Viscoelastic Properties of Plasticized PVC Reinforced with Cellulose Whiskers

L. CHAZEAU,[1] J. Y. CAVAILLÉ,[1] G. CANOVA,[2] R. DENDIEVEL,[2] B. BOUTHERIN[1]

[1]Centre de Recherche sur les Macromolécules Végétales (CNRS), Université Joseph Fourier, B.P. 53 X, F-38041 Grenoble cedex 9

[2]Génie Physique et Mécanique des Matériaux, ENSPG, U.R.A. CNRS, B.P. 46, F-38042 St Martin d'Hères cedex

ABSTRACT: New nanocomposites are processed with a plasticized poly(vinyl chloride) matrix reinforced by cellulose whiskers whose characteristics are a high aspect ratio and a large interface area. Dynamic mechanical analysis performed on samples reinforced with a filler fraction of up to 12.4 vol % gives the viscoelastic properties of the composite above and below its glass transition temperature. Different theoretical predictions are proposed to describe this behavior, but none of them is found wholly satisfactory for describing the reinforcing effect of these fillers. A model based on the Halpin–Kardos equation, with the assumption of an immobilized phase around the whiskers, is developed to account for significant decrease in the modulus drop, on passing above the glass transition temperature. The small discrepancy between this model and the experimental modulus measured in the rubber plateau is discussed as a possible effect of a percolating whisker network whose crosslinks are assured by chains adsorbed onto the whisker surface. Swelling experiments support this hypothesis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1797–1808, 1999

Key words: composite; cellulose; plasticized PVC; mechanical properties; swelling

INTRODUCTION

Many cellulosic products, such as wood shavings, have long been used as a filler in polymers, in order to decrease their cost without degrading their mechanical properties. For 20 years, cellulose fibers such as wood fibers or cotton have been increasingly studied for their potential as reinforcement agents in composites. They combine good mechanical properties, that is, a strength and a modulus of the same order of those of mineral fillers, with the advantages of cellulose, which is biodegradable and renewable.[1] Nowadays, cellulose fibers are used as fillers in the majority of resin composites;[2] they are also used in rubber composites.[3] For several years, thermoplastic composites reinforced with cellulose fibers have been the subject of increasing interest.[4–6] The literature on these materials focuses on the problem of the dispersion of the fibers during processing and on the compatibility between cellulose, which is hydrophilic, and the hydrophobic polymer matrix.

Due to the high viscosity of the matrix fiber mixture during the processing (although this latter occurs largely above T_g), it is very difficult to avoid fiber aggregates. The fibers are generally long and entangled, and too strong a mechanical dispersion process can lead to a dramatic decrease in their length and, therefore, in their reinforcing properties.[7] Lastly, the wettability of

the polar cellulose is problematic with usually nonpolar synthetic polymer,[8] leading also to an agglomeration of the fibers in the composite. The solutions proposed by different authors consist generally in grafting on the fiber surfaces with polymers, which assures a better affinity with the matrix and/or a better dispersion.[9,10] One of the solutions we explored to solve these problems was to use a dispersion step of fibers in the matrix, in an aqueous suspension. Thus, both fillers and polymer matrix must be prepared in aqueous medium, and both suspensions must be stable, at least during the time necessary for mixing of the two components.[11,12] By this method, if the fibers are sufficiently well dispersed in the aqueous medium, it seems possible to avoid aggregate formation after evaporation of the water.

Suspension, microsuspension and emulsion processes are widely used in industry to produce polymers in an aqueous medium. The polymer synthesized by this way is obtained, before the drying step, as microdroplets in a water suspension, with the stability being provided by suspension or emulsifying agents. Two types of cellulose nanoscopic fibers have been made in our laboratory. One is derived from pulps of sugar beets.[13] The suspensions obtained are stable. The nanoscopic size of these fibers make possible the processing of small thickness composites and a possible transparency of the final product. Moreover, their very large aspect ratio and their mechanical properties provide them with a great industrial potential for the reinforcement of polymer matrices. Due to their shape of infinitely long and flexible fibers, it is, however, more difficult to study their reinforcing effect in polymer than it would be with rigid rods. That is the reason why we preferred to study cellulose whiskers as a preliminary approach. They have the same nanoscopic size, a large aspect ratio, and a high modulus. They are rod-shaped monocrystals prepared, in this case, from tunicates. Whiskers were firstly studied by Favier and coworkers,[12,14] who was interested in their reinforcing effect in a poly(styrene–butyl acrylate) matrix. She showed a drastic improvement of the composite modulus in the rubbery state of the matrix. This effect was attributed to the formation of a whisker network linked by hydrogen bonds between the cellulose whiskers.

The aim of the present study is to understand the effect of these fillers still in thermoplastic matrix but when the process, different from the simple casting described by Favier, includes hot-mixing and hot-moulding, which should avoid the formation of the hydrogen-bonded network. Composites with different whisker contents are prepared. For both fundamental and industrial interest, plasticized poly(vinyl chloride) (PVC) is chosen as the matrix. Dynamic mechanical measurements and tensile tests are performed to estimate the viscoelastic behavior of the materials as a function of temperature. Different models usually used for composites are presented and discussed. The hypothesis of the existence of a flexible network is also evoked, highlighted by swelling experiments and a theoretical estimation by finite element modelling of the lower and upper limits of such a network modulus.

EXPERIMENTS

Materials

The cellulose whiskers are obtained from sea animals, namely, tunicates, after a treatment described by Sassi.[15] The final aqueous suspension of whiskers does not sediment or flocculate due to the electrostatic repulsion between the surface sulphate groups grafted during the sulphuric acid treatment. The whisker average dimensions, determined by transmission electron microscopy, are 1 μm length and 15 nm diameter.

The PVC was supplied by Elf-Atochem (isotacticity 19%; syndiotacticity 34%; molecular weight $\bar{M}_n$ = 40000; polymolecularity indice I_p = 2). The whiskers suspension was blended with the PVC microsuspension (bead diameter 0.2 μm) and then freeze-dried. The blend of this freeze-dried powder, 30 phr (that is, per hundred ratio of PVC) of plasticizer [di-ethyl-hexyl phthalate (DOP), provided by Elf-Atochem], 4.5 phr of tin stabilizer (CIBA-GEYGY), and 1.5 phr of lubricant (stearic-acid-based compound), was processed by hot-mixing at 180°C during 5 min in a Brabender mixer. This mixture was then pressed into sheets by compression moulding at 200°C during 3 min. We made composites with 0, 6, 9, 12, 16, and 24 phr, that is, 0, 3.4, 5, 6.6, 8.4, and 12.4% respectively, by volume of whiskers contents. In the present article, plasticized PVC matrix will be called pPVC.

Preliminary Characterization

Differential scanning calorimetry (DSC; Perkin–Elmer DSC7 system) was used to determine the glass transition temperature. Typical sample weight was 15 mg. The analysis was done from

190 to 380 K with a heating rate of 10 K/min. The presence of plasticizer strongly increases the width of the transition.[16] The temperature of the transition beginning T_{g1} was found to be 261 K; the temperature of the transition ending T_{g4} was 305 K. Similar temperatures were found for the composites, and were independent of the whisker content.

The composite films remain transparent, even at 12.4 vol % of whiskers. Due to their size, the whiskers only appear as luminous point under scanning electron microscopy (SEM). However, this technique seems to show a good dispersion of the whiskers. The use of the electron transmission microscopy was impossible since no sufficiently thin microtome was available.

Small angle X ray scattering (SAXS) and small angle neuron scattering (SANS) were performed on the composites. The results are described in other references.[17] It lead to the conclusion that we had an isotropic dispersion of the filler without aggregates. The isotropic character of the whisker dispersion was also confirmed by comparisons and analogies with the description of whisker-filled composites described in Hajji et al.[18]

A study, by transmission electron microscopy (TEM), of whiskers extracted of the composite[17] allowed confirmation that the typical length of the whiskers was not modified during the processing of the composites.

Study of Materials

Mechanical Tests

Mechanical behavior was measured with a mechanical spectrometer described previously.[19] It consisted of a forced oscillation pendulum, working in the temperature range of 100 to 700 K and the frequency range of 5×10^{-5} to 5 Hz. Since the maximum strain was less than 10^{-4}, the viscoelastic behavior of the samples was considered independent of the applied stress over the whole strain amplitude range in all temperature ranges used for the experiments. The storage (G') and loss (G'') moduli of the complex shear modulus (G^*) and the internal friction tan ϕ (G''/G') were measured as a function of temperature T, between 100 and 420 K, for a fixed frequency of 0.1 Hz. Resolution for tan ϕ was better than 5×10^{-4}. Sample dimensions were about 15 mm length, 6 mm width, and 1.5 mm thickness.

The error made on the thickness of the samples lead to a three times higher uncertainty on the modulus value from shear tests. Therefore, micro-tensile tests were performed on a RSA II Rheo-metrics. The strain rate was 10^{-4} s^{-1}. The testing temperature was 240 K. The tensile modulus E was deduced from the slope at the origin of the stress–strain curve. The shear modulus was calculated through the equation $G = E/2(1 + \nu)$ with ν, the Poisson ratio, equal to 0.35.

Swelling Experiments

Swelling is a method currently used to determine if fillers create supplementary crosslinks inside a composite.[20,21] The choice of the solvent used is of importance. This latter must be a good solvent of the matrix to allow its swelling or its dissolution, but it must not be able to break the eventual links between the matrix and the filler. If this last condition is not respected, the experiments cannot be conclusive.

Tetrahydrofuran (THF) or ketones are known to be good solvents for PVC.[22] Preliminary tests of swelling with THF were inconclusive: composites immersed in THF were fractionated in little aggregates, which were impossible to weigh. This solvent might be strong enough to break the links between the matrix and the whiskers. Therefore methyl ethyl ketone was used.

Cubic-shaped samples of about 30 g weight were immersed in methyl ethyl ketone for 2 weeks. The solvents were changed every day for the first 3 days. To be sure that 2 weeks were sufficient for the samples to reach their equilibrium, kinetic experiments were performed, which consisted of measuring the weight of the samples as a function of time. It was found that equilibrium was reached after only 2 days. It was also checked that the experiments were weight-independent by recording the same swelling ratio for samples weighing from 15 up to 50 g. Once swollen, the samples were weighed after a drying step, which consisted of putting them under vacuum at 60°C for 1 day (60°C is 40°C below the initial T_g of the samples). DSC scanning showed an increased T_g of the samples, independent of filler concentration. This was due to an extraction of plasticizer by the solvent. Thus, all the samples were found to lose about 60% plasticizer during experiment (this percentage was deduced from their glass transition temperature). This was taken into account, as was the weight of the whiskers, for the calculation of the swelling ratio Q_m, by subtracting these two weights to the final weight of the dry samples. Q_m was given by the following relation:

$$Q_m = 1 + \frac{\rho_m}{\rho_s}\left(\frac{W_m - W_f}{W_d - W_f} - 1\right) \qquad (1)$$

Figure 1 Shear elastic modulus measured by Dynamic Mechanical Analysis (frequency = 0.1 Hz) of composites reinforced with 0% (Δ), 3% ($\blacklozenge$), 5% ($\times$), 6.6% ($\square$), 8.4% (+), 12.4% vol. ($\bigcirc$) of whiskers.

ρ_m and ρ_s are, respectively, the density of the composite and of the solvent, as follows: ρ_m = 1.35, and ρ_s = 0.8. W_m is the swollen sample weight, W_f is the weight of the whiskers inside the composite, W_d is the dry sample weight.

RESULTS AND DISCUSSION

Elastic Behavior

Dynamic mechanical analysis (DMA) experiments were performed on the composites reinforced with 3, 5, 6.6, 8.4, and 12.4 vol % of whiskers. The elastic modulus as a function of the temperature is shown in Figure 1. Below T_g, the increase of the modulus with whisker content is moderate. By contrast, the whiskers efficiency above T_g is drastically high. The slope of the rubber plateau is slightly higher for the composite than for the matrix. This can be explained by an increasing contrast between the fiber and the matrix modulus when the matrix modulus decreases. Indeed, this contrast is known to have a great influence on the reinforcement effect of the fillers. However, the difference between the slopes is small. This excludes the presence of a rigid whiskers network.[19] For a higher temperature, that is,

Figure 2 Elastic modulus E measured below T_g, at 235 K ($\bullet$) and theoretical modulus deduced from Reuss ($\bullet\bullet\bullet$) and Voigt ($\bullet\bullet\bullet$) bounds, the Halpin Kardos model (– – –) and the "cluster" model (———).

the temperature of pPVC flow, the flow of the composite is observed in the same temperature range as for pure pPVC.

Figures 2 and 3 show the shear modulus as a function of the fillers volume fraction, respectively, at 235 (below T_g) and 380 K (above T_g). They are compared with two theoretical models, the Halpin–Kardos one,[23] and the cluster model developed by Molinari and El Mouden.[24]

The Halpin–Kardos Model

The Halpin–Kardos model considers the composite as a quasi-isotropic short-fiber laminate con-

Figure 3 Elastic modulus E measured at 380 K (above T_g); same legend as for Figure 2.

sisting of a thickness-symmetric arrangement of 4 plies of unidirectional material making angles of $\pi/4$ with respect to each other. The mechanical properties of each unidirectional ply is given by the following:[25]

$$\frac{E_{ii}}{G_m} = \frac{2E_{fii}(1 + \nu_m)(1 + \xi_{ii}X_f) + 4\xi_{ii}(1 + \nu_m)^2(1 - X_f)G_m}{E_{fii}(1 - X_f) + 2(\xi_{ii} + X_f)(1 + \nu_m)G_m}$$

$$\frac{G_{12}}{G_m} = \frac{G_f(1 + \xi_{12}X_f) + \xi_{12}(1 - X_f)G_m}{G_f(1 - X_f) + (\xi_{ii} + X_f)G_m} \tag{2}$$

where E_{fii} is the Young modulus of the fiber in the direction i ($i = 1, 2$), G_f and G_m are the shear modulus of the fiber and the matrix, ν_m is the matrix Poisson factor, and X_f is the fiber volume fraction. ξ_{ii} depends on L, l, and e, which are the length, the width, and the thickness of the fibers, respectively, as follows:

$$\xi_{11} = 2\left(\frac{L}{e}\right) \quad \xi_{22} = 2\left(\frac{l}{e}\right) \quad \xi_{12} = \left(\frac{l}{e}\right)^{\sqrt{3}}$$

These results are inserted by a macromechanic approach into the quasi-isotropic calculation (laminates description), giving finally

$$G = \frac{E_{11} + E_{22}(1 - \nu_{12})}{8(1 - \nu_{12}\nu_{21})} + \frac{G_{12}}{2} \tag{3}$$

where the Poisson factors are

$$\nu_{12} = X_f\nu_f + (1 - X_f)\nu_m \quad \text{and} \quad \nu_{21} = \nu_{12}\frac{E_{22}}{E_{11}}$$

with ν_f, as the fiber Poisson factor.

The Halpin–Kardos model, firstly developed to describe semicrystalline polymers, has been validated since its creation by experimental measurements[12,26] and has been shown to be correct whether the fibers are randomly oriented in plane or in volume. The advantage of this model is to propose a simple analytic expression for the composite modulus, which take into account the form factor and the anisotropy of the mechanical properties of the inclusions and which can be easily extended to a viscoelastic description of the material. But the Halpin–Kardos model does not take into account the mechanical interaction between the fibers.

The Cluster Model

Conversely, the cluster model takes into account these interactions. This model can be seen as a refinement of the classical models based on inclusion calculations (for example, self-consistent models). Moreover, the cluster model has the advantage over more classical homogenization techniques as it accounts for the effects of both the morphology of the reinforcing fibers and their spatial distribution. It can be described as follows. A set of 100 fibers (or inclusions) Ω_f randomly spread and oriented in an elementary cube of length L is used, and this elementary volume is reproduced in the three directions of space. A cluster C_f is then defined by a spherical volume of radius R_c, which acts as the representative volume element (RVE), that is, the one in which the mechanical properties are identical to the corresponding macroscopic ones. It is possible to discretize the space and, assuming uniformity of strain inside the fibers, to obtain the localization equations for each fiber f, as follows:

$$\varepsilon_f = E + \sum_{f,} \Gamma_{ff,} : (\delta L_{f,})\varepsilon_{f,} + E_0 : \sum_{f,} X_{f,}\delta C_{f,} : \varepsilon_{f,} \tag{4}$$

where E is the macroscopic elastic strain and X_f is the volume fraction of the fiber f in the RVE. E_0 is the average strain in the matrix taken as the reference medium. δC_f, is the difference between the rigidity tensor of the fiber f' ($C_{f'}$) and the one of the matrix (C_m). This is a linear system of equations with unknown ε_f, with the coupling tensors between pairs of fibers f and f', defined as

$$\Gamma_{ff,} = \frac{1}{V_f} \int_{V_f} \int_{V_{f,}} \Gamma(r - r')drdr' \tag{5}$$

which is a double integral over the volumes V_f and $V_{f'}$. $\Gamma(r - r')$ is the Green operator associated with the rigidity tensor of the matrix. The interest of the tensor $\Gamma_{ff'}$ is to include both the morphology and the spatial distribution of f and f'. Writing the average conditions both on strains and stresses leads to the following global stiffness:

$$C_{eff} = X_mC_m : \Lambda_m + \sum X_fC_f : \Lambda_f \tag{6}$$

with Λ_m and Λ_f, the localization tensors, given by

Table I   Parameters Used for the Halpin–Kardos Modelling

Symbol	Designation	Value
E_{f11}	Longitudinal modulus of the cellulose whiskers	130 GPa[a]
E_{f22}	Transverse modulus of the cellulose whiskers	15 GPa[b]
G_m	Shear modulus of the matrix	0.74 GPa (at 235 K)
		0.53 MPa (at 280 K)
G_f	Shear modulus of the fiber	5 GPa[c]
ξ_{11}		133[d]
ξ_{22}		2[d]
ξ_{12}		1[d]
ν_f	Fiber Poisson factor	0.3
ν_m	Matrix Poisson factor	0.35 (at 235 K)
		0.5 (at 280 K)

[a] Average values of the literature.[27–32]
[b] They are the lowest value of the 2 transverse modulus of the whiskers[30] since the Halpin–Kardos model is bidimensional.
[c] The average value of the shear modulus in the 2 transverse directions.[30]
[d] Deduced from the average whisker dimensions.

$$\varepsilon_f = \Lambda_f : E \quad \text{and} \quad \varepsilon_m = \Lambda_m : E$$

Molinari and El Mounden have shown that this method converges towards the exact solution when the cluster size increases. In our case, $R_c = 3L/2$ seemed to be a sufficiently high value to obtain a convergence of the calculated results.

Comparison Between Experiments and Theoretical Predictions

Calculations with these two models have been made using the parameters respectively listed in Tables I and II and deduced from literature.[27–32] For the cluster model, we used the program developed in the GPM2 laboratory of the ENSPG by G. Canova. It was modified to take into account the anisotropy of the mechanical properties of the cellulose whiskers through the definition of their elastic tensor (that is, the elastic tensor of a rigid fiber).

The results of the calculation below T_g (235 K) are plotted in Figure 2 with the basic calculation of the Reuss and Voigt boundaries. The models give quite different predictions. Taking into account the anisotropy of the whisker mechanical properties does not significantly change the results calculated with the cluster model. Indeed, like in Favier et al.,[12] in which this anisotropy was not taken into account, the same under-estimation of the composite modulus is found. On the other hand, the Halpin–Kardos prediction largely overestimates the data. Peyroux[33] found that the

Table II   Parameters Used for the Cluster Modelling

Symbol	Designation	Value
E_l	Longitudinal modulus of the cellulose whiskers	130 GPa[a]
G_m	Shear modulus of the matrix	0.74 GPa (at 235 K)
		0.53 MPa (at 280 K)
G_{tt}	Shear modulus of the cellulose whiskers (transverse direction)	5 GPa[c]
G_{lt}	Shear modulus of the cellulose whiskers (longitudinal direction)	5 GPa[c]
K_l	Compression modulus of the whiskers	12.5 GPa[a]
N	Number of whiskers	100
f	Form factor of the whiskers	1/67[d]

[a] Average values of the literature.[27–32]
[b] They are the lowest value of the 2 transverse modulus of the whiskers[31] since the Halpin–Kardos model is bidimensional.
[c] The average value of the shear modulus in the 2 transverse directions.[31]
[d] Deduced from the average whisker dimensions.

Figure 4 Evolution of the viscous modulus as a function of temperature measured by DMA on composite samples (frequency = 0.1 Hz); same legend as for Figure 1.

Halpin–Tsai model, on which the Halpin–Kardos equation is based, gives results above the classical self-consistent models. This is probably even enhanced by the quasi-isotropic laminate representation of the composite. However the model was firstly used to describe a semicrystalline polymer in which the inclusions are randomly oriented in the volume. Therefore, this representation is *a priori* valid for our composite, as it has been validated in several studies. Due to the high modulus of the matrix below T_g, the aspect ratio value has very little effect on the calculated results. Moreover, transmission electron microscopy (TEM) of whiskers extracted from the composites showed that the process did not modify their typical dimensions.[17] Therefore, a possible decrease of the whiskers length during processing cannot be an explanation of the observed overestimation. The predominant factor in the Halpin–Kardos calculation of the modulus, below T_g, is the whisker modulus, but literature shows that this latter must be considered correct. Therefore, there is no obvious explanation of the overestimation of the composite modulus by the Halpin–Kardos equation. It can, however, be concluded that the modulus of the composite below its glass transition temperature is in between the values predicted by the two models. Thus, the reinforcement in this domain can be described by a charge transfer.

Figure 3 shows the comparison between the Halpin–Kardos equation, the cluster model, and the experimental values measured above T_g.

Generally, with fiber-filled elastomer, the filler efficiency is much smaller, even when these composites are unidirectional.[34–36] The modulus of the composites increases exponentially with whisker content, and yet both models predict a more or less linear increase. Thus, the reinforcing effect above T_g cannot be described by both models used. However, it is noteworthy that the Halpin–Kardos offers a closer description of the experiments.

If the results below T_g and above T_g are now considered, it can be concluded that the cluster model or the Halpin–Kardos equation are not satisfactory. The cluster model is better below T_g than the Halpin–Kardos prediction, but it is the contrary above T_g. In term of modulus drop, both models are equivalent and make a quite similar prediction.

Viscoelastic Behavior

The DMA experiments also provides the evolution of the viscous modulus G'' and the loss factor curves of the composites as a function of temperature (compare Figs. 4 and 5). The α and β relaxations are observed, respectively, at around 150 and around 300 K. The behavior of plasticized PVC confirms the literature results.[16] The α relaxation, like the glassy transition, is widened by the presence of the plasticizer and shifted towards a lower temperature; the β relaxation is decreased by the presence of the plasticizer and

Figure 5 Loss factor as a function of temperature measured by DMA on composite samples (frequency = 0.1 Hz); same legend as for Figure 1.

partly overlaps with the α relaxation. These two relaxations are still present in reinforced pPVC. The whiskers do not seem to shift the tan ϕ peak temperature of the relaxations measured at 0.1 Hz. These results confirm the DSC measurements that showed that T_g remains unchanged with whiskers content. Similar observations have been reported for various composite systems.[37]

The maximum of G'' is shifted towards the high temperatures, and its value increases with increasing whiskers content. We observe an increase of tan ϕ measured in the rubber plateau domain. Nielsen[38] stated that it could be generated by interfiller slippage, which occurs when the matrix does not constrain the filler anymore because of a difference in the dilatation coefficients between filler and matrix. This effect requires the presence of aggregates that are not present in the present case, as shown by the optical observation of the composites and SANS experiments.[24] The maximum of the tan ϕ peak for the α relaxation decreases with increasing the whisker content as reported for other filled composites.[37] The decrease of the β relaxation maximum might result from the decrease of the α relaxation, as these two relaxations overlap in this temperature range. A simple decrease of the volume fraction of the matrix cannot explain these observations. Boluk assumed that a fraction of the matrix is immobilized around the fillers. Although the literature using this approach[21,39–41] is relatively abundant, it is still questionable as it is assumed that the interphase has the same stiffness as the fillers.

In the present work, the principle of equivalence between elastic and viscoelastic solutions[26,42] is applied to the Halpin–Kardos model. This model is preferred to the cluster model since it provides a simple analytical equation that is easy to extend in the viscoelastic domain. This is obtained by replacing the elastic modulus by complex values. As seen previously, the parameters used do not allow a good fit for G' nor G'' (compare Fig. 6). However, it is interesting to notice that the Halpin–Kardos model leads to an increase in the G'' peak.

Limitations in modelling of the composite behavior is much more drastic above T_g than below T_g. Below T_g, the Halpin–Kardos model leads to an almost linear increase of the modulus versus the whiskers content, such as $G_{cHK} = 4.10^{11}\phi + G_m$ (c and m subscripts refer, respectively, to the matrix and the composite), as shown in Figure 2. The experimental increase of the modulus follows $G_c = 10^{11}\phi + G_m$. It is, therefore, possible

Figure 6 Viscoelastic modulus of a composite with 12.4% vol. of whiskers content: $G'(\square)$ and $G''(\bigcirc)$. Comparison with the viscoelastic prediction of the Halpin–Kardos model: $G'(\text{———})$ and $G''(---)$.

to extrapolate an empirical law below T_g, between the experimental values and the ones predicted by Halpin–Kardos, as follows: $G_c = (G_{cHK} - G_m) \times \phi \times 0.25 + G_m$. In fact, this could correspond to a corrective factor to the quasi-isotropic representation of the whiskers. The correction has a relatively low effect on the model above T_g since this latter already drastically underestimates the experimental data. It leads to the Halpin–Kardos model being considered only in terms of the prediction of the modulus decrease during the glass transition. But this correction, the modulus decrease, is still incorrectly described.

An interphase of immobilized matrix in the neighborhood of the whiskers might be an explanation of the high values of experimental data. This interphase should have about the same form factor as the whiskers, with the modulus of the matrix alone measured below T_g. The assumption is made that our composite is equivalent to a matrix filled with cellulose whiskers and pPVC whiskers with the same aspect ratio and no glass transition (in the expected temperature domain of the matrix glass transition). This assumption is consistent with the increase of tan ϕ with the increasing whisker content well above T_g, that is, in the range of 340–400 K. Indeed, this phenomenon could be explained by the beginning of the glass transition of this interphase.

Figure 7 Modelling of the elastic shear modulus of the composite with 6.6% vol. whiskers, by a two step Halpin–Kardos model, considering 6.6% vol. of immobilized matrix domains. G' of the unreinforced matrix (Δ), G' of the composite ($\bigcirc$), G' of the modelling (————), G' of the simulated matrix in presence of whiskers (– – –).

To model this feature, the Halpin–Kardos model is applied in two steps, firstly to account for the matrix containing pPVC whiskers, and then secondly to calculate the reinforcing effect due to the cellulose whiskers. The adjustable parameter is the volume fraction of pPVC, which remains stiff. It is adjusted so that the glass transition be described well, considering both G' and G''. The best fit is obtained for a volume fraction of immobilised matrix equal to the whisker volume fraction (compare Figs. 7 and 8). This suggests the presence of an interphase of about 3 nm thickness (calculated from the cellulose whisker dimensions) around each whisker. This value is relatively small and is of the same order of magnitude as the gyration radius of PVC chain.

Effect of an Eventual Whiskers Connectivity

It is clearly visible on Figures 7 and 8 that this model, although it provides an improvement in the description of the composites, cannot accurately describe the reinforcement effect observed in the rubber plateau domain. In order to understand this under-estimation, it is worth considering a possible effect of whiskers percolation. A computer simulation of randomly dispersed whiskers leads to the calculation of a geometric percolation threshold of 0.8 vol %. This low value can explain the mechanical behavior of the composites made by Favier et al.,[12] in which the material

processing allows the formation of hydrogen bonds between the whiskers. In the present case, during the processing of the materials, the hot-mixing step should drastically limit the formation of hydrogen bonds between whiskers. Moreover, the presence of rigid whisker network would lead to a quasi-constant rubber plateau. In fact, we observe a slope of the composite rubber plateau that is quite similar to the one of the matrix. However, since the interwhisker distance is small, it is possible that polymer chains immobilized on the whisker surfaces make a link between the whiskers, creating a flexible network whose the properties are largely dependent on the modulus of these chains. To check this assumption, swelling experiments were performed on the plasticized PVC and the composites with different whiskers contents, as described in the experimental section. Methyl ethyl ketone does not dissolve pPVC probably because of microcrystalline domains of the more regular syndiotactic sequences that are present in PVC.[43,44] On the other hand, specific interactions between carbonyl group C=O of DOP and Cl—CH group of PVC[45] can create bridges between the polymer chains.[46] Assuming that such links act as crosslinking nodes, the molecular weight between nodes M_c can be determined by the Rehner–Flory equations,[47] from the swelling ratio. This requires the additional assumptions (1) of a small molecular weight between crosslink in comparison with the initial weight of the polymer chains, (2) of a

Figure 8 Modelling of the elastic shear modulus of the composite with 12.4% vol. whiskers, by a two step Halpin–Kardos model considering 12.4% vol. of immobilized matrix domains; same legend as for Figure 7.

Figure 9 Inter-crosslink weight M_c calculated from swelling measurements, as a function of the whisker volume fraction, and trend line.

Gaussian statistic for the polymer chains, and, finally, (3) of small deformations in the case of which there is no chain reptation, as follows:

$$M_c = \frac{V_s \rho_p \left[\dfrac{2}{fQ_m} - \left(\dfrac{1}{Qm} \right)^{1/3} \right]}{\ln\left(1 - \dfrac{1}{Q_m} \right) + \dfrac{1}{Q_m} + \chi \left(\dfrac{1}{Q_m} \right)^2} \qquad (7)$$

V_s is the molar volume of the solvent, χ is the interaction parameter, f is the node functionality, and ρ_p is the matrix density. $V_s = 90.12$ cm^3/mol; $\rho_p = 1.35$ g/cm^3; the interaction parameter χ is estimated from the interaction parameter values of the THF ($\chi = 0.14$) and the acetone ($\chi = 0.63$). It is necessary between these 2 values since it was noticed experimentally that MEK is a better solvent than acetone, but not as good a solvent as THF. It was taken as $\chi = 0.2$. In fact, this value has only a small influence on the results discussed below.

Figure 9 shows that an increasing whisker content leads to a decrease of the calculated M_c value of the composite. The same observations were done by Ibarra[21] with short-fiber elastomer composites and by Bogonuk in filled elastomers.[20] Following their conclusion, the presence of adsorbed chains on the whiskers surface seems to act like supplementary crosslink points.

An attempt was made to estimate the mechanical behavior of such a network in which the interwhisker bonds are assumed to result of adsorbed polymer chains. The calculation based on previous work[14] was focused on the whiskers' skeleton properties. From the simulation of a randomly dispersed whiskers network in a cubic cell, a set of nodes was obtained, considering all the intersection points of whiskers. Two whiskers were considered to cross whenever they met within a distance lower than their diameter. The boundary nodes were defined as the intersection between the whiskers and the cubic faces. Whisker segments between nodes were assumed to be linked together within two extreme conditions. In the first case, there was no force transfer at the nodes; whisker segments acted as bars. In the second case, whiskers were assumed to act as Euler beams; the links between them were perfect, that is, infinitely rigid, so that both displacements and rotations were fully transmitted. The calculation of beam and bar network mechanical properties gave the lower and upper bounds, respectively, of the real whiskers network.

The Young modulus of the whiskers were taken of 130 GPa with an aspect ratio of 1/67 and Poisson ratio of 0.3. The network stiffness was calculated within the two hypotheses (bar or beam elements) with the CASTEM 2000 finite elements code. Homogeneous strain conditions were applied at the boundaries; that is, the displacements of the boundary nodes were set so that they fulfill a prescribed displacement gradient. The elastic parameters of the network were deduced from an identification of the external work with the elastic deformation energy. Due to the limitation of computer memory, the maximum whiskers number, used for the determination of network nodes, was 2000. This number depended on the whiskers volume fraction since the higher was this latter; the more numerous were the nodes and the segments of the simulated network. For this reason, the calculations were done for a maximum whiskers concentration of 7%. The isotropy of the simulated networks was checked, meaning that the whisker number used was sufficient. We noticed a dispersion of the results, which increased when the whisker volume fraction decreased. The results are plotted in Figure 10.

The simulation of the rigid network (beams) leads to a shear modulus lower than in previous reports.[14] This is probably due to the higher number of whiskers considered in this work, leading to a more realistic modelling of the network. It is

Figure 10 FEM simulated Young modulus for the "flexible" network of bar elements ($- - -$) and for the rigid network of beam elements ($\bigcirc$ and trend line ——), as a function of the whisker volume fraction. Comparison with experimental modulus measured at 333 K ($\square$).

noticeable that the percolation threshold appears clearly as an increase of the modulus. Values calculated for bar element simulation are widely spread. In that case, the reinforcement effect is only provided by a tetrahedralization of the bars, which is statistically less frequent than the simple intersection of whiskers. Increasing the number of elements leads to a modulus which tends toward 2 Mpa for volume fraction in between 5 and 7%. For lower whiskers content, no reinforcement effect is detected: the intersection points are too few statistically to allow the occurrence of efficient tetrahedralization of the elements. The calculation for bar element networks leads to an underestimation of the modulus since each whisker segment is supposed not to transmit momentum, even between bars of the same whiskers.

Whatever be the limitation of this modelling, it shows that even a low transfer of stress between whiskers can provide a reinforcement of the composite in which they are embedded. For comparison, experimental data for composites, measured at 333 K, are plotted in Figure 10. They are in between the two calculated bounds. Besides, in Figure 3, the discrepancy between the Halpin–Kardos model and the experimental values measured above T_g becomes evident for whisker contents higher than 4%, that is, close to the calculated threshold of reinforcement of bar networks.

CONCLUSION

New thermoplastic matrix nanocomposites with well-dispersed fillers have been prepared. The particularities of these fillers reside in their high aspect ratio and, due to their very small size, an unusual large interface area. The mechanical properties measured at small deformation revealed all the potential interest in such materials. Advantages include their transparency and their suitability for processing as small thick pieces. The theoretical models based on mean field assumption, which took into account the shape and the anisotropy of the mechanical properties of the whisker fillers, did not fully fit the experimental values of the modulus if the stiffness and size were those of each phase considered independently.

Among the models tested, the Halpin–Kardos equation was chosen for its simplicity and ability to account for the viscoelastic behavior. It was found to overestimate by about a factor of 2 the modulus below T_g, and to underestimate by a much higher factor the modulus in the rubber plateau region. To overcome the overestimation below T_g, a correction factor calculated from the modulus of the composite below T_g was applied. The existence of an interphase of immobilized matrix in contact with the whisker surface was assumed. Thus, the matrix of the composite was described, in the first approximation, like a medium containing whiskers of matrix without glass transition and with the same aspect ratio as the cellulose whiskers. With this assumption, the composite was modelled in two steps with the Halpin–Kardos equation applied successively for the calculation of the modulus of the matrix and then of the composite. However, calculated values were still under-estimated, and this could be a consequence of whisker connexity, which should occur around 1 vol %.

The geometric percolation threshold of such large aspect ratio cellulose whiskers is very low, and so the assumed interphase might make a link between the whiskers, thus allowing the formation of a flexible network. This scheme was supported by swelling experiments, which showed a large decrease in swelling with increasing whisker content. However, the existence of a part of the matrix whose the properties are modified by the whiskers was not revealed by DSC or isochronal DMA measurements. It might be due to either the absence of relaxation within this interphase or the lack of precision with these experiments. Only an increase of the loss factor with

whiskers content in the rubber plateau domain was observed. A further study of the molecular dynamic of the matrix mechanical spectroscopy would be desirable because it could provide a comparison between the relaxation time of the matrix with and without fillers and a better partition between the different relaxations that occur. That is the purpose of a further work.

REFERENCES

1. Maldas, D.; Kokta, B. V. Trends Polym 1993, 1, 174.
2. Flodin, P.; Zadorecki, P. Composite Systems from Natural and Synthetic Polymers; L., Salmen, A. de Ruvo, J. C. Seferis, E. B. Stark, Eds.; Elsevier Science: pp 59–83.
3. Varghese, S.; Kuriakose, B.; Thomas, S. J Appl Polym Sci 1994, 53, 1051.
4. Klason, C.; Kubat, J.; Strömvall, H.-E. Int J Polym Mater 1984, 10, 159.
5. Felix, J. M.; Gatenholm, P. J Mater Sci 1994, 29, 3043.
6. Sain, M. M.; Kokta, B. V. J Appl Polym Sci 1994, 54, 1545.
7. Anthoine, G.; Arnold, R.; Boustany, K.; Campbell, J. Rubber India Sept 24, 1976.
8. Dalväg, H.; Klason, C.; Strömvall, H.-E. Int J Polym Mater 1985, 11, 9.
9. Trejo O'Reilly, J. A., Ph.D. Thesis, INPG, Grenoble, France, 1996.
10. Matuana-Malanda, L.; Park, C. B.; Balatinecz, J. J. Cell Plast 1996, 32, 449.
11. Boldizar, A.; Klason, C.; Kubat, J.; Näslund, P.; Saha, P. Int J Polym Mater 1987, 11, 229.
12. Favier, V.; Chanzy, H.; Cavaille, J. Y. Macromolecules 1995, 28, 6365.
13. Dinand, E.; Vignon, M.; Chanzy, H.; Vincent, I.; Maureaux, A. Brevet francais 1995, 95-11-555.
14. Favier, V.; Dendievel, R.; Canova, G.; Cavaillé, J.-Y.; Gilormini, P. Acta Mater 1997, 45, 4, 1557.
15. Sassi, J.-F., Ph.D. Thesis, Joseph Fourier University of Grenoble, France, 1995.
16. Kinjo, N.; Komatsu, T.; Nakagawa, T. Nippon Kagaku Zasshi (J Chem Soc Jpn) 1971, 92, 27.
17. Chazeau, L., Ph.D. Thesis, Joseph Fourier University of Grenoble, France, 1998.
18. Hajji, P.; Cavaillé, J.-Y.; Favier, V.; Gauthier, C.; Vigier, G. Polym Compos 1996, 17, 612.
19. Cavaillé, J.-Y.; Salvia, M.; Merzeau, P. Spectra 2000 1988, 16, 37.
20. Bogonuk, C., Ph.D. Thesis, Joseph Fourier University of Grenoble, France, 1994.
21. Ibarra, L.; Chamorro, C. J Appl Polym Sci 1991, 43, 1805–1819.
22. Adelmann, J.; Klein, A. J Polym Sci 1958, 31, 77.
23. Halpin, J. C.; Kardos, J. L. J Appl Phys 1972, 43, 2235.
24. Molinari, A.; El Mouden, M. Int J Solids Struct 1996, 33, 3131.
25. Halpin, J. C.; Kardos, J. L. J Appl Phys 1972, 43, 2235.
26. Jourdan, C. Ph.D. Thesis, INSA, Lyon, France, 1987.
27. Sakurada, I.; Nukushima, Y.; Ito, T. J Polym Sci 1962, 57, 651.
28. Matsuo, M.; Sawatari, C.; Iwai, Y.; Ozaki, F. Macromolecules 1990, 23, 3266.
29. Nishino, T.; Takano, K.; Nakamae, K. J Polym Sci, Part B: Polym Phys 1995, 33, 1647.
30. Tashiro, K.; Kobayashi, M. Polym Bull 1985, 14, 213.
31. Tashiro, K.; Kobayashi, M. Polymer 1991, 32, 1516.
32. Kroon-Batenburg, M. J.; Kroon, J.; Northolt, M. G. Polym Commun 1986, 27, 290.
33. Peyroux, R. Ph.D. Thesis, Université des Sciences et Techniques du Languedoc, France, 1990.
34. Weber, M. E.; Kamal, M. R. Polym Compos 1992, 13, 2.
35. O'Connor, J. E. Rubber Chem Technol 1977, 50, 945.
36. Ibarra, L.; Chamorro, C. Polymer Composites 1989, 10, 4, 256.
37. Boluk, M. Y.; Schreiber, H. P. Polymer Composites 1986, 5, 295.
38. Nielsen, L. E. J Appl Polym Symp 1969, 12, 249.
39. Amdouni, N. Ph.D. Thesis, INSA, Lyon, France, 1989.
40. Ziegel, K. D. J Colloid Interface Sci 1969, 29, 1, 72.
41. Isaaka, K.; Shibayama, K. J Appl Polym Sci 1978, 22, 3135.
42. Dickie, R. A. J Appl Polym Sci 1973, 17, 45.
43. Morrison, J. D.; Burgess, A. N.; Stephenson, R. C. Polymer 1994, 35, 11, 2272.
44. Ballard, D. G. H.; Burgess, A. N.; Dekoninck, J. M.; Roberts, E. A. Polymer 1987, 28, 3.
45. Monteiro, E. E. C.; Mano, B. E. J Polym Sci 1984, 22, 533.
46. Mutin, P. H.; Guenet, J. M. Macromolecules 1989, 22, 843.
47. Flory, P. J.; Rehner Jr., J. J Chem Phys 1943, 21, 521.