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Modified woodflour as thermoset fillers
Part I. Effect of the chemical modification and percentage of filler on the mechanical properties

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Abstract

Composites made from an unsaturated polyester/styrene thermoset matrix and esterified woodflour have been prepared and tested. Different degrees of esterification of the wood particles with maleic anhydride were obtained by using different times of reaction, which lead to materials with varied final properties. Water absorption performed on treated particles indicates that they are more hydrophobic than the untreated ones. Flexural, compression and dynamic-mechanical tests were performed on composites to find out an optimum level of chemical modification of the woodflour. Moreover, the relationship between the filler content and the composite final properties was also studied for a selected filler treatment. An important increment in particle dispersion was obtained by modifying the woodflour with maleic anhydride.

Keywords: Woodflour; Composites; Chemical treatment

1. Introduction

The use of vegetable fibers and/or particles as reinforcement fillers for polymeric matrices has been enjoying a continuous growing interest in the past decade from the academic and applied points of view. Applications go beyond the widely used particleboard and efforts are being made to produce insumes for the construction, packaging and automotive industries among others. Because of the shortage of high-quality wood, reconstituted wood materials, such as particleboards, plywood, and fiberboards, are important products of wood-based industries [1]. Moreover, natural fibers are very cheap, easily available, and renewable. Therefore, products based on natural fiber reinforced polymers result in less expensive manufactures than the original matrices [2]. Besides, these products are completely degradable at the end of their use life, by means of biodegradation and/or combustion.

Polymers with particulate fillers or short fiber reinforcements are enjoying a rapid increment in the volume and number of applications because of their good processability. A wide variation of mechanical and physical properties can be developed through an appropriate compounding of polymer and fillers. Fillers are added into the polymer matrix with the aim of improving thermal and mechanical properties. There are, however, some adverse effects: addition of high modulus wood fiber to a plastic matrix usually results in increased brittleness. In other words, the increment of the stiffness and strength of wood fiber composites are obtained at the expense of their toughness and ultimate elongation [3]. However, vegetal fillers/fibers, like sawdust, woodflour, sisal, and bagasse, are utilized because of their low density, coupled to their relatively good mechanical properties and reactive surface. Nevertheless, the main drawbacks of using such fibers in composites are their hygroscopicity and the difficulties in achieving acceptable dispersion levels in a polymeric matrix. These problems are usually reduced by acting on the interface, which properly modified can produce important effects on dispersion quality and adhesion between polymer and filler.

In a previous work, woodflour was chemically modified with maleic anhydride (MAN) in order to improve dispersion/adhesion with a thermoset resin unsaturated polyester (UPE). It was found that the treatment was effective in decreasing the hygroscopicity of the fibers, but the excessive degree of esterification achieved in that study (weight gain = 58%) led to the deterioration of the woodflour,

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adversely affecting its mechanical properties [4]. Thus, lower esterification levels of woodflour were used in this work to obtain an improved dispersion of the fibers in the polyester matrix. Different degrees of esterification of the wood particles were achieved by using different times of reaction. The first step in the modification was an alkaline pretreatment. Several authors suggest that wood alone does not react significatively with etherifying/esterifying reagents since the hydroxyl groups in wood are not readily accessible. Hence, the raw material must be pretreated with NaOH as a swelling agent, and water as a solvating agent [5].

Water absorption, flexural, compression and dynamic-mechanical tests were performed on the composites to find out an optimum relation between the degree of modification and the final properties of the composites. Moreover, the relationship between the filler content and the composite final properties was also studied for one of the esterified woodflours.

2. Experimental

2.1. Materials

The matrix was an UPE based on bisphenol A-fumarate obtained in the form of pellets (RQ 426, Perlinac S. A., Argentine), which was dissolved and crosslinked with styrene in a 60:40 weight proportion with no additives. The initiator was benzoyl peroxide (Lucidol 0.75, Akzo Chemical S. A.), 1.5 wt% with respect to the total reaction mixture. The initiator was added to the polyester–styrene solution in the last 10 min of mixing.

Woodflour from *Eucalyptus saligna* was selected for this work because of its availability and because this wood is widely used in Argentina. 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 μm.

Woodflour was dried at 70°C for 24 h in a vacuum oven and part of it was treated with an aqueous solution of NaOH (10 wt%). The filler was immersed in the solution during 1.5 h at room temperature and then washed several times with distilled water.

Part of the NaOH treated woodflour was immersed in a 0.6 N solution of MAN in xylene and then heated at reflux temperature (140°C) during 4, 7 or 24 h (depending on the desired reaction level). Then, the esterified wood particles were separated from the xylene solution and intensively washed with distilled water in order to eliminate the unreacted anhydride. Finally, the woodflour was dried at 70°C in a vacuum oven until constant weight was achieved.

2.2. Compounding and molding

The filler and the solution of UPE in styrene were mixed in a Brabender type mixer 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 force of 6.4 ton during 1.5 h. After that time, it was post-cured in an oven for 2 h at 150°C. In order to save material, in some cases, the test specimens were cut from small plates (metal mold, 30 mm of diameter and about 3 mm of thickness).

Samples of neat resin were obtained by pouring the mixture into a 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.

Three different types of mixtures woodflour/polymer were prepared:

(a) polymer—untreated woodflour (WC);
(b) polymer—NaOH treated woodflour (NaOH); and
(c) polymer—esterified woodflour (MAN).

In all cases the weight percentage of woodflour was indicated between brackets, i.e. WC(40) indicates 40 wt% of untreated woodflour, and the level of esterification was indicated before the word MAN, i.e. 10MAN(40) indicates a composite made with 40 wt% of woodflour treated with MAN with a weight gain of 0.1 g MAN/g neat woodflour.

2.3. Characterization

Woodflour ester content. The ester content of the MAN modified woodflour was calculated from the acid and saponification values using the techniques described elsewhere [6].

Water Retention Value (WRV). Water retention is a technique used in the characterization of textile fibers (ASTM D 2402-90). It was used in this work in order to reveal changes in the hygroscopicity of the samples, due to the chemical treatments. Fibers were immersed in distilled water for 5 min and then, separated by centrifugation 15 min at 1000*g*(gravity acceleration). The technique measures the water that can not be extracted by mechanical means. Water retention values are calculated as the difference between the weight of the wet and dried samples ratioed by the latter.

Equilibrium Moisture Content (EMC). Humid environments were prepared in hermetic boxes maintained at 20 ± 2°C and containing flasks with aqueous solutions of sulfuric acid (18 and 38 wt%) to ensure 90 and 60 of relative humidity (RH), respectively. Treated and untreated woodflour samples of about 1 g were dried until constant weight prior to be exposed to wet environments. The weight changes due to moisture absorption were recorded until no change was detected. The EMC was calculated as the difference between the final and the initial (dry) weight, ratioed by the later and expressed as percentage.

Scanning electron microscopy (SEM). The SEM photographs of the surface of untreated and treated wood particles

Table 1
Acid number, saponification value (both in mg KOH/g sample) and ester content of MAN (in gMAN/100 g woodflour) of the *E. saligna* woodflour as a function of the esterification reaction time

Woodflour Treatment	Acid number	Saponification value	Ester content of MAN
NaOH	Negligible	82.3 ± 0.6	–
10MAN (4 h)	75.3 ± 0.4	214.1 ± 6.7	10.96
30MAN (7 h)	120.9 ± 3.3	337.2 ± 1.8	30.58
58MAN (24 h)	229.0 ± 0.7	522.1 ± 18.0	58.30

and the fracture surface of the composites were taken with a scanning electron microscope Philips model SEM 505. The samples were previously coated with gold.

2.4. Mechanical tests

2.4.1. Dynamic mechanical tests

A Perkin–Elmer dynamic mechanical analyzer (DMA 7) was used in these experiments to obtain the storage modulus (E'), and loss tangent (tan δ) of the samples. The tests were carried out using the temperature scan mode, and the three point bending fixture with a specimen platform of 15 mm length and 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, and the linear dimensions were measured up to 0.01 mm.

2.4.2. Compression tests

The 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).

2.4.3. Bending tests

Three point bending tests were carried out at room temperature at a crosshead speed of 1 mm/min and tested using a span of 50 mm in a Shimadzu Autograph S-500-C Universal testing machine. The composites were cut from the molded plates (transversal area of 13×3 mm^2). The neat resin specimens were cut to a transversal area of 12×2.4 mm^2 and tested using a span of 40 mm (procedure A, ASTM D 790-86).

Table 2
EMC (%) and WRV for woodflours with different treatments

Treatment	EMC (%)		WRV
	60 RH	90 RH	
Untreated	11.28	14.72	4.80 ± 0.30
NaOH	21.69	29.89	5.72 ± 0.18
10MAN (4 h)	9.81	12.91	3.41 ± 0.07
30MAN (7 h)	8.54	10.38	3.29 ± 0.02
58MAN (24 h)	9.80	12.22	3.63 ± 0.21

3. Results and discussion

3.1. Chemical modifications of the filler

The efficiency of the MAN chemical modification after alkaline pretreatment was verified in different ways. The ester content of the MAN modified woodflour was calculated from the acid and saponification values listed in Table 1. These values indicated that the degree of chemical reaction between the –OH groups of woodflour and the maleic anhydride (MAN) (i.e. g of maleic anhydride/100 g of neat woodflour) is a function of time at a given temperature, as was pointed out previously by other authors [7].

Table 2 shows the EMC (at 60 and 90 RH) and the WRV of the untreated and treated woodflours. It is noticed that the hygroscopicity of the woodflour is increased when it is treated with alkali, but the esterification reduces the OH concentration (substitution of the hydroxyl by maleate groups due to the esterification of the woodflour) and thus, reduces the water sorption. It is noticed that EMC and WRV decrease with the level of the esterification reaction. These results are in correspondence with that found for other authors. For example, Gauthier et al. [8] affirm that if cellulose fibers are treated (by an esterification reaction) with small molecules, which penetrate in the bulk of the fiber, a better control of the water sorption, and therefore, of the dimensional stability of the fibers is achieved. However, our results also show that if an excessive degree of chemical modification is achieved (24 h of treatment), the hygroscopicity of the MAN treated samples begins to increase. Since, the water uptake of natural fibers is related to the number of hydroxyl groups, which in these particles are extensively reacted, the high values of EMC have to be attributed to a high degree of deterioration of the fibers instead, which was verified by optical microscopy.

The surface topology of the wood particles was studied by SEM, which indicates an uneven surface for untreated samples as shown in Fig. 1. It can be observed that certain globular protrusions are present on the surface of untreated fibers. When the fibers were treated with MAN, these protrusions practically disappeared, leading to the formation of a rather smooth surface as MAN concentration increases (MAN acting as a coating layer, evenly distributed onto the surface). The micrographs also suggest that some plasticization of the particles may have taken place, since they show a structure smooth and even. The fiber surface is

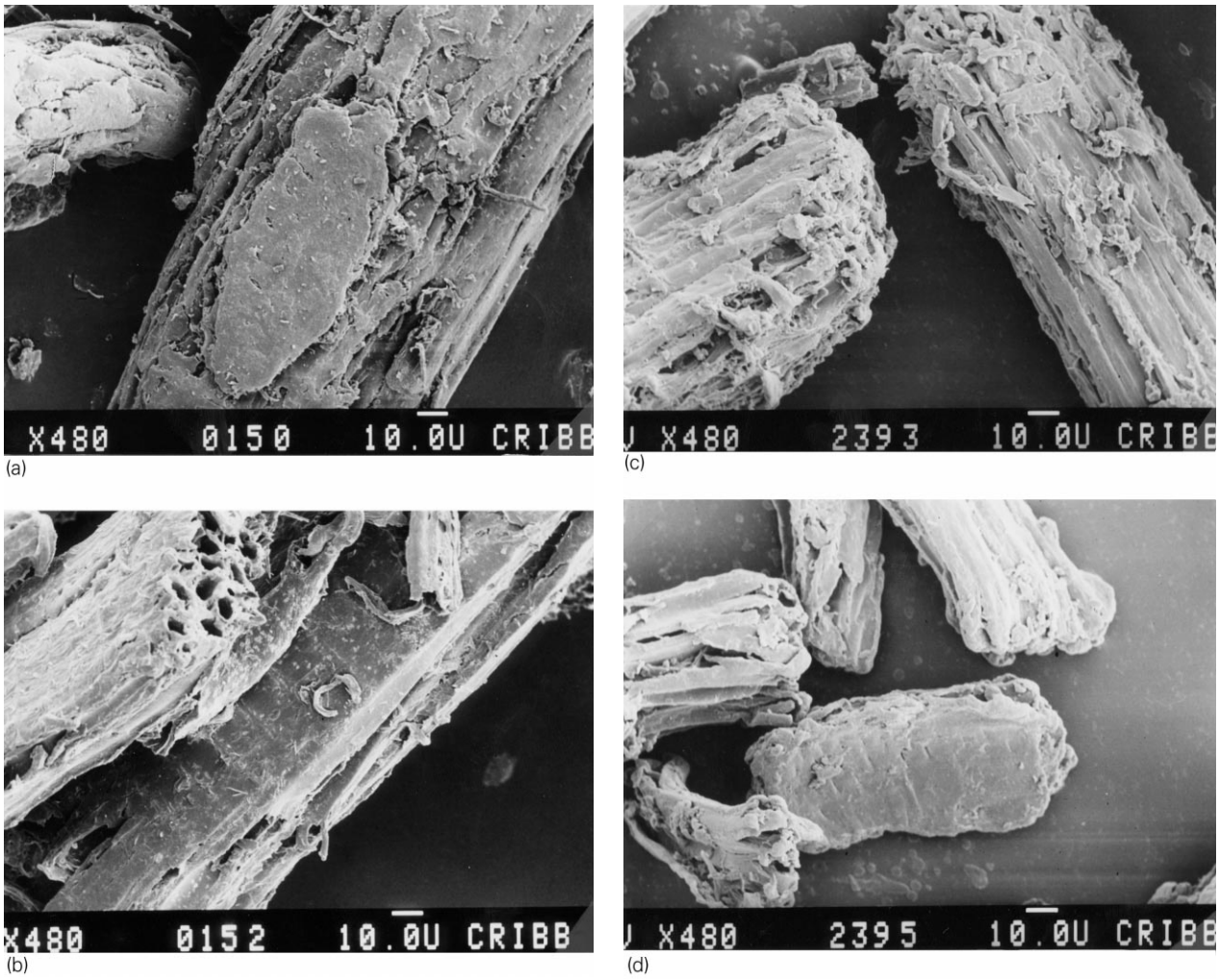


Fig. 1. Scanning micrographs of woodflour particles (× 480). Largest side of micrographs correspond to 185 μm. (a) Untreated: uneven surface with globular protrusions. (b) NaOH treated: rough surface. Notice fibrillation of fibers and empty capillaries. (c) 10% MAN treated: rather smooth and even surface, plasticized particles. (d) 30% MAN treated: smooth and even surface, plasticized particles.

also severely affected by the alkaline treatment. Alkaline treated particles exhibit a very rough surface in comparison with non-treated or MAN treated particles and fibrillation of fibers is also recognized. Takase and Shiraishi [9] argue that it is expected that this fibrillation leads to an enlargement of the surface area of the fiber and consequently, to an enhancement of the adhesion between the polymer matrix and filler. Mercerization treatment is also believed to improve the fiber surface adhesive characteristics by removing natural and artificial impurities, which should produce a rough surface topography [10].

Table 3
Dependence of the compressive modulus (E_c), yield strength (σ_Y), ultimate deformation (r_u) and toughness for samples containing 40 wt% of woodflour with different treatments

Treatment	E_c (GPa)	σ_Y (MPa)	r_u	Toughness
Matrix	2.5 ± 0.1	111.4 ± 4.1	0.305 ± 0.074	33.7 ± 11.2
WC(40)	3.9 ± 0.3	140.9 ± 2.6	0.084 ± 0.027	10.5 ± 3.8
NaOH(40)	3.7 ± 0.2	130.1 ± 11.8	0.099 ± 0.017	11.8 ± 1.13
10MAN(40)	4.2 ± 0.3	138.2 ± 4.8	0.168 ± 0.041	26.4 ± 6.5
30MAN(40)	4.1 ± 0.1	136.8 ± 0.8	0.214 ± 0.038	30.7 ± 7.4
58MAN(40)	3.9 ± 0.3	138.6 ± 6.3	0.207 ± 0.075	28.5 ± 13.5

3.2. Composites

3.2.1. Effect of the chemical modification of the filler

Table 3 summarizes the dependence of the compressive modulus, yield strength, ultimate deformation and toughness for samples containing 40 wt% of woodflour with different treatments. The toughness in compression was calculated as the area under the true stress–strain curve [11]. These results indicate that the incorporation of woodflour to the resin increases the compression modulus and the yield stress but decreases the ultimate deformation and the toughness in all cases.

There were no large differences between the modulus and yield stress values of WC and MAN composites, but a clear

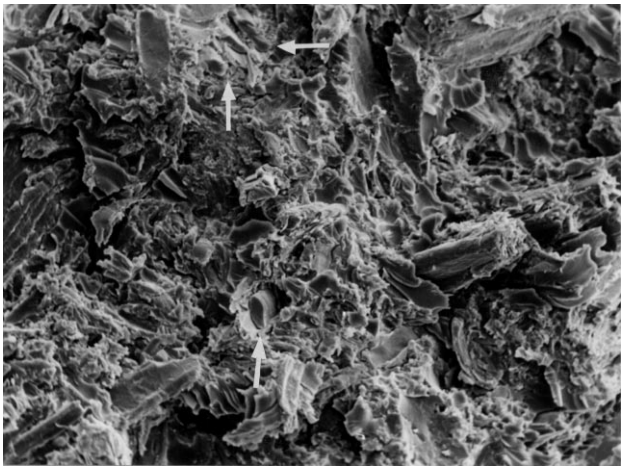


Fig. 2. Scanning micrographs of 30MAN(40) composites. Surface fracture from compressive test. Largest side of micrograph corresponds to 182.5 μm. Arrows indicate places where the fibers cell walls were deformed due to the applied load.

improvement in ultimate deformation and toughness was noticed. For example, in the 30MAN(40) samples, the reduction of the toughness with respect to the matrix is less than 9%, while the reduction for the WC(40) specimens is larger than 65 wt%. No improvement was found when the fibers were esterified during 24 h instead of 4 or 7 h. This behavior could be attributed to the deterioration of the fibers due to the severe reaction conditions. Moreover, the important weight gain could also change severely the chemical structure of the wood particles. Thus, the hydrogen bonding present in wood, which provides a significant portion of the strength of the fibers, is reduced due to the esterification with MAN, adversely affecting the woodflour mechanical properties. It is also noticed that the pretreatment of the woodflour with alkali reduced the compression strength of the composite. This result shows the opposite trend to that reported by Bisanda and Ansell [12] for sisal – epoxy composites (21% rise in compressive strength with fiber volume fraction = 0.40). They state that mercerization greatly improves the resin pick up or wettability of the fibers. They believe that this treatment results in an improvement of the interfacial bonding by giving rise to additional sites of mechanical interlocking, hence promoting resin/fiber interpenetration.

Table 4
Dependence of the flexural modulus (E_b), ultimate strength (σ_u) and ultimate deformation (r_u) for samples containing 40 wt% of woodflour with different treatments

Sample	E_b (Gpa)	σ_u (MPa)	r_u ($\times 1000$)
Matrix	2.9 ± 0.2	93.5 ± 0.6	36.12 ± 2.40
WC(40)	5.44 ± 0.22	54.06 ± 1.96	9.94 ± 0.37
NaOH(40)	5.02 ± 0.05	45.05 ± 3.48	8.97 ± 0.69
10MAN(40)	5.23 ± 0.22	52.82 ± 4.79	10.14 ± 1.28
30MAN(40)	5.26 ± 0.26	52.28 ± 7.42	9.9 ± 0.96
58MAN(40)	4.28 ± 0.21	44.46 ± 6.01	10.39 ± 1.40

The presence of fibers ends within the body of a short fiber composite means that there is considerable stress concentration taking place near the fiber ends where microcracks are formed and fibers debond from the matrix even in ductile matrices. The interactions between neighboring fibers constrain the matrix flow significantly, resulting in a deteriorating effect of matrix embrittlement. Thus, the reduction of the toughness of WC(40) with respect to that of the matrix is associated with the matrix embrittlement by constraint imposed by the stiff non treated particles and the interaction between neighboring short fibers. Matrix fracture is predominant over other failure mechanisms, such as interfacial debonding and fiber pull out, because of the very short fiber length. On the other hand, the plasticizing effect of MAN treatment on the fibers can also be responsible for the increment in the toughness of the treated composites. MAN treated fibers could suffer larger plastic deformation than untreated fibers, and if a large-scale fragmentation of brittle matrix is accompanied by plastic deformation of fiber, substantial amounts of energy would be required under these circumstances [13]. The plasticizing effect on woodflour due to the chemical modification is also supported by SEM microscopy. Fig. 2 shows the fracture surface of a 30MAN(40) sample tested in compression. The arrows indicate places where the fiber cell walls are deformed due to the applied load.

Table 4 shows a comparative study of the flexural mechanical properties of the composites made with 40 wt% of woodflour with different treatments. Compared to the original resin, the flexural modulus is improved with the addition of the filler, with only small differences due to treatment. The lowest values of E_b and σ_u corresponds to 58MAN(40), probably due to the deterioration of the fibers and probable plasticization occasioned by the high degree of esterification. The ultimate stress and the elongation at break are smaller than that of the neat polymer for all the composites. No additional improvement was found with respect to WC when the MAN treatment was applied to the filler. The relative low strength of the NaOH composites (compared with untreated composites) indicates that the increment of the woodflour interfacial area due to the mercerization step [14] is not the only factor that affects the mechanical anchorage of the matrix in the filler.

It is known that fillers with higher stiffness than the matrix can increase the modulus of composites, but generally cause a dramatic decrease in the elongation at break. 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 [15,16]. The important decrease in elongation at break noticed in all the composites (compared with the pure resin) suggests a good degree of interfacial compatibility between particles and resin in all the materials, independently of the treatment of the woodflour.

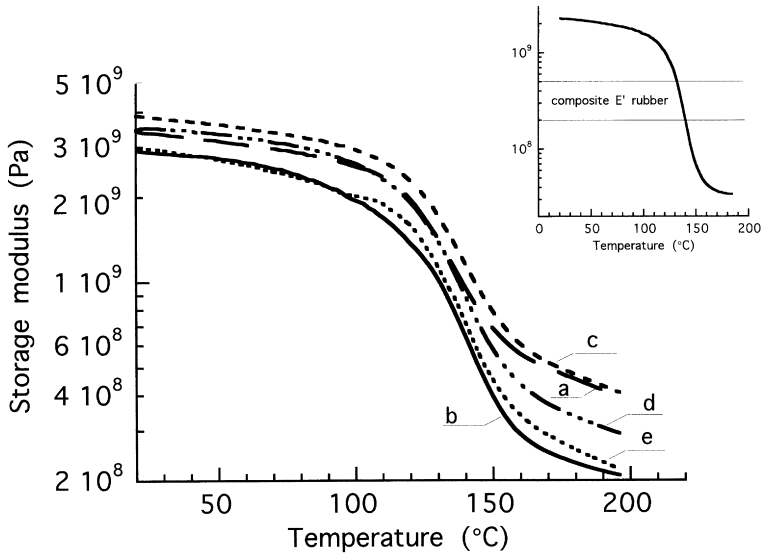


Fig. 3. Temperature scans of E' of 40% composites. Inset: neat matrix. (a) — — WC, (b) — NaOH, (c) – – – 10MAN, (d) – - - - — 30MAN, and (e) –– 58MAN.

The effect of the chemical treatments of the filler on the dynamic mechanical properties was also studied. Fig. 3 shows the classical steep drop of E' with temperature corresponding to the transition glass–rubber state of the UPE resin, which occurs about 140°C (see inset) and the variation of the storage modulus with temperature for composites containing 40% of untreated, NaOH, 10MAN, 30MAN and 58MAN treated woodflour. All the composites show the expected steep decrease of E' with the temperature when the matrix undergoes the glass–rubber transition. All fillers have a large effect on the rubbery modulus of the system, due principally to the fact that the ratio between the modulus of the filler to the modulus of the matrix is larger when the matrix is in the rubber state instead of in the glassy state. The rubbery modulus of the composites decreases in the following order: 10MAN $\approx$ WC $>$ 30 MAN $>$ 58MAN $>$ NaOH. Composites made with untreated woodflour and 10MAN woodflour (low degree of esterification), show similar E'. However, if higher degrees of esterification are considered there is a decreasing trend in E' as the MAN gain in the woodflour increases. This may be related with the plasticizing effect of the esterification, which reduces the wood bending modulus at these high temperatures.

Table 5 shows the temperature of the peak of tan δ for samples containing 40 wt% of woodflour with different treatments. The peak of tan δ of all these specimens (including the matrix) appears at approximately the same temperature. This is an indication of the absence of free MAN in the composites made with esterified woodflour, because unattached MAN would have a plastificant effect on the matrix [16].

From the above results it can be concluded that the short time esterification reaction improved the performance of the woodflour–polyester composites, at least in compression and no extra benefits can be deduced from the use of larger reaction times for the modification of the filler. No enhancement of the other mechanical properties (flexural, dynamical at room temperature) is found when the MAN composites are compared to the WC.

3.3. Effect of the filler content

A very important observation during preparation of the samples was the impossibility to obtain composites with more than 40 wt% of NaOH treated woodflour or 50 wt% of untreated woodflour [16]. At these filler loads, there is macroscopic decohesion of the composite components, which makes especially difficult to cut samples from the molded plates. Nevertheless, it is possible to cut specimens from composites made up to 75% of 10MAN woodflour. The introduction of a coating onto fibers surface improves dispersion of the particles, reducing agglomeration by reducing the hydrogen bonding that holds them together. The 10MAN molded samples exhibit a high degree of macroscopic homogeneity within the entire range of fiber concentration covered by these tests.

Although the MAN treatment of the woodflour did not

Table 5
Temperature of the tan δ peak for samples containing 40 wt% of woodflour with different treatments

Sample	WC(40)	NaOH(40)	10MAN(40)	30MAN(40)	58MAN(40)
Tan δ	140.9 ± 0.8	144.2 ± 0.5	140.1 ± 0.8	141.1 ± 1.1	142.6 ± 2.7

Table 6
Dependence of the compressive modulus (E_c), yield strength (σ_Y), ultimate deformation (r_{ul}) and toughness for samples containing different wt% of woodflour 10MAN treated

Filler wt%	E (Gpa)	σ_Y (MPa)	r_{ul}	Toughness
40	3.3 ± 0.4	128.3 ± 4.8	0.199 ± 0.050	22.0 ± 6.5
50	3.3 ± 0.2	169.7 ± 0.8	0.122 ± 0.018	18.8 ± 1.4
60	3.9 ± 0.4	172.8 ± 8.2	0.137 ± 0.011	14.3 ± 6.7
65	4.5 ± 0.2	156.2 ± 3.0	0.081 ± 0.005	8.9 ± 0.5
70	4.1 ± 0.4	128.1 ± 3.2	0.065 ± 0.007	5.2 ± 0.3
75	3.0 ± 0.7	63.9 ± 12.3	0.035 ± 0.004	1.1 ± 0.1

produce major improvement in mechanical properties of the composites at 40% load, it is clear that the 10MAN or 30MAN treated samples are a successful combination of enhanced dispersion/compressive properties and low cost filler treatment (only 4 or 7 h of reaction). 30MAN composites shows a slightly better performance in compression, but 10MAN composites require a shorter time of treatment. Thus, in this section the properties of 10MAN composites at different filler content will be evaluated.

Table 6 shows the dependence of the compressive properties of 10MAN composites as a function of the concentration. The samples tested were cut from small plates, thus the

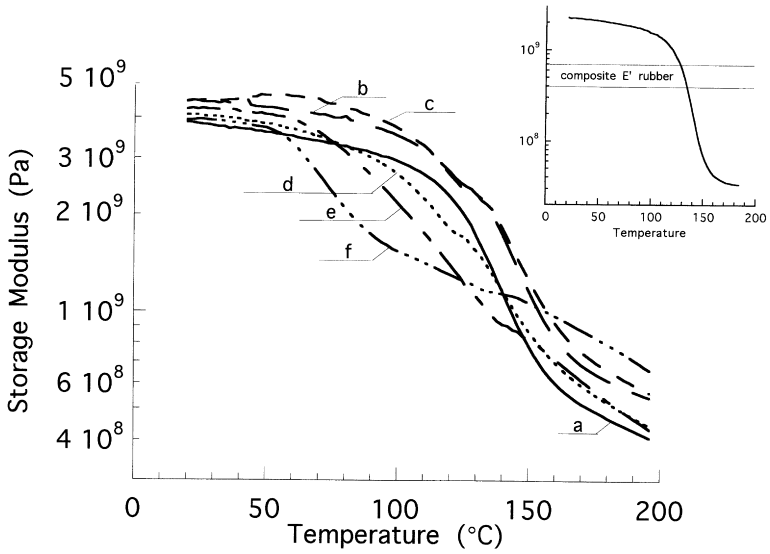


Fig. 4. Temperature scans of E' of 10MAN composites. Inset: neat matrix. (a) — 40%, (b) — — 50%, (c) – – – 60%, (d) - - - ; 65%, (e) — – — 70% and (f) —- – - — 75%.

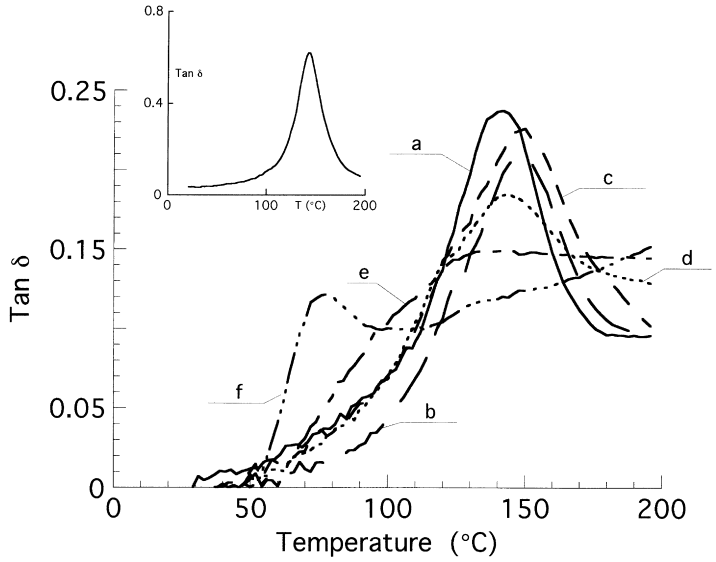


Fig. 5. Temperature scans of tan δ of 10MAN composites. Inset: neat matrix. (a) — 40%, (b) — — 50%, (c) – – – 60%, (d) - - - 65%, (e) — – — 70% and (f) — - – - — 75%.

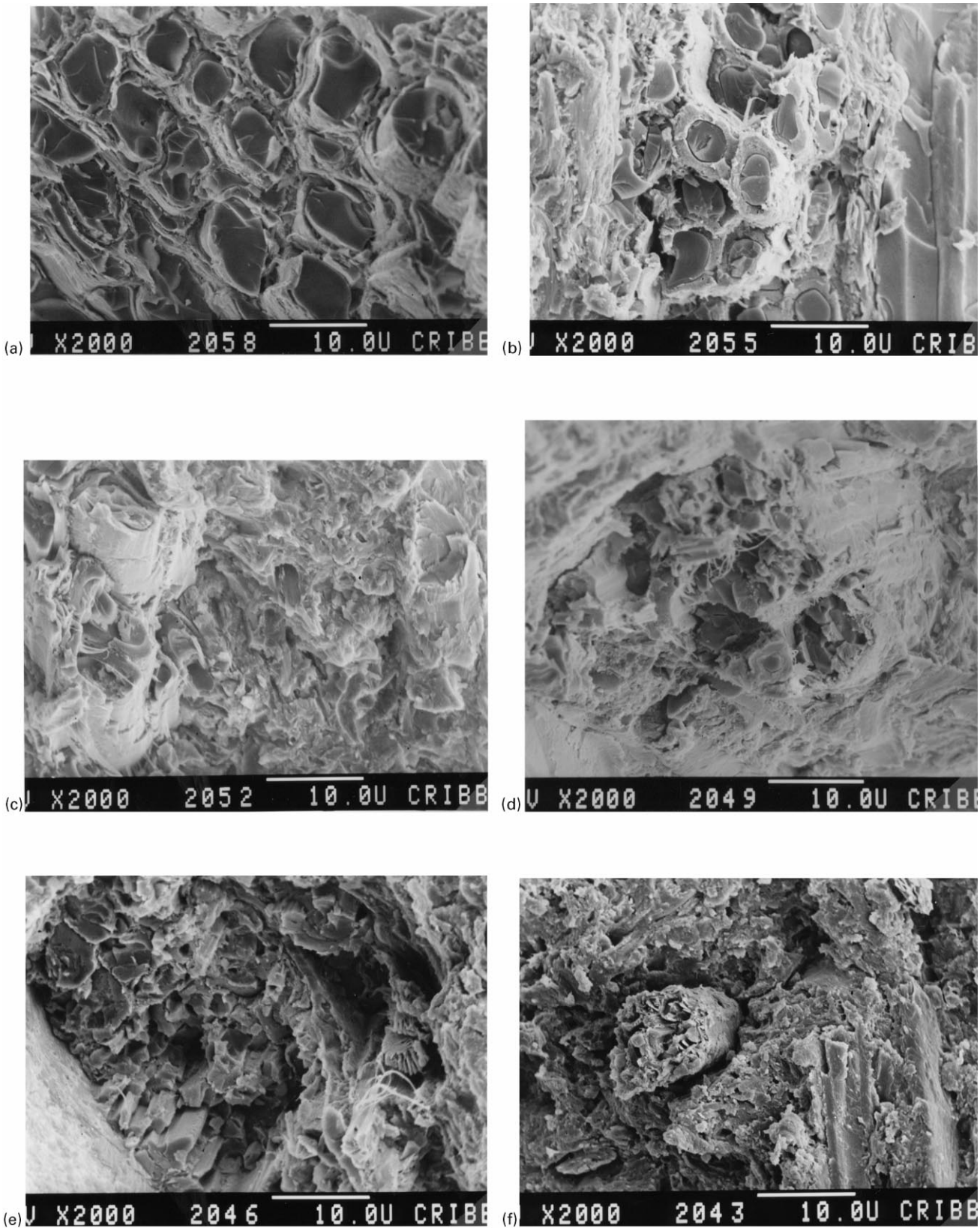


Fig. 6. Scanning micrographs of 10MAN composites. Largest side of micrographs correspond to 47 μm. (a) 40%, (b) 50%, (c) 60%, (d) 65%, (e) 70% and (f) 75%. All photos do not show indication of fiber pull out, which means good adhesion between matrix and fiber. Notice wood capillaries completely filled with matrix and matrix fragile fracture in micrographs (a)–(c). Notice several empty capillaries (matrix insufficient to wet completely the filler) and agglomeration of wood particles in micrographs (e) and (f).

results are not directly comparable with those of Table 3. However, the measured density of these specimens is comparable to that of the samples molded from larger plates (e.g. for 10MAN(40) $\rho = 1.26 \pm 0.018$ for large plates and $\rho = 1.28 \pm 0.001$ for small plates)

Compressive modulus shows a steady increase with the filler content until a maximum, at 65 wt% of treated woodflour, and then it decreases. A similar behavior it is noticed for the yield stress, but the maximum corresponds to 60 wt% of woodflour. Therefore, the compressive modulus for 10MAN(65) is 81% higher than that of the neat resin, while the ultimate stress for 10MAN(60) is 25% higher than that of the matrix. On the other hand, the ultimate deformation and toughness decrease steadily with the increment in woodflour content, which is consistent with the behavior of polymers reinforced with rigid fibers.

It is clear that the MAN treatment allows us to use higher woodflour loads because of the improved dispersion, which besides improves properties, leading to a potentially cheaper product.

The variations of the dynamic flexural storage modulus, E', and the loss tangent (tan δ), with the temperature for samples containing 0, 40, 50, 60, 65, 70 and 75% by weight of 10MAN treated woodflour are shown in Figs. 4 and 5, respectively.

Fig. 4 shows that the addition of a rigid filler increases substantially the modulus of the composite in the rubber phase (as was previously mentioned), and thus the E' change in the transition is noticeably smaller than that for the neat resin. The storage modulus of the composites increases with increasing filler contents up to 60% of woodflour and then decreases for higher loads in the whole temperature range studied, but it is always greater than the matrix one. No tendency was found for the behavior of concentrated samples for temperatures above T_g, which could be attributed to problems of agglomeration of particles due to the high loads used. In all cases the rubbery moduli of the composite materials are at least one order of magnitude larger to that of the neat resin. At the concentrations used in this work, this effect is due to the fact that load transfer in the composite occurs mainly 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.

Fig. 5 shows that the maxima of tan δ for 10MAN(40), 10MAN(50), 10MAN(60) and 10MAN(65) appear at approximately the same temperature. Small variations could be attributed to different residual moisture contents, which are possible in dried samples because of the different loads of woodflour. When filler content continues to increase, the tan δ peak becomes more flat and appears at lower temperature than that of the neat resin. In the case of 10MAN(75) composite the matrix transition appears only insinuated and a peak at approximately 76°C is observed. This peak is assigned to a transition of the woodflour particles. The damping of the rigid filler is very low compared with that of the polymer, hence at low concentrations of filler, MAN treated woodflour transitions are masked by the glass–rubber transition of the matrix. At high fiber concentrations, more than 65 wt%, the transition of the treated woodflour becomes more noticeable and it is evident at 75 wt% content.

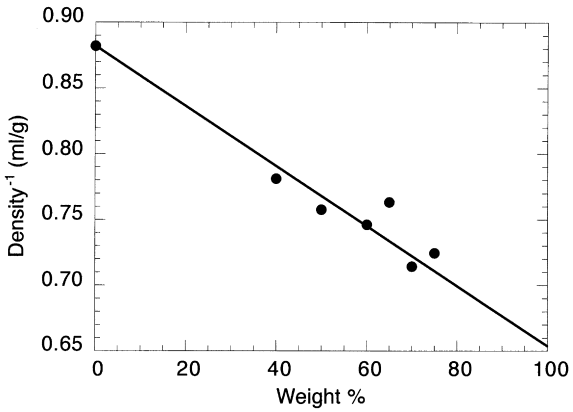
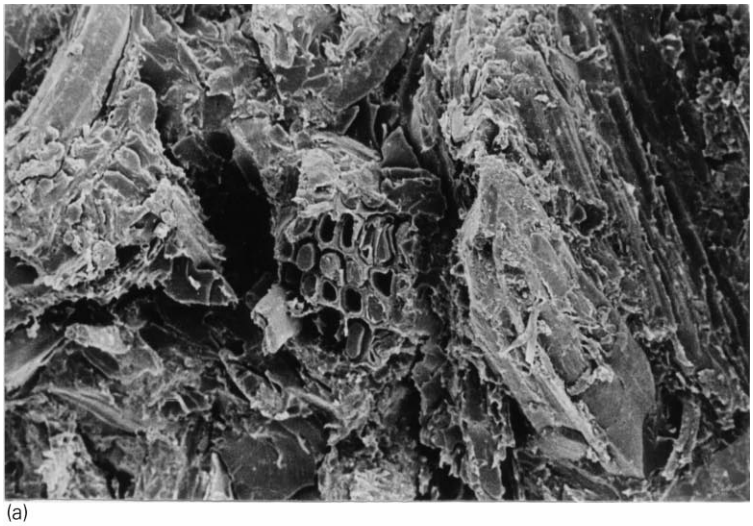


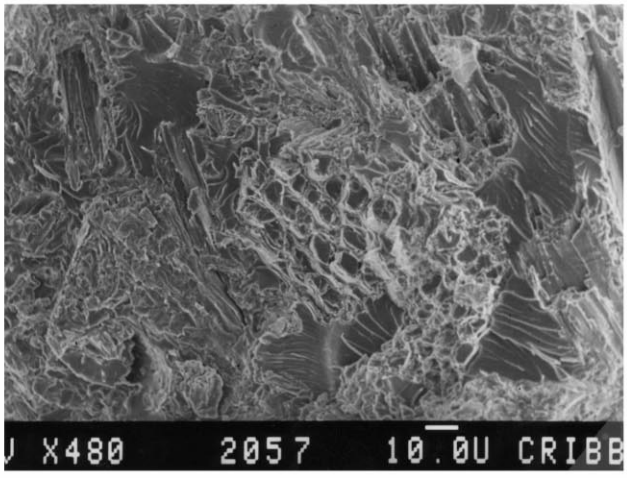
Fig. 7. 1/Density vs. wt% of 10MAN composites. ● experimental measurements; — theoretical values given by rule of mixtures.

The thermal dynamic-mechanical behavior of a dry *E. saligna* sample was presented in a previous work [17]. Wood devoid of moisture exhibited a broad thermal transition in the range of 20–90°C and a steep increase in tan δ at about 220°C. These transitions were also studied by Kelly et al. [18] and they found similar thermal transitions in the range of −30–140°C, depending on the wood species and the moisture content of the samples.

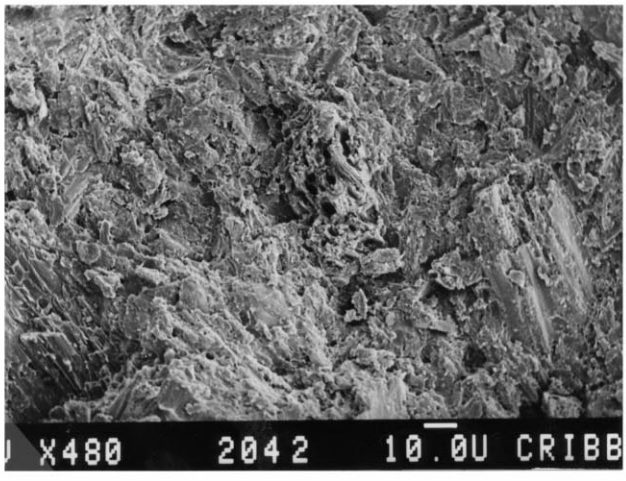
Fig. 6 shows the micrographs (SEM) of fracture surface for the composites made with 10MAN treated woodflour. Fiber pull out is not observed in any case, which indicates that there is good adhesion between fiber and matrix. It can be observed that there are no important differences between the fracture surface of composites with 40, 50 and 60 wt% of woodflour. In all cases, the capillaries of the wood are filled completely with the resin, which exhibit fragile fracture. However, the surface is substantially more irregular than the fracture surface of the neat UPE resin. Wood particles are unaltered. The behavior of 70–75% composites is different: the amount of matrix is insufficient to join the filler particles together, there are fibers with empty capillaries and agglomeration of wood particles. The presence of empty capillaries in the most concentrated samples does not have an important effect on the density of the composites. Fig. 7 shows the inverse of the measured density of 10MAN composites as a function of the woodflour wt%. The straight line shows the behavior expected if the density of the composites follow the rule of mixture (ρ matrix = 1.1335, experimental value and ρ cell wall = 1.53 [19]). Selecting the density of the cell wall as the expected density of the woodflour means that no voids are expected in the composite. The experimental data fall very close to the theoretical straight line in Fig. 7 indicating that the amount of voids is



(a)



(b)



(c)

Fig. 8. Scanning micrographs of composites (× 480). Largest side of micrographs correspond to 185 μm. (a) WC(40): notice several empty capillaries attributed to a poor dispersion of the fibers into the matrix. (b) 10MAN(40): notice all capillaries completely filled with the matrix, due to the improved dispersion of the fiber into the matrix. See also Fig. 6a, which is a magnification of the central zone (wood fiber) of (b). (c) 10MAN(75): notice empty capillaries indicating that the resin is insufficient to wet all the wood particles.

negligible, and that the existing voids had no detectable effect on the composite density, even at high loads.

Fig. 8 shows SEM micrographs at lower magnification (×480) of WC(40), 10MAN(40) and 10MAN(75). It is noticed that there are several empty capillaries in the WC(40) samples, while all capillaries of 10MAN(40) specimens are filled with resin. This behavior is attributed to the improved dispersion obtained with MAN treatment, since the concentration in both samples is the same. On the other hand, the empty capillaries found also in 10MAN(75) are attributed to the high concentration of filler. In this case, the resin is insufficient to wet all the fibers and get into the capillaries.

4. Conclusions

The degree of chemical modification between the –OH> groups of woodflour and MAN can be varied by changing the reaction time. The esterification of the woodflour reduces the water sorption respect to that of the untreated or NaOH treated woodflours. SEM microscopies indicated the formation of a rather smooth layer of the surface of the treated fibers as MAN concentration increases.

The most important effect of the chemical treatment of filler is the improved dispersion observed for the esterified particles. This allows us to use high concentration of woodflour in the composites. Composites made from non-treated woodflour can be loaded up to about 50% by weight of filler, while this value is only 40% for the alkaline treated woodflour composites and can reach about a 75% for the MAN treated woodflour. This would allow us to reduce the cost of the composite, since less resin is required in the manufacture of the piece. MAN composites show a clear improvement in ultimate deformation and toughness (calculated from compressive tests) when compared with WC or NaOH composites.

The flexural and compressive properties of composites made with woodflours with different degrees of esterification did not show important differences, thus, it is possible to use a short time in the chemical treatment.

SEM micrographs indicated that the matrix penetrated into fiber capillaries. The opposite behavior is common when working with thermoplastic matrices. The principal reason is the low viscosity (about 200 cp) of the UPE resin during the compounding step, which facilitates the filling of the capillaries. At high concentrations of MAN treated woodflour the resin is insufficient to wet completely the filler, hence empty capillaries were found. The presence of these “voids” do not influence the expected density of the composites. Empty capillaries were also found in relatively low concentrated composites, e.g. WC(40), because of the lower dispersion of the untreated particles in the resin.

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