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ORIGINAL CONTRIBUTION

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Rheology of particle suspensions in viscoelastic media. Wood flour-polypropylene melt

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Abstract The dynamic mechanical behavior of suspensions of wood flour in polypropylene (PP) melts was investigated at varying filler concentrations. The main observed features were related to the viscoelastic nature of the polymer and to the filler aggregation, where the process of formation and destruction of particle clusters is governed by the polymer chain dynamics. The effect of the wood flour particles at low and large deformations was analyzed. The sample containing a wood flour concentration of 50% (by weight) showed a solid like behavior at low frequencies and was identified as the sample closer to a liquid-solid transition (LST). The values of the Newtonian viscosity obtained from sinusoidal oscillations at low frequencies were related to the concentration of filler in the suspensions. Moreover, a filler concentration scaling was found, that allows to obtain a master curve using the neat polymer as the reference and from which it is possible to calculate the dynamic mechanical behavior of all the suspensions. Apparently, for this system, the relaxation mechanisms of the neat polymer are not changed by the presence of the filler. However, the corresponding relaxation times are increased as a function of the filler concentration.

Keywords Polypropylene · Wood flour · Dynamic mechanical properties · Particle concentration scaling

Introduction

For years, fillers have been used extensively to improve the mechanical properties of polymeric materials. Besides the increment usually obtained in stiffness, hardness or abrasion resistance, and the reduced cost of the filled material, the addition of fillers to polymers also modify their flow behavior and consequently their processability(Friedrich et al. 1995). The matrix and particles interact thermodynamically according to their surface potentials and hydrodynamically through flowfield interactions (Solomon and Lu 2001). The presence of direct mechanical contacts between embedded particles or fibers can also give rise to many non-linear rheological features, which strongly manifest themselves at high concentrations of filler(Chaouche and Koch 2001). Thus, the presence of filler enhance the non-linear behavior of polymers and can contribute with new non-linear effects especially at high concentrations. Some of these non-linear responses are shear thinning and yield stress, which appear when the particles can form flocs that are held together by adhesive forces. Shear thinning occurs when viscosity decreases with increasing shear rate, while yield stress appears in suspensions that do not flow until that critical stress value is overcome. The probability of direct interaction between the particles increases as the concentration of filler increases. The formation of separate individual clusters is also possible even at small concentrations, affecting the flow properties of the viscoelastic melt(Aranguren et al. 1992). These non-linear effects are enhanced when the particles show rod-like or irregular geometries. In particular, carbon black or fumed silica have been used for decades as reinforcing fillers in the rubber industry and since they show extensive clustering, the rheological properties of the filled unvulcanized rubbers show many of the above mentioned effects. Gosh and Chakrabarti(2000) studied the addition of carbon black to an ethylene-propylene-diene monomer (EPDM) and reported the formation of a 3D filler network above 25 parts per hundred of filler. They measured the rupture of the structure with increasing amplitude of applied sinusoidal oscillations and saw that the network broke at smaller deformations as the concentration increased, while the shear thinning of the samples increased. Cai and Salovey(1999) also reported this type of structure for polymer particles in a polymer matrix. They studied the recovery of the structure after the external shear stress was removed and found a fast initial recovery that got slower with time. They related the strength of these structures to the yield stresses measured in each case.

Much of the published literature deals with the behavior of colloidal suspensions (size <1 μm), but commercial systems of polymers reinforced with fibers or particles (with sizes above the micron) are of highly practical interest, and have not been as frequently considered.

During the last decade a renewed interest in using natural sources for reactants and fillers has arisen. In particular, there has been a very large increment in the development and commercial use of wood-polymer composites mainly in the automotive and construction applications. The polymeric materials are filled with vegetable fibers usually in the form of short fibers or particles, as it is the case for wood flour composites. These type of short agrofibers or wood flour particles show an aspect ratio larger than 1.0, although they are not exactly rod-like. Instead, they show very irregular surfaces, with complex internal composition and morphology and present polar surfaces, so that they are also capable of interactions among themselves through mechanical and H-bonding interactions. Thus, they can potentially enhance the viscoelastic characteristics of the polymeric matrices.

Although the number of publications dedicated to the study and characterization of natural fiber composites has increased, there are still a very reduced number of articles dealing with the rheological characterization of these materials, which is of paramount interest in the processing of the filled melts. Kumar et al.(2000) have reported on the rheological properties of composites prepared from SBR and short sisal fibers. As is the case in other types of suspensions, they also found a shear-thinning behavior with pseudoplasticity increasing with the fiber content.

An alternative analysis of the viscoelasticity of suspensions has also been proposed in a scarce number of rheological studies of filled viscoelastic fluids. Sumita et al. (1983) analyzed the behavior of nylon 6 composites filled with ultrafine inorganic particles and found that the different yield stress curves as a function of the strain rate could be reduced with respect to filler content to a single master curve. Analogously, Gleissle and Baloch (1984) could generate a single master curve from the viscometric functions of suspensions by simply shifting the curves laterally along the axis representing the shear rate. The resulting dimensionless shift factor was interpreted as a shear rate amplification factor. Later on, Trappe and Weitz (2000) found that weakly attractive particles in a viscoelastic medium exhibit a scaling behavior as the particle volume fraction is varied, so that the storage and loss moduli could be scaled onto a single master curve and a similar scaling is obtained from nonlinear rheologic data.

In the present work, the rheological behavior of polypropylene-wood flour composites is analyzed. Small amplitude oscillations was the selected technique for investigating the viscoelastic behavior of the melts. The effect of chemically treating the filler or adding a compatibilizing copolymer in such a way as to affect the interfacial interactions between filler and matrix has been also considered. The Newtonian viscosity and the breakage of the filler structure were related to the filler concentration and the frequency of the tests. The scaling of the dynamic-mechanical properties of the suspensions with respect to the filler concentration was investigated and applied to generate master curves that allow a rapid calculation of other viscoelastic properties from a single reference master curve.

Brief theoretical background

The viscosity of suspensions is greatly affected by the concentration of the particles in the mixture. One of the many different equations proposed to model the functionality of the viscosity measured at low frequencies, η_0, with the nominal volume fraction of the particles, ϕ, is shown below (Poslinski et al. 1988):

$$\eta_0 = \eta_{0solv.}(1 - \frac{\phi}{\phi_m})^{-b} \tag{1}$$

where $\eta_{0\mathrm{solv.}}$ is the Newtonian viscosity at zero shear rate of the solvent (in the present case, the thermoplastic unfilled melt, $\eta_{0,\mathrm{PP}}$), ϕ is the volume fraction of particles, ϕ_m is the volume fraction at maximum packing, and b is an exponent, which usually takes the value of 2 for spherical particles, but can take higher values for irregular or rod-like particles.

As ϕ approaches ϕ_m the Newtonian viscosity becomes infinite, indicating that the particles are touching and the material behaves as a solid.

The complex viscosity, η^*, shows a functionality with the frequency of a sinusoidal oscillation test, ω (rad/s), similar to that of the steady shear viscosity, η, vs shear rate, γ, and so it has been used in some cases to predict steady shear properties from dynamic mechanical properties, which is known as the Cox-Merz rule (Bird et al. 1987). The steady shear viscosity of polymers can been modeled using the versatile and simple equation known as the Carreau-Yasuda model, which can be applied to non-Newtonian fluid flows as follows:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = [1 + (\lambda_{av}\dot{\gamma})^a]^{(n-1)/a} \tag{2}$$

where η is the shear viscosity, η_0 is the Newtonian viscosity at zero shear rate, η_∞ is the Newtonian viscosity at large shear rate, $\dot{\gamma}$ is the shear rate, λ_{av} is a relaxation time, n is the pseudoplastic exponent (quantifying the slope of the curve at "intermediate" shear rates), and finally a is an adimensional parameter that is related to the curvature of the curve in the transition zone.

In many cases, for thermoplastic melts, a good correlation has been found if $a = 2$ and $\eta_\infty = 0$, which is known as the Carreau model (Bird et al. 1987). In this work, this form of Eq. (2) was utilized, replacing the shear viscosity by the complex dynamic viscosity and the shear rate by the frequency of the test, as is shown in Eq. (3a):

$$\eta* = \eta_0[1 + (\lambda_{av}\,\omega)^2]^{(n-1)/2} \tag{3a}$$

For highly concentrated samples a simple power law expression can represent the observed behavior:

$$\eta* = h(\omega)^{(n-1)} \tag{3b}$$

The linear viscoelastic properties of the materials are frequently analyzed using the generalized Maxwell model, which represents the time dependence of these properties, by including the elasticity and the time relaxation of the sample. Since polymers are complex materials that have many mechanisms of relaxation, the model includes the response of a series of Maxwell elements. Thus, the dynamic mechanical moduli and the damping function (tan δ) can be written as

$$G'_{(\omega)} = \sum_i G_i \frac{\omega^2 \lambda_i^2}{1 + \omega^2 \lambda_i^2} \qquad G''_{(\omega)} = \sum_i G_i \frac{\omega \lambda}{1 + \omega^2 \lambda^2}$$

$$\tan\delta = \frac{G''_{(\omega)}}{G'_{(\omega)}} \tag{4}$$

where G′(ω) is the storage modulus, G″(ω) is the loss modulus, ω is the frequency expressed in rad/s, G_i is the modulus of the i-*th* Maxwell element, and λ_i is the relaxation time for that same element.

Addition of fillers to viscoelastic mediums originate suspensions with enhanced non-linear behaviors, which can go from viscoelastic liquids at low filler concentrations to viscoelastic solids at high filler loads. Winter and Mours(1997) have discussed largely the behavior of materials close to the gel point, interpreting this expression in a broad sense that includes different types of liquid-solid transitions, such as chemical crosslinking, crystallization, liquid crystal phase transitions, percolating suspensions, etc. In their studies they found out that in all cases the systems show a power decay of G(t) at the LST, which appears as a positive power law relation of G′ and G″ with the frequency in dynamic tests, ω^m. At the transition, G′ and G″ are parallel in a wide frequency range (theoretically, at all frequencies). This means that tan δ is a constant and frequency independent.

At the transition there is also a relation between the exponent m and the phase angle, δ_c, measured in the dynamic experiments as shown:

$$m = 2\delta_c/\pi \tag{5}$$

Since the dynamic properties moduli and viscosity are related as $\eta^* = G^*/\omega$, it turns out that the exponent "*m*" is the same as the "*n*" ("pseudoplastic exponent") presented above, for the special case of the sample at the LST.

Experimental

Materials Wood flour from *Eucalyptus Sp.* (Argentina) was selected as the filler. Only particles that pass through a sieve of mesh 100 (Tyler series) were used in this study, thus the maximum particle average diameter was 147 μm. The nominal density of the wood flour particles was taken as 1.53 g/cm^3, that is the density of the wall cells(Marcovich et al. 2001). This value was utilized in the calculation of the nominal filler volume concentration in the suspensions.

The polymeric matrix was powder polypropylene Moplen (MFI: 17.2 g/10 min), gently provided by Himont (Italy), while maleic anhydride modified polypropylene, PPMAN (MFI: 6.6 g/10 min, gently provided by University of Simon Bolívar, Venezuela), was used as compatibilizer agent. The MAN content in the copolymer was 0.3 ± 0.05 g MAN/g copolymer(Nuñez et al. 2002). The compatibilizer was added in the proportion of 5 g of PP-MAN for each 100 g of untreated wood flour.

Solid sheets of the injected composite materials were obtained from a Sandretto Series 8 model 60 t injection-molding machine. The barrel temperature profiles were chosen as 180, 200, and 220 °C (extrusion zone) and 220 °C (injection zone) and the pressure was maintained at 125 bar in the extrusion zone and 50 bar in the injection zone.

Dynamic mechanical tests Discs were cut from 3 mm thick plaques and mounted between parallel plates of 2.5 cm of diameter for the dynamic mechanical tests. The samples were heated at 200 °C and allowed to melt, the thickness between plates was adjusted down to 2 mm and the excess of material was retired from the edge of the plates. Runs were performed in a Rheometrics Analyzer, model

Advanced Rheometric Expansion System at 200 °C, using dynamic shear mode.

Results and discussion

Thixotropic behavior

The rheology of concentrated dispersions of irregular particles in polymeric fluids can be very complex(Ziegelbaur and Caruthers 1985). The response of these materials depends on shape, size and concentration of the particles besides the nature of the polymeric medium and the nature of the interactions at the particle- fluid interface. Frequently, these types of suspensions show thixotropy, that is the properties of the material change with time, and this change depends on its deformation history. The polymeric fluid shows an intrinsic time-dependent response because of its viscoelastic nature, while the suspension behavior shows an additional strong contribution due to the structure of the particles in the suspending medium.

Repeatability problems have been frequently associated to these systems (Aranguren et al. 1992) due to the sensitivity of the materials response to the state of agglomeration of the fillers, which, as stated above, depends strongly on the deformation history of the material. In the present study, the same protocol was followed for the loading and testing of all the samples. To select those conditions, the recovery of the most viscous sample after specimen loading (large compression deformation) was investigated. This sample required the longest time (of the composite series studied) for recovery of the original structure.

When the material is loaded, the distribution of particles in the viscoelastic medium is perturbed because of the large deformation suffered while pressing the sample and closing the plates to reduce the gap separation. Finite clusters can be initially disrupted and broken leading to smaller aggregates or even particles (low concentration). If a dynamic mechanical test at low strains (to avoid further breakage of structure) is performed immediately after loading the sample, a value of storage modulus is measured that corresponds to that broken structure. However, if the material is left at rest for increasing lengths of time, and the measurements are repeated, the measured values of the storage modulus grow, as seen in Fig 1 for the melt sample corresponding to a 50% by weight of untreated wood flour in polypropylene. It can be noticed that the most important recovery occurred during the first 10 min. Runs performed at 20 min show that the recovery occurred between 10 and 20 min is lower. This observation is not new; the rate of recovery is maximum at the beginning of the rest time and then it decreases, since the material gets closer to the final achievable structure, and thus the driving force decreases with the time.

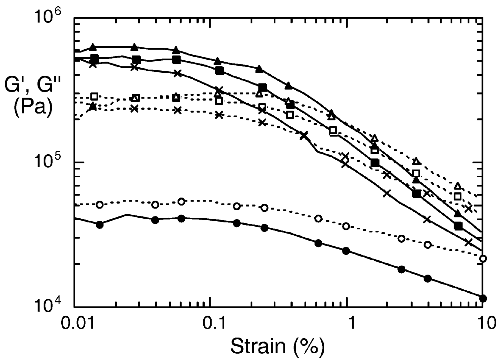

Fig. 1 Strain sweep of the sample containing 50 wt% of wood flour at different resting times. *Continuous lines* correspond to storage modulus, G′; *dotted lines* to the loss modulus; *circles* rest time = 0; *squares* rest time = 10 min, *triangles* rest time = 20 min; *crosses* rest time = 30 min

As seen in Fig. 1, there is still a small increment of G′ between 10 and 20 min of resting time of the sample. However, if the sample is allowed to rest for 30 min, the modulus decreases. This behavior is explained as the result of the degradation of the sample at the temperature of the test, probably due to some oxidation of the polymer melt, and mainly the degradation of the vegetable fibers that cannot stand such high temperatures for too long periods of time(Nuñez et al. 2002). Consequently, the protocol followed for testing all the samples was the following: loading the solid disk, melting the composite (less than 1 min), closing the plates down to 2 mm, cleaning the excess material from the edges, and let the sample rest for 15 min before beginning the dynamic mechanical measurements.

It is also interesting to notice (Fig 1) that the response of the sample at low strains changes from that of a viscoelastic liquid to that of a viscoelastic solid, that is, G″ > G′ at zero rest time, which reverts to G′ > G″ for the rested samples.

Non-linear behavior and filler agglomeration Particulate suspensions in polymeric media present large nonlinear viscoelastic effects under many conditions of work. Thus, the region of linear viscoelasticity was determined as a first step of the study. Figure 2 shows the storage modulus vs strain for the sample prepared with untreated wood flour at 40% by weight. The scans are shown at different frequencies. From this plot, it is obvious that the linear viscoelastic (LVE) region is very small for these type of suspensions, although at lower wood flour concentrations (not shown in the figure) the effect of filler structure is smaller and consequently the LVE region is larger. A strain of 0.05% was selected for the frequency scan tests, taking into account the linear viscoelastic range observed

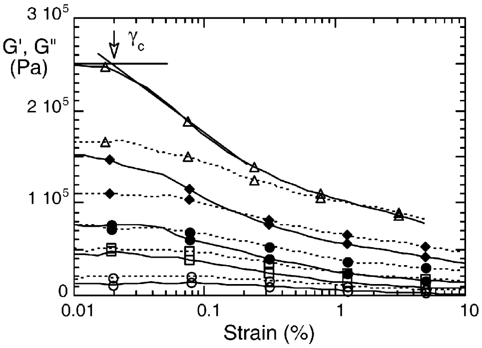

Fig. 2 Strain sweep of the sample containing 40 wt% of wood flour at different frequencies of the test. *Continuous lines* correspond to storage modulus, G′; *dotted lines* to the loss modulus. Symbols: *open circles* 0.1; *open squares* 0.5; *filled circles* 1; *filled diamonds* 5; *open triangles* 10 Hz

in the strain scan tests and the sensibility of the equipment.

The most striking feature in the strain scan tests is the large drop of the modulus as deformation increases. This effect is due to the disruption of the initial structure of the filler in the PP melt. At the highest concentrations studied there, clusters of filler exist in the material, which can further agglomerate or break depending on the imposed external conditions. As the overall deformation is increased, the filler agglomerates are also deformed until the distance between individual clusters or particles is large enough for breakage to occur. This cluster or agglomeration destruction increases as the deformation of the sample increases. This process has been described in the literature previously. Probably the oldest mention to this effect has been in the area of filled elastomers(Payne 1960), where it is known as the Payne effect. In that case, even more dramatic non-linear effects have been observed, which is directly related to the much smaller size of the fillers utilized (carbon black, silica).

When the tests are run at low frequencies, the mechanism of destruction of the clusters has a strong viscoelastic contribution due to the comparatively fast molecular dynamics. The behavior could be described as typical of a viscoelastic liquid, the contacts filler-polymer-polymer-filler have enough time to relax and new contacts can be made in the meantime. At high frequencies, the deagglomeration is essentially the result of an elastic response to the deformation. The behavior is more typical of a solid. The contacts are destroyed faster than the chain dynamics allows the macromolecules to relax or to form new links. This is also illustrated in Fig 2, which shows G′ as solid lines and G″ as dotted lines. In the LVE region (low strains), and at low frequencies (0.1 and 0.5 Hz), G″ > G′, as expected for viscoelastic liquids. However, at high frequencies (5 and 10 Hz), G′ > G″, as expected for viscoelastic solids. At 1 Hz the elastic and the viscous contributions are similar in the region of small deformations. These results indicate that the dynamic of cluster formation or breakage is governed by the viscoelastic polymer melt.

The nature of the filler network connections has been the subject of discussion many times in the literature (Aranguren et al. 1992; Kosinski 1985; Chahal and St Pierre 1969), and certainly it depends on the nature of the matrix, the filler, and the type of interactions that can occur between filler particles, between filler and matrix, as well as between the polymer chains themselves. If the links forming the network are all due to direct filler-filler interactions, one expects that at a small critical deformation of the sample, the agglomerates become essentially broken down independently of the frequency of the test. However, if there is a significant number of connections between particles that occur through linked/entangled polymer chains (filler-polymer-polymer-filler), then one expects that the viscoelastic response of the chains affect the form in which deagglomeration takes place. Thus, in the latter case, the breakage of structure will depend on the strain and frequency of the test. To quantify the strain at which destruction of the filler structure takes place, given by the onset of non linearity in the G′ vs strain curves, a critical strain was measured. The value of γ_c is taken at the intercept of the horizontal line drawn at the level of the initial linear viscoelastic plateau ($G'_{\omega \to 0}$) and the line tangent to the G′ curve in the zone of decreasing G′, as shown in Fig 2. It is obvious from the plot that the value of the critical strain depends on the frequency of the test. This is further illustrated in Fig 3. At low frequencies, the polymer chains linking the filler structure had enough time to separate and reform new links, thus a larger γ_c is measured. As the frequency is increased, the chains have less time to rebuild the links being destroyed by deformation of the sample and the measured γ_c is reduced. This dependency on frequency should also

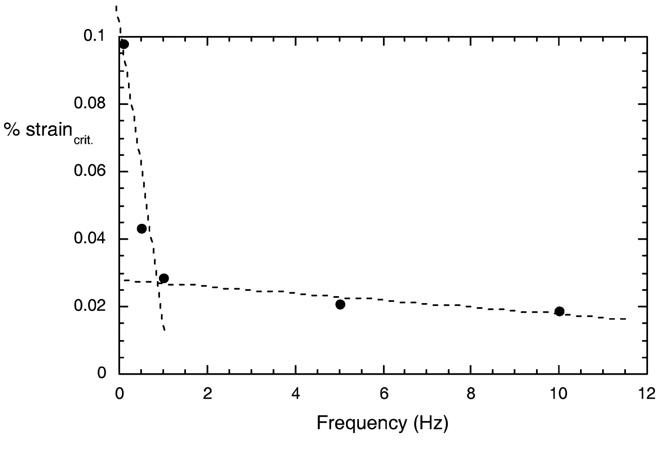

Fig. 3 Critical strain as a function of the frequency of the test

become less important as the frequency of the test is increased, and the rate of link re-building is overcome by the rate of deagglomeration. This is exactly what is observed experimentally in Fig 3.

Effect of the wood flour content Figure 4 shows strain sweep curves at a fixed frequency of 1 Hz for the samples prepared with untreated wood flour at different concentrations. As the filler concentration increases, the value of the storage modulus in the linear viscoelastic region (low strains) increases dramatically. The increment is more important for wood flour concentrations above 26% (by weight). As the strain is increased the filler structure is broken and clusters/ particles are separated. The difference in storage modulus between the samples at large deformations is much smaller in this region, where hydrodynamic effects should be the major contribution to the G′ increment with respect to that of the unfilled melt. Due to the high viscosity of the samples, it was impossible to reach very high deformations without appearance of edge instabilities, so that, data only up to approximately $\gamma \approx 10\%$ are shown in Fig 4.

Figure 5 shows the effect of the wood flour addition to the storage and loss moduli as a function of the frequency in the LVE region. At the low strains utilized in the test, the neat PP as well as the 10% wood flour suspension show liquid viscoelastic features (G″ > G′) in all the frequency range measured. The elastic and viscous components of the material response are about the same order of magnitude for samples prepared with 26 and 40% of wood flour, and clearly G′ > G″ occurs at a concentration of 50% of wood flour. The fact that G′ > G″ has been frequently interpreted as the condition at which the filler particles are connected throughout the sample.

Moreover, following Winter and Mours (1997) approach, it can be seen from Fig 5 that at 50% WF, G′ and G″ are almost parallel in the frequency range observed experimentally. Correspondingly, the plot of tan δ vs frequency (Fig 6) shows that at that concentration tan δ is almost independent of ω. Winter and Mours(1997) stated that values of m in the range of 0.19 to 0.92 have been measured, where the lowest values were found for physical networks. In our case, as mentioned above, the 50% wood flour sample presents the highest connectivity of the particles in the suspension. This feature correlates very well with the very low m value obtained from data in Fig 6, $m = 0.20$–0.23, as measured from the G′ and G″ curves, respectively.

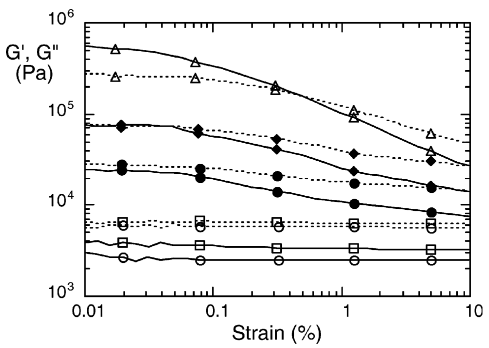

Fig. 4 Strain sweep of wood flour composites at different filler concentrations. *Continuous lines* correspond to storage modulus, G′; *dotted lines* to the loss modulus; *open circles* neat PP; *open squares*10%; *filled circles* 26%; *filled diamonds* 40%; *open triangles* 50%

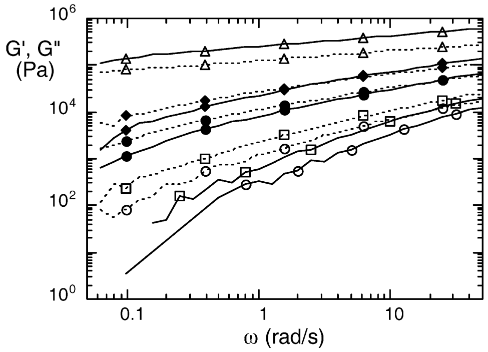

Fig. 5 Frequency sweep of wood flour composites at different filler concentrations. *Continuous lines* correspond to storage modulus, G′; *dotted lines* to the loss modulus; *open circles* neat PP; *open squares*10%; *filled circles* 26%; *filled diamonds* 40%; *open triangles* 50%

Calculation of m from tan δ data gives a value of $m = 0.28$ (Eq. 5), close to the 0.20–0.23 reported above. The difference is interpreted as the fact that the 50% WF sample may be close to, but not exactly at the LST transition.

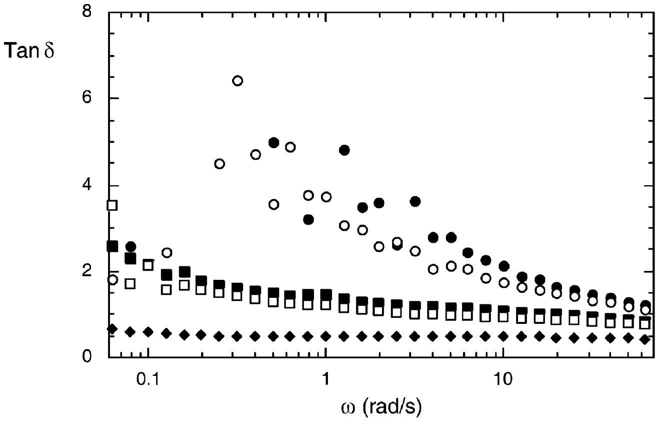

Fig. 6 Tan δ as a function of the frequency for wood flour composites at different filler concentrations; *filled circles* neat PP; *open circles* 10%; *filled squares* 26%; *open squares* 40%; *filled diamonds* 50%

Analysis of the viscosity of the suspensions Figure 7 shows the complex viscosity vs frequency at low strains, for the melts with different percentages of untreated wood flour. As the concentration increases, the viscosity also increases, although the increment is larger in the region of low frequencies. At 50% wood flour the curve shows practically no Newtonian region. As other authors have noticed in different suspension systems, the differences between curves obtained at different filler concentrations are smaller at high frequencies, while the exponent of the Carreau model (*n*) decreases with increasing concentrations (Chaouche and Koch 2001;Rueb and Zukoski 1998). All samples show shear-thinning behavior as previously observed in other filled melts (Ghosh and Chakrabarti 2000). The reason for shear thinning at the low strains utilized in these systems is related to the viscoelastic behavior of the matrix and polymer links between particles/clusters. As mentioned before, at high frequencies there is not enough time for the polymer chains to reform the original filler particle distribution.

Although the dynamic viscosity vs frequency is reported, the shape of the curve is similar to that of a viscosity vs shear rate curve, and so analogous models were utilized to fit the experimental points. In fact, this similitude has been previously used in the study of unfilled systems and some suspensions to predict steady shear curves from dynamic measurements, which is known as the Cox-Merz rule. In particular, if the Carreau model (Eq. 3a) is used to adjust the experimental points, the fit is very good, as illustrated in Fig 7. The values of the parameters utilized in fitting the experimental points are reported in Table 1. The table includes values obtained from fitting the 50% wood flour sample according to a power law equation (Eq. 3b). It was concluded that the fitting is almost equally good for η_0 varying from 3.18×10^6 to infinity. This low sensitivity is due to the fact that there is essentially no linear plateau at low frequencies. The sensibility of the fitting parameters greatly improves as the concentration of wood flour is reduced, in which cases the calculated value η_0 can also be directly read from the curve.

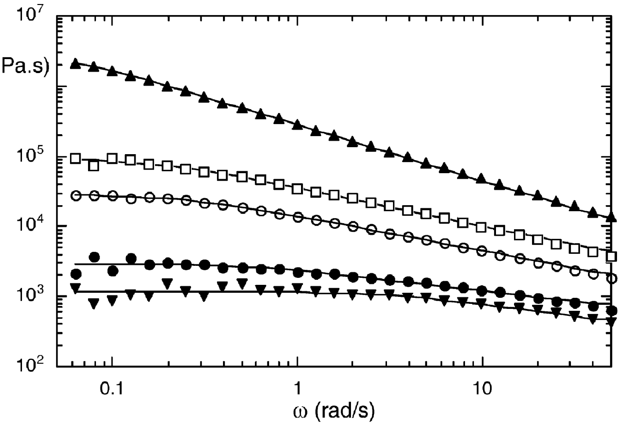

Fig. 7 Complex viscosity as a function of the frequency of the test in the LVE region for composites at different wood flour concentrations. *Continuous lines* correspond to the Carreau model fitting; *filled inverted triangles* neat PP; *filled circles* 10%; *open circles* 26%; *open squares* 40%; *filled triangles* 50%

Table 1 Fitting parameters of the Carreau model for the PP filled with different percentages of untreated wood flour

%WF	ϕ	η_0 (Pa-s)	λ_{av}(s)	*n*
0	0	1.176 e3	0.319	0.652
10	6.2	2.967 e3	1.888	0.695
26	17.3	2.815 e4	4.060	0.506
40	28.4	9.255 e4	5.920	0.459
50	37.3	3.177 e6 (∞)	20.935 (*)	0.203 (0.283)

Values in parenthesis correspond to the fitting parameters calculated using the power law equation (Eq. 3b)
(*) corresponding *h* value of Eq. (3b) equals 13000 Pa s^n

It has been postulated that since highly loaded melts show longer relaxation times than the corresponding unfilled melts, there should be a dependence of λ_{av} with the filler concentration (Ghosh and Chakrabarti 2000; Utracki, 1984). Much in the same way, it has been reported that the inclusion of fillers in a melt polymer enhance the shear thinning behavior, observed by the reduced value of the exponent, *n*, in the power-law region of a viscosity vs shear rate (or dynamic viscosity vs frequency) plot (Chaouche and Koch 2001; Rueb and Zukoski 1998). This effect is illustrated in Table 1; there is a clear reduction in the pseudoplasticity exponent above 26% of WF. The 50% wood flour composite shows an exponent of 0.203 to 0.283 compared to 0.65 of the neat PP. These values are in the same range as those reported in the literature for filled melts (Gosh and Chakrabarti 2000). Analysis of the parameters presented in Table 1 allows one to observe that the λ_{av} parameter increases with wood flour concentration, especially at high loads. At loads as high as 50% wood flour, there is little "bulk matrix" and the relaxation time of the PP is highly affected by the presence of the filler. Note that the pseudoplastic exponent obtained from the dynamic viscosity data is $n = 0.203$ to 0.283 for the 50% WF sample (Table 1), in agreement with the decay exponent measured before, $m = 0.20$–0.23 (or 0.28 from tan δ), as it was expected for a sample close to the LST.

Effect of the fiber treatment on the LVE behavior of the samples Although the nature of the specific interactions between the components of the suspensions does not usually appear in the theoretical treatments, it produces large changes in the behavior of the suspensions (Cai and Salovey 1999; Aranguren et al. 1992). Figure 8 shows the storage modulus vs frequency in the linear viscoelastic region (low strains) for samples prepared at

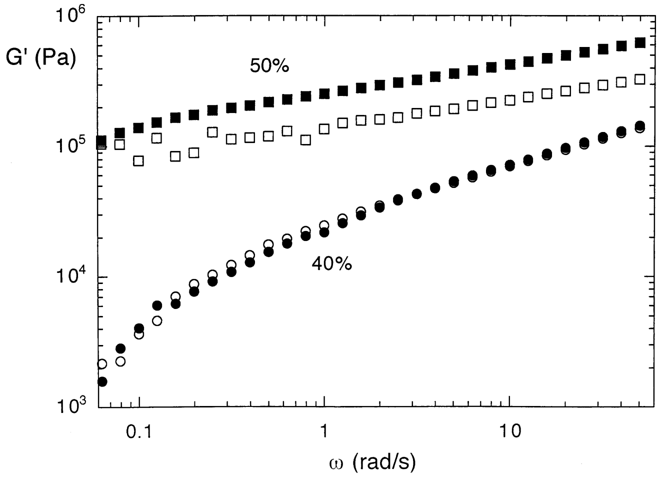

Fig. 8 Frequency sweep of wood flour composites prepared at different concentrations of wood flour, with and without the addition of a coupling agent, PPMAN. *Filled symbols*: wood flour composites; *unfilled symbols*: wood flour composites + PPMAN; *circles*: 40 wt% of wood flour; *squares*: 50 wt% of wood flour

different concentrations of wood flour, with and without the addition of a coupling agent, PPMAN.

There are not appreciable differences at 40% WF, but at 50% WF, with an incremented probability of particles touching and directly interacting, the effect of the PPMAN compatibilizer becomes more evident. It seems that in the melt state, the compatibilizer acts reducing the number of connected particles and allows a better flow of the clusters/particles one with respect to the others. At the highest concentration considered, in the uncompatibilized mixtures, there must be a large number of untreated wood flour particles or clusters that interact frequently and become mechanically entangled due to their irregular shapes and surfaces and/or physically linked through surface H-bonding. Relative movement of one particle/cluster with respect to the others results hindered by these reasons. The behavior of the samples with added compatibilizer is welcomed, because besides the improved processability (extrusion/injection) of the material, it also leads to final composites of better mechanical properties (i.e., lower creep, Nuñez et al. 2003a, 2003b).

Scaling of the viscoelastic properties with the concentration filler in the suspension

Scaling of different viscoelastic properties with the temperature of the experiment is a common technique known as time-temperature superposition. This method allows construction of a master curve for the property studied by shifting the curves obtained at different temperatures along the frequency (or time) axis. This method is generally applied to one-phase systems that do not suffer morphological or chemical changes in the temperature range of interest. In this way, only the relaxation times of the material vary with the temperature of the test, and are responsible for the change in the response of the material. However, the scaling of viscoelastic properties of suspensions with the content of filler have been mentioned only sporadically in the literature. In those cases, the application of this type of scaling has been shown to dramatically simplify the analysis of the wide variation of the dynamic moduli with the particle concentration (Trappe and Weitz 2000). Surprisingly, in spite of the differences, the data were successfully scaled onto a single master curve.

In the present study, the same observation as above can be made. The scaling was accomplished by shifting each moduli curve, corresponding to different wood flour concentrations, along the frequency axis (horizontal shifting) without other corrections in the moduli axis (vertical shifting). The resulting master curve is shown in Fig 9, with the neat PP used as the reference material. A very good superposition of the data is observed, with G″ > G′ at low frequencies, which reverts at high frequencies due to the presence of the filler. The application of the scaling to these materials implicitly indicates that the nature of the relaxation mechanisms of the polymer are not changing with the addition of the filler, in such a way that only the times required for the specific relaxation to take place are varying. It is probable that the good scaling obtained is due to the fact that most of the samples are below the LST.

The horizontal shifting, a_ϕ, is related to the ratio of the suspension viscosity and that of the reference PP melt, much in the same way as the traditional a_T, equals to η_T/η_{Tref}. In Fig 10 the shifting factors, a_ϕ, are plotted together with the ratios of the Newtonian viscosities of the filled materials with respect to the neat PP calculated

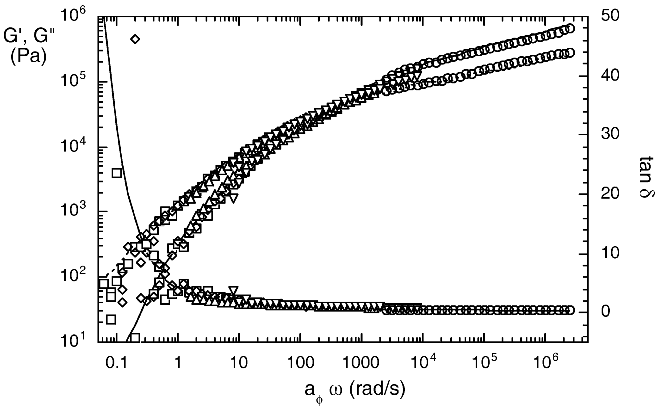

Fig. 9 Master curve with the neat PP as the reference material. *Lines*: fittings using the Maxwell model with eight elements; *open squares* neat PP; *open diamonds* 10%; *open triangles* 26%; *open inverted triangles* 40%; *open circles* 50%

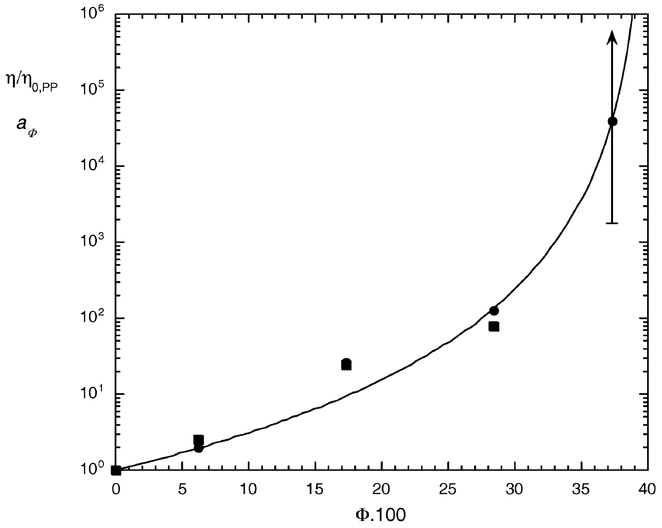

Fig. 10 Ratios of the Newtonian viscosities, and a_φ (*horizontal shifts*) of the filled materials with respect to the neat PP as a function of the volumetric fraction of wood flour. *Line*: Fitting of a_ϕ vs ϕ using Eq. (1); *filled squares* $\eta_0/\eta_{0,PP}$; *filled circles* a_ϕ

from fitting of the dynamic viscosities by Eq. (1) and reported in Table 1. Note the uncertainty in the fitted η_0 value of the sample with the highest wood flour concentration (50%), and the overall similar trends of the two sets of data. The fit of a_ϕ vs ϕ using Eq. (1) is shown as a continuous line in Fig 10. The match of the fitted curve to both experimental set of data is good, but the functionality is stronger than the theoretical value of $b = 2$, derived for suspensions of spherical particles. An exponent $b = 3.97$ was found, which indicates a strong dependence of η_0 with the filler concentration. One possible reason is the nonspherical and very irregular shape of the wood flour particles. Irregular particles are known to increase the viscosity of suspensions well above the values expected for spheres. Besides, a value of $\phi_M = 0.40$ was calculated as the maximum packing of wood flour particles expressed as a volumetric fraction. This value is in the experimental range reported in the literature for particulate suspensions (Van der Werff and de Kruif 1989). Figure 10 also indicates that the 50% wood flour ($\phi = 0.373$) sample is close to that maximum value. Actually, given the experimental errors, including the error involved in the calculation of the nominal volume fractions, this sample can be considered as one in which particles are extensively connected and interacting. This would be in agreement with the solid like behavior of the sample exhibited under dynamic mechanical oscillations.

The fact that the response of the material is controlled by the polymer dynamics, but at the same time it shows thixotropy, would indicate that the particles recover their "statistical equilibrium position" at rest, as the result of the chains movements controlled by polymer molecular diffusion. However, once that the particles are close they can interact mechanically (irregular rough surfaces) or through H-bonding due to the many hydroxyl groups present in the particles. This is also consistent with the reduced modulus obtained by addition of an interfacial compatibilizing agent, which avoids the direct contact between particles.

Table 2 Parameters utilized in the generalized Maxwell model for the master curve of PP (reference)

G_i (Pa)	λ_i (s)
7.75×10^5	8×10^{-08}
2.95×10^5	1×10^{-06}
1.90×10^5	1×10^{-05}
1.325×10^5	1×10^{-04}
8.0×10^4	1×10^{-03}
2.50×10^4	1×10^{-02}
6.5×10^3	0.1
6.5×10^2	0.8

The previously obtained master curve was modeled according to a generalized Maxwell model of eight elements. For a set of relaxation times, the G_i parameters were optimized, to obtain the best fitting of the G′ and G″ curves. The fitting curves are shown in Fig 9 and the parameters utilized in the model are reported in Table 2.

Once the master curve is modeled and the shifting factors determined, the dynamic mechanical properties measured can be calculated for all the samples. To reproduce an experimental curve one only needs to use the model and the shifting factors corresponding to the given wood flour %. The predictions can be directly obtained by replacing the λ_i values corresponding to the neat PP (as tabulated in Table 2) by $a_\varphi\lambda_i$, the

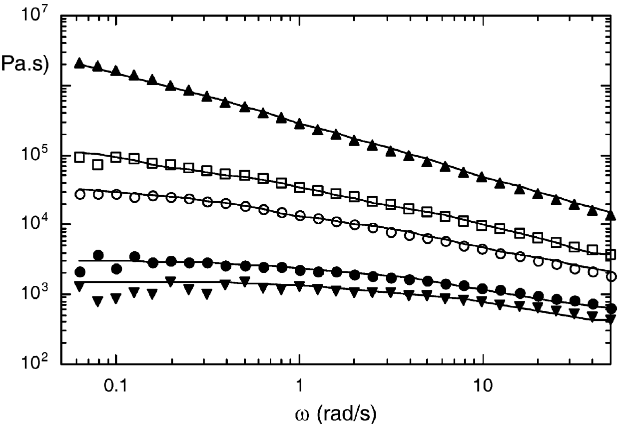

Fig. 11 Complex viscosity as a function of the frequency of the test in the LVE region for composites at different wood flour concentrations. *Continuous lines* correspond to the Maxwell model with eight elements; *filled inverted triangles* neat PP; *filled circles* 10%; *open circles* 26%; *open squares* 40%; *filled triangles* 50%

relaxation time corresponding to the suspension. Figure 11 shows the experimental points and the predicted curves for the dynamic viscosity of the samples. All predicted curves present the Newtonian region and the pseudoplastic regime. In this region, the pseudoplastic exponent is just the result of the linearization of the log-log curve in the range of frequencies considered. The agreement is very good for all the curves giving the observed increment in Newtonian viscosity and reduction of the pseudoplastic exponent as the suspension becomes more concentrated.

This type of scaling behavior has been only occasionally discussed in the literature and although it is not expected to be universally applicable, it has interesting implications with respect to the nature of the structure of the studied suspensions and the simplifying mathematics involved in their modeling. As already seen a single master curve can be used to describe all the suspensions if only the amplification of the relaxation times (shifting factors) is known. Since the study is restricted to the LVE region one set of parameters would suffice to predict the behavior in different test conditions (at least theoretically). In the future, it would be interesting to analyze the volume fraction scaling concept applied to non-linear viscoelastic functions.

Summary and conclusions

The LVE behavior of wood flour-PP mixtures in the melt state was analyzed. Simple equations, such as the Carreau model, allowed one to describe correctly the dynamic viscosity behavior for different wood flour concentrations. The low frequencies-Newtonian viscosity increased with the wood flour %, while the "pseudoplasticity" exponent of the suspensions decreased.

Analysis of the storage and loss moduli curves in frequency sweep tests (LVE range) indicates that the added compatibilizer acts reducing the probability of particle interactions in the melt, at least at high wood flour concentrations. The main reason would be the coating of the particles by the compatibilizer, which hinders mechanical particle interlocking or H bonding interactions.

Winter criterion for determining liquid-solid transitions was utilized to investigate if any of the samples was at the critical concentration. Analysis of the G′, G″, tan δ, or Newtonian viscosity all indicate that the samples studied were below the transition, with the exception of the 50% WF sample which was at (or very close to) the LST.

The dynamic mechanical properties were scaled with respect to the filler content and superposed onto a single master curve. The Newtonian viscosity ratios (with respect to $\eta_{0,\mathrm{PP}}$) and the horizontal shift factors, aϕ, showed a similar functionality with the nominal volume fraction of particles. The modeling of the master curve together with the use of the shifting factors allow the calculation of all the dynamic properties for the different samples. This is possible because only the relaxation times of the polymer relaxation processes were affected (increased) by the presence of the filler.

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