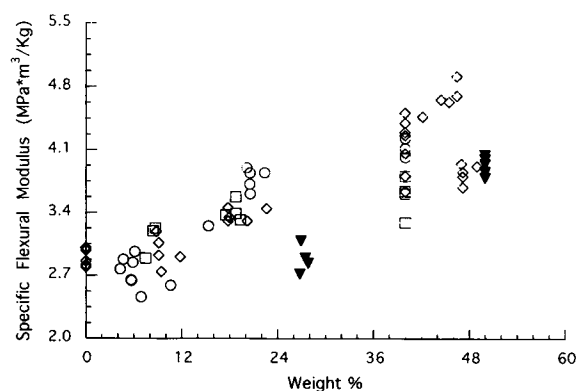
Figure 2   Specific flexuarl modulus as function of the filler content. ◇ SC, □ MSC, ○ WMSC, ▼ calcium carbonate.
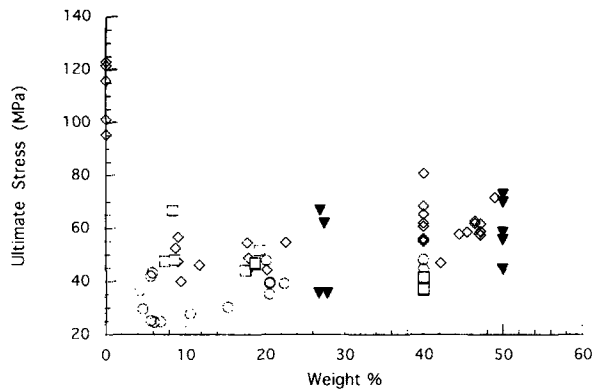
Figure 3 Ultimate stress of the composite material as a function of the filler content. ◇ SC, ☐ MSC, ○ WMSC, ▼ calcium carbonate.

Figure 4 Elongation as a function of the filler content. ◇ SC, ☐ MSC, ○ WMSC, ▼ calcium carbonate.
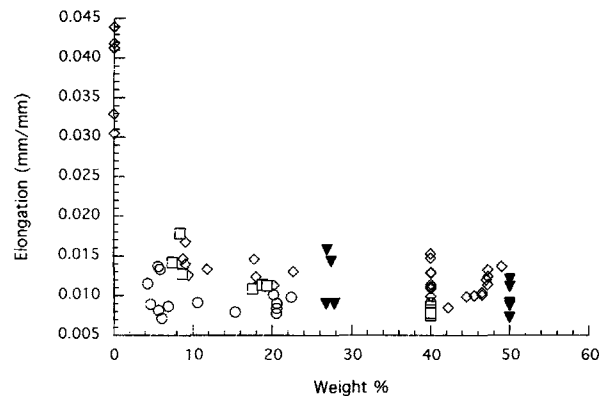
trix.[3] However, in the present case, poor adhesion (nontreated sawdust) or low concentration of co-valent bonds (low interfacial area, particles of less than 0.1 mm have a BET area of 1.3 m^2/g) between particles and polymer, added to a smaller interphase region (essentially maleic anhydride) are suspected to be responsible for the decreasing trends in certain mechanical properties, particularly elongation and stress.

For the reasons summarized above, no improvement of the mechanical properties was noticed for the composites prepared with maleic anhydride-treated sawdust. The low interfacial area of the particles did not allow to distinguish the effect of the used treatment. Further studies will be performed with small-size particles (wood flour) and alkaline pretreatment, in order to increase the area of particle–polymer contact.

Dynamic Mechanical Tests

The variations of the dynamic flexural storage modulus, E', and the loss tangent, tan δ, with the temperature for samples containing 0, 10, 20, 40, and 50% by weight of nontreated sawdust are shown in Figures 5 and 6, respectively.

E' decreases as temperature increases, and the change is larger for samples with lower filler content. For example, the storage modulus of the neat resin drops (α transition) from 1×10^9 to 4×10^7 Pa when the temperature changes from 100 to 150°C, while the dynamic modulus of SC(40) changes from 3×10^9 to 5×10^8 Pa in the same range. Differences in the rubbery moduli of the materials are partially due to hydrodynamic effects of the filler particles embedded in a viscoelastic medium. A number of other contributions to the modulus of filled rubbers

have been suggested; for example, the shape factor effect. The data can be reasonably fitted to the Guth equation[15] if the aspect ratio of the fibers were 5.9, but this value appears to be too large, according to microscopy results. Hence, it must be concluded that although shape factor effects probably contribute to the modulus of the rubbery region, the addition of hydrodynamic and shape factor effects still does not account for the total increment observed. At the concentrations used in the work, the effect is most probably due to the fact that load transfer in the composite is through filler particles, which are touching each other. Moreover, the particles introduce an elevated degree of mechanical restraint that reduces the mobility and deformability of the rubber matrix.

Figure 6 shows that the maximum of tan δ appears at lower temperatures as the fibers content increases. This was thought to be due to the plasticizing effect of adsorbed water, which increases with wood par-
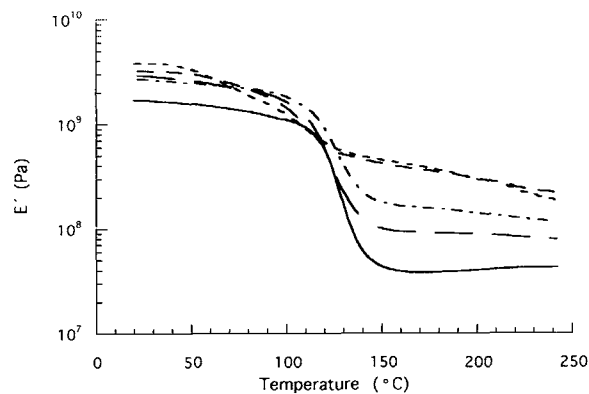
Figure 5 Flexural storage modulus, E', as a function of the temperature for SC samples. — SC(0), — — SC(10), — · — SC(20), - - SC(40), ---- SC(50).
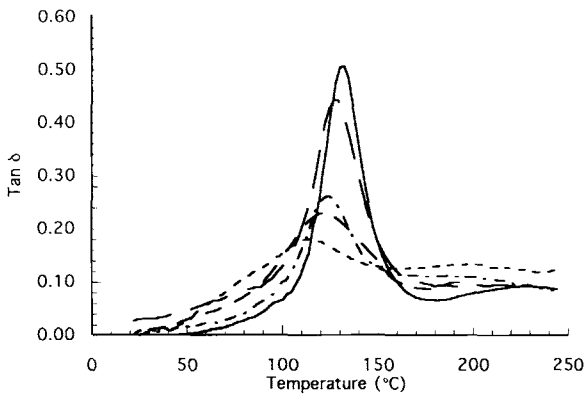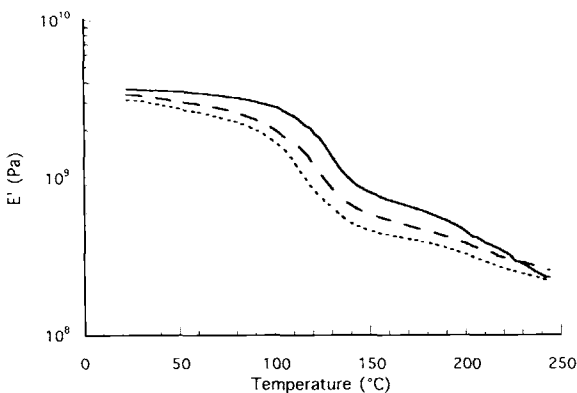
Figure 6 Loss tangent, tan δ, as a function of the temperature for SC samples. — SC(0), — — SC(10), — · — SC(20), - - SC(40), ---- SC(50).
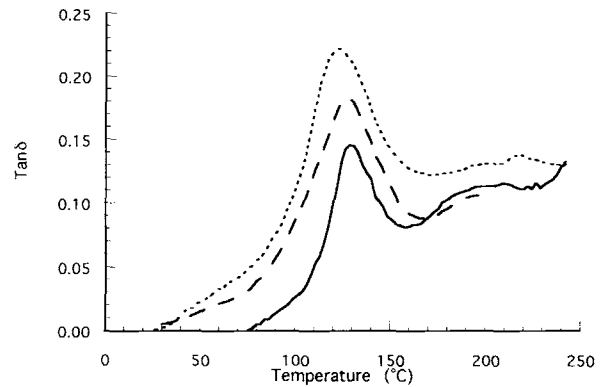

Figure 8 Temperature scans of tan δ for SC(40) samples. —— dried for 2 h at 120°C, - - in equilibrium with room humidity and temperature, ---- immersed in distilled water during 24 h.

ticles content. To confirm this hypothesis, the behavior SC(40) composites in different humidity conditions were analyzed.

Figure 7 and 8 show the temperature scans of E' and tan δ for SC(40) samples acconditionated in three different ways: (1) dried for 2 h at 120°C, (2) in equilibrium with room humidity and temperature, and (3) immersed in distilled water during 24 h.

There is a decrease in the bending modulus with increasing moisture in the composites. The greater drop in E' for humid-wetted material can be assigned to the plasticizing effect of water on the polymer matrix. That water affects the viscoelastic behavior of SC is evident from the temperature scan of loss tangent, for oven-dried and humid composites. It is observed that moisture lowered the α-transition temperature, which can be explained by the fact that plasticizer reduces the activation energy required for chain motion. This material shows approximately
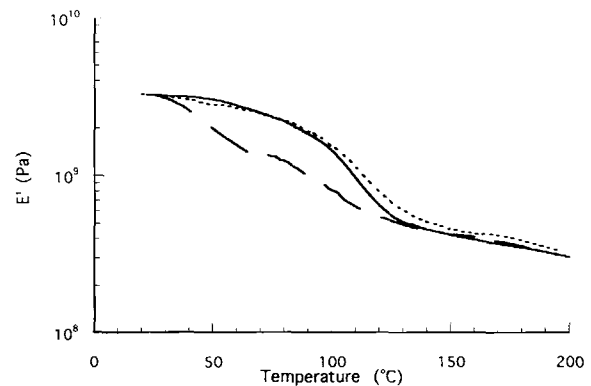
an 1.5% of increase in volume after 1 day of immersion in water, which should modify the free volume available for chain motion.

The variation of E' with temperature for *Eucaliptus saligna* wood samples acconditionated in the same ways that the 40% sawdust composites were also performed. For example, the dried sample showed a storage modulus of 3.72 × 10^8 Pa at 30°C. At the same temperature, the specimens in equilibrium with room humidity and immersed in water gave E' values of 2.82 × 10^8 and 2.00 × 10^8 Pa, respectively. The decrease of E' with increasing humidity is attributed to the plasticizing effect of water on wood cell wall components. The disruption of highly ordered hydrogen bonds in the wood structure, through formation of less ordered water–water hydrogen bonds, weakens the resistance of wood to applied stress and, hence, results in the loss of strength and stiffness as moisture content increases.[16] Then, the decrease in E'

Figure 7 Temperature scans of E' for SC(40) samples. —— dried for 2 h at 120°C, - - in equilibrium with room humidity and temperature, ---- immersed in distilled water during 24 h.
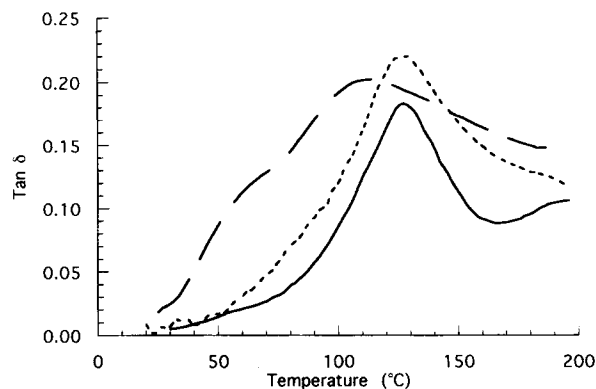

Figure 9 Temperature scans of E' for SC(40), MSC(40), and WMSC(40) samples. — SC(40), - - MSC(40), ---- WMSC(40).

Figure 10 Temperature scans for tan δ for SC(40), MSC(40), and WMSC(40) samples. — SC(40), – – MSC(40), ---- WMSC(40).

of the SC can be attributed to both effects, wood and matrix plastification.

Figures 9 and 10 show the temperature scans of E' and tan δ for SC(40), MSC(40), and WMSC(40) samples. The decrease of E' for the MSC(40) specimen with the temperature is important even at temperatures as low than 50°C. On the other hand, it is observed that the peak of tan δ for SC(40) and WMSC(40) remains at the same temperature, while the MCS(40) sample exhibit at least two maxima, both of them at lower temperatures than the previous specimens. The behavior of the composite with treated and unwashed sawdust is attributed to the plastificant effect of the unreacted maleic anhydride. Moreover, as was previously mentioned, no differences in the behavior of SC and MSC composites was noticed.

CONCLUSIONS

The specific mechanical properties of the sawdust composites are compared satisfactorily with respect to the inorganic composites.

No improvement in mechanical properties was found when the sawdust was chemically modified. A low interfacial area is suspected to be responsible for this fact. Besides, the small molecule used as modifier agent can reduce the hygroscopicity, but creates a rather rigid interphase, contributing to reduce the yield stress and the elongation of the composites. To improve this behavior, a longer chain coupling agent could be utilized. On the other hand, composites properties would be improved if a large degree of modification is achieved. Pretreatments such as immersion in alkaline medium or maceration increase the interfacial area and break cellulose H-bonding. This would allow for a larger degree of chemical modification.

Composites of wood particles–unsaturated polyester can be used at higher temperatures (up to 200°C) than the neat resin, because the E' drop at a transition is much reduced.

The main drawback of the organic filler composites is their water sorption capacity, which impairs the material final properties, as has been demonstrated by the dynamical mechanical tests.

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