

# POLYANILINE MODIFIED NANOCELLULOSE AS REINFORCEMENT OF A SHAPE MEMORY POLYURETHANE

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## ABSTRACT

Shape memory polymers (SMPs) are smart materials capable of “remembering” and autonomously recovering their original shape after being deformed, as a response to a stimulus. Segmented polyurethanes (PU) that present a two-phase microstructure consisting on hard and soft segments, can show this type of behavior.

In this work, electrically conductive cellulose nanocrystals were used to reinforce shape memory polyurethanes, adding an extra variable to tune up the properties of these nanocomposites. The modified nanocrystals were prepared by an in situ polymerization method, growing polyaniline (PANI) on the surface of the cellulose nanofibrils. These crystals combine the good mechanical properties of the cellulose nanocrystals and the conductive properties of the PANI. The crystals were added to a thermoplastic-segmented polyurethane showing shape memory properties. Electrical measurements were performed to characterize the conductive properties of the resulting composite films. Reinforcement was clearly observed in the polyurethane nanocomposites at cellulose concentrations above 4-10 wt%. This range was higher than that observed previously in non-conductive nanocellulose composites, probably due to agglomeration of the crystals after PANI modification. The shape memory behavior was studied and compared with that of the unfilled commercial system. Addition of the conductive nanocellulose improved fixity, but reduced shape recovery.

## 1. INTRODUCTION

Intelligent composites that act as a response to an external input are prepared from shape memory polymers (SMPs). These intelligent materials show unusual properties, such as shape-memory behavior, pseudoelasticity or large recoverable strain, high damping capacity, and adaptive properties, which derive from reversible phase transitions in the materials [1]. Polymers with shape memory behavior have both a temporary form and a stored permanent form [2]. Segmented linear polyurethanes can present this type of behavior. They are biphasic materials, in which the thermally reversible phase allows fixing a transient shape and the “frozen” phase is responsible for the polymer recovery to its original shape. This last phase, that gives the polymer the capacity of “remembering” its shape, can be a crystalline or a glassy phase, or it can be a physical or chemical network structure. When a shape memory polymer is heated above the phase transition temperature ( $T_s$ ) of the reversible phase, the modulus of the material suffers a large drop, which can be due to the melting of the crystalline phase or to the glass-rubber transition of the reversible phase [3]. The transient shape can be imposed in this condition, while the material is maintained below the phase transition of the “frozen” phase, and then cooled to fix this transient shape. If the material is reheated above  $T_s$ , it recovers the original shape.

In this work, a new approach to the tailoring of the properties of these materials has been investigated. It consisted in the addition of nanofillers that potentially can: i)

change the temperature of the transitions by changing the molecules mobility, ii) change the crystals structures by affecting the phase separation of PU segments, iii) modify the relaxation processes of the polymer phases, iv) modify the mechanical/shape memory properties of the nanocomposites.

Cellulose was selected as the source for the preparation of the nanoreinforcements to be introduced in the segmented PU. Cellulose is the most abundant natural polymer in nature and it constitutes the primary structural material in plants. It also has hydroxyl groups that can strongly interact with other polar materials, such as polyurethanes. This is important to reach good interfacial adhesion [4], essential to obtain composites with good mechanical properties .

Additionally, the use of electrically conductive cellulose crystals was interesting because it allows producing composites with combined properties (mechanical and electrical), turning the nanocomposites potentially susceptible to the action of an electrical field. The use of electrically conductive cellulose nanocrystals as reinforcement of shape memory polyurethanes was investigated in this work. The dispersion of the nanocrystals was analyzed by microscopy, while rheological and electrical measurements were performed to determine the effect of the nanocrystals addition. Finally, the shape memory behavior of the composites was investigated by mechanical and temperature cycling tests.

## **2. MATERIALS AND METHODS**

Cellulose crystals were prepared from microcrystalline cellulose (Avicel PH101 MCC, FMC BioPolymer, USA) by acid hydrolysis, as it was described elsewhere [4]. The crystals obtained in aqueous suspension were freeze-dried and redispersed in dimethylformamide (DMF) by ultrasonication. A high performance polyester thermoplastic PU (IROGRAN PS455-203, Hunstman) that exhibits shape memory behavior was selected as the matrix.

The crystals suspension was incorporated into a DMF-PU solution and composite films were prepared by casting at 80°C for solvent evaporation.

Conductive cellulose crystals were prepared by grafting polyaniline of their surface. To achieve this goal, polyaniline (PANI) doped with hydrochloric acid was in-situ polymerized in an aqueous suspension of cellulose nanocrystals, using ammonium persulfate as oxidant (monomer / oxidant = 4/1) [5]. The aniline concentration was varied from 3 to 7  $10^{-4}$  mol and the modified crystals were dialyzed to eliminate by-products of the synthesis.

Fracture surfaces were coated with gold and analyzed by scanning electron microscopy (scanning electron microscope Philips model SEM 505).

Samples in the molten state ( $T \sim 160^\circ\text{C}$ ) were subjected to rheological testing in the linear viscoelastic range (small strains, 1%), using a rheometer (AR-G2, TA instruments) with parallel plates geometry (diameter = 25 mm).

The electrical conductivity of the composites prepared with different concentrations of nanocrystals was determined at room temperature using a two-probe method.

Shape memory behavior was studied by performing thermo-mechanical cyclic tests on films specimens of 5 mm x 25 mm using a universal testing machine equipped with a heating chamber (INSTRON 8501). The specimens were conditioned at 60°C in the chamber and then elongated to 100% deformation at a speed of 20 mm/min. After that, the specimens were cooled down to 0°C and unloaded. Then, the samples were heated back at 60°C and let recover for ten minutes at that temperature. The loading-unloading cycle at the given temperatures was repeated.

The “fixity” and “recovery” ratios ( $R_f$  and  $R_r$ , respectively) were calculated from these tests as follows:

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \times 100\% \quad R_r = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \times 100\% \quad (1)$$

where  $\varepsilon_m$  is the maximum strain in the cycle (100%),  $\varepsilon_u$  is the residual strain after unloading at 0°C and  $\varepsilon_p$  is the residual strain after recovery.

### 3. RESULTS AND DISCUSSION

#### 3.1 Microscopy

Figure 1.a illustrates the good dispersion of the PANI modified -cellulose nanofibers/crystals (CNF-Pani) in the commercial PU matrix. The micrograph corresponds to a sample with 1 wt.% of filler. The minute white points are the cellulose nanocrystals. Notice the roughness of the cryogenic fracture surface indicating that the crystals disturb the advance of the fracture. The unfilled PU shows, under the same conditions, a featureless surface Figure 1b (small spots are imperfections of the film). It is also interesting to observe the large area covered by the crystals at only 1 wt. %.

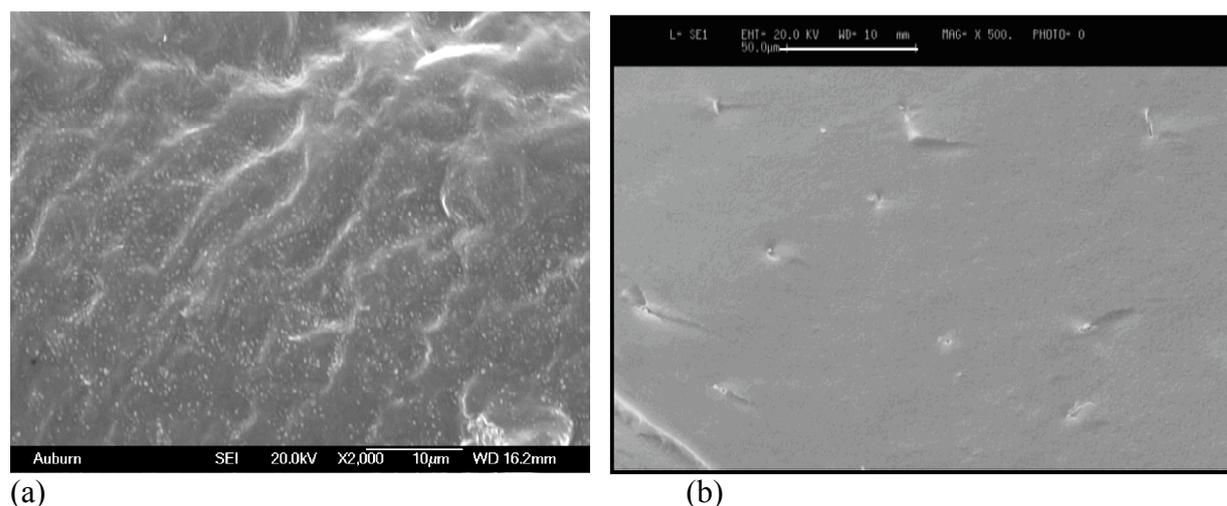


Fig. 1. Fracture surface of (a) reinforced PU with 1wt.% of CNF-Pani and (b) unreinforced PU.

#### 3.2 Rheological characterization

The existence of a threshold concentration of nanocrystals percolating the films was investigated by measuring the mechanical, electrical and rheological properties of systems reinforced with different concentrations of nanocrystals.

Figure 2 shows the storage modulus ( $G'$ ) vs frequency for PU samples reinforced with CNF-Pani in the molten state. As it is usual in these cases, the largest differences appear at low frequencies. A clear low-frequency plateau appears at 10 wt.% concentration. The presence of an equilibrium modulus, solid-like behavior for the viscoelastic material, indicates that a nanocrystal network is percolating the sample. The lower concentrations investigated in this work shows no equilibrium plateau, a typical behavior of viscoelastic liquids, which suggests that the threshold concentration

is in the 4-10 wt.% range.

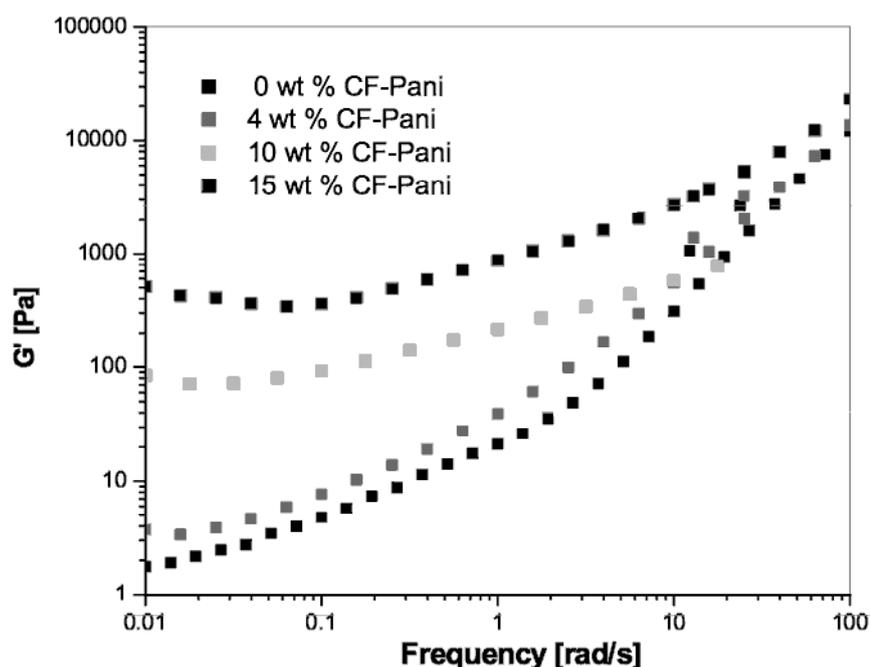


Fig. 2. Storage modulus ( $G'$ ) as a function of the frequency for reinforced PU with CNF-Pani

### 3.3 Electrical Conductivity

The values of resistivity of the samples containing different concentrations of modified cellulose crystals are summarized in Table 1. These preliminary data show that an important change occurs in the range 4-10 wt.% of CNF-Pani, much in the same way as it was detected by rheological measurements. Further measurements need to be done in order to identify the concentration at which the major change in electrical properties occurs.

Table 1. Resistivity values vs. CNF-Pani concentration.

Sample	Resistivity ( $\Omega$ cm)
0 wt% CNF-Pani	$> 10^{11}$
2 wt% CNF-Pani	$> 10^{11}$
4 wt% CNF-Pani	$> 10^{11}$
10 wt.% CNF-Pani	$2.2 \cdot 10^{10}$
15 wt% CNF-Pani	$2.7 \cdot 10^{10}$
100 wt% CNF-Pani	$5.3 \cdot 10^5$

### 3.4 Shape memory Behavior

Figure 3 shows the curves that represent the response of the commercial unfilled PU under the thermal-mechanical cycling. The first cycle is, generally, different from the subsequent ones [6-8] and the material response tends to be repeatable after two or three cycles. The same type of behavior was observed for the nanocomposite films, which indicates that the shape memory behavior is not lost with the addition of the nanocrystals.

Table 2 summarizes the results for the unfilled sample and for two different CNF-

Pani concentrations. Samples with higher cellulose crystals concentrations were not tested in cycling because as more reinforcement is added the elongation to rupture of the material is reduced and a 10 wt.% sample breaks under tension at deformations below the 100% (approx. 35% strain).

Table 2 shows that the addition of nanoparticles to a shape memory polymer reduces the recovery of the material, which can be explained as the restraint imposed by the particles to the mobility of the chains in the thermally reversible phase [9].

Table 2. Shape memory behavior. The fixity and recovery percentages are calculated from eqn. 1.

<b>0 wt%</b> (unfilled PU )	$\epsilon_u$ (%)	$\epsilon_p$ (%)	% fixity	% recovery
1st cycle	93.40	23.72	93.40	76.28
4th cycle	94.08	30.16	94.08	69.84
<b>2 wt% CNF-PANI</b>				
1st cycle	94.72	26.00	94.72	74.00
4th cycle	94.20	45.16	94.20	54.84
<b>4 wt% CNF-PANI</b>				
1st cycle	90.72	25.00	90.72	75.00
4th cycle	78.44	34.88	78.44	65.12

#### 4. CONCLUSIONS

The results of this work show that it is possible to graft polyaniline on cellulose nanocrystals previously obtained by acid hydrolysis and to utilize these modified crystals to reinforce a shape memory polyurethane. Electronic microscopy indicates that there is a good dispersion of the crystals in the matrix. Rheological and electrical measurements indicated that an important change in the properties of the nanocomposites occur in the range of 4-10 wt.% of CNF-Pani. The shape memory behavior of the material is maintained, although the recovery ratio is reduced by the presence of the crystals.

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