Mechanical Properties of Woodflour Unsaturated Polyester Composites

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ABSTRACT: Agrowastes and woodflour are a potential and attractive alternative of cheap reinforcement for brittle polymeric materials because they can reduce costs and, at the same time, improve certain properties. On the other hand, their high moisture sorption and low microbial resistance are disadvantages that need to be considered and, as far as possible, corrected. Polyester resins are widely used throughout the world, and can be processed with reinforcing agents very easily. In this work, the effect of the addition of chemically modified woodflour on the final properties of unsaturated polyester composites was studied. The filler was treated with an alkaline solution to increase its interfacial area and then modified with maleic anhydride (MAN) under severe reaction conditions (140°C, 24 h). No improvement in the mechanical behavior of polyester-woodflour composites was found when particles were only alkali treated, while the composites prepared with MAN-treated woodflour offered better performance under compressive loads. Simple mechanical models used to fit the experimental flexural behavior indicated that a good compatibility between filler and matrix was obtained regardless of the kind (treated or untreated) of reinforcement used. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2121-2131, 1998

Key words: woodflour composites; mechanical properties; surface treatment; mathematical approach; vegetable fillers

INTRODUCTION

Agrowastes and woodflour have played an important role in the plastic industry. The field of woodflour filled composites is, of course, very old, being that woodflour-filled phenolics-based composites one of the oldest commercial materials. The earliest phenolics were mixed to woodflour to reduce cost and improve resin processing. As an example, commercial particle boards used in the fabrication of furniture have a modulus of elasticity between 2.8 and 4.5 GPa, with a flexural strength varying around 20 MPa.¹ Presently, natural vegetable fibers/particles are used in composites made from other polymeric matrices when high strength and stiffness are not the first priority. Natural vegetable fillers reduce the total mass of a given composite volume, because they have low density. This kind of filler is a potential and attractive alternative of cheap reinforcement for polymeric materials. In general, its use reduces costs and at the same time improves certain properties.² However, lignocellulosic materials present high moisture sorption and low microbial resistance, which are disadvantages that need to be considered and, as far as possible, corrected.

The composite properties depend on those of the individual components and on their interfacial compatibility. Many research work has been carried out to identify the parameters that govern

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mechanical behavior of particulate composites. Generally, it has been found that the reinforcement effect increases with decreasing particle size and with increasing adhesion to the matrix.³ In the case of vegetable fillers, it has been shown that the waxy substances are the cause of poor fiber wettability and adhesion characteristics,⁴ but they can be eliminated by extraction with organic solvents.

Surface treatments of vegetable particles affect the dispersion in the polymeric matrix and, consequently, the mechanical properties of the composites. This problem^{5,6} has been addressed by several authors for the case of thermoplastic resins. Dispersion aids and adhesion promoting agents were used with polyolefinic matrices.⁷ Other authors worked with aspen fibers modified with maleic anhydride⁸ and demonstrated that the esterification reduced the equilibrium moisture content of the fibers and eliminated the irreversible thickness swelling of the fiberboards. Han et al.,⁹ who used woodflour as reinforcement of unsaturated polyester resins, found that an addition of maleic anhydride during the kneading step had a significant effect on the mechanical properties of the final composite. Gatenholm et al.⁵ discussed the effect of the acid-base interaction of the polymer-filler pair on the dispersion of fillers in the polymer matrices and showed that it varied widely with the surface treatment given to the filler.

Most of the reported works have been focused on the reinforcement of thermoplastics and only occasionally on the reinforcement of thermosets,^{9,10} except for phenolic and ureic matrices. On the other hand, polyester resins are widely used throughout the world mainly mixed with reinforcing agents. Although, cured unsaturated polyesters exhibit brittleness in their unfilled state, the physical or chemical characteristics of the filler can influence extensively not only the properties of the cured resin but also its processability in the uncured state.

The aim of this work is to investigate the effect of chemically modified woodflour on the final properties of unsaturated polyester composites. Previous results¹¹ obtained from composites made from sawdust modified with MAN indicated that there were no improvement on the mechanical properties due to the chemical treatment of the filler surface with respect to those of the untreated sawdust composites. A low interfacial area added to a low modification degree were suspected to be responsible for this fact. In the present work, woodflour instead of sawdust is used to enhance the interface effect through a larger polymer-filler contact area. The particles were pretreated with an alkaline medium and then reacted with maleic anhydride under severe reaction conditions (140°C, 24 h). A large degree of chemical modification was achieved in the woodflour (a weight gain of 58% was measured due to esterification of the particles).

Finally, different theoretical models that lead to relatively simple expressions were used to analyze the flexural response of the composites.

MATHEMATICAL APPROACH

The ability to predict the mechanical properties based on the knowledge of filler and matrix properties is an important step for the development of composites.

The macroscopic behavior of particulate composites is affected by the size, shape, and distribution of inclusions. Interfacial adhesion is also important. Simple expressions can be found in the literature, which were derived to predict the elastic properties of two-phase systems containing discontinuous reinforcements. To obtain these equations the composite microstructure is represented as a unit cell formed by isostrain and isostress type elements arranged in different ways.

The use of several theoretical models in the prediction of experimental data for modulus, strength, and ultimate deformation as a function of filler volume fraction (V_f) has been reviewed extensively by Ahamed and Jones¹² and is discussed briefly below.

The most simple models commonly used to predict the behavior of the elastic modulus of a fiber reinforced material are the parallel (upper bound) and series (lower bound) equations. Uniform strain and uniform stress, respectively, are used in the derivation of these expressions.

$$E_c = E_m V_m + E_f V_f$$
 upper bound (1)

$$E_c = \frac{E_f E_m}{V_f E_m + V_m E_f} \qquad \text{lower bound} \qquad (2)$$

where E represents the elastic modulus and V the volumetric fraction. The subcripts c, f, and m indicate composite, fiber, and matrix, respectively.

The Kerner equation has been widely used in describing the modulus of particle-filled composites. Kerner's derivation is based on the calculation of the shear modulus and bulk modulus of a macroscopically isotropic and homogeneous composite, and can be used to describe the bulk, shear or elastic (Young's) moduli of filled composites.¹³ In this expression, ν_m is the matrix Poisson ratio.

$$\frac{E_c}{E_m} = 1 + \frac{15V_f(1-\nu_m)}{(1-V_f)(8-10\nu_m)}$$
(3)

The Hirsch model proposes a relation for E_c , which is a weighed average of eqs. (1) and (2). The parameter x and (1-x) are the relative proportions of material conforming to the upper and lower bound solutions, respectively.¹²

$$E_{c} = x(E_{m}V_{m} + E_{f}V_{f}) + (1-x)\frac{E_{m}E_{f}}{(E_{f}V_{m} + E_{m}V_{f})} \quad (4)$$

The model, for a two-phase system proposed by Counto¹² assumes perfect bonding between the particle and the matrix. The modulus of the composite is given by:

$$\frac{1}{E_c} = \frac{1 - V_f^{1/2}}{E_m} + \frac{1}{(1 - V_f^{1/2})/V_f^{1/2}E_m + E_f}$$
(5)

For the approximate solution obtained by Paul,¹² the constituents are assumed to be in a state of macroscopically homogeneous stress. Adhesion is assumed to be maintained at the interface of a cubic inclusion embedded in a cubic matrix. When a uniform stress is applied at the boundary the elastic modulus of the composite is given by:

$$E_{c} = E_{m} \left(\frac{1 + (E_{f}/E_{m} - 1)V_{f}^{2/3}}{1 + (E_{f}/E_{m} - 1)(V_{f}^{2/3} - V_{f})} \right)$$
(6)

Using the same model, for uniform displacement at the boundary, Ishai and Cohen obtained the following equation

$$E_{c} = E_{m} \left(1 + \frac{V_{f}}{(E_{f}/E_{m})/(E_{f}/E_{m}-1) - V_{f}^{1/3}} \right) \quad (7)$$

The models for the strength of filled systems are less developed than that for the moduli.¹² The quantitative relation between strength and relative amount of a particulate filler for composites with a rigid matrix has, in particular, been the object of many investigations; these have produced a number of theoretical or empirical equations that fit well with the experimental results. A large number of these approaches appears to be the consequence not only of several implicit difficulties in the theory of fracture, but also of the widely diverse experimental behavior of different materials.¹⁴ Two kinds of models have been formulated, for the two cases of adhesion and no adhesion between filler particles and matrix.

The most versatile model developed for the case of no adhesion is the power law:

$$\sigma_c = \sigma_m (1 - a V_f^n) \tag{8}$$

where the subindex have the same meaning as for the moduli and the constants a, n, related with particle shape, and arrangement in the composite are used as fitting parameters.

The Nielsen equation was derived for the case of adhesion, assuming, for the tensile strength, rigorous Hookean behavior up to breaking strains:

$$\sigma_c = \sigma_m \frac{E_c}{E_m} \left(1 - V_f^{1/3} \right) \tag{9}$$

Danusso and Tieghi¹⁴ suggested, on a purely empirical basis, the following estimation with three fitting parameters (a, b, and c):

$$\sigma_c = \sigma_m \left(\frac{1 - V_f}{a + bV_f + cV_f^2} \right) \tag{10}$$

Pukanszky et al.,¹⁵ assuming that the yield stress of the composite is determined by the decrease of the effective load bearing cross section of the matrix (due to filling) and by the polymer– filler interaction, propose the following equation:

$$\sigma_c = \sigma_m \left(\frac{1 - V_f}{1 + 2.5 V_f} \right) \exp(BV_f) \tag{11}$$

where B is a parameter characterizing the interfacial interaction.

EXPERIMENTAL

Materials

The matrix was an unsaturated polyester (UPE) based on bisphenol A-fumarate (RQ 426, Perlinac S. A., Argentine), crosslinked with styrene in a 60:40 weight proportion and no additives. The initiator was benzoyl peroxide (Lucidol 0.75, Akzo

Chemical S.A.), 1.5% wt with respect to the total reaction mixture.

Woodflour from *Eucalyptus saligna* (Entre Rios, Argentina) was used in this work. 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 μ mm.

Woodflour was dried at 70°C for 3 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 for 1.5 h at room temperature and then washed several times with distilled water, then three times with a mixture of water–ethanol (50:50), and finally, once with ethanol.

Part of the NaOH-treated woodflour was immersed in a 4.08 N solution of MAN in xylene and then heated at reflux temperature for 24 h. Then, the esterified wood particles were separated from the xylene solution and intensively washed with distilled water to eliminate the unreacted anhydride. Finally, the woodflour was dried at 70°C in a vacuum oven until constant weight was achieved.

Compounding and Molding

The compounding and molding steps were carefully described in a previous publication.¹⁰ Three different types of woodflour/resin mixtures were prepared: (a) composites where the woodflour was incorporated without treatment (WC); (b) composites where the woodflour was pretreated with NaOH (NaWC); (c) composites where the woodflour was pretreated with NaOH and then treated with maleic anhydride (MANWC).

In all cases the weight percentage of filler will be indicated between brackets, for example, WC(40) indicates a composite made with untreated woodflour in a 40:60 (filler:matrix) proportion.

Mechanical Tests

Dynamic Mechanical Test

A Perkin-Elmer dynamic mechanical analyzer (DMA 7) 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 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

Table	I Acie	d and Saj	ponification	Values
for Sa	mples	of Treate	d Woodflou	r

Sample	Acid Value	Saponification Value
NaOH treated MAN treated	Negligible 228.99 ± 0.72	$\begin{array}{r} 82.29 \pm \ 0.55 \\ 522.98 \pm 18.03 \end{array}$

analysis were cut to $20 \times 3 \times 2 \text{ mm}^3$ approximately, and the dimensions were measured up to 0.01 mm.

Compression

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. An aspect ratio between 1.5 and 2 was maintained for all the samples (ASTM D 695–85).

Three-Point Bending

Three-point bending tests were also 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 $13 \times 3 \text{ mm}^2$). The neat resin specimens were cut to a transversal area of $12 \times 2.4 \text{ mm}^2$ and tested using a span of 40 mm (procedure A, ASTM D 790–86).

RESULTS AND DISCUSSION

Chemical Modifications of the Filler

The efficiency of the alkali pretreatment and the MAN chemical modification was verified in different ways.

The ester content of the MAN-modified woodflour was calculated from the acid and saponification values listed in Table I, using the techniques described elsewhere.¹⁶ This value indicated that there were 58.3 g of maleic anhydride/100 g of neat woodflour, which was further confirmed by weight gain.

Table II shows the BET area (*Micrometrics*, model *Accusorb 2.100* E) for the treated and untreated woodflour. The important reduction of BET area after the MAN esterification is the result of the large weight gain, which indicates that

Sample	No	NaOH	MAN
	Treatment	Treatment	Treatment
BET area (m²/g) WRV	$\begin{array}{c} 2.0 \pm 0.14 \\ 4.8 \pm 0.30 \end{array}$	$\begin{array}{c} 9.1 \ \pm 0.14 \\ 5.72 \pm 0.18 \end{array}$	$\begin{array}{c} 0.55 \pm 0.07 \\ 3.63 \pm 0.21 \end{array}$

Table IIWater Retention Value (WRV) and BET Area for DifferentSamples of Woodflour

not only the surface, but also internal wood cavities (capillaries and pores), must have participated of the reaction.

The water retention value (WRV) is a technique used in the characterization of textile fibers (ASTM D 2402–90). The technique measures the water that cannot be extracted by mechanical means. WRV are calculated as the difference between the weight of the wet and dried samples rationed by the latter. The measurement are done by immersing woodflour in distilled water for 5 min and then separating by centrifugation (15 min at $1000 \times g$).

Table II also shows the WRV for the modified and unmodified woodflour. NaOH-treated wood particles are more hygroscopic than untreated ones. As expected, MAN woodflour shows the lower WRV. Water sorption of lignocellulosic materials occurs through hydrogen bonding, favored by the presence of hydroxyl groups (—OH). The substitution of the hydroxyl by maleate groups due to the esterification of the woodflour reduces the water affinity of the fibers.

Analysis of the data indicates that the reduction in water affinity due to the MAN treatment is larger than expected from a simple linear relation



Figure 1 Scanning micrographs of woodflour particles. (A) Untreated; (B) NaOH treated; (C) MAN treated.



Figure 2 Temperature scans of *E'* of composites. (——) Matrix; (— –) WC(40); (— —) NaWC(35); (– –) MANWC(40); (---) MANWC(55).

with the BET area obtained from nontreated and alkali-treated particles.

Figure 1 shows scanning micrographs (SEM) for different woodflour particles. The fiber surface is severely affected by the alkaline and MAN treatments. Alkaline-treated particles exhibit a very rough surface in comparison with nontreated particles. This fact explains the increment in the specific surface area for the NaOH treated. MANtreated particles have a rather smooth surface due to the MAN coating layer, which is evenly distributed onto the surface.

In fact, the mechanical properties of the maleic treated particles may be lower compared with the nontreated filler, specially when the esterification degree is too high. The esterification of wood particles can be represented by the following equation:

wood $-OH+MAN \rightarrow$

wood—OOC—CH₂=CH₂—COOH

Because severe reaction conditions were used during the chemical treatment, the internal structure of the wood particles changed, leading to weakening of their mechanical properties. Results like these were reported by Chotorou et al.⁶ for chemicothermomechanical pulp fibers treated with acetic anhydride (weight gain 18.3%).

Dynamic Mechanical Test

Figures 2 and 3 show the temperature scans of E' and tan δ for WC(40), NaWC(35), MANWC(40), and MANWC(55) dry samples. All the composites

show a decrease of E' with the temperature, but the dynamical modulus of MANWC(55%) remains higher than the other composites for the whole temperature range, and the differences are more important for the rubber state. Furthermore, the difference between glass and rubber moduli is much smaller in the composites than in the matrix (e.g., $E_{g'}/E_{r'} = 13.08$ and 61.33 for WC(40) and matrix, respectively). This fact was attributed to the combination of the hydrodynamic effects of the particles embedded in a viscoelastic medium and to the mechanical restraint introduced by the filler at high concentrations, which reduced the mobility and deformability of the matrix.

On the other hand, it is observed that the peak of tan δ for all the samples (including the matrix) appears at approximately the same temperature. MAN has a plastificant effect on the matrix;¹¹ thus, a lower glass transition temperature should be measured if unreacted MAN were present. In this case, there are no changes in the tan δ peak of matrix of the MANWC (with respect to the neat resin), indicating that there is no free MAN in the matrix phase, that is, the MAN is strongly attached to woodflour.

Figure 3 indicates that the height of the tan δ peak of the composites is smaller than that of the neat resin. As was indicated elsewhere,¹⁷ the height of the main tan δ peak is a relative measure of the amount of material taking part in the transition. Thus, as the amount of polymeric resin decreases when woodflour concentration increases, a reduction in the height of the tan δ peak is expected. Moreover, the width of the peak of



Figure 3 Temperature scans of tan δ of composites. (—) Matrix; (— –) WC(40); (— —) NaWC(35); (– –) MANWC(40); (---) MANWC(55).

Material	Total Filler (%)	Modulus (GPa)	Yield Stress (MPa)	Ultimate Strain (mm/mm)
Matrix	0	2.5 ± 0.1	111.4 ± 4.1	0.31 ± 0.07
WC	20	3.7 ± 0.4	135.8 ± 1.8	0.25 ± 0.06
	40	3.9 ± 0.3	140.9 ± 2.6	0.08 ± 0.03
NaWC	20	3.1 ± 0.7	108.3 ± 25.7	0.18 ± 0.04
	35	3.6 ± 0.1	135.3 ± 4.9	0.16 ± 0.03
	40	3.7 ± 0.2	130.1 ± 11.8	0.10 ± 0.02
MANWC	20	3.3 ± 0.1	125.5 ± 6.3	0.22 ± 0.02
	40	3.9 ± 0.3	138.6 ± 6.3	0.21 ± 0.08
	55	4.4 ± 0.1	157.4 ± 2.9	0.12 ± 0.02

 Table III Compressive Properties for Composites

the composites made from similar concentrations of woodflours [e.g., WC(40), NaWC(35) and MANWC(40)] are comparable, while they become broader than that of the matrix and narrower than that of the MANWC(55). In other words, this behavior suggests that there are molecular relaxations in the composites that are not present in the pure matrix. The molecular motions at the interfacial region generally contribute to the damping of the material apart from those of the constituents.¹⁸ Hence, the width of the tan δ peak increasing with filler concentration is indicating that the volume of interface increases.

Compression Tests

Table III summarizes the dependence of the compressive modulus, maximum strength, and ultimate deformation with filler content and type of treatments. The compressive modulus and strength increase with woodflour content of the composites. For example, the compressive modulus of the WC(40) is 57% higher than that of the neat resin, while the ultimate stress for the same sample is 26% higher than that of the matrix. On the other side, the ultimate strain decreases with filler concentration [the ultimate deformation of the matrix is 3.6 times greater than that of the WC(40)].

MAN-treated woodflour allows one to use higher filler loads because of the improved dispersion, which besides the improved properties, should result in a cheaper product. MAN contributes to the formation of a soft film of hydrophobic material on the surface of the hydrophilic particles. In addition, strong fiber-fiber interaction due to intermolecular hydrogen bonding might also be diluted, which would lead to better dispersion of the wood particles. This point was reflected in the fact that we could load the matrix up to 55% of MAN-treated particles, while only 40% of untreated or 35% of NaOH-treated woodflour could be compounded. On the other hand, there is only 6.32 g of woodflour every 10 g of filler because a high esterification degree was achieved. Thus, 55% of MAN-treated filler corresponds to 35% of neat woodflour.

For the particular case of NaWC, the stress decreases for filler contents greater than 35%. This is due to the relatively high BET area of the mercerized woodflour (compared with the specific surface area of the other woodflours) and the inability of resin to completely wet the filler particles at higher concentrations. Thus, it was not possible to obtain a good material with more than 35% of this kind of filler.

The ultimate deformation of the materials decreases with the increase in filler weight percent, but again in this case, the less affected is the material made from MAN-treated woodflour.

Three-Point Bending Tests

Table IV shows the bending modulus (E_b) , the maximum stress (σ_u) , and the ultimate deformation of the composites made from woodflour with and without treatments as a function of the filler content.

It is well known that the modulus of a filled system depends on the properties of both components, filler, and matrix; thus, the modulus of the woodflour was higher than the one of the matrix, and the moduli of the filled composites are higher than that of the neat polymer resin. However, there are no significant differences between the moduli of untreated sawdust and alkaline-pretreated woodflour composites at the same filler content, except for NaWC(40).

On the other hand, the esterified woodflour composites exhibit significantly smaller flexural

Material	Total Filler (%)	Modulus (GPa)	Ultimate Stress (MPa)	Ultimate Strain (× 10 ³ , mm/mm)
Matrix	0	2.9 ± 0.2	93.5 ± 0.6	36.12 ± 2.40
WC	20	4.3 ± 0.3	63.3 ± 4.7	14.80 ± 1.41
	40	5.4 ± 0.2	54.1 ± 2.0	9.94 ± 0.37
NaWC	20	4.4 ± 0.2	50.2 ± 4.8	11.38 ± 1.16
	35	5.5 ± 0.4	58.2 ± 3.1	10.34 ± 0.02
	40	5.0 ± 0.1	45.0 ± 3.5	8.97 ± 0.69
MANWC	20	3.8 ± 0.2	59.4 ± 2.3	15.47 ± 0.90
	40	4.3 ± 0.2	52.5 ± 6.0	10.39 ± 1.39
	55	5.4 ± 0.4	56.2 ± 3.1	10.86 ± 0.58

Table IV Flexural Properties for Composites

moduli. This fact was anticipated because the mechanical properties of this filler may be very different of those of the untreated woodflour. First, the severe condition of the reaction could damage the fibers, and second, the important weight gain would severely change the chemical structure of the wood particles. Besides, the deterioration in hydrogen bonding in woodflour (due to the esterification with MAN), which provides a significant portion of the strength of the fibers, appears to decrease the woodflour mechanical properties. However, if the composite behavior is compared on the basis of "neat woodflour" content differences in the elastic moduli become considerably smaller. Figure 4 shows this comparison.

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



Figure 4 Bending modulus (E_b) as a function of neat woodflour content. ($--\Phi$) WC; (\bigcirc) NaWC; (\Box) MANWC.

present a σ_u smaller than that of the unloaded matrix.

There is a slight decrease of the ultimate stress with filler content for WC, while NaWC shows a maximum for 35% of filler. Flexural properties for NaWC(40) were lower than NaWC(35) because incomplete wetting of the woodflour by the resin occurs (a similar behavior was found for compression results). However, stress data for all samples are rather dispersed, and there is no significant difference between them.

The ultimate deformation is lower for the composites than for the neat matrix and decreases with the increment of the filler content in all the samples.

Moreover, the deterioration of the MANtreated woodflour properties is only reflected on the modulus of MANWC, because for the same filler content, ultimate stress and deformation maintain similar values for all the composites tested.

Thus, it may be concluded that, although the modifier (MAN) is firmly bonded to the filler particles (as was demonstrated by analytical techniques and dynamic mechanical properties), no enhancement of final mechanical properties is found when compared to the WC, probably because of the MAN low molecular weight, which creates a brittle interphase.

Mathematical Validation

To improve our understanding of the mechanical behavior of the composites, the experimental response in three-point bending was compared to simple theoretical or empirical expressions. To do that, the modulus of the woodflour (E_f) was taken as 14 GPa according to Buttrey,¹⁹ while the modulus and ultimate strength for the matrix $(E_m = 3.278 \text{ GPa}; \sigma_m = 93.54 \text{ MPa})$ were experimen-



Figure 5 Experimental modulus of WC and theoretical values given by the lower an upper bounds [eqs. (1) and (2), respectively].

tally determined. The matrix Poisson coefficient (ν_m) was taken as 0.35 (typical value for unsaturated polyester resins).

Figure 5 is a comparison of the lower and upper bounds [eqs. (1) and (2)] with experimental data of the modulus of WC. Both predictions are widely separated and are of limited predictive value. This was expected because the assumptions of either uniform stress or uniform strain used in the derivation of these expressions were clearly an oversimplification.

The theoretical curves predicted by the models of Kerner, Hirsch, Counto, Paul, and Ishai-Cohen [eqs. (3) to (7)] are compared with experimental



Figure 6 Experimental modulus of WC and theoretical curves predicted by eqs. (3) to (7). (— — —) Kerner; (—) Hirsch; (— –) Counto; (– – –) Paul; (---) Ishai-Cohen.



Figure 7 Comparison of experimental strength of MANWC and theoretical predictions. (- - -) Power law; (____) Nielsen; (__ -) Danusso and Tieghi; (- -) Pukanszky et al.

values in Figure 6. It is noticed that the Kerner equation overestimates the data, whereas Counto and Ishai-Cohen estimations give lower values than the experimental ones. The data fall on the curves predicted by the Hirsch model and Paul's upper bound.

To account for the composite complex stress and phase distribution, the Hirsch equation consider a combination of the upper and lower bound of the law of mixtures. This expression requires an empirical factor, which is determined by a curve fitting routine, to furnish a phenomenological description of the experimental data. Therefore, the data would be necessarily represented by the Hirsch model. On the other hand, the good agreement of experimental data with Paul's expression indicate that the system is satisfactorily represented by an uniform stress distribution.

In Figure 7, the strength predictions from eqs. (8) to (11) and the experimental values determined for MANWC are compared. It can be seen that the power law is ineffective in describing the data [eq. (8)], as well as the Nielsen's equation (expression 9) and the Pukanszly's model [eq. (11)]. On the other hand, experimental results were reasonably fitted by the empirical expression suggested by Danusso and Tieghi [eq. (10)], which was developed for the case of interfacial adhesion.

Micromechanical analysis of stress transfer between matrix and spherical particles with perfect adhesion indicate that σ_c should decrease initially with V_f , but beyond a critical volume content of filler it should increase. As a matter of fact, the results for different materi-



Figure 8 Comparison of experimental ultimate deformation of composites and theoretical predictions. (\bullet) WC; (\bigcirc) NaWC; (\square) MANWC.

als with a high degree of interfacial adhesion show in general a nonmonotonic decrease pattern of σ_c at low values of the volume fraction of the filler, frequently steeper than that for the case of no adhesion, followed by a minimum and a later increase.¹⁴ Experimental results in Figure 7 show a minimum for a volume fraction of 0.35, which indicated that the system is better described as a material with perfect adhesion between filler an matrix than to one without adhesion.

The scatter of the strength data is not surprising, considering the severity of the chemical modification of the woodflour and the mechanical processing conditions.

With respect to the predictions of ultimate deformation, Nielsen²⁰ proposed two models for the cases of perfect adhesion and no adhesion. Figure 8 shows experimental data of all the composites and the curves for ultimate deformation predicted by Nielsen approach. The lower curve suggests that the deteriorating effect of filler in elongation is relatively greater at very low levels of filler, as long as adhesion is maintained and aggregation is absent. The results for MANWC are very well fitted by the prediction corresponding to the perfect adhesion case, while the data obtained from WC and NaWC are a bit overestimated by the same curve. Furthermore, all the ultimate deformation data are definitely well below from the theoretical predictions for the case of no adhesion. This fact is indicative of a good degree of interfacial compatibility between particles and resin in all the materials (independent of the treatment of the woodflour).

CONCLUSIONS

Alkaline modification of woodflour was successful to increase the particle-specific area, also producing a rough surface that could facilitate the mechanical coupling with the matrix. On the other hand, the MAN molecule was firmly attached to the filler particles, as was established by analytical and physical techniques. Important weight gain was achieved in the esterification reaction, indicating that the —OH groups of the woodflour are highly reactive.

MAN treatment decreased the hygroscopicity of the fibers as was demonstrated by the WRV technique; thus, the water sorption capacity of the composites could be diminished using this kind of woodflour.

Unfortunately, the excessive degree of esterification lead to the deterioration of the woodflour, diminishing its mechanical properties. This fact, added to a low molecular weight of the modifier, are suspected to be responsible for the decreasing trends (with respect to the neat resin) in certain mechanical properties, particularly flexural deformation and stress. Although the chemical modification of the filler was improved with respect to previous results (mild treatment conditions), no improvement of the flexural mechanical properties with respect to those of WC was noticed in MANWC.

The MAN chemical modification proved to be very effective in improving the dispersion of the filler in the polymer, as it was established by the larger weight percent of esterified woodflour particles that could be incorporated into the resin. Besides, when the compressive properties were evaluated, the composites made with MANtreated woodflour offered the best performance, mainly due to the better dispersion of the particles.

The mechanical behavior of NaWC was similar (flexural) or worse (compression) than the WC or MANWC ones, suggesting that the increase in the contact area of particle–polymer is not the single feature to look for if an improvement on composite final properties is wanted.

Flexural moduli was well represented by the Paul equation, derived for a cubic inclusion in a cubic matrix, when perfect adhesion is maintained at the interface and the constituents are in a state of homogeneous stress. The strength and ultimate deformation theoretical models applied to flexural results indicated that all the materials, independent of the treatment of the woodflour, had a good degree of interfacial compatibility between filler and resin.

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