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Yves Bréchet, Jean-Yves Cavaille, Emmanuelle Chabert, Laurent Chazeau, Rémi Dendievel, et al.. Polymer based nanocomposites: effect of filler-filler and filler-matrix interactions. *Advanced Engineering Materials*, 2001, pp.571-577. <10.1002/1527-2648(200108)3:83.0.CO;2-M>. <hal-00475327>

HAL Id: hal-00475327

<https://hal.science/hal-00475327v1>

Submitted on 9 Apr 2024

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Polymer Based Nanocomposites: Effect of Filler-Filler and Filler-Matrix Interactions

By Yves Bréchet, Jean-Yves Y. Cavaillé,* Emmanuelle Chabert, Laurent Chazeau, Rémy Dendievel, Lionel Flandin, and Catherine Gauthier

Nanocomposite materials present specific features, mainly due to their very high interfacial area, and a very short distance between reinforcing particles surface. For polymer based nanocomposites, reinforcing particles are most of the time much stiffer than the matrix. In that case, the percolation of those particles which occurs at a threshold fraction which depends on their shape factor (and on their dispersion characteristics) is shown to play a drastic role, especially if they form a rigid network. Such a network may result from strong interactions between the surface of the dispersed particles, but softer network may appear if the particles are bound together through the interactions of their surface with polymer chains. In order to analyze and to predict the behavior of nanocomposite materials, a modeling of this type of interactions is proposed, and allows to better understand the origin of the high reinforcing effect, generally observed. However, the complete prediction of composite materials with percolating dispersed fillers is still a difficult problem and requires further developments. It exemplifies for the special case of composites a general problem of two phase materials: the effect of scaling down the reinforcement and the properties of entangled structures.

1. Introduction

Since many years, polymer based nanocomposite materials are actively studied especially because they may have unusual combinations of properties. In fact, among this class of materials, some of them have been used for a long time like for instance, carbon black filled rubber in automotive industry. However, a well-known non-linear behavior like "Payne"^[1] or "Mullins"^[2] effects is still analyzed only empirically. More generally, several effects are observed, most of them being a consequence of the extremely high interfacial area (hundreds m²/g of materials) and of the very short distance between the surface of the reinforcing fillers.

In addition, some years ago,^[3] we showed that a drastic reinforcing effect may be observed, but also that this effect is closely dependent on the material processing step. For this reason, a part of the present investigations has been focused on the effect of particles percolation, especially when they are much stiffer than the matrix. Four main routes were explored, (i) the study of the percolation effect on the linear mechanical properties,^[4] (ii) the study of non linear behavior below the glass rubber transition temperature T_g of the matrix,^[5, 6] and above it (rubbery state),^[7] (iii) the percolation itself through the electrical conductivity of modified fillers^[8] dispersed in a

soft matrix and its behavior under given strain rate and stress relaxation experiments,^[9] and (iv) the modeling of the reinforcing effect by analytical and numerical calculations.^[10] This paper will give an overview of these different aspects, bringing together experimental data and modeling results.

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2. Experimental Aspects

The particle shape factor is the only parameter able to shift the percolation threshold when particles are randomly dispersed within a matrix. Two main types of fillers were used, namely spherical and rod like. Both were in the nanoscale range.

2.1. Spherical Nanofillers

The effects of both nature and concentration of the fillers on mechanical properties can be addressed by the study of reinforced soft thermoplastic matrices.^[11] Different composites, based on the mixture of a film forming latex (matrix) with aqueous suspension of fillers in required proportions, were obtained by evaporation under controlled atmosphere. Choice was made of a poly(butyl acrylate) matrix (PBA, $T_g = -50^\circ\text{C}$) filled with spherical particles of either polystyrene (PS, $T_g = 100^\circ\text{C}$) or silica, both of diameter 120 nm. The filler content varies around the geometric percolation threshold ($\sim 24\%$), from 10% to 50% vol. Such elaboration process is convenient to incorporate large amounts of fillers, but it does not prevent from filler aggregation, as frequently observed in nanocomposites.

The dynamic modulus (G' , G'') of composites have been measured as a function of temperature, with an home-made inverted pendulum working in an helium atmosphere. These curves were normalized in the glassy region (to avoid experiment uncertainty), using a 3 phase model (that accurately accounts for the slight reinforcement observed in this region^[12]). Figure 1a shows the shear modulus as a function of temperature of PBA-PS filled composite, PBA-silica filled composite and the pure PBA matrix. In addition to a higher level of relaxed modulus, the evolution of composite modulus with temperature differs from that observed for the pure matrix. Considering PS/PBA "as dried" systems (i.e. just after the coalescence of PBA latex at room temperature), the com-

posite modulus falls with increasing temperature until 70°C , and then increases before falling again above the PS main relaxation temperature. This increase can be associated with morphological evolution of the PS phase, i.e. thermally assisted increase of contact area between neighboring PS particles. Beside, similar tests have been performed on PS filled composites heated at 140°C , to achieve the PS particles coalescence. As shown on Figure 1a, the annealing treatment leads to a higher relaxed modulus. Moreover, the decrease of G' with increasing temperature follows the evolution measured for pure PS. So, in this case, the temperature dependence of the modulus is governed by the stiffest connected phase, PS. These experiments underline the differences in mechanical behavior between a system in which particles are just in contact and a system in which particles are strongly bounded. When filled with silica particles, the composite exhibits higher modulus value than with PS particles, and a weaker temperature dependence. The influence of filler content is shown in Figure 1b: as expected, the reinforcement above T_g (PBA) increases with the filler content. One can notice that the relaxed modulus does not increase linearly with filler fraction and a much faster increase is even observed around 20%vol, i.e. in the vicinity of the geometric percolation threshold. Moreover, it can be observed that particle-particle interaction has an influence on the mechanical properties even below the geometric percolation threshold, as evidenced on Figure 1b. The results for PS and silica fillers suggest that the strength of filler/matrix interaction plays also an important role. As a conclusion, the relaxed modulus increases with increasing filler concentration, contact area, connectivity and the strength of the filler interaction.

2.2. High Aspect Ratio Rod-Shape Nanofillers

In the past few years, there has been an important development of new nanofibers with a large aspect ratio. These new materials combine the advantages of a large interface area (more than $100\text{ m}^2/\text{g}$) with a much lower percolation threshold than particles. Cellulose whiskers, made from tunicates, are quasi-perfect crystals with $18 \times 9\text{ nm}$ lateral dimensions^[13] and an aspect ratio of around 100. They have a tensile modulus (150 GPa) much higher than the usual modulus of polymers (around 3 GPa below the glass transition temperature T_g) and can form hydrogen bonds with their neighbors thanks to the numerous hydroxyl groups on their surface.

Intensive studies have been performed with these fillers, which can be obtained as a stable aqueous suspension. A number of works, using

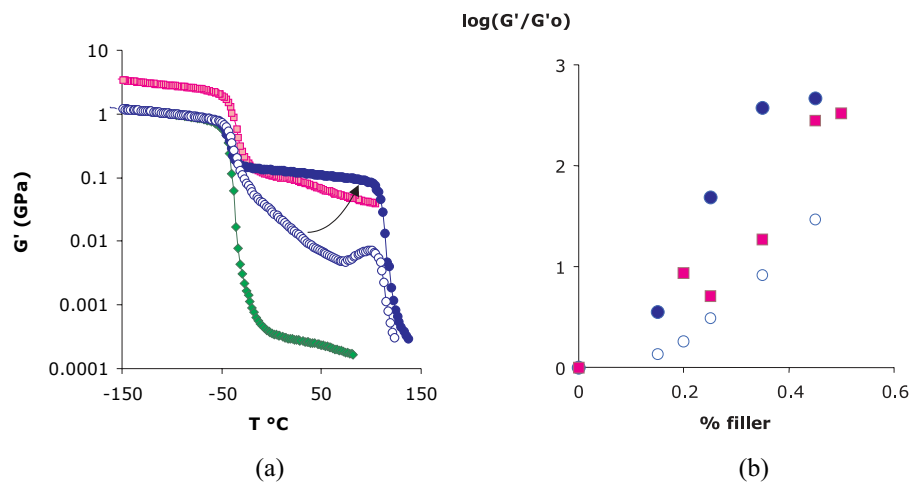


Fig. 1. Experimental elastic modulus measured by dynamic mechanical analysis ($f=1\text{ Hz}$). a) - vs. temperature for 45% filled PS, as dried (\circ) and after annealing treatment at $T > T_{gPS}$ (\bullet), for 45% filled silica (\blacksquare) and for PBA matrix (\diamond); b)- reinforcement at 0°C vs. filler content: case of PS (as dried \circ and after annealing treatment \bullet) and silica \blacksquare .

different matrices such as a copolymer P(S-BA) latex^[4] ($T_g = 0^\circ\text{C}$), plasticized PVC^[14] (here after called pPVC, $T_g = -10^\circ\text{C}$), Epoxy resin,^[15] polypropylene,^[16] etc. show the very important reinforcing effect of these fillers when introduced in polymer matrices above the glass transition temperature. This reinforcement is again extremely dependent on the way of processing the composites. Figure 2a shows the torsion modulus of pPVC matrix composite and P(S-BA) latex composite as a function of temperature. Both materials are processed in a very different manner. In the former case, the pPVC suspension is mixed with the whiskers aqueous suspension, then freeze dried, hot mixed in a Brabender (Banburry S.A.), and pressed as a 2 mm thick sheet. For P(S-BA) matrix, the aqueous suspension of whiskers and P(S-BA) droplets is simply dry-cast in a mould. T_g of P(S-BA) is well below the room temperature and leads to a film formation by the simultaneous water evaporation and the inter-diffusion of the polymer chains. The microstructural characterization of both composites by electron microscopy, and small angle neutron scattering^[13] shows the homogeneous dispersion of the whiskers inside the matrix and the absence of aggregates.

When tested by dynamic mechanical analysis, P(S-BA) composite shows a drastic increase of the modulus when the whisker concentration increases (Fig. 2b). This increase reaches a three decades factor for only 6 % whiskers content. It is also found that the modulus of this composite is almost constant above T_g , up to the temperature of cellulose degradation (200°C), though P(S-BA) modulus dramatically decreases in this temperature range. The increase of the modulus of plasticized PVC is much more progressive and does not show any percolation threshold.

These results suggest that the formation of a cellulose whisker network occurs when the processing allows the formation of strong hydrogen bonds between whiskers. Below

the temperature of cellulose degradation, the bonds strength is slightly temperature dependent, and leads therefore to a constant modulus of the network. This latter is present in P(S-BA) composite, for which the evaporation casting process allows the whiskers contact formation. The existence of a whisker network is confirmed by swelling experiment in toluene. This solvent totally dissolves non reinforced P(S-BA), but only swells the reinforced sample. Moreover, the swelling ratio Q decreases drastically with increasing whisker content ($Q = 60$ for 1 % filler content, $Q = 30$ for 6 %).

The hot mixing process used for PVC composites probably leads to a destruction of the whisker - whisker bonds. This explains the much smaller reinforcement observed with this material, compared to P(S-BA). However, the experimental value for the modulus remains much higher than the calculated ones with classical model (see below) when concentration is above 5 %. This indicates the formation of a soft network in which the junctions between whiskers are made of adsorbed PVC chain. This is in agreement with the fact that the composite modulus decreases like that of the pure matrix modulus at increasing temperature (Fig. 2a).

These differences of interaction between whiskers inside both composites were confirmed by large deformation experiments. When tensile tests are performed above T_g ,^[5] the stress-strain curve of P(S-BA) composite with 6 % filler content shows a sudden decrease of its slope for deformation of few %, but not a fracture of the sample. This indicates the irreversible damage of the whiskers-whiskers network inside the composites. By contrast, tensile tests on PVC composites show a progressive damage of the materials without any critical value of the deformation above which a decrease of the mechanical properties could be observed.^[7]

The role of a rigid or semi-rigid whisker network, (i.e. with hydrogen bonds or bonded by the way of the matrix) was confirmed by other experimental results on epoxy resin composites^[15] and polypropylene composites.^[16] In the former case, the material was processed by an *in situ* crosslinking of the epoxy resin (previously under the form of emulsion in a whiskers aqueous suspension). In the latter case, the whiskers originally obtained in aqueous suspension were stabilized as a toluene suspension thanks to the use of surfactant. This suspension was then mixed with polypropylene in toluene, and then dry cast. One can notice the advantages of these two other processes, which enable the use of cellulose whiskers as fillers in most of the commercial polymers, and therefore enlarge their possible application in the composite field. The modulus of these composites is

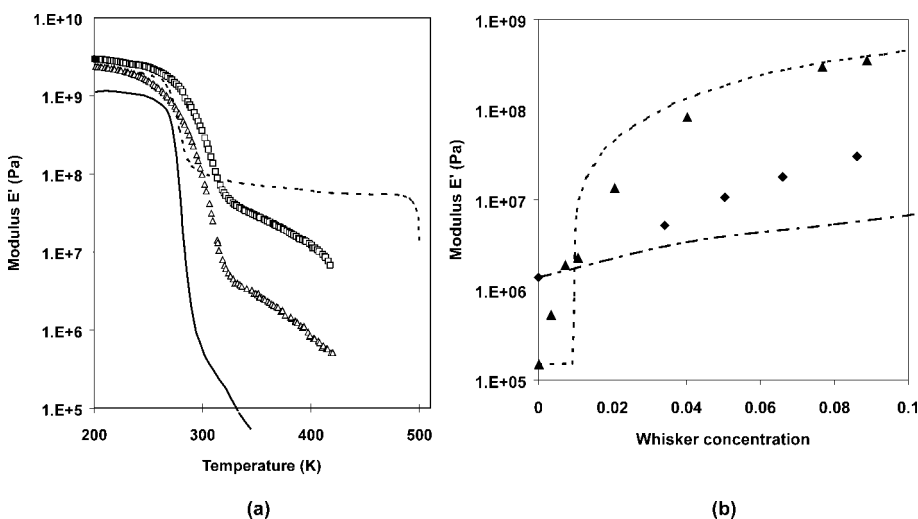


Fig. 2. Experimental elastic modulus measured by dynamic mechanical analysis ($f=0.1$ Hz): a) vs. temperature for pPVC matrix (Δ), pPVC reinforced with 6.6 v/v% of whiskers (\square), PS-Abu (bold line), PS-Abu reinforced with 6 v/v% of whiskers (dashed line), b) as a function of filler content of pPVC composites (\blacklozenge , $T = 60^\circ\text{C}$) and PS-Abu composites (\blacktriangle , $T = 52^\circ\text{C}$). Theoretical modulus deduced from the "percolation theory" for PS-Abu composite description (----). Theoretical modulus deduced from the "cluster model" with pPVC as matrix (-.-.-).

highly increased by the fillers and is again explained by the formation of a whiskers network.

2.3. Percolation and Electrical Measurements

In order to check that the filler percolation plays the main role in the composite reinforcement, a set of experiments has been focused on the preparation and the characterization of an homogeneous composite material composed of electrically conductive fillers dispersed in a thermoplastic insulating matrix. These fillers were chosen to have either a spherical shape or a rod-like shape with a high aspect ratio (70). Processing of these conductive polypyrrole particles, which were obtained either through a classical polymerization of pyrrole in the presence of stabilizer, or polymerization onto the surface of cellulose whiskers, is detailed elsewhere.^[8] Matrix was made with the same P(S-BA) copolymer. The relationship of filler content in the composite to electrical and mechanical properties was investigated. Among the main results, the mechanical behavior of these materials was shown to correspond to the case where no strong interactions exist between the whiskers (polypyrrole inhibits hydrogen bonding), but here again, the reinforcement is much higher than expected from classical mean-field theory. Moreover, in order to characterize the connectivity of the fillers in the matrix, electrical measurements were performed and appeared to be in good agreement with the predictions of the statistical percolation theory. This is also an indication that the filler dispersion is almost random, i.e. no large aggregates are formed during the process. The next step was to record simultaneously AC electrical conductivity and stress – strain curves, which allows to follow the damage of the percolated network versus strain or time. The main point is that with rods (whiskers) but not with spherical conductive particles, this damage is recovered during the stress relaxation (i.e. when $d\varepsilon/dt = 0$) after deformation up to 0.2, within less than 2 hours (see Fig. 3).^[9]

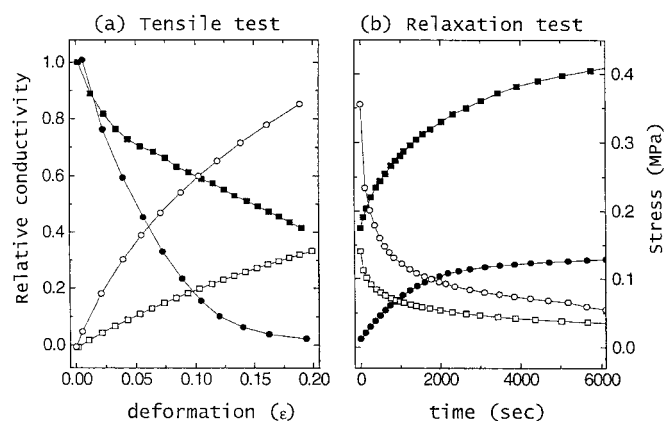


Fig. 3. Evolution of the normalized real conductivity at low frequency (1kHz) under tensile and relaxation tests for composites containing 10% of stick-like filler (■) and 20% of spherical filler (●) and corresponding mechanical stress (opened symbols).

3. Modeling Approaches

The materials investigated here are a challenge for micro-mechanical models. From a very general point of view, the elastic modulus of a filled polymer is affected by (i) the elastic properties of its constitutive phases (i.e., modulus and Poisson ratio), (ii) the volume fraction of filler (iii) the morphology (i.e., shape, aspect ratio, and distribution of the filler into the polymeric matrix) and (iv) the interactions between fillers. Various models are proposed in the literature to understand the complex interplay between these parameters and to display a prediction of the elastic modulus of polymer composites. It is generally accepted that these elastic calculations can be extended to the description of the viscoelasticity of filled polymers through the correspondence principle of Hashin.^[17]

The first class of approaches are usually based on variational methods (e.g., Voigt and Reuss bounds). However, in the case of composites materials based on a polymeric matrix, the bounds are generally too far apart to allow reliable predictions (e.g., Young modulus of silica ~ 70 GPa, glassy polymer ~ 3 GPa, rubber ~ 1 MPa). The second class of theoretical predictions corresponds to phenomenological approaches (e.g., series-parallel model of Takayanagi).^[18] The description of the elastic behavior of the composite is deduced from empirical or semi-empirical equations, introducing one or more adjustable parameters. Although they are not rigorous enough, these approaches can be very useful as a first step to roughly estimate the effect of the mechanical coupling in a biphasic system. The third class of mechanical modeling are established on the definition of a "representative volume element" (R.V.E.), either with geometrical considerations (e.g., Kerner's model),^[19] or self consistent assumptions (e.g., Christensen and Lo's,^[20] Herve and Zaoui).^[21] When the RVE displays a single uniform reinforcing phase included in a continuous matrix, an analytical formulation is obtained, generally referred to as 3-phase model. This formulation appears to be well suited for homogenization of elastic and viscoelastic modulus when particles are well dispersed in the matrix and far apart from each other. However, as soon as particle aggregation occurs and especially when the rubbery plateau modulus is concerned, the 3-phase model fails to represent the data. This has been reported in the case of fillers when the volume fraction of the fillers is high (> 20% vol.), and even at very low fraction of particles in the case of nanocomposites. For instance, the cluster model, developed by Molinari et al.,^[22] which is an extension of the self-consistent model, though including the geometry of the whiskers, their anisotropic properties and their interaction via a Green operator, does not describe correctly the mechanical properties of pPVC composite (Fig. 2b). This model largely underestimates the composite modulus of the P(S-BA) latex, for which the strong hydrogen bonds between the cellulose whiskers must be accounted. The key issue behind this constant discrepancy is the failure of the inclusion/matrix concept to describe these systems close or beyond the percolation threshold. A new attempt is presented below, to describe the previous experimental data.

3.1. Spherical Nanofillers

The solution now proposed has the aim, via a Discrete Element approach, to explicitly take into account both initial spherical morphology of PS and PBA particles and nature of the contacts between them. A RVE made of hundreds of spheres is chosen, with a given volume fraction of PS and PBA particles. At each contact is associated a constitutive relation between forces and torques transmitted through the contact and the kinematics variables

(displacement and rotation rate) defined at the particle center. By analogy with Jagota and Scherer^[23], this relation involves normal, tangential, flexural and rotational viscous moduli. These moduli depend on the intrinsic viscosities of PS and PBA and on the contact radii. Three types of relationships are used, for PS/PS, PS/PBA and PBA/PBA contacts. For PS/PS, the contact radius is temperature dependent, which allows to describe the beginning of the coalescence observed above 70 °C. In the case of annealing treatment, the contact radius is assumed to be constant and of the same order than the particle radius. Moreover, the intrinsic viscosity of the PBA matrix is chosen higher for PBA/PS contacts than for PBA/PBA, but the difference decreases at increasing temperature. The equilibrium equations of the particle assembly are solved, with homogeneous imposed kinematics conditions at the boundaries. The resulting forces are deduced and thus the effective viscosity in the temperature range [-10 °C; +100 °C], i.e. above T_g and below T_f . The initial ratio for the PS and PBA moduli is 5.10^3 . In Figure 4a, it can be seen that the evolution of the effective shear modulus with temperature is qualitatively described for different volume fractions of reinforcing particles. In particular, the larger the volume fraction of PS, the more important is the decrease of the modulus with temperature. The beginning of the coalescence is also retrieved for PS concentrations larger than 30%. In Figure 4b is shown the effect of the annealing treatment. Experimental results at 50 °C, before and after annealing are plotted. The numerical results illustrate the difference between the "geometrical percolation" (a skeleton of PS particles is formed with small contact radii) and the "mechanical percolation" (the same skeleton of PS particles is formed, but with large contact radii). The last one occurs at about 20-25 % of PS reinforcements.

3.2. High Aspect Ratio Nanofillers

A first attempt to model the whisker composites is called the "percolation model" and can be derived from the phe-

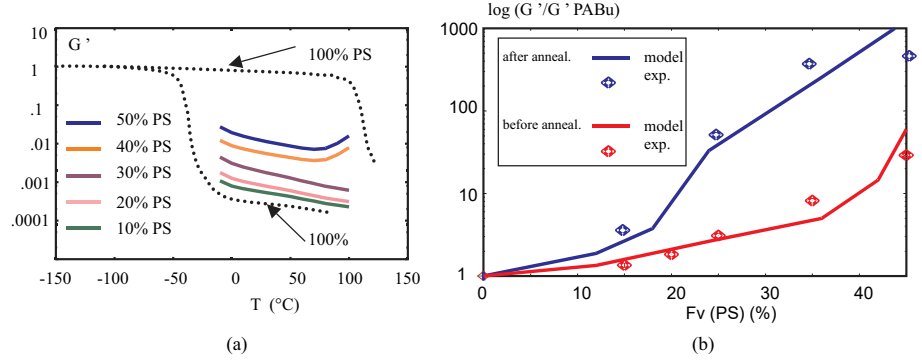


Fig. 4. a) - $G'(T)$ for different volume fractions of PS. Experimental values for PS and PBA are reported in dotted line. b) - $G'=f(\text{volume fraction of PS})$, at $T=50$ °C before and after annealing.

nomenological approaches. The composite is described as a parallel mechanical coupling of a rigid phase (made of the theoretical volume fraction of whisker network) and of a soft one (made of the matrix reinforced with the whiskers out of the network).^[4] This model is an important improvement of the description of P(S-BA) composite, as shown in Figure 2b, but it overestimates the PVC composite behavior. Therefore the evaluation of the network modulus as a function of the mechanical properties of the link between the whiskers is necessary. This work, in progress, is now described. The calculations are performed in two steps: (i) the generation of whisker networks (definition of intersection nodes, of elements between nodes, and of the linking elements between two whiskers in contact) and (ii) the calculation of the mechanical properties of the network with a finite element code CASTEM 2000 (DMT-CEA software). In the first step, whiskers (cylinder of length L and diameter d) are generated, with random orientation (for isotropic network). Their number depends on the aspect ratio, the volume fraction of whiskers, and the calculation capacity of the computer. Due to the high aspect ratio of the fillers, a procedure to account for boundary effects is adopted. Two whiskers are considered to intersect each other when the distance in between has a value below the diameter length. This leads to the definition of nodes and linking elements. These nodes are slightly displaced along the whisker length so that the link element length is constant. When there is a path linking each face of the sample to the opposite side (i.e. percolation), there is a continuous whisker network that can be mechanically tested. Due to the finite element calculation limit, the calculations are performed for volume fraction up to 9%. In the second step, using CASTEM 2000, the whiskers and the linking elements are considered as beams, i.e. nodes transmit displacement and rotation. The whisker modulus is 150 GPa, and the Poisson's ν , 0.35. The link beam has an adjustable stiffness. Its section is defined so that the apparent shear modulus is a third of its tensile modulus. The network is tested with symmetry conditions, in tensile test. The apparent tensile modulus is deduced from the summation of the forces applied on the nodes of the displaced face. Figure 5 presents preliminary calculations giving

the modulus of a whisker network, versus the whisker volume fraction, for different link beam properties. The curve shape is very similar whatever the "link beam" modulus. For small link modulus (below 1 GPa), the modulus of the network seems to linearly increase with the link modulus: in that case, the deformation mainly occurs in the links. Then for increasing value of the link modulus, the modulus of the network tends toward the value for totally rigid link. All the value calculated are below 1 GPa, meaning that the contribution of the whisker network is negligible in the reinforcement observed in the glassy state. Above T_g , for whisker fraction equal or below 5 %, the calculated value is also below the experimental tensile modulus of pPVC composite (at 60 °C). This suggests that, at this concentration, the network is too weak to have an influence on the modulus of the composite. This is confirmed by the reasonable agreement between experimental value and the "cluster model" for whisker content below 4 %.

Concerning P(S-BA) composites, their mechanical properties are mainly due to the whisker network properties when the volume fraction is above 6 %. For smaller fraction, the calculated modulus is lower than the experimental ones, even for high modulus of the links. Moreover, it must be noticed in Figure 2b that no clear percolation threshold appears on the mechanical properties. By contrast, the calculation necessarily leads to a steep increase of the modulus above 1 % whisker concentration. Different assumptions are currently investigated to explain this disagreement: the percolation threshold might be lower than the simulated one since the calculation of the intersections does not take into account the possible inter-phase thickness. A slight orientation of the whiskers parallel to the surface of water evaporation exists in the P(S-BA) composite, and the possibility of concentration heterogeneity is not excluded. However, the promising preliminary results suggest that the calculation presented here might be an alternative method to the classical models that are currently not efficient to describe the mechanical properties of such composites.

4. Conclusion

The experimental work and modeling presented in this paper shed some light on the specific role of the skeleton formation of dispersed stiff particles within a soft matrix. This skeleton is generally speaking flexible, as it results from the more or less random percolation of the particles during the material processing. However, in some cases where the particle/matrix interface has a high energy, a very stiff network

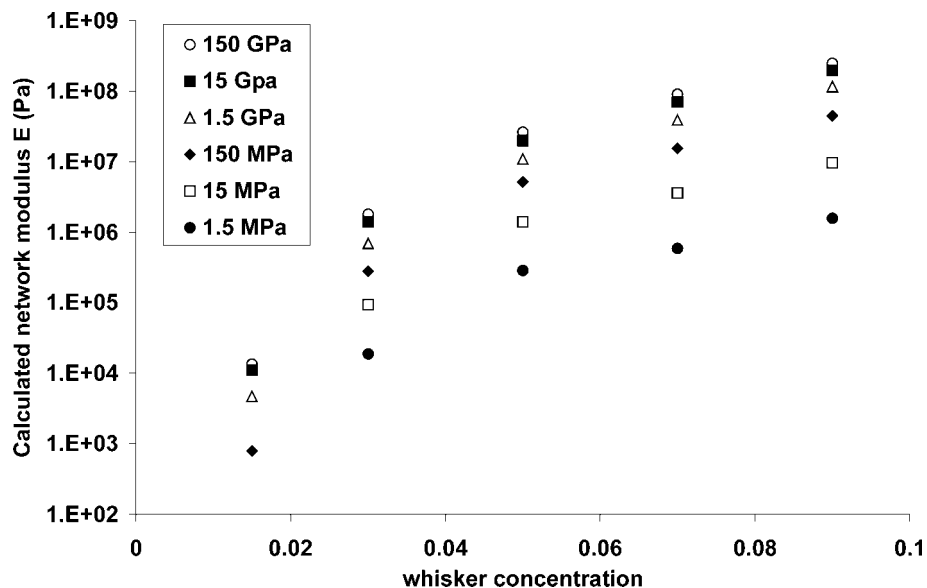


Fig. 5. Calculated modulus of a whisker network as a function of the whisker volume fraction, for different tensile modulus of the bond between the whiskers.

can be formed. When this is the case, i.e. the stiffness of the matrix is much lower than the network stiffness, the mechanical behavior of the composite material can be rather well predicted on the basis of a structural modeling (by finite element, for instance) assuming that the matrix behavior can be neglected. When the network is more flexible (resulting from just geometrical contact between particles, or when the surface particles are linked together by polymer chains), then classical mechanical coupling approaches are still not efficient and must be revisited. Several way can be experimented, such as the Discrete Element Approach presented above, but we can think also of an adaptation of homogenization techniques,^[24] as a work in progress.

- [1] A. R. Payne, *J. Appl. Polym. Sci.*, **1962**, 19, 57.
- [2] L. Mullins, *J. of Rubber Res.*, **1947**, 16, 275.
- [3] J. Y. Cavaille, R. Vassoille, G. Thollet, L. Rios, C. Pichot, *Colloid Polym. Sci.*, **1991**, 269, 248.
- [4] V. Favier, J. Y. Cavaille, H. Chanzy, A. Dufresne, C. Gauthier, *Polym. for Adv. Technol.*, **1995**, 6, 351–55. V. Favier, H. Chanzy, J. Y. Cavaille, *Macromol.*, **1995**, 28, 6365–67.
- [5] P. Hajji, J. Y. Cavaille, V. Favier, C. Gauthier, G. Vigier, *Polym. Comp.*, **1996**, 17, 612.
- [6] L. Chazeau, J. Perez, J. Y. Cavaille, *J. Polym. Sci. Polym. Phys.*, **2000**, 38, 383–92.
- [7] L. Chazeau, J. Y. Cavaille, P. Terech, *Polymer*, **1999**, 44, 5333–44.
- [8] L. Flandin, G. Bidan, Y. Brechet, J. Y. Cavaille, *Polym. Comp.*, **2000**, 21, 165–74. see also L. Flandin, T. Prasse, R. Schueler, K. Schulte, W. Bauhoffer, J. Y. Cavaille, *Phys. Rev. B*, **1999**, 59, 14349–55.
- [9] L. Flandin, Y. Brechet, R. Dendievel, J. Y. Cavaille, *J. Mater. Sci.*, **1999**, 34, 1753–59.

- [10] V. Favier, R. Dendievel, G. R. Canova, J. Y. Cavaille, *Acta Mater.*, **1997**, *45*, 1557–65.
- [11] E. Chabert, Ph.-D. Thesis, *INSA-Lyon*, in progress.
- [12] E. Reynaud, Ph.-D. Thesis, *INSA-Lyon*, **2000**.
- [13] P. Terech, L- Chazeau, J. Y. Cavaille, *Macromolecules*, **1999**, *32*, 1872–1875.
- [14] L. Chazeau, J. Y. Cavaille, G. Canova, R. Dendievel, B. Boutherein, *J. Appl. Polym. Sci.*, **1999**, *71*, 1979–1808.
- [15] M. Matos Ruiz, C. Graillat, J. Y. Cavaille, A. Dufresne, J. F. Gérard, *Composite Interfaces*, **2000**, *7*, 117–31.
- [16] C. Bonini, Ph.-D. Thesis, *Institut National Polytechnique de Grenoble*, **2000**.
- [17] Z. Hashin, *J. Appl. Mech.*, **1983**, *50*, 481–505.
- [18] M. Takayanagi, S. Uemura, S. Minami, *J. Polym. Sci. C*, **1964**, *5*, 113–122.
- [19] E. H. Kerner, *Proc. Phys. Soc. London*, **1956**, *69B*, 808–813.
- [20] R. M. Christensen, K. H. Lo, *J. Mech. Phys. Solids*, **1979**, *27*, 315–330.
- [21] E. Herve, A. Zaoui, *Int. J. Engin. Sci.*, **1993**, *31*, 1–10.
- [22] A. Molinari, M. El Mouden, *Int. J. Solids Struct.*, **1996**, *33*, 3131.
- [23] A. Jagota, G. W. Scherer, *J. Amer. Ceram. Soc.*, **1995**, *78*, 521–528.
- [24] M. Bornert, E. Chabert, C. Gauthier, A. Zaoui, J. Y. Cavaille, in progress.