

# Composites From PMMA Modified Thermosets and Chemically Treated Woodflour

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The mechanical behavior of composites made from woodflour and a modified thermoset unsaturated polyester resin has been examined. Polymethylmethacrylate (PMMA), a common low profile additive (LPA), was used as the matrix modifier. Woodflour, the reinforcing filler, was used "as received" and was also modified with a commercial alkenyl succinic anhydride (ASA), in order to enhance the compatibility with the resin. The composites exhibited higher flexural and compressive modulus and compressive yield stress than the neat resin, while flexural strength and ultimate strain were reduced. The addition of PMMA to the unfilled thermoset led to a LPA morphology and decreased the flexural modulus, but produced an increment in flexural strain at break, impact energy and toughness of the UP resin. No enhancement in the mechanical behavior of the composites was found when treated woodflour instead of unmodified woodflour was used.

## INTRODUCTION

The use of vegetable fibers and/or particles as reinforcement/filler of polymeric matrices has attracted growing interest in the past decade from both the academic and the applied points of view. Natural vegetable fibers reduce the total mass of a given composite volume, because they have a relatively low density. This kind of filler is a potentially attractive alternative of inexpensive reinforcement for polymeric materials; in general its use reduces cost and at the same time improves certain properties (1, 2), i.e. the stiffness of the composites, owing to the high modulus of the fiber/filler. In addition, compared with inorganic fillers, natural fibers produce low wearing of the processing machinery. Currently, woodflour and sawdust are considered wastes of the local forest industry. They are partially burned to generate energy, or sent to the paper industry, while the major part just accumulates without any expected application and with the consequent environmental risk (3). However, the widespread use of these resources is hampered by their polar nature (which affects the degree of dispersion of the fibers in the polymeric matrix and the macroscopic homogeneity of the structural piece (4) and also by their high moisture sorption and a relatively low degradation temperature.

Surface treatments of vegetable particles affect dispersion in and compatibility with the polymeric matrix and consequently the mechanical properties of the composites. This problem has been addressed by several authors, and different surface modifications have been proposed. For example, Razi *et al.* (2) modified southern yellow pine using silanes of different structures and molecular weights and found that these treatments improved the polymer (HDPE)/wood interface bond. Raj and Kokta (4) esterified Kraft pulp of aspen with stearic acid to improve the dispersion of the fibers in a polypropylene matrix. Felix and Gatenholm (5) treated cellulose fibers with one commercial alkylsuccinic anhydride and two polypropylenes modified with maleic anhydride of different molecular weights in order to improve the interfacial adhesion with polypropylene.

Styrene crosslinked unsaturated polyester resins (UP) are widely used as matrices in composites (6), because they have a relatively low cost and a low viscosity. However, as with many thermoset polymers, the use of UP resins are limited by their brittleness, the high shrinkage that occurs during polymerization, and the poor resistance to crack propagation. Although the addition of fillers and reinforcements into the UP resins can reduce the volume shrinkage, problems such as wavy surfaces or fiber-pattern appearance in molded parts, internal void and cracks, etc., due to the polymerization shrinkage cannot be totally excluded (7). For these reasons, the UP resins are

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often used with modifiers to obtain improved surface properties and/or toughness, by reducing the resin shrinkage during the curing step (8). These modifiers are called "low profile additives" (LPA) and the purpose of their inclusion in a UP resin is to compensate for the thermal and polymerization shrinkage of the resin at a minimum cost of the other properties. Standard low shrink and low profile additives include polyethylene (PE), polystyrene (PS), poly(vinyl acetate) (PVAc), poly(methyl methacrylate) (PMMA), poly(styrene-co-butadiene), polyurethanes and other less common thermoplastics. Among them, PVAc and PMMA based low profile additives are most widely used (9–12). These additives are used in commercial applications in the range of 5–20 wt% (10). The addition of a thermoplastic modifier offers two advantages over more conventional rubber-toughening processes: it avoids the important loss of modulus that is a necessary consequence of adding rubber particles, and it operates in thermosetting resins that are too tightly cross-linked to absorb significant amounts of energy, offering in this way some toughening effect (13).

The morphology of the final composite materials and the resulting mechanical properties depend on several variables: resin molecular weight and molecular weight distribution, curing temperature, additive and filler concentrations and compatibility with the resin (10, 14, 15).

The general aim of the work is to obtain composites from modified unsaturated polyester resins and vegetable fibers, facilitating woodflour dispersion in the UP resin through the chemical modification of the fibers, and improving the toughening of the neat resin and composites by the addition of a thermoplastic polymer.

## EXPERIMENTAL

### Materials

The matrix used was an unsaturated polyester resin (UP) based on bisphenol A-fumarate (RQ 426, Perlinac S. A., Argentina), crosslinked with styrene in a 60:40 weight proportion. The initiator was benzoyl peroxide (Lucidol 0.75, Akzo Chemical S. A.). Polymethyl methacrylate (PMMA, Súbiton, Prothoplast SAIC) was used as the thermoplastic modifier. It was added in 3, 5 or 8 wt% to the styrene-polyester resin mixture. To improve the dispersion of the LPA into the styrene-polyester mixture, the selected amount of PMMA powder was allowed to swell in styrene monomer (50 wt% of the total amount of styrene was used in this step) during one day. After that time, the PMMA-styrene blend was mixed with the styrene-polyester solution (prepared using the other 50 wt% of the total styrene), at room temperature using mechanical agitation.

Woodflour from *Eucalyptus saligna* (Argentina) was selected for this work because of its availability and wide use in the region. Only particles that pass through a sieve of mesh 250 (Tyler series) were used in this study; thus the maximum particle average diameter

was 57  $\mu\text{m}$ . Woodflour is a particulate filler with aspect ratio between 1 and 3. However, the complex structure of this filler is that of a fibrous cellulose natural composite in a lignin-hemicellulose matrix, and thus it shares some of the features of the short fiber fillers.

Woodflour was esterified in order to improve its compatibility with the matrix using a commercial alkenyl succinic anhydride (ASA, Lasar 2019 CE, Akzo Nobel). The particles were dried at 70°C in a vacuum oven until constant weight was reached. The esterification reactions were carried out by immersing the woodflour in a solution of acetone containing 96 g/l of Lasar and catalyst (4-dimethylaminopyridine, Fluka, 8.75 g/l) and then heating at reflux temperature (56.5°C) for 4 hours. The esterified wood particles were separated from the acetone solution and intensively washed with distilled water in order to eliminate the unreacted materials. Finally, the woodflour was dried at 70°C in a vacuum oven until constant weight was achieved.

### Compounding and Molding

The untreated and treated woodflours were dried at 70°C in a vacuum oven until constant weight was reached. Then, the filler and the solution of unsaturated polyester in styrene (containing PMMA in the case of modified matrices) were mixed in a Brabender type mixer for about 1 hour. 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 force of 6.4 tons during 1.5 h. After that time, it was postcured in an oven for 2 hours at 150°C. Samples of neat or PMMA modified resin were obtained by pouring the mixture inside a glass plate mold of 2.4 mm thickness and using the same curing cycle mentioned above. Composites were prepared using 40 wt% of untreated or ASA-treated woodflour, UC and LC, respectively.

### Physical Characterization

The ester content of the ASA modified woodflour was calculated from the saponification values using the techniques described elsewhere (16, 17).

Diffuse reflectance infrared (DRIFT) spectra of the woodflour samples were obtained by adding 64 scans and using a 2  $\text{cm}^{-1}$  resolution. The samples were not diluted in KBr powder. The equipment utilized was a Mattson Genesis II.

Optical micrographs from the UP-styrene mixtures were taken using a Leica model EMLB microscope equipped with a Linkan THMS 600 hot stage.

Scanning electron micrographs (SEM) of the fracture surface of the composites and PMMA modified UP-systems were taken using a scanning electron microscope, Philips model SEM 505. The samples were previously coated with gold.

## Mechanical Testing

A Perkin Elmer dynamic mechanical analyzer (DMA 7) was used to obtain the dynamic flexural storage modulus ( $E'$ ), and loss tangent ( $\tan \delta$ ) of the samples. The tests were carried out using the temperature scan mode, three-point bending fixture with a specimen platform of 15 mm length and dynamic and static stresses of  $3 \times 10^5$  and  $5 \times 10^5$  Pa, respectively. The frequency of the forced oscillations was fixed in 1 Hz. All specimens for dynamic mechanical analysis were cut to  $20 \times 3 \times 2$  mm<sup>3</sup> approximately, and the dimensions were measured up to 0.01 mm.

Three-point bending tests were carried out at room temperature at a crosshead speed of 1 mm/min according to ASTM D 790-86 in a Shimadzu Autograph S-500-C Universal testing machine.

Compressive tests were carried out at room temperature at a crosshead speed of 0.5 mm/min in an Instron 8501 Universal testing machine. Square bars (3.5 mm side) were cut from the molded plaques. The aspect ratio of all the samples was kept between 1.5 and 2 (ASTM D 695-85).

Izod unnotched impact strength was measured at room temperature in a Fractovis Ceast falling ball machine. The velocity of the test was set as 1 m/s and the striker minimum mass (3.6 kg) was used, thus the impact energy was 1.8 J.

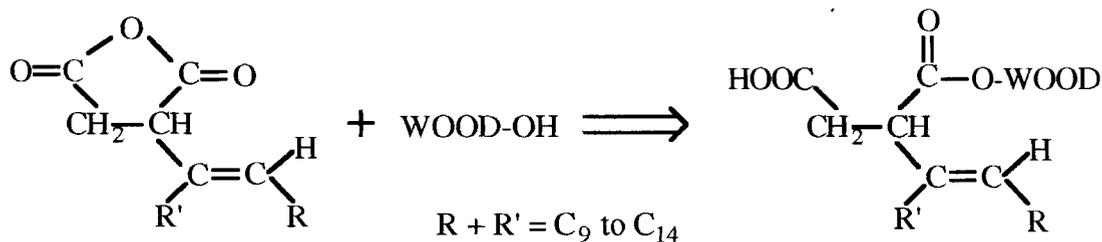
All the specimens used for mechanical tests were previously dried at 70°C in a vacuum oven until constant weight.

## RESULTS AND DISCUSSION

### Filler Modification

Woodflour was esterified using a commercial alkenyl succinic anhydride (ASA). This modifier is a low price reagent, commonly used as a sizing agent in the paper industry, which can potentially react, through its own double bond, with the unsaturations of the UP-styrene system. The expected reaction scheme is shown in Scheme 1. The anhydride group of the ASA reacts with one of the free hydroxyls of the woodflour, generating an ester linkage and a new acid group on the woodflour surface.

The efficiency of the chemical modification was evaluated using analytical techniques: saponification values (performed on washed samples) indicated that there were 0.46 mole of ASA attached to 1 Kg of treated woodflour ( $\approx 166$  g/Kg treated woodflour).



Scheme 1. Expected reaction between woodflour and ASA.

Changes introduced at the woodflour surface by the ASA treatment were monitored by FTIR. Figure 1a shows the spectra of the neat ASA. In the interest of the following discussion, the C-H region around 2900  $\text{cm}^{-1}$ , and the C=O vibration corresponding to the anhydride group at 1867 and 1784  $\text{cm}^{-1}$  (18, 19) are indicated in the figure. It is noticeable that the C=C stretching vibration is not detectable in the 1650  $\text{cm}^{-1}$  region, as it is also well known to occur in the *trans* long-chain unsaturated fatty acids, in which the double bond is situated towards the center of the chain. The spectrum also shows a peak at 968  $\text{cm}^{-1}$ , which is assigned to the out of plane =CH deformation vibration corresponding to disubstituted *trans* ethylenes, in agreement with the previous discussion (19).

The spectra of the untreated and chemically treated woodflours are also included in Fig. 1 (1b and 1c, respectively). The CH region increases in intensity because of the ASA attached to woodflour particles. However, the C=O peaks assigned to the anhydride vibration are absent in the spectrum of treated woodflour, indicating that there is no unreacted ASA in the sample.

The difference spectrum (treated-untreated) in the 1600 and 1800  $\text{cm}^{-1}$  region is shown in Fig. 2. The band at 1700–1750  $\text{cm}^{-1}$  is a double peak with maxima at about 1710  $\text{cm}^{-1}$  and 1735–1740  $\text{cm}^{-1}$ , which are assigned to absorption of carbonyl bonds in carboxylic acids and in esters, respectively (18, 19). This observation, together with the absence of the anhydride peaks and the increase of the intensity in the CH region, indicates that ASA becomes attached to the woodflour through reaction of the OH group of the wood with the anhydride group, which generates an acid and an ester groups. The difference spectrum also shows the appearance of a peak at 1650  $\text{cm}^{-1}$ , which is in the region of the C=C stretch vibrations. The appearance of this peak is also consistent with the disappearance of the peak at 968  $\text{cm}^{-1}$ , present in the unreacted ASA. It is believed that the reaction to the woodflour particles leads to some steric change in the attached molecule and for that reason the asymmetric vibration becomes detectable with this technique.

### Matrix Modification

The unsaturated polyester resin was modified using PMMA as low profile additive (LPA). Shrinkage occurs during crosslinking of most thermoset resins because

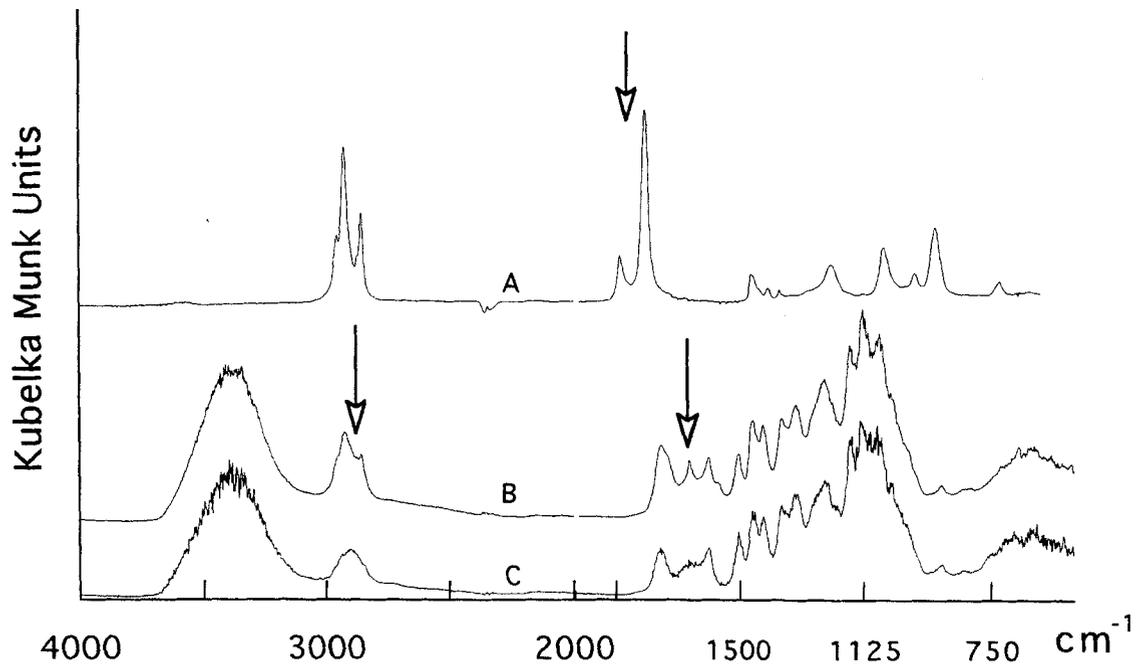


Fig. 1. FTIR spectra of A) neat ASA; B) treated and C) untreated woodflours.

of the volume change of the resin during cure and the thermal contraction that takes place as the part cools from the cure temperature. This undesirable effect manifests itself both in distortion of the part and in uneven surface. The surface of the part develops an "orange peel" appearance, due to the differential contraction between the resin phase and the other solids present. The cure contraction and thermal contraction of the resin are hindered to some extent by the presence of fibers and filler particles, so the resin surrounding these particles is left in a state of hydrostatic tension. Near the surface of the mold, this tension can be relieved by local resin contraction, which leaves visual evidence of the fibers just below the surface of the part. That is, the shrinkage forces create internal stresses, which lead to surface and structural flaws (12, 20). In order to eliminate most of the problems mentioned above, low profile additives are widely used in the curing of UP resins to compensate for the resin shrinkage (12, 20, 21). The LPAs are usually specific elastomers (i.e. butadiene-nitrile rubbers) or thermoplastic polymers, such as poly(vinyl acetate), poly(methyl methacrylate), thermoplastic polyurethane, polystyrene, etc. (7), which are compatible or partially compatible with the styrene-unsaturated polyester resin mixture before cure, and become incompatible at some time during the cure.

An optical microscope equipped with a heated plate was used to monitor the changes in the morphology of the different systems with temperature. The heating rate selected was 5°C/min, and the temperature was varied from 20°C to 150°C. Figure 3 shows optical micrographs of the UP-styrene copolymer modified with

two different percentages of PMMA. The micrographs were taken at room temperature after cooling down from the final maximum temperature (150°C). They also represent the morphology of the systems before heating, since no appreciable changes in morphology were observed with the temperature.

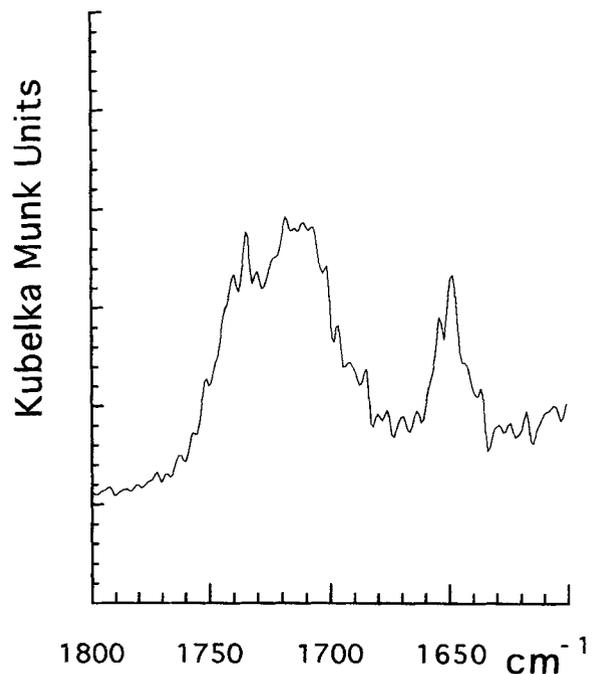


Fig. 2. Difference DRIFT spectra (treated woodflour-untreated woodflour).

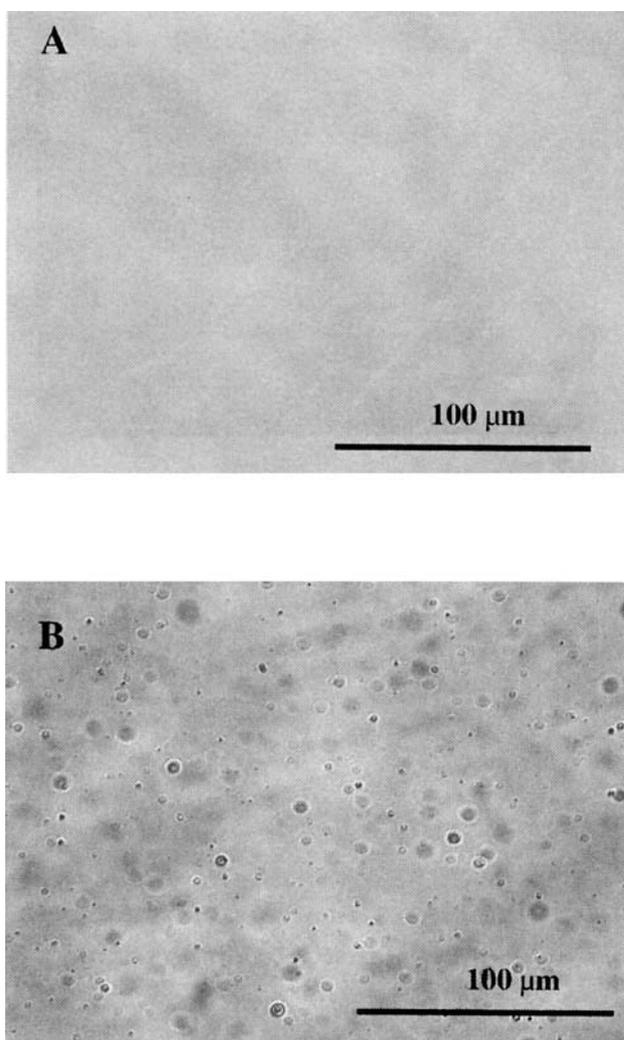


Fig. 3. Optical micrographs of UP-styrene solutions with different percentages of PMMA. A) 3%; B) 5%.

The systems containing low concentrations PMMA (lower than 3%) are totally homogeneous before curing, and remain unchanged after crosslinking. On the other hand, the systems containing higher PMMA concentrations are phase separated before the reaction and remain heterogeneous after curing. It is known that when a common solvent such as styrene is added to form a UP-LPA-common solvent system, the LPA and UP usually cannot coexist in a homogeneous phase. For a given UP-styrene mixture, the addition of a LPA beyond a certain percentage generally leads to the formation of two phases in equilibrium. The exact percentage for phase separation depends on the chemical nature and the molecular weight of the LPA and resin, the molar ratio of styrene to UP unsaturations in the mixture, and the temperature (7).

Figure 4 shows scanning electronic micrographs of the bending fracture surface of unfilled UP-S thermoset

with the addition of different amounts of PMMA (0, 3, 5, 8 wt%). The unmodified system shows brittle fracture and the fracture surface exhibits longitudinal ridges that are sometimes referred to as "river patterns." Although the fracture surface of the 3 wt% PMMA modified system shows also brittle fracture, there are some nodules in the surface that were not present in the UP-S thermoset. This feature indicates some change in the material that can be due to two reasons: 1) the PMMA was incorporated homogeneously to the resin or 2) an incipient phase separation. However, it should be noticed that the cured sample was completely transparent even under an optical microscope, which indicates that if some separation occurred it should be restricted to extremely small domains.

Samples prepared with larger amounts of thermoplastic additive show two-region-morphology. One region shows the same characteristics as those of the unmodified resin. This is the UP-rich phase, which shows brittle fracture. There are also some relatively large, more or less spherical domains (on the order of 100 µm) with a complex internal structure. This is the PMMA-rich phase, which is not a pure phase. This type of morphology has been previously described for UP and vinyl ester resins cured with styrene and modified with elastomers or thermoplastics (UP: 22, 23; Vinyl ester: 21, 24).

The modified systems at 5% and 8% PMMA are initially heterogeneous, and thus, good mixing is then a paramount variable in this type of formulation, commercially utilized. In particular, in this work, the copolymerization reaction was carried out at relatively high temperature (80°C), which initially reduced this problem, since in the system, the viscosity is lowered and miscibility increases with temperature (7, 20). However, some heterogeneity remains as seen from the optical micrographs (Fig. 3), and it is the reason for the presence of the large PMMA-rich spheroidal domains. These domains contain initially some UP resin and S, and the reaction proceeds in their interior. Microgels of cured UP are formed, which produce the internal nodules as the reaction proceeds and intermicrogel bonds are formed. The additive is segregated from these nodules and surrounds them, so they performed a segregating effect and the nodular structure is preserved until the end of the reaction. There is a shrinkage of the UP-S nodules and main UP-rich phase, which generates stresses inside the PMMA rich domain. Towards the end of the reaction, microcracks develop internally inside this domain, which partially compensate for the volume shrinkage of the material. This phenomena is well known in low profile systems and has been described by different authors with few modifications depending on the materials being studied (20, 21), although the overall mechanism is the same. Microvoids could also occur around the fillers and fibers in composites (8).

The initial partial incompatibility of the present system leads to large LPA-rich domains and a main phase

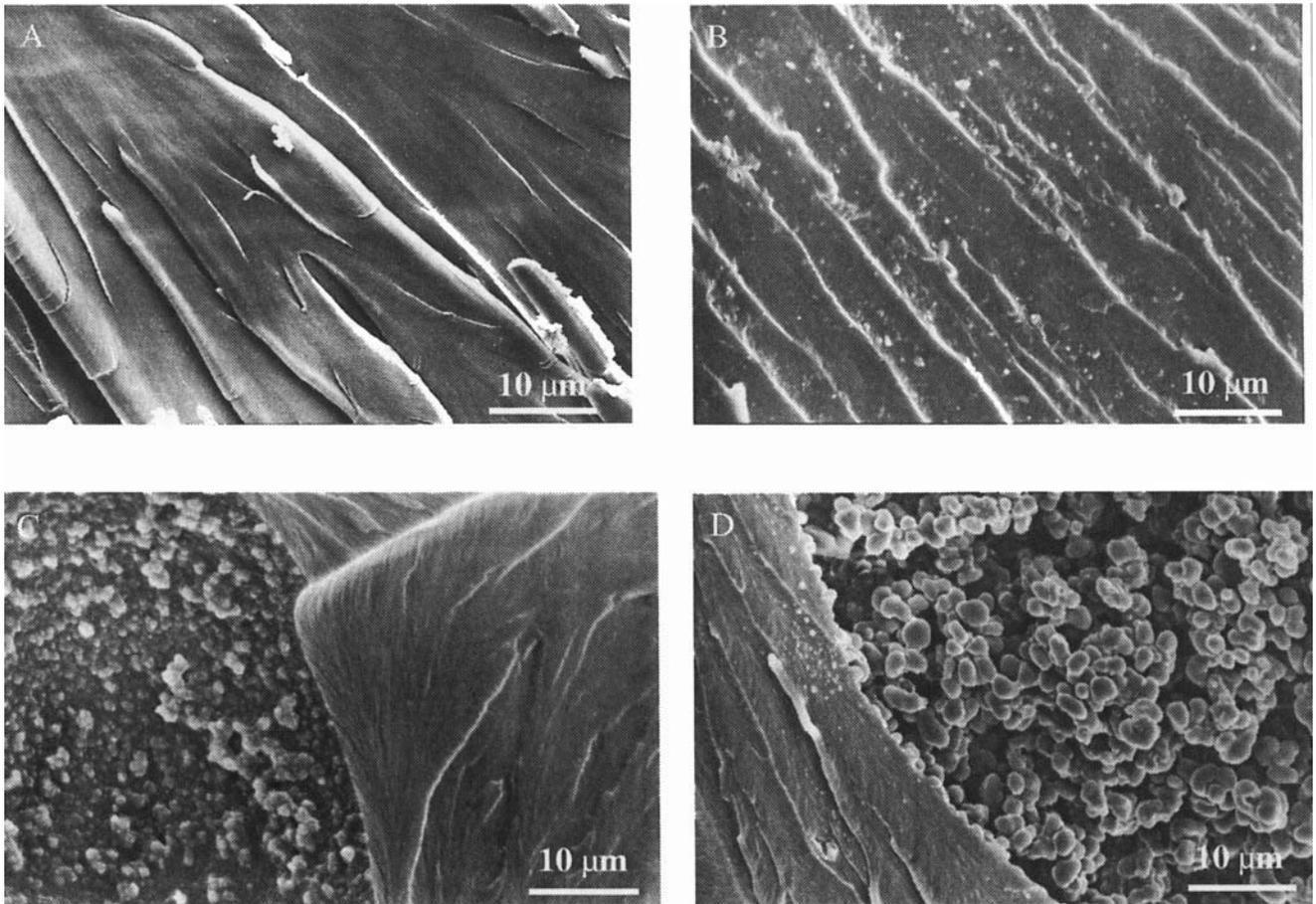


Fig. 4. SEM micrographs of UP-styrene systems with different percentages of PMMA. A) 0%; B) 3%; C) 5%; D) 8%.

with little modification. The sample with 8% of PMMA was more difficult to prepare, because of the high viscosity of the additive and the increased heterogeneity of this mix. The UP-S nodules were more clearly defined and had larger size in the 8% sample with respect to the 5% PMMA sample (2–3  $\mu\text{m}$  and 0.5–1  $\mu\text{m}$ , respectively, from Fig. 4). This trend has been previously reported for similar systems (21, 23, 25). Although the main phase probably contains some additive, the usual segregation that takes place during curing, generating second-phase inclusions in the main phase (as it is observed in epoxy-rubber systems), is not observed here. The characteristics of the continuous main phase are similar to those observed in the 3% PMMA sample.

Figure 5 shows the results of the dynamic mechanical test of the neat resin modified with different percentages of PMMA. It is observed that the peak of  $\tan \delta$  for all the samples, including the neat UP, appears at approximately the same temperature (about 151°C). This peak corresponds to the main glass-rubber transition of the UP-rich phase, showing only some width increase with LPA addition. The  $\tan \delta$  position confirms that the content of thermoplastic modifier in the

main phase is low. On the other hand, the curves corresponding to samples containing PMMA show a shoulder between 120°C and 130°C, which increases its intensity as the PMMA content increases, and corresponds to the PMMA transition.

### Mechanical Properties

#### Bending

The morphologies just described result in the improvement of the control of the volume shrinkage through restricted internal microvoiding, but at the same time they have a correlation to the mechanical and fracture behavior of the materials.

The flexural performance of the UP-S systems and composites made from untreated and treated woodflour is reported in Table 1. The amount of PMMA was reported as a weight percentage of the neat UP-styrene mixture in all cases. The flexural modulus slightly decreases with the addition of PMMA in all cases, while the ultimate strength and deformation are improved by the PMMA addition and they pass through a maximum, located between 3% and 5% of the thermoplastic polymer content. The last feature is more noticeable

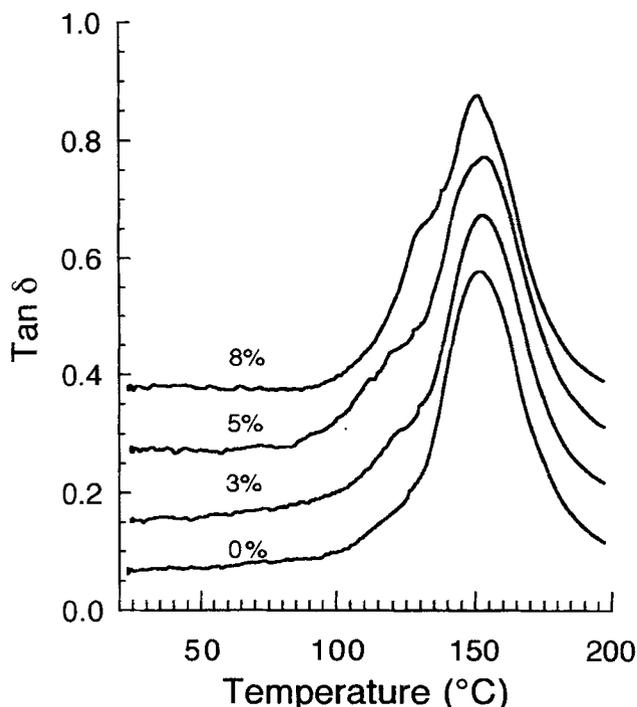


Fig. 5. Temperature scans of  $\tan \delta$  of UP-S systems modified with PMMA. The curves have been vertically shifted to facilitate the comparison.

for the unfilled systems and practically negligible for the composite materials. In particular, the mechanical properties of the 8% PMMA system show a large drop in the strength with respect to the samples with lower PMMA content, which was attributed to the large number of microvoids (localized in the PMMA dispersed phase) of this sample, and to the resulting reduced cohesion of the material. This effect was also found by other researchers in similar systems (21, 25).

Compared to the unfilled materials, the flexural modulus is improved with the addition of the filler, with noticeable differences due to treatment. On the other hand, the addition of woodflour reduces the

strength of the matrix and causes a dramatic decrease in the elongation at break. It is known that almost all the elongation occurs in the matrix if the filler is more rigid than the matrix. If there is good adhesion between the filler and the matrix, a decrease of elongation at break, even with a small amount of filler, can be expected. If the adhesion is poor, the elongation at break may decrease more gradually (15, 26). The important decrease in elongation at break noticed in all the composites suggests a good degree of interfacial compatibility between particles and resin in all the materials, independently of the treatment of the woodflour.

The lowest values of  $E_b$  and  $\sigma_u$  in the composites correspond to the LC sample, probably because of plasticization of the fibers occasioned by the esterification reaction (17, 27, 28) and perhaps because of some flexibilization of the matrix near the fiber.

### Compression

Typical compressive stress-strain curves for the samples without PMMA are shown in Fig. 6. It can be seen that when loaded in compression, all the samples undergo considerable plastic deformation, contrary to what happens in bending, where they exhibit elastic behavior up to the rupture. The addition of woodflour increases the compression modulus and the yield strength, but reduces the ultimate deformation of the matrix. Table 2 lists compressive modulus, yield strength, ultimate deformation and toughness for the unfilled material and composite samples containing 40 wt% of woodflour. The toughness in compression was calculated as the area under the true stress-strain curve (29). The toughness of the UP-S systems is clearly influenced by PMMA concentration and again, it goes through a maximum at about 3% to 5%. The toughness of the ASA treated woodflour composites (LC) was always lower than that of the untreated woodflour composites (UC), which could be the result of an improved adhesion (covalent bonding) between filler and matrix. This adhesion favors the brittle fracture mode with relatively low energy absorption (30).

Table 1. Flexural Modulus ( $E_b$ ), Ultimate Strength ( $\sigma_u$ ) and Ultimate Deformation ( $r_u$ ) for the Neat Resin and Composite Samples Containing 40 wt% of Woodflour With Different Treatments. Reported Values Are the Average of the Properties of Six Specimens  $\pm$  the Standard Deviation.

Sample	PMMA (%)	$E_b$ (GPa)	$\sigma_u$ (MPa)	$r_u$ (mm/mm)
Matrix	0	$2.67 \pm 0.33$	$74.32 \pm 9.56$	$27.84 \cdot 10^{-3} \pm 1.81 \cdot 10^{-3}$
	3	$2.41 \pm 0.17$	$98.99 \pm 4.66$	$39.91 \cdot 10^{-3} \pm 1.08 \cdot 10^{-3}$
	5	$2.23 \pm 0.15$	$103.95 \pm 9.63$	$53.01 \cdot 10^{-3} \pm 0.85 \cdot 10^{-3}$
	8	$2.23 \pm 0.12$	$71.72 \pm 2.33$	$32.50 \cdot 10^{-3} \pm 0.84 \cdot 10^{-3}$
UC	0	$4.20 \pm 0.22$	$47.13 \pm 4.20$	$11.22 \cdot 10^{-3} \pm 0.72 \cdot 10^{-3}$
	3	$3.36 \pm 0.07$	$48.85 \pm 7.51$	$14.74 \cdot 10^{-3} \pm 2.51 \cdot 10^{-3}$
	5	$3.34 \pm 0.20$	$49.09 \pm 4.78$	$17.62 \cdot 10^{-3} \pm 3.67 \cdot 10^{-3}$
LC	8	$3.23 \pm 0.20$	$43.38 \pm 11.06$	$16.23 \cdot 10^{-3} \pm 3.46 \cdot 10^{-3}$
	0	$3.05 \pm 0.12$	$33.18 \pm 1.18$	$11.31 \cdot 10^{-3} \pm 0.58 \cdot 10^{-3}$
	3	$2.81 \pm 0.18$	$36.87 \pm 5.62$	$13.95 \cdot 10^{-3} \pm 0.93 \cdot 10^{-3}$
	5	$2.77 \pm 0.09$	$31.54 \pm 5.87$	$13.11 \cdot 10^{-3} \pm 2.61 \cdot 10^{-3}$
	8	$2.74 \pm 0.12$	$30.37 \pm 3.34$	$12.03 \cdot 10^{-3} \pm 2.24 \cdot 10^{-3}$

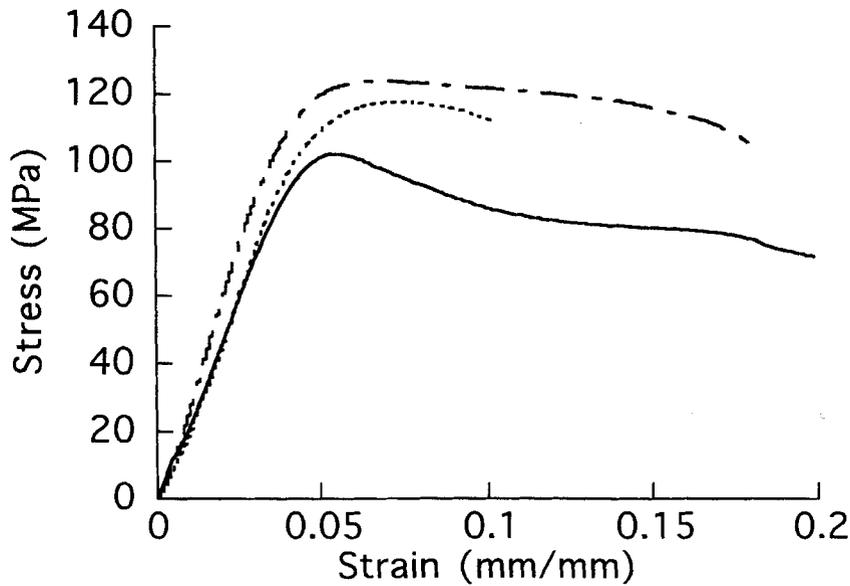


Fig. 6. Compressive stress-strain curves of neat resin and composites (without PMMA). — neat resin; --- UC; ..... LC.

**Impact**

**PMMA Addition to Unfilled Systems**

Figure 7 shows the impact energy of the matrix and composites as a function of PMMA content. The impact strength of the UP-styrene system exhibits a high improvement with the addition of PMMA when fillers are not present. At 3% PMMA the impact energy of the sample is almost six times that of the unmodified system. Thus, although there is no optical indication of phase separation (the sample is transparent), the small differences observed in the fractured surface of this material with respect to the pure system are in agreement with the result of the impact test.

Larger microstructure variations were observed for increasing amounts of additive (Fig. 4). However, the variations in impact energy are almost negligible with respect to the 3% PMMA sample. The reason for this moderate effect is the large segregation of PMMA in a second phase of large complex domains, which do not

contribute markedly to the toughening of material, although they do to the surface quality of the pieces. Besides, this segregation leaves the continuous main phase poorer in PMMA than the nominal percentage added, and consequently, the behavior of this main phase is not much different from that of a low % PMMA modified system.

At 8% PMMA a similar effect takes place, but at the same time microcracking and segregation are clear at this percentage of modification (Fig. 4c), which actually increases brittleness of the material. It should be also noticed the large error bars on the results corresponding to this sample, which is the result of the heterogeneity of the system.

**Untreated Woodflour Addition**

The addition of woodflour increases the impact strength of the unmodified matrix, the untreated woodflour being more effective than the treated one. This behavior was also observed in other systems

**Table 2. Dependence of the Compressive Modulus ( $E_c$ ), Yield Strength ( $\sigma_y$ ), Ultimate Deformation ( $r_u$ ) and Toughness for the Neat Resin and Composite Samples Containing 40 wt% of Woodflour with Different Treatments. Reported Values Are the Average of the Properties of Six Specimens  $\pm$  the Standard Deviation.**

Sample	PMMA (%)	$E_c$ (GPa)	$\sigma_y$ (MPa)	$r_u$ (mm/mm)	Toughness (MPa)
Matrix	0	2.55 $\pm$ 0.15	103.24 $\pm$ 5.25	0.213 $\pm$ 0.026	15.26 $\pm$ 2.82
	3	2.40 $\pm$ 0.04	106.35 $\pm$ 4.36	0.245 $\pm$ 0.033	18.61 $\pm$ 4.19
	5	2.40 $\pm$ 0.09	112.30 $\pm$ 2.56	0.280 $\pm$ 0.014	23.24 $\pm$ 2.00
	8	2.35 $\pm$ 0.39	109.43 $\pm$ 9.00	0.262 $\pm$ 0.013	20.18 $\pm$ 1.78
UC	0	2.72 $\pm$ 0.23	135.95 $\pm$ 5.22	0.168 $\pm$ 0.012	19.98 $\pm$ 1.78
	3	3.01 $\pm$ 0.32	140.28 $\pm$ 5.00	0.167 $\pm$ 0.032	22.02 $\pm$ 1.88
	5	3.08 $\pm$ 0.25	126.90 $\pm$ 4.61	0.176 $\pm$ 0.031	20.04 $\pm$ 0.93
	8	2.97 $\pm$ 0.32	135.83 $\pm$ 6.91	0.177 $\pm$ 0.011	23.24 $\pm$ 2.8
LC	0	2.87 $\pm$ 0.79	130.79 $\pm$ 3.42	0.108 $\pm$ 0.018	12.70 $\pm$ 2.14
	3	2.61 $\pm$ 0.89	124.41 $\pm$ 5.41	0.134 $\pm$ 0.044	12.01 $\pm$ 4.04
	5	2.16 $\pm$ 0.72	124.63 $\pm$ 3.16	0.129 $\pm$ 0.028	10.70 $\pm$ 1.42
	8	2.15 $\pm$ 0.16	132.97 $\pm$ 3.31	0.153 $\pm$ 0.021	17.71 $\pm$ 0.57

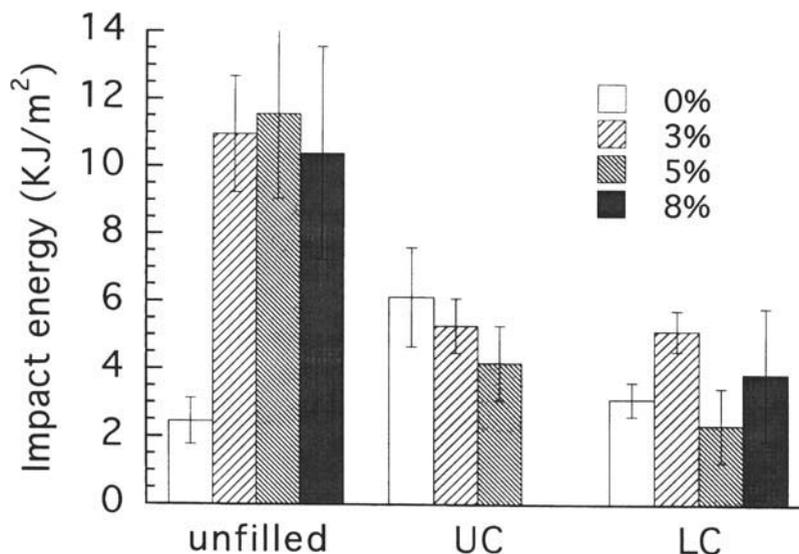


Fig. 7. Impact strength of UP-styrene systems and composites as function of the percentage of PMMA.

formed by brittle matrices filled with rigid fillers, i.e. epoxy resins filled with small glass spheres (31, 32). Kim and Mai (30) indicate that it is generally accepted that for relatively brittle matrix materials, such as epoxy and polyester resins, the fracture toughness of short fiber composites increases systematically with the volume fraction of filler, and the contribution of the matrix toughness to the total fracture toughness is insignificant. Clearly, the degree of enhancement in mechanical properties depends upon a number of parameters, where the volume fraction of filler and the surface treatment are among the most important (33).

Some controversy still exists regarding the precise mechanisms responsible for the observed improvements in toughness in brittle polymers reinforced with rigid fillers. Several authors have suggested that the presence of the rigid particles serves to pin the advancing crack forcing it to bow out and hence increasing the fracture energy (31, 34, 35). Evans *et al.* (36) observed the same behavior in epoxy resins filled with glass particles, and they suggested that substantial debonding of the filler phase may occur around the crack tip creating microcracks and leading to a reduction in the magnitude of the stresses in the process zone.

Although addition of PMMA has a positive effect on the impact properties of unsaturated polyester-styrene networks, and the addition of woodflour has also a moderate positive effect, the addition of PMMA to the untreated filled thermosets do not show an additive positive effect. Probably the addition of a rigid filler alters the morphology of the two-phase system, inhibiting the effect of the LPA component.

Scanning electron micrographs taken from the fracture surface of untreated composites broken in flexion with different PMMA concentrations are shown in Fig. 8. These micrographs shows that the fracture behavior of the matrix changes from fragile (0%–3% PMMA)

to a more ductile one (5% PMMA or more), as the amount of PMMA increases. Figure 8 shows clear evidence of ductile tearing in the 8% PMMA untreated woodflour composite. The macroscopic study of the fracture surfaces suggests that there is plastic deformation of the matrix in the composites. The addition of rigid fillers to an already ductilized matrix has the contrary effect of reducing toughness, as is already known in thermoplastic composites. The brittle unmodified UP-S system is toughened by the addition of a rigid filler with a weak interphase (untreated woodflour composites), while the more ductile LPA modified systems suffer a high reduction of this property with the woodflour addition.

#### Addition of Treated Woodflour

Figure 9 shows the fracture surface of untreated and treated composites at two different PMMA contents. There are pulled-out fibers in the untreated composite longer than those observed in the treated woodflour composites. Thus, one of the major sources of fracture toughness in untreated composites is fiber pullout following interface debonding, as was previously observed in similar systems (30). On the other hand, the fibers visible in the treated composites are shorter, which would suggest that the fracture advanced with little changes in the plane cracking, mostly breaking the fibers instead of pulling them out. It is known that the cracks in composites can propagate preferentially along the fiber-matrix interfaces or transversely right through the fiber and matrix, depending on the properties of the interface relative to fiber and matrix (30). Thus the described behavior would indicate that the adhesion was improved as a result of the chemical modification of the woodflour.

Although the esterification of the woodflour facilitates the mixing and dispersion of the fibers in all the

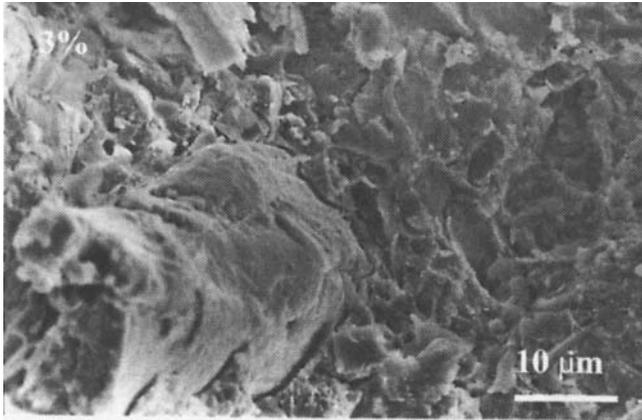
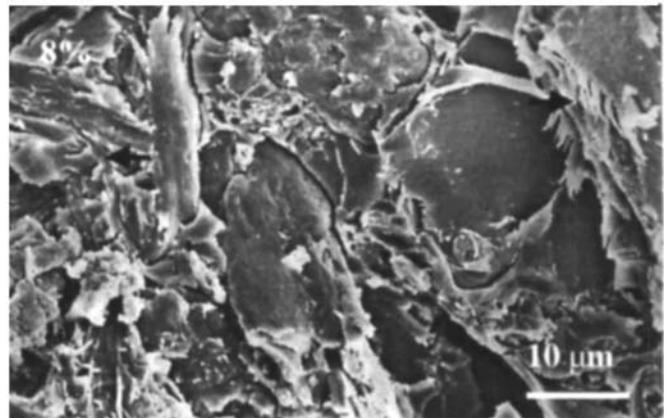
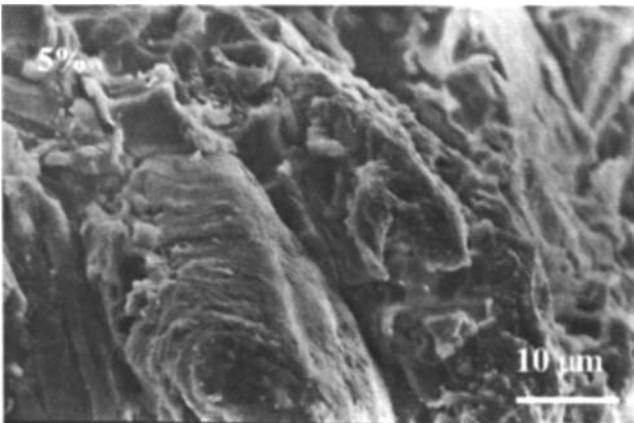


Fig. 8. SEM micrographs of the fracture surface of untreated composites containing different percentages of PMMA.



UP systems and apparently improves interfacial adhesion, it also reduces the modulus of the derived composites as well as the strength of the material and also produces a reduction of the impact strength of the sample. For this system, it seems more convenient to use untreated woodflour, and if surface quality is not a major concern, the use of PMMA should be avoided in the formulation of the composites.

### CONCLUSIONS

High PMMA concentrations lead to a LPA morphology in the UP-S system, which was verified using SEM microscopy.

Woodflour surface was successfully modified using a commercial ASA. The efficiency of the esterification reaction was verified by saponification values and FTIR spectroscopy.

The addition of woodflour to the unmodified polyester resin increases flexural and compressive modulus and the compressive yield stress. It also produces an increase of the impact energy and toughness, but decreases flexural strength and ultimate strain.

The addition of PMMA to the neat UP-S network decreases flexural modulus, but increases flexural strain at break, impact energy and toughness. On the other hand, the addition of PMMA to the untreated filled

thermosets does not show any positive effect, although the addition of woodflour shows also a moderate improvement on the impact properties.

Woodflour plastification due to the chemical treatment could explain the reduced flexural and compressive properties of the composites made from treated woodflour. The improved adhesion between the treated woodflour and the matrix reduces the impact properties of the resulting composites.

### NOMENCLATURE

- PMMA: polymethylmethacrylate
- LPA: low profile additive
- ASA: alkenyl succinic anhydride
- UP: unsaturated polyester resin
- HDPE: high density polyethylene
- PE: polyethylene
- PS: polystyrene
- PVAc: poly(vinyl acetate)
- UC: untreated woodflour composites
- LC: ASA-treated woodflour composites
- DRIFT: diffuse reflectance infrared spectroscopy
- SEM: scanning electron micrograph, scanning electron microscopy
- E': dynamic flexural storage modulus
- tan  $\delta$ : loss tangent

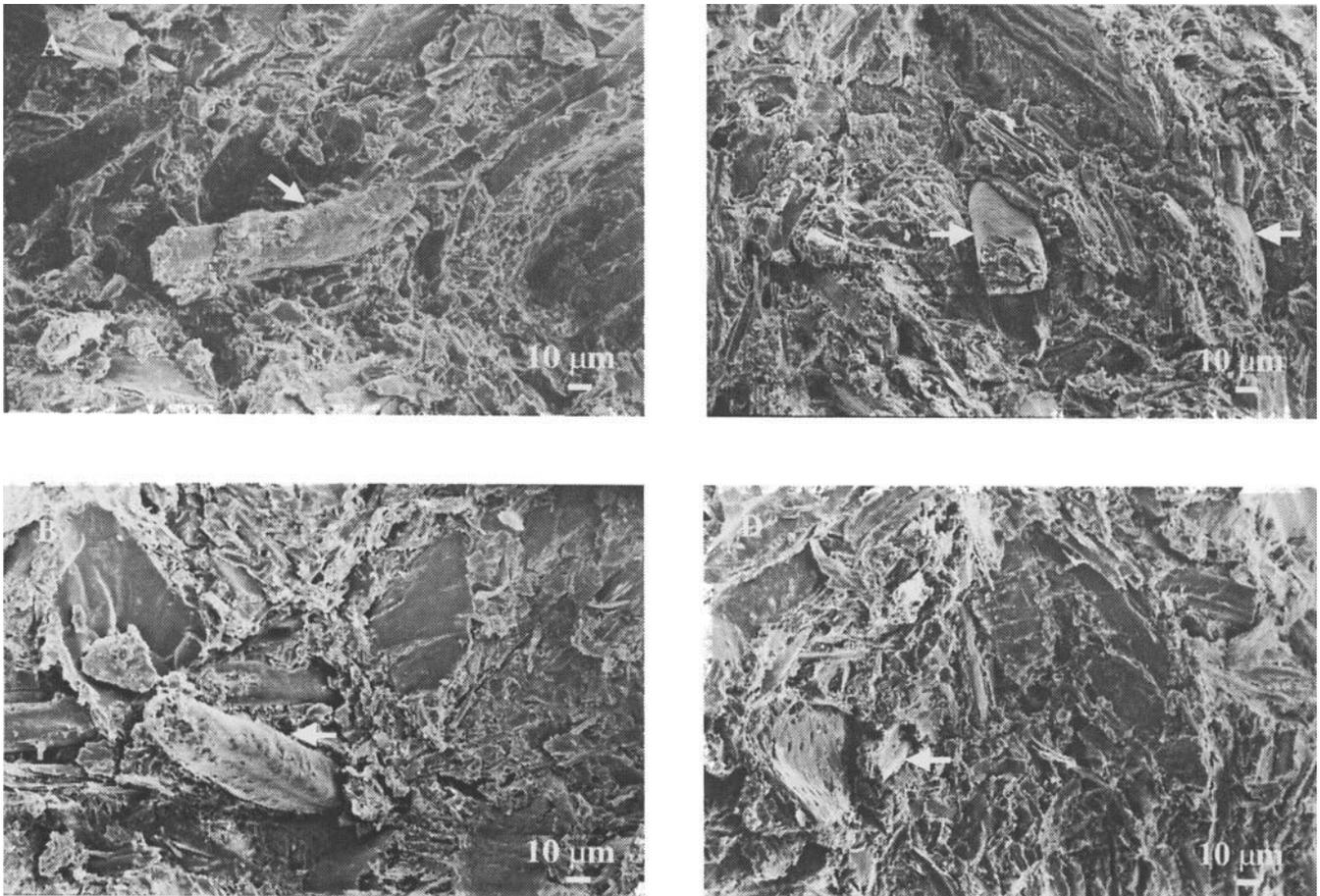


Fig. 9. SEM micrographs of the fracture surface of untreated and treated composites containing different percentages of PMMA. A) untreated woodflour, 3% PMMA; B) untreated woodflour, 8% PMMA; C) treated woodflour, 3% PMMA; D) treated woodflour, 8% PMMA.

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