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# New Waterborne Epoxy Coatings Based on Cellulose Nanofillers

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**Summary**: New nanocomposites based on a waterborne epoxy emulsion and a suspension of cellulose crystallites were prepared by film casting in order to obtain coatings displaying both flexibility and stiffness. Tunicin cellulose whiskers are attractive reinforcing fillers due to their high aspect ratio, large interface area, and, significant mechanical properties). Typical processing problems for this type of composite are related to high viscosity values of filled polymers in the in the molten state, the incompatibility between hydrophobic matrices and hydrophilic cellulose and the formation of hydrogen bonds between cellulose of this type of natural fibres in an epoxy matrix. The aim of this work is to solve some of the problems above mentioned by selecting the nature of the components used for coating synthesis film processing. The dynamic mechanical properties display an important improvement of the composite modulus in the rubbery state of the matrix at low concentrations of fillers, which can not be expected other cellulose based fibers.

**KEYWORDS**: waterborne epoxy, cellulose whiskers, processing, and nanocomposites.

## Introduction

One of the principal challenges in the coating domain is to obtain an "ideal structure" which lead to produce flexible and stiff films at the same time. A compromise between these two contradictory properties must be achieved. A material having a two-phase structure -it means, a soft phase and a stiff one – is proposed in the literature as a possibility to obtain such compromise [1,2]. In other words, the soft phase could be a heterogeneous crosslinked

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polymer and, the hard phase based on stiff particles (microgels, silica particles) well dispersed in a continuous medium.

Waterborne coatings have been widely used as industrial coatings since they display several advantages compared to the solvent-based counterparts as: lower toxicity, reduced risk of flammability and reduction of voc. In addition, waterborne epoxy coatings have good adhesion with steel or concrete substrates and a relatively good chemical resistance [3-7].

As the viscosity of a polymer emulsion is independent on the molecular weight of the polymer, then, large amounts of solvents are not necessary to achieve low viscosity for applications. As a matter of fact, this kind of initial polymer component can be used to solve problems associated with dispersion of fillers into polymer matrices. Indeed, it is well known that emulsion polymerization can lead to the easy processing of materials, either by film casting (water evaporation) or by freeze drying followed by the classical extrusion process [8-12]. Common limits in composites processing are often related to high viscosity of molten filled polymer matrices. The common incompatibility between hydrophobic matrices and hydrophilic fillers, which usually leads to low performance of the resulting composites and, to the fact that long fibers tend to entangle which results in aggregates formation [13,14]. One of the keys proposed in the literature [15-17] is to graft functional groups onto the fiber surface in order to improve the interactions and/or the dispersion between the matrix and the fibers. In our work, we chose a dispersion step of fibers in the matrix, in an aqueous suspension as a way to solve these problems. Thus, both fillers and polymer matrix are prepared in aqueous medium and both suspensions must be stable, at least during the time necessary for mixing of the two components [16].

This work focuses on the use of cellulose whiskers, consisting of rigid rod shaped monocrystalline cellulose particles (whiskers) prepared in water from hydrolyzed mantles of tunicates (sea animals). Moreover, the very large aspect ratio (around 70), a high specific area ($150 m^2/g$), the high rate of crystallinity (95%), a reactive surface (hydroxyl groups) and, a high longitudinal Young modulus, $E_{11}$ (from 130 to 150 GPa) provide them with a great potential for the reinforcement of polymer matrices [8-14]. Favier et al. [8-10] studied the effect of tunicin whiskers in a poly(styrene-co-butyl acrylate) matrix. They demonstrated a large improvement of the composite modulus in the rubbery state of the matrix. This effect was attributed to the formation of a network of whiskers from the hydrogen bonds existing between the cellulose whiskers. This was confirmed by finite element calculation [10, 11].

In the present study we describe the dispersion and the reinforcing effect of an aqueous suspension of microcrystalline animal cellulose fillers into an epoxy matrix. According to the type of processing and nature of cellulose fibers, coatings having both stiffness and flexibility can be prepared.

## Experimental Part

### *Materials and processing*

**Cellulose whiskers**

Stable colloidal dispersions of tunicates (sea animals) cellulose were prepared according to a method described previously [19]. The microfibrils consist of rod shaped monocrystalline cellulose domains (whiskers) prepared as a suspension in water from hydrolyzed mantles of tunicates. The dimensions of the whiskers, determined by transmission electron microscopy, were 1μm long and from 10 to15 nm diameter. The solid fraction of the cellulose whiskers in water was 0.6wt%.

**Water-based epoxy emulsion**

The matrix was based on an aqueous emulsion of a diglycidyl ether of bisphenol A prepolymer (Reapox 164) supplied by Bakelite (Mn=380g/mol, n=0.15). A polyoxypropylene triamine (Jeffamine T403) from Hunstman (Mn=432g/mol; functionality=5.3) was selected as curing agent as it is soluble in water. A non-ionic emulsifier, the nonyl phenol polyethylene oxide (Igepal CO897) ( $\overline{M}$n=2,225g/mol; n=40; HLB=17.8) supplied by Rhône-Poulenc was used as 3%wt to obtain a 60% solids content epoxy emulsion, in order to prepare the "mother emulsion" (ME). The stoichiometric ratio aminohydrogen-to-epoxy was equal to 1 [3]. This epoxy emulsion was prepared under high-speed stirring (11,000 rpm for 15 minutes) using an Ika Ultraturrax mixer (S25KV dispersion tool). From these conditions of processing, the particle size of the emulsion droplets in the emulsion was 1.7± 0.1 μm.

**Films of nanocomposites**

The whisker suspension, the epoxy emulsion, and the curing agent were mixed together. The wet reactive system was applied using a bar-coater as 150-μm thick layers. Such a method leads to 150 μm-thick dried (i.e. cured) films. Composites based on 0.5, 1, 2.5, and 5% by weight of whiskers were processed. According to the formulation, the processing of nanocomposites requires two coexisting phenomena which can be denoted as "reactive drying": (i) the removal of water, i.e. drying and, (ii) the polymerization process. The drying step should be slow enough in order to avoid a vitrification of the surface, which could induced a limiting removal of water. The cure schedule was 40°C for 6 hours followed by 4 hours at 80°C. The glass transition temperature of the films depends on the process and on the whisker content as discussed below (see Table I). In all the cases Tg is between 20 and 50°C, which allows to perform mechanical tests both in the glassy state (T<Tg) and rubbery state (T>Tg) by slightly changing the temperature of testing from room temperature.

### Morphology characterization

Transmission electron microscopy (TEM) of nanocomposites was performed on specimens prepared by ultramicrotomy (Ultracut S from Leica) which were exposed to osmium tetroxide, $OsO_4$, for 3 hours. A Philips CM 120 microscope was used operating at 80 kV.

### Thermal analysis

Differential scanning calorimetry (Mettler TA 3000) was used to determine the glass transition temperature of the cured films. The temperature range used in this study was in between 173 and 423 K with a heating rate of 10K/min. Samples weights were about 15mg.

### Preliminary characterization of suspensions

The viscosity, $\eta$, as a function of shear rate, $\gamma$, of the initial epoxy emulsions and the non-reactive (before polymerization) system epoxy/suspension of whiskers were studied using a rheometer SR 2000 from Rheometrics. A cone-plate geometry (cone angle=0.02 rad and plate diameter=50 mm) was used for testing the viscosity as a function of shear rate at room temperature.

### Dynamic mechanical spectroscopy

Dynamic mechanical tests were performed by using a spectrometer RSA-II from Rheometrics in a rectangular torsion mode in a temperature range between –120 to 150°C. The mean deformation was 0.6%. The testing conditions were such that the dynamic mechanical behavior of the samples was in the linear viscoelastic domain. Specimens were rectangular with dimensions of 30 x 3 x 0.2 mm. The storage (E'), and loss (E'') part of the elastic complex modulus (E*) and the internal friction tan $\phi$ (E''/E') were measured as a function of temperature at 1Hz.

## Results and Disusssion

### Filler dispersion

Figure 1 shows the influence of the addition of cellulose whisker suspension on the viscosity, $\eta$, of the initial epoxy emulsion as a function of shear rate, $\gamma$, at room temperature. For example, at low shear rates, the addition of 1% wt of tunicine microcrystals induces a large increase (10 times) of the viscosity by comparison with the epoxy emulsion containing the same amount of water. It is noteworthy that this increase of viscosity in aqueous medium is so high that it makes impossible the dispersion of whiskers within pure epoxy. In addition the fact that cellulose whiskers were prepared as aqueous suspension leads to process composites in aqueous medium. In the following, the epoxy matrix prepared from an emulsion containing the same amount of water as included in the corresponding amount of whiskers, but without whiskers, will be so called "neat matrix". Then, for preparing a nanocomposite film based on 1 wt% of whisker suspension, an initial epoxy emulsion containing the same amount of water was considered as a reference for the neat epoxy matrix

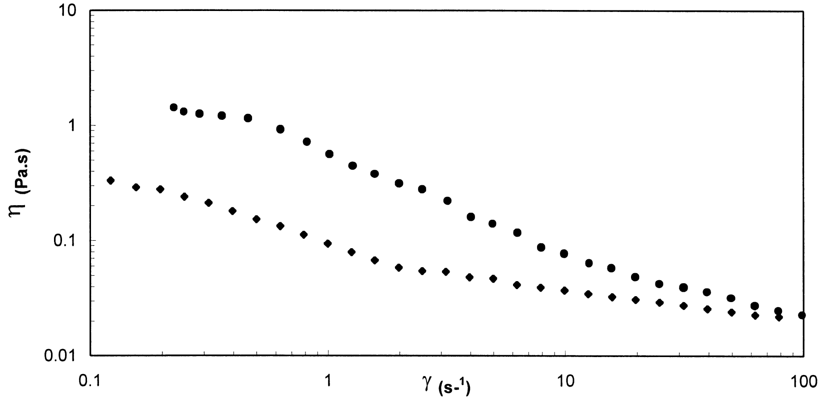

Figure 1: Evolution of the viscosity as a function of the shear rate at room temperature for the waterborne epoxy emulsion (ME) (◆) and for a 1% wt cellulose whiskers suspension (●).

## Control of the emulsion stability

The stability of the initial emulsion determines, among other parameters, the quality of the final coating. In order to study the influence of the average size and the size distribution of the particles on the stability of the emulsion and on the filmification process, several processing parameters are changed during the preparation of the waterborne epoxy resin emulsion:

*i)* Different amounts of emulsifier, i.e. from 1.5 to 6 wt. %, were used to determine the influence on the particle size (Table I).

Table I. Control of the stability of the epoxy waterborne emulsion: comparison between different parameters (emulsifier amount, time of mixing, shear rate, and Tg) and the emulsion droplet diameter.

| % of emulsifier | $d_p^{*1}$ (µm) | Shear rate (rpm) | $d_p^{*2}$ (µm) | Time of mixing (min) | $d_p^{*3}$ (µm) | Tg onset of matrix film (°C) | $d_p^{*}$ (µm) | Tg onset of 5% wt whiskers composite film (°C) | $d_p^{*}$ (µm) |
|---|---|---|---|---|---|---|---|---|---|
| 1.5 | 3.5 | 8,000 | 2.3 | 10 | 2.5 | 19.5 | 10 | 25.4 | 10 |
| 3 | 2.3 | 11,000 | 1.5 | 15 | 2.3 | 45.5 | 2.6 | 20.3 | 2.6 |
| 6 | 2.5 | 13,000 | 1.1 | 30 | 1 | 49.4 | 1.6 | | |
| | | 16,000 | 0.9 | | | | | | |

$d_p$ : droplet average diameter of the initial waterborne system : mixing for 15 min

[1] Parameters kept constant: % emulsifier=3 ; time of epoxy emulsion (ME)

[2] Parameters kept constant: shear rate=8,000 rpm ; time of mixing=15 min

[3] Parameters kept constant: % emulsifier=3 ; shear rate=8,000 rpm

As expected, higher is the amount of emulsifier, smaller the epoxy droplets are (and narrower the distribution of particle sizes is). The so-called equilibrium value of the average particle size beyond which no further change is observed. 3 wt. % of emulsifier. This amount was chosen for the standard formulation to be sure that the water/epoxy interface is fully covered by the emulsifier.

*ii)* The shear rate was varied by changing the rotation speed of the mixer from 8,000 to 16,000 rpm leading to values of sizes of the epoxy droplet diameter from 2.3 to 0.9 µm, respectively.

*iii)* The third parameter studied was the time of mixing which can allow to obtain particle diameters from 2.5 to 1 µm as time of mixing was varied from 10 to 30 minutes, respectively.

The curing process which occurs simultaneously with drying of the waterborne emulsion, denoted ME, seems to be strongly dependent on the average droplet size as reported in Table I. In fact, the final glass transition temperature, Tg, of the resulting film depends significantly on the initial epoxy particle size. In the case of a film prepared from the epoxy emulsion with the larger particles (about 10 μm), the Tg of the neat epoxy matrix is close to 20°C whereas for films prepared from emulsions with smaller particles, i.e. 2.6 and 1.5 μm, the glass transition temperatures are 45 and 49°C, respectively. This fact was already reported in the literature [4,5]. The authors proposed that in emulsions having smaller droplets, the interfacial area is large and the hardener can diffuse inside the entire initial droplets leading to an homogeneous mixture and as a consequence to an homogeneous cured film. In such a case, the stoichiometric ratio is the same whatever the location is. On the other hand, for larger initial particles, the interfacial area remains low and the hardener concentration close to the surface is higher. As a consequence, the curing process occurs rapidly in the outer shell of the large droplet avoiding the rest of the hardener to diffuse into the core of the particle, leading to heterogeneous films. In fact, the stoichiometric ratio, i.e the crosslink density in the resulting cured film, is not the same everywhere and the structure of the film keeps a memory of the initial distribution of droplet sizes.

The effect of the addition of cellulose whiskers on the glass transition temperature is also shown in Table I. The Tg values of the nanocomposites based on 5 wt. % of whiskers are about 20°C and doesn't depend strongly on the average particle size of the epoxy emulsion used for mixing with the whiskers suspension, i.e. 10 μm vs 2.6 μm.

Works are in progress to study the surface energy of pure components in order to understand and determine the type and intensity of possible interactions between the reactive cellulose surface, the epoxy resin, and the amine hardener. [20]

## Reinforcing effect of the cellulose fillers

Using the parameters from processing reported previously, i.e. 3 wt % of emulsifier, 11,000 rpm, and a time of mixing of 15 minutes, the average particle size of epoxy droplets is 1.7± 0.1 μm. 150μm-thick and transparent films can be obtained from reactive drying of whiskers suspension and epoxy emulsion mixtures. A good dispersion of these nano-objects in the epoxy matrix is evidenced from transmission electron microscopy (Figure 2 ). In addition, the dimensions of the initial whiskers is verifed and the transparency of the films confirmed the good dispersion of the nanofillers, i.e. no aggregates are present. This means that during the drying step and especially during removal of water no aggregates of the whiskers are formed even if the stabilization of the whisker suspension is broken down.

## Dynamic mechanical properties

In Figures 3a and b, the storage modulus E', and the loss factor, tan $\phi$, as a function of temperature at 1 Hz are displayed. The spectra corresponding to the neat matrix is typical of a dynamic mechanical behaviour of a crosslinked epoxy. At temperatures below $T\alpha$, the main mechanical relaxation associated with the glass transition temperature, the storage modulus of the matrix remains constant (about 1 GPa) and decreases rapidly in the $T\alpha$ region. Nevertheless, the well-known secondary relaxation, denoted $\beta$, is evidenced at around –60°C and is associated with motions of the hydroxyether units [21,22] Above the $\alpha$ relaxation i.e. in the rubbery state, E' remains constant with increasing temperature (rubbery plateau) indicating that no further crosslinking occurs during heating for measurement. Thus, the maximum of epoxy conversion was reached during curing and the epoxy network is fully cured whatever the amount of cellulose whiskers is. The mechanical loss factor, tan $\phi$, exhibits a maximum at about 28°C, denoted as $T\alpha$, for the neat matrix.

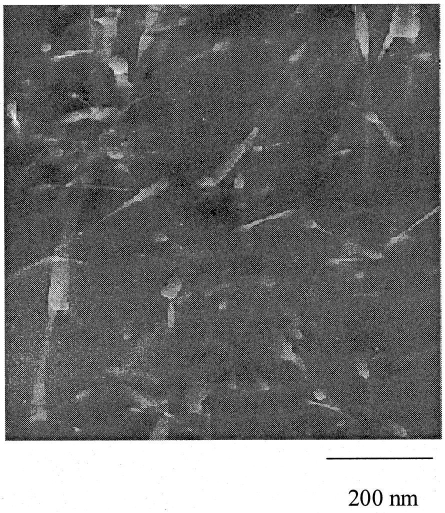

Figure 2: Transmission electron micrograph of an ultramicrotomed cross-section of a nanocomposite with 5 wt% of tunicin whiskers and epoxy (staining with $OsO_4$ ).

For the nanocompositesr, it can be seen that even with a low amount of cellulose whiskers (1 wt. %), the polymer films display an improved mechanical behaviour at temperatures above the glass transition temperature, i.e. in the rubbery state. For example, nanocomposites based on 2.5 wt; % of tunicin cellulose whiskers display a slight increase of the storage modulus below Tα, whereas the decrease of E' associated at the α relaxation is strongly reduced (at the the rubbery plateau E' is 38 MPa and 1.9 MPa for the nanocomposite based on 2.5 wt % of cellulose whiskers and neat matrix, respectively). The mechanical relaxation peak is also greatly changed by the presence of cellulose whiskers, as it is shifted from 28°C to 58°C. This effect could be related to interactions between the polyepoxy chains (polar sites of the epoxy chains) and the reactive surface of cellulose which contains a high density of hydroxyl groups [23]. As a consequence, the thermomechanical resistance is associated with a reduced molecular mobility of the epoxy/amine network chains close to the cellulose whiskers surface. The shift of the α relaxation is in agreement with the DSC data experiments.

In a previous work [23], we demonstrated, by means of different theoretical mechanical approaches that, the formation of a whisker network is responsible of the film stiffness at high temperatures, i.e. as the matrix is a rubbery state. In fact, the rubbery plateau is the same for all the nanocomposites whatever the whiskers content is. This phenomenon confirms that a ridig cellulose whiskers network has been formed which provide a large reinforcing effect at high temperatures [10, 24, 25]. The formation of such a network from H-bonds between whiskers requires to reach a percolation threshold which was evidenced in different types of non-reactive polymer matrices such as PVC and latexes. In the present work, such an effect can also occurs with additional interactions with the polymer network which minimize the mechanical effect of the existence of the whiskers network.

## Conclusions

New thermoset matrix nanocomposites with well-dispersed nanofillers have been prepared following a methodology for materials processing (reactive filmification process) for well-known components. The most important parameters determining the quality of emulsions and then the reactive drying of the waterborne epoxy-amine matrices are the distribution of epoxy droplets size of the initial emulsion. The glass transition temperature, Tg, of the resulting epoxy/amine film composite depends significantly on the initial epoxy particle size. It seems that in the presence of cellulose whiskers, the nanofillers act as stabilizers of the emulsion as Tg becomes slightly dependent of the initial emulsion droplet diameter. From such a waterborne epoxy matrix and cellulose whiskers, it is possible to obtain a desirable balance between flexibility and stiffness of the composite films from a suitable design of the epoxy matrix (Tg, $M_w$, type of hardener, etc) and the amount of whiskers. The dynamic mechanical properties of composites demonstrate significant improvement of the modulus in the rubbery state even at low amount of cellulose whiskers. The formation of a filler network from H-bonds between the cellulose whiskers in addition to strong interactions between cellulose surface and the polymer chains could explain this effect.

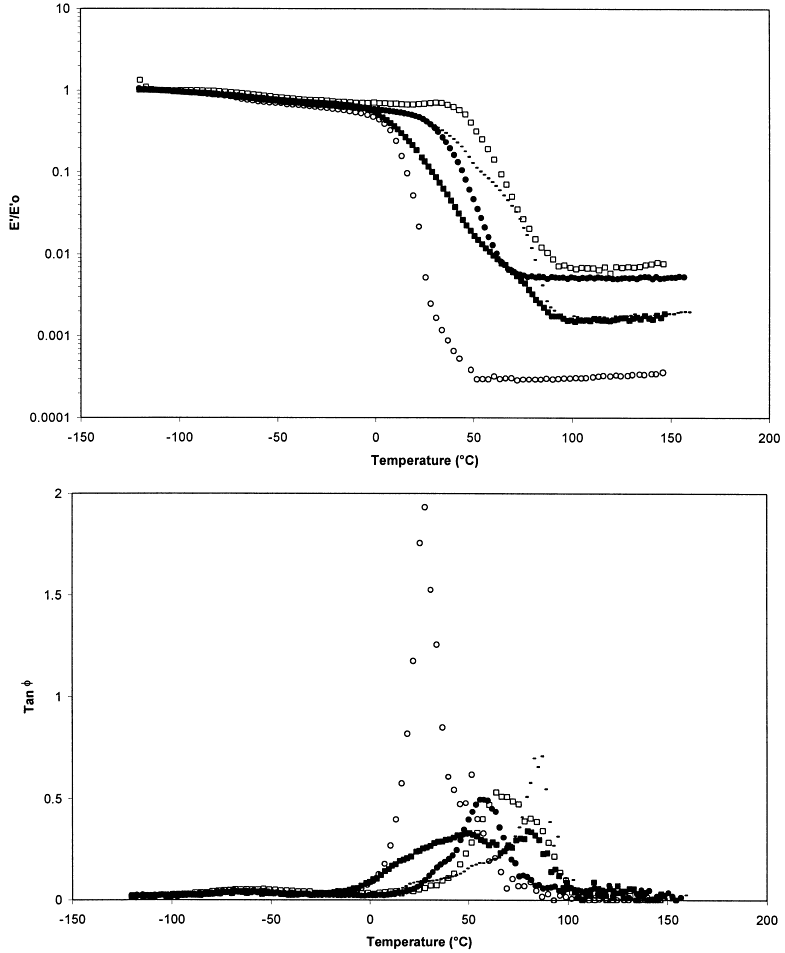

Figure 3: Storage modulus E' (a) and Tanϕ (b) vs. temperature at 1 Hz for nanocomposites based on 0.5 wt % (■) and, 2.5 wt % (●) of cellulose whiskers

The corresponding neat matrices (□) and (○) based on the same amount of water as in the nanocomposites initial mixtures and, the "mother emulsion" (ME) (–) are also represented.

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