PROCESSING AND CHARACTERIZATION OF NEW THERMOSET NANOCOMPOSITES REINFORCED BY CELLULOSE WHISKERS

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SUMMARY: In the present study we describe the processing and the mechanical properties of a nanocomposite based on an aqueous suspension of microcrystalline animal (tunicier) cellulose fillers and a thermoset epoxy matrix. According to the type of processing and nature of cellulose fibers, we expect to solve common problems for this kind of composite processing related to high viscosity values in the molten state, the incompatibility between hydrophobic matrices and hydrophilic cellulose and the formation of hydrogen bonds between cellulose fibers which leads to aggregates formation. We are particularly interested in the reinforcing effect of this type of natural fibers in an epoxy matrix. The dynamic mechanical properties showed an important improvement of the composite modulus in the rubbery state of the matrix.

KEYWORDS: water-based epoxy, cellulose whiskers, processing, nanocomposites, dynamic mechanical properties

INTRODUCTION

Cellulose fibers are gaining importance as a reinforcing phase in thermoplastic matrices. They combine good mechanical properties and their ability to be biodegradable and renewable. Many works in the literature emphasizes (i) on the dispersion of short fibers into the matrix during processing and (ii) on the incompatibility between hydrophobic thermoplastic matrices and hydrophilic cellulose filler, which usually leads to low performance of the resulting composites. Processing problems related to the high viscosity of the molten polymer/fiber system, the formation of hydrogen bonds between cellulose fibers, and the fact that these fibers are generally long and entangled which results in aggregates formation were reported in the literature (1,2).

In the present study we describe the processing of a nanocomposite based on an aqueous suspension of microcrystalline animal cellulose fillers and a thermoset matrix. According to the type of processing and nature of cellulose fibers, we expect to solve the problems listed previously.

MATERIALS AND PROCESSING

The microfibrils consist of rod shaped monocrystalline cellulose domains (whiskers) prepared as a suspension in water from hydrolyzed mantles of tunicates (sea animals). An efficient reinforcement can be expected according to their highly crystallinity (95%), a large aspect ratio (about 100) and a high Young modulus (between 130 and 150 GPa) (3,4). The dimensions of the whiskers, determined by transmission electron microscopy, were 1μm length and 10-15 nm diameter. The solid fraction of the cellulose whiskers in water was 0.6wt%.

In order to achieve a good dispersion, the introduction of the whiskers in the epoxy matrix was done in an aqueous medium. The matrix was based on an emulsion in water of a prepolymer of diglycidyl ether of bisphenol A (Reapox 164) supplied by Bakelite (Mn=380g/mol, n=0.15, and a polyoxy propylene triamine (Jeffamine T403) from Hunstman (Mn=432g/mol ; functionality = 5.3) as a curing agent. A non-ionic emulsifier, the nonyl phenol polyethylene oxide (Igepal CO897) (Mn=2225g/mol; n=40 ; HLB=17.8) supplied by Rhône-Poulenc was used as 2.5%wt to obtain an epoxy emulsion (60% solids content; average diameter of particules: 2μm). The stoichiometric ratio aminohydrogen-to-epoxy was equal to 1. Thus, the whiskers suspension, the epoxy emulsion, and the curing agent which is soluble in water were mixed together. Composites based on 1, 2.5 and 5% by volume of whiskers contents were processed.

According to the formulation, the precessing of nanocomposites imply to phenomena: first the water evaporation of water and then, the polymerization process. Thin and transparent films (200μm) were obtained. The drying step should be slow enough in order to avoid a vitrification of the surface. The cure schedule was 40°C for 6 hours followed by 4 hours at 80°C. The glass transition temperature of the films is around 45°C which allows to perform mechanical tests at the glassy (T<Tg) or rubbery states (T>Tg) by changing the temperature of testing.

MECHANICAL PROPERTIES

Even with a low concentration of cellulose whiskers (5 wt%), the thermoset polymer films display improved mechanical properties specially at temperatures above the glass transition temperature (Tg). In Figure 1, the storage shear modulus G', and the loss factor (tan Φ) as a function of temperature at 0.1 Hz are showed. The curve corresponding to the neat matrix is typical of a thermoset dynamic mechanical behavior. At temperatures below Tα, the main mechanical relaxation associated with Tg, the shear modulus of the matrix remains constant (around 1 GPa) and decreases rapidly in the Tα region. Nevertheless, a secondary relaxation, denoted β is evidenced and is associated with motions of the hydroxyether units. Above the α relaxation i.e. in the rubbery state, G' remains constant with increasing temperature (rubbery plateau). The nanocomposites based on 5% of tunicin cellulose whiskers display a slight increase of the shear modulus below Tα, whereas, the decrease associated with α is reduced. The mechanical loss factor (tanΦ) exhibits a maximum around 300K (Tα) for the neat matrix. Tα is slightly modified by the presence of 5 wt % of cellulose whiskers, as it is shifted at 320K. This effect could be related to interactions between the matrix and the reactive surface of the cellulose. The shift of the α relaxation is in agreement with the DSC experiments.
In order to elucidate about the reinforcing effect (interactions between fibers and epoxy/fibbers or mechanical effect?) of the tunicin cellulose whiskers into an epoxy/amine matrix, a comparison between different mechanical theoretical approaches and the experimental data is in progress.

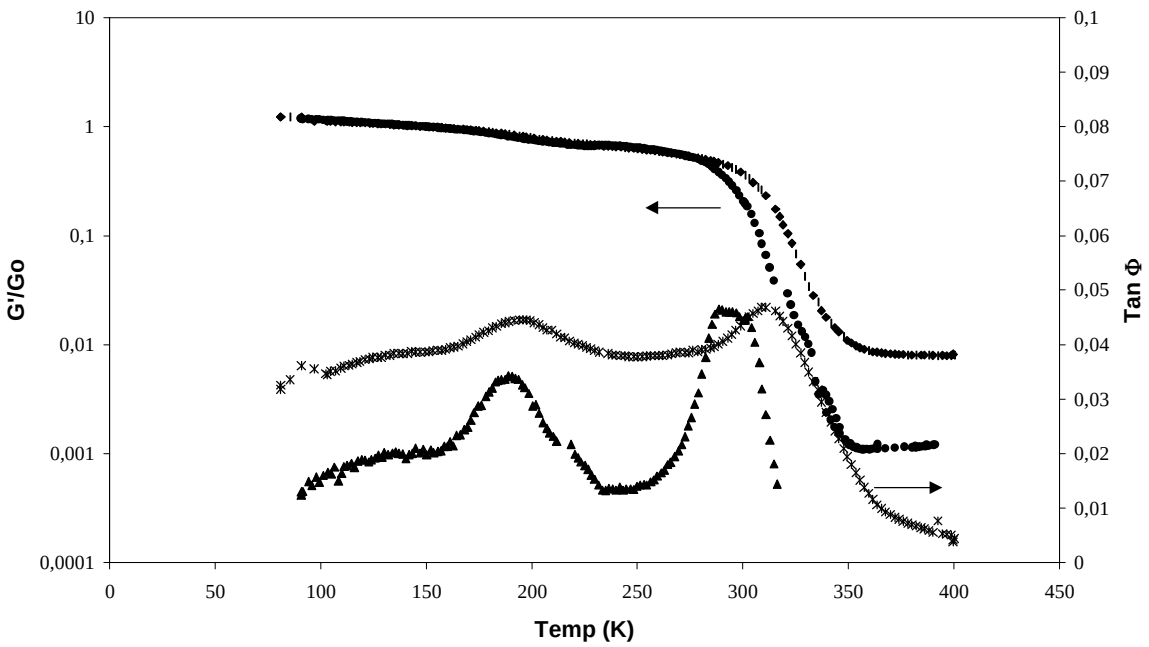

Fig. 1: Shear modulus G' and Tanϕ vs. temperature at 0.1 Hz for nanocomposites based on 0 wt% (• and ▲) and 5 wt% (♦ and ✻) of cellulose whiskers.

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REFERENCES

1. Klason C ., Kubat J., Strömvall H.E, "The efficiency of cellulosic fillers in common thermoplastics. Part 1: Filling without processing aids or coupling agents", *Intern. J. Polym. Mat*., Vol. 10, pp. 159-187, 1984.

2. Hajji P., Cavaillé J.Y., Favier V., Gauthier C., Vigier G., "Tensile behavior of nanocomposites from latex and cellulose whiskers", *Polym. Composites*, Vol. 17, No. 4, pp. 612, 1994.

3. Favier V., Chanzy H., Cavaillé J.Y., "Polymer nanocomposites reinforced by cellulose whiskers", *Macromolecules*, Vol. 28, No. 18, pp. 6365-6367, 1995.

4. Nishino T., Takano K., Nakamae K., "Elastic modulus of the crystalline regions of cellulose polymorphs", *J. Polym. Sci :B :Polym.Phys*., Vol. 33, pp. 1647-1651, 1995.