PROCESSING AND MECHANICAL PROPERTIES OF A PLASTICISED PVC REINFORCED WITH CELLULOSE WHISKERS

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SUMMARY: The use of fillers with nanometric dimensions is actually intensively developed as reinforcing particles in thermoplastics, rubber and thermosets. In most of the cases, such particles are spherical, and it is known that the reinforcing effect is expected to be much higher with high aspect ratio fillers. In this work, cellulose monocristals (whiskers) with an average diameter of 15 nm and average length of 1µm are dispersed within polyvinyl chloride matrix. The mechanical properties are analyzed in both the linear and non linear domains and compared with data from modeling. In particular, the interfacial characteristics are discussed.

KEYWORDS: nanocomposite, cellulose, PVC, viscoelasticity, plastic deformation, molecular dynamics, modeling

INTRODUCTION

Since a long time polymers are usually filled by particles having a typical size below µm, as for instance carbon black to reinforce rubber, or more recently silica nanometric particles for thermoplastics and rubber. As shown in recent works, the mechanical stiffness can be drastically enhanced if the shape factor of the fillers is far from unity. The major problem is the achievement of a random dispersion of fillers, especially, if their surface energy is much higher than the matrix. One of the ways we explored to solve these problems was to perform a dispersion step of fillers in the matrix, in an aqueous suspension. By this method, it is possible to avoid aggregates formation after water evaporation or freeze drying. Suspension, micro-suspension and emulsion polymerization are widely used in industry to produce polymers in aqueous medium. On the other hand, cellulose whiskers are rod shaped monocrystals (extracted from the biomass, with a typical length of 1 µm, and a diameter of 15 nm) prepared, in this case, from tunicates. Whiskers were firstly studied by Favier et al.[1] 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 et al., includes hot-mixing and hot-molding which should avoid the formation of the hydrogen bonded network. Composites with different whisker contents are prepared. For both fundamental and industrial interest, PVC plasticized by di-ethyl-hexyl phthalate (DOP) is chosen as the matrix[2]. 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 modeling of the lower and upper limits of such a network modulus.

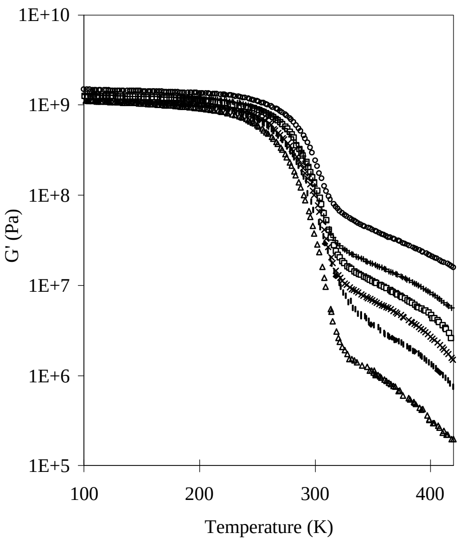
MATERIALS

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 sulfate groups grafted during the sulfuric acid treatment. Poly-vinyl-chloride was supplied by Elf-Atochem (molecular weight $\overline{M_n}$ =40000, polymolecularity indice I_p=2). The whiskers suspension was blended with the PVC micro-suspension (bead diameter 0.2 µm) and then freeze-dried. The blend of this freeze-dried powder, 30 phr (i.e. per hundred ratio of PVC) of plasticizer D.O.P (di-ethyl-hexyl phthalate 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 mixer Brabender. This mixture was then pressed into sheets by compression molding at 200°C during 3 min. We made composites with 0, 6, 9, 12, 16, 24 phr, i.e. respectively, 0, 3.4, 5, 6.6, 8.4, 12.4 % by volume of whiskers contents.

RESULTS AND DISCUSSION

The mechanical behavior has been measured within linear conditions (by mechanical spectroscopy) and non linear below and above Tg (compressive and tensile tests). Typical results are reported in Figures 1 and 2.
The improvement of both the shear modulus is much higher (by about a factor 10) than predicted by classical model for mechanical coupling analysis based on mean field approach, which may result from the interactions between the whiskers (spatial constraints); the plastic flow stress can be analyzed from the DMA data, taking into account the stress concentration around the whiskers ends. It is worthy to point out that the overall plastic behavior results from various parameters, such as, the plastic behavior of the matrix alone, the mechanical coupling between fillers and matrix, the effect of stress concentration around the fillers and the damage of the material which corresponds mainly to interfacial decohesion [3-5].

The "quasi point defect theory" developed by Perez et al. and the account for fluctuations of plasticizer concentration within PVC, allowed a good analysis of the matrix behavior [4]. Furthermore, with the same set of parameters it is possible to provide a reasonable fit of experimental data (i) coming from dynamic mechanical analysis and mechanical spectroscopy as discussed in our previous work (i.e. within linear stress - strain condition), and (ii), given here by compressive tests (i.e. when the behavior is strongly not linear).
About the compressive mechanical behavior of nanocomposite samples, a procedure which consists in calculating the tangent modulus of the composite along the load path, from the tangent modulus of the matrix, and from the experimental relationship between the matrix



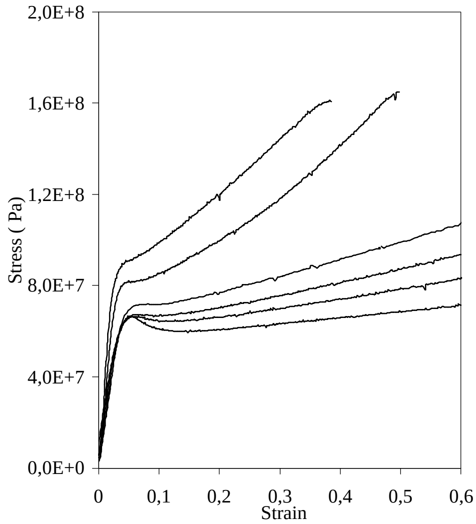


Figure 1: shear elastic modulus measured by dynamic mechanical analysis (0.1 Hz) of composites reinforced with 0% (Δ), 3% (♦), 5% (×), 6.6% (□), 8.4% (+), 12.4%vol. (○) of whiskers

Figure 2: Compression tests on plasticized PVC reinforced with (from bottom to top) 0, 3.4, 5, 6.6, 8.4, 12.4 %vol. of whiskers; T=253 K ; $d\varepsilon/dt=1.3\ 10^{-3}\ s^{-1}$

modulus and the composite modulus as measured by DMA, is proposed to predict the composite behavior. Stress concentration induced by the whiskers in the matrix is assumed to strongly enlarge the yield stress peak in stress - strain curves, leading almost to its disappearance. This concentration in turn, probably leads to damage which is evidenced by the whitening of samples. In order to evaluate the effect of stress concentration, a semi quantitative model is proposed. Finally, one of the key point of this work is thus the modeling of materials under large deformation can be entirely deduced from the study of materials under linear condition.

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