

# Unsaturated Polyester–Poly( $\epsilon$ -caprolactone) Hybrid Nanocomposites: Thermal–Mechanical Properties

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This paper reports on the thermal behavior and mechanical properties of nanocomposites based on unsaturated polyester resin (UP) modified with poly( $\epsilon$ -caprolactone) (PCL) and reinforced with an organically modified clay (cloisite 30B). To optimize the dispersion of 30B and the mixing of PCL in the UP resin, two different methods were employed to prepare crosslinked UP–PCL–30B hybrid nanocomposites. Besides, two samples of poly( $\epsilon$ -caprolactone) of different molecular weight (PCL2:  $M_n = 2.10^3 \text{g.mol}^{-1}$  and PCL50:  $M_n = 5.10^4 \text{g.mol}^{-1}$ ) were used at several concentrations (4, 6, 10 wt%). The 30B concentration was 4 wt% in all the nanocomposites. The morphology of the samples was studied by scanning electron microscopy (SEM). The analysis of X-ray patterns reveals that intercalated structures have been found for all ternary nanocomposites, independently of the molecular weight, PCL concentration and the preparation method selected. A slight rise of the glass transition temperature,  $T_g$ , is observed in UP/PCL/4%30B ternary nanocomposites regarding to neat UP. The analysis of the tensile properties of the ternary (hybrid) systems indicates that UP/4%PCL2/4%30B nanocomposite improves the tensile strength and elongation at break respect to the neat UP while the Young modulus remains constant.

## INTRODUCTION

Thermosetting polymers are in general versatile and widely accepted matrices for advanced materials, but because of their high crosslinking degree, they are brittle. The addition of a second elastomeric or thermoplastic phase increases their toughness but decreases the elastic modulus at temperatures above the glass transition temperature ( $T_g$ ) of the thermoplastic [1, 2]. Unsaturated

polyester (UP) resins are one of the most widely used thermosetting materials because they are relatively inexpensive and have good mechanical properties. Nevertheless, polymerization shrinkage, inherent brittleness, and low resistance to crack propagation limit its application, being necessary the inclusion of low-profile additives [3, 4]. The addition of a low-profile additive causes an increase of the elongation at break, whereas the Young's modulus decreases as it occurs in the UP/poly( $\epsilon$ -caprolactone) (PCL) system [3, 5]. Many different kinds of additives may be added to a thermosetting polymer to obtain materials with a wide range of engineering applications. Among the inorganic materials used as reinforcing additives to improve physical and mechanical properties of thermosetting polymers, layered silicates (clays) organically modified, such as montmorillonites (MMTs), are one of the most widely used; their fairly aspect ratio provides an important increase of the interface between matrices and nanoparticles. Related with the state of dispersion of the organoclay in the polymer structures and depending on the method of preparation and the interaction between the clay and the polymer, three types of morphologies can be generated, which correspond to: total phase separation of the two components, intercalated nanocomposite structures, and nanocomposites where exfoliation is achieved [6]. In nanocomposites with layered silicates in which exfoliation is reached, it was found that the more clay is exfoliated, the more it prevents coalescence of the dispersed domains in the matrix [7].

Intensive research efforts have been devoted to the study of binary systems nanocomposites based on polyester thermosets reinforced with silicate layers [8–18] or other nanoparticles [19, 20]; their mechanical and thermal properties can be improved by adding low concentration of nanoparticles. However, there are few works dealing with ternary nanocomposites formed by polyester thermoset/thermoplastic/nanoclay [21–25]. The objective of this work is to study the thermomechanical properties and morphology of ternary thermoset/thermoplastic/nanoclay systems. Specifically, the nanocomposites studied consist

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of UP resin toughened with PCL and modified by using an organically modified MMT, cloisite 30B as nano-reinforcement. Two samples of poly( $\epsilon$ -caprolactone) of different molecular weights have been selected; two different methods were used to prepare the nanocomposites to optimize the dispersion of 30B and mixing of PCL in the UP resin. It has been analyzed whether the preparation method of the nanocomposite and the molecular weight of the thermoplastic have a significant effect on the dispersion state of the cloisite when PCL coexists with UP. The effect of the nanoscaled 30B layers on the non-isothermal crystallization degree of PCL [26–28] has also been investigated. The influence of the nanoclay dispersion on the thermal behavior and the mechanical properties are reported and related with the morphologies generated.

## EXPERIMENTAL

### Materials

The UP, Norsodyne 44233, used in this study is commercially available and was kindly supplied by Cray Valley. The isophthalic UP resins contain 38 wt% of styrene. Nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) was used to characterize the UP that consists of isophthalic anhydride (IA), maleic anhydride (MA), and 1,2-propylene glycol (PG). The relative composition calculated was IA:MA:PG = 1.5:1:3. The number average molecular weight is 4,550 g/mol. The molar ratio of styrene to polyester C=C bonds was MR 3/1. To cure the resin, benzoyl peroxide was used as initiator and was supplied by Pan-reac. The organophilic clay used as the reinforcement filler was cloisite 30B, provided by Southern Clay Products. Cloisite 30B is an MMT modified with a quaternary ammonium salt that contains: one methyl group, two 2-hydroxyethyl groups, and a tallow (average composition ~65%  $\text{C}_{18}$ , 30%  $\text{C}_{16}$ , and 5%  $\text{C}_{14}$ ). The modifier concentration or cation exchange capacity is 90 meq/100 g clay. To study the effect of the molecular weight of the PCL on the UP/PCL/30B nanocomposites, two PCL samples were used: PCL2 ( $M_n = 2.10^3$  g/mol) supplied by Aldrich Chemical Company and PCL50 ( $M_n = 5.10^4$  g/mol) provided by Polyscience.

### Sample Preparation

Two different methods were used to obtain the best dispersion of 30B and the mixing of PCL in the UP resin. Irrespective of the process used for sample preparation, well-dispersed mixtures and stable suspensions of 30B and PCL components in the polyester resin were obtained. In all the nanocomposites, the percentage of cloisite was 4% by weight related to the UP/PCL content. The cloisite content was chosen as a consequence of a previous work [15], where the binary nanocomposites systems UP/cloisite (with different contents 2–10 wt%) were studied,

being a 4 wt% of 30B content the optimum to get the best mechanical nanocomposite properties [11, 15].

**First Method (P1): UP/PCL/4% C30B.** The percentage of thermoplastic PCL (4, 6, and 10% by weight) was added to 30 g of resin and stirred until it was completely dissolved in the matrix (1 h). Next, 4 wt% of the total mass (thermoplastic + resin) of cloisite 30B was added, and the mixture was heated at 50°C for 3 h until total dissolution of the cloisite.

**Second Method (P2): UP/PCL/4% 30B.** Cloisite 30B was first dispersed in the UP resin. A total of 4 wt% of cloisite 30B was added to 30 g of resin, taking into account the weight of the resin plus the mass of PCL that would have to be added. The sample was stirred for 2 h at 50°C until total dispersion of cloisite. The percentage of PCL was added to the UP/30B dispersion and stirred at 200 rpm at 50°C for 3 h.

### Curing Reaction

Crosslinking reaction was initiated by adding 1.5 wt% of benzoyl peroxide to UP/PCL/30B mixtures. The mass of benzoyl peroxide was calculated in relation to the UP content. The mixture was achieved by stirring at 400 rpm, at room temperature. Next, the reactive mixtures were pressed in  $140 \times 10 \times 1.5$  mm aluminum molds and were cured in an oven at 80°C for 1 h. Postcuring was also performed for 3 h at 110°C.

### Measurements

**Wide-Angle X-ray Diffraction.** Wide-angle X-ray diffraction (WAXD) patterns were performed at room temperature in reflection mode using a Panalytical X'Pert PRO Alpha1 diffractometer equipped with a curved Ge111 primary beam monochromator and a fast detector X'Celerator (Cu  $\text{K}\alpha 1$  radiation ( $\lambda = 0.15406$  nm), 45 kV, 40 mA). The measurement range of  $2\theta$  was from 1.5 to 40°, and step size was 0.0167°. Bragg's law was used to calculate the crystallographic d-spacing.

**Scanning Electron Microscopy.** Scanning electron microscopy (SEM) has been used to study the morphology of UP nanocomposites. A Fei-Inspect-S instrument was used with beam energy of 10 kV, verifying that these experimental conditions did not produce severe damage on the samples. The magnification in the study varied from 475x to 4375x. The fracture surfaces were observed.

**Differential Scanning Calorimetry.** The calorimetric measurements reported were performed under nitrogen atmosphere at 20  $\text{Kmin}^{-1}$  heating rate, in a Mettler Toledo mod.821e differential scanning calorimetry (DSC) instrument. Pans of aluminum of 40  $\mu\text{L}$ , were used in all the cases, and the weight of the samples were kept in the

range 7–14 mg. The temperature scale was calibrated using indium and zinc, and the measurements were registered at a heating rate of 10°C/min. The scans ranged from –90 to 300°C. The curing heat reaction was determined from the integral under the exothermal peak of the corresponding thermograms.  $T_g$ s were taken at the midpoint of the heat capacity change.

**Dynamic Mechanical Thermal Analysis.** The dynamic mechanical thermal analysis (DMTA) experiments were performed on a DMTA V instrument from Rheometric Scientific, with the dual cantilever bending mode at 1, 2, 5, 10, and 50 Hz. All measurements were performed within the range 20–250°C and a heating rate of 3°C/min. The storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) were determined. The maximum of the  $\tan \delta$ -temperature curves was associated with  $\alpha$ -relaxations corresponding to the glass transition.

**Tensile Test.** Tensile mechanical properties of the nanocomposites were measured using a MTS machine, QTest 2L model, a MTS extensometer, model number 63411F-54, and a load cell of 2 kN capability. The specimens were loaded at a constant rate of 1 mm/min until fracture. Stress–strain curves were recorded for five or six specimens at least of each sample, to obtain the average value of the mechanical properties: tensile modulus, tensile strength, and strain at break.

## RESULTS AND DISCUSSION

### WAXD

WAXD was used to calculate the basal spacing ( $d$ -spacing) of the nanoclay. The value of basal spacing indicates how the layered silicate nanoclays are dispersed within a polymer matrix. When the  $d$ -spacing value remains nearly identical to its pristine state, polymer molecules are unable to penetrate into the galleries and therefore a heterogeneous dispersion is formed. Nevertheless, an intercalated nanocomposite is formed when several polymer chains are inserted between interlayers, and as a consequence, the  $d$ -spacing value is expanded to a limited extent.

The WAXD patterns of the 30B, UP/30B, PCL/30B binary nanocomposites and UP/PCL/30B hybrid nanocomposites with different content of PCL obtained following P1 and P2 preparation methods are shown in Fig. 1, and the corresponding data are collected in Table 1.

Cloisite 30B exhibits  $d_{001}$  reflection at  $2\theta \approx 4.8^\circ$  (basal spacing = 1.8 nm). WAXD patterns of the binary nanocomposites and ternary systems UP/PCL/30B prepared following both preparation methods P1 and P2, with different percentages of PCL2 are shown in Fig. 1a and 1b. All the binary systems and both hybrid nanocomposites show a similar behavior with a peak corresponding to a basal reflection around  $2\theta \approx 2.3^\circ$  ( $d_{001} \approx 3.8$  nm). The peak at  $2\theta \approx 4.9^\circ$  could correspond to the second order diffraction

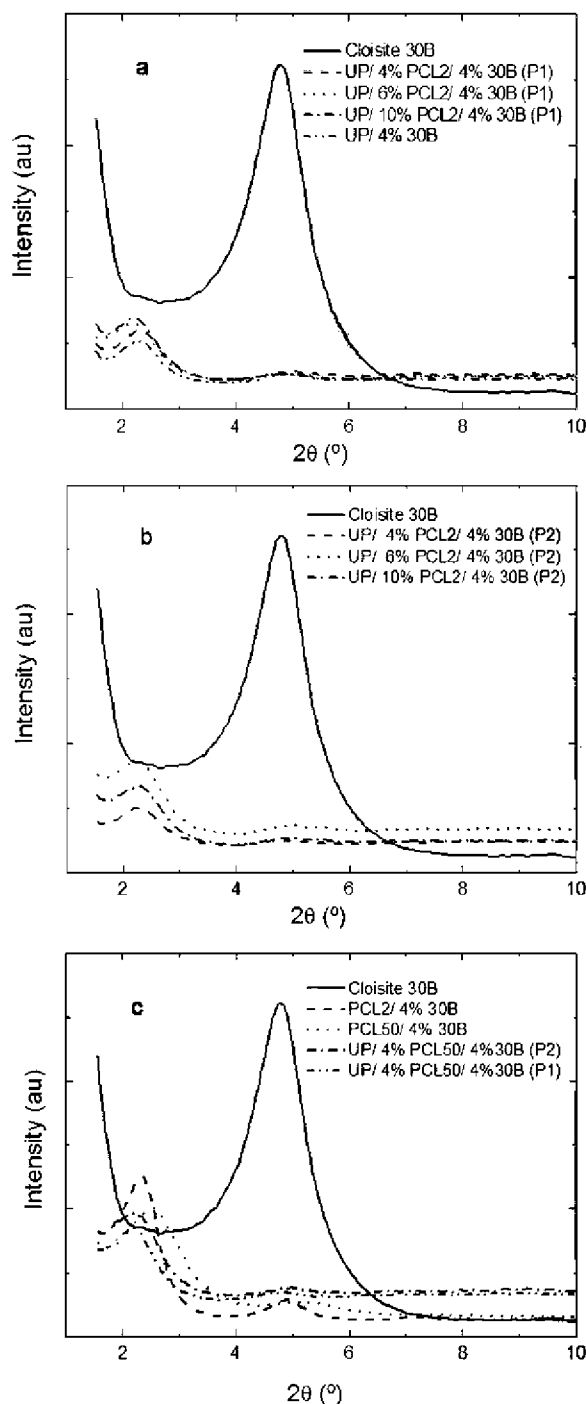


FIG. 1. XRD patterns of 30B and UP/PCL nanocomposites.

$d_{002}$ . This indicates the formation of a nanocomposite with the disappearance of the peak corresponding to the basal spacing of the pure clay and that the mixtures UP/PCL2 are intercalated between silicate layers. As a consequence, an increase of 2 nm on 30B  $d_{001}$  spacing is observed (see Table 1). Analogous results were obtained in other binary 30B/polyester nanocomposites systems [11]. Figure 1c shows the X-ray diffraction patterns for nanocomposites with 4 wt% clay loading and 4 wt% of PCL2, and PCL50. Figure 1c includes also the diffractograms of the

TABLE 1.  $d$ -spacings  $d_{100}$  (nm) for Cloisite 30B, UP/30B, PCL/30B, and UP/ PCL/30B ternary nanocomposites.

System	$d$ -basal spacing (nm)
Cloisite 30B	1.8
UP/4%30B	3.7
PCL2/4%30B	3.7
PCL50/4%30B	3.4
UP/4%PCL2/4%30B (P1)	3.8
UP/6%PCL2/4%30B (P1)	3.8
UP/10%PCL2/4%30B (P1)	4.0
UP /4%PCL2/4%30B (P2)	4.0
UP /6%PCL2/4%30B (P2)	3.7
UP /10%PCL2/4%30B (P2)	3.7
UP/4%PCL50/4%30B (P1)	4.0
UP/6%PCL50/4%30B (P1)	3.7
UP/10%PCL50/4%30B (P1)	3.9
UP/4%PCL50/4%30B (P2)	3.9
UP/4%PCL50/4%30B (P2)	3.7
UP/4%PCL50/4%30B (P2)	3.8

corresponding ternary nanocomposites, obtained from P1 and P2 preparation methods. The analysis of WAXD patterns shows that there is no significant difference in the capacity of the UP/PCL blends for accessing to the galleries between silicate layers, independently of the molecular weight of the PCL, and the preparation method of the ternary nanocomposites. In addition, a narrower and intensive peak at  $2.3^\circ$  for binary PCL2/30B systems is observed, suggesting that a more regular layered silicate structure is maintained in these cases [29].

### SEM

The morphologies of the nanocomposites were examined using SEM measurements. In neat UP, the fracture surface was found homogeneous and uniform according to the transparency observed by visual inspection of the samples. As it was seen in a previous work [5], the cleavage surface of the neat polyester is smooth, and the crack propagation lines are almost parallel to one another. This indicates that the neat polyester is brittle as expected.

Figure 2 shows the fractured surfaces of binary UP/4%30B, PCL2/30B, PCL50/4%30B systems at different magnifications. The micrographs of the UP/30B show fractured flakes with cleavage borders showing that the interface between 30B and the polyester matrix is weak, being observed a heterogeneous dispersion of clay in UP matrix. Nevertheless the micrographs of the PCL2/30B and PCL50/30B show the fractured surfaces of the nanocomposites with the spherulites of the PCL and without any river-like crack and fractured flakes; a more homogeneous dispersion of 30B in PCL can be observed in comparison to UP/30B system. Figure 3 includes the micrographs of the hybrid UP/4%PCL2/4%30B (P1), UP/4%PCL2/4%30B (P2), and UP/4%PCL50/4%30B (P2) nanocomposites. Once again it can be noticed in both systems, that PCL favors a more homogeneous dispersion of

intercalated aggregates of clay sheets in the polyester matrix (particularly in UP/4%PCL2/4%30B (P1) system) in comparison to UP/30B binary nanocomposite. Similar behavior has been found for other ternary systems containing polyester resin such as UP/30B/CSR (core-shell rubber) [25].

### DSC

Dynamic DSC measurements were performed on cured UP/PCL/4%30B systems with different content of PCL2 and PCL50 (4–10 wt%), at 5, 10, 15, 20, 25, 30°C/min. As an example the dynamic heating curves at several heating rates for UP/4%PCL2/4%30B are shown in Fig. 4. For dynamic experiments, the temperature of the exothermal peak depends on the heating rate and it can be observed in Fig. 4 that the maximum of the peaks shift toward the lower temperature region as the heating rate decreases. The total heat of curing reaction,  $\Delta H$ , values calculated from the area of exothermal peak in the curves, are given in Table 2 for all the ternary systems studied obtained from protocols P1 and P2. This Table also includes values for neat UP, UP/30B, and UP/PCL binary systems. The values of  $\Delta H$  were taken as the average of the enthalpy values obtained at different heating rates. In all the cases,  $\Delta H$  remains practically constant with the heating rate.

The values of activation energy  $E_a$  were calculated from the slope of the linear variation of the logarithm of heating rate with the inverse of temperature, using the Ozawa [30] calculation procedure, and are also collected in Table 2. The average value of activation energy  $E_a = 82 \pm 2$  kJ/mol for ternary systems, compared with  $E_a = 86 \pm 1$  KJ/mol for neat UP confirms that any significant change is observed. Therefore the presence of different contents of PCL in the UP/PCL/30B nanocomposites, independently of PCL2 and PCL50, and the differences in preparation methods P1 and P2, do not change significantly the kinetic mechanism of curing the UP resin.

The  $T_g$  (achieved after curing) is one of the most significant properties for establishing the thermal behavior of polymer nanocomposites.  $T_g$  values of UP/PCL/4%30B nanocomposites are given in Table 2. The UP  $T_g$  increases with 30B content in the nanocomposites, as it was found in a previous work [15] and in UP/30B similar systems studied for other authors [11]. On the other hand, the addition of PCL2 to neat UP provokes an opposite effect, a decrease in the  $T_g$  [5]. In Table 2, it can be observed that the  $T_g$  of the UP decreases with 4–10% of PCL2 contents, although this tendency changes in UP/6%PCL2 system. The  $T_g$  value, found for the UP+6%wt PCL2, was not expected, but the overall tendency to decrease the  $T_g$  with the PCL content (4–10% wt) remains. The rise of  $T_g$  value observed in UP/PCL/30B ternary nanocomposites related to UP/PCL binary systems could be a consequence of different effects depending on the PCL molecular weight. In any case, the main factor

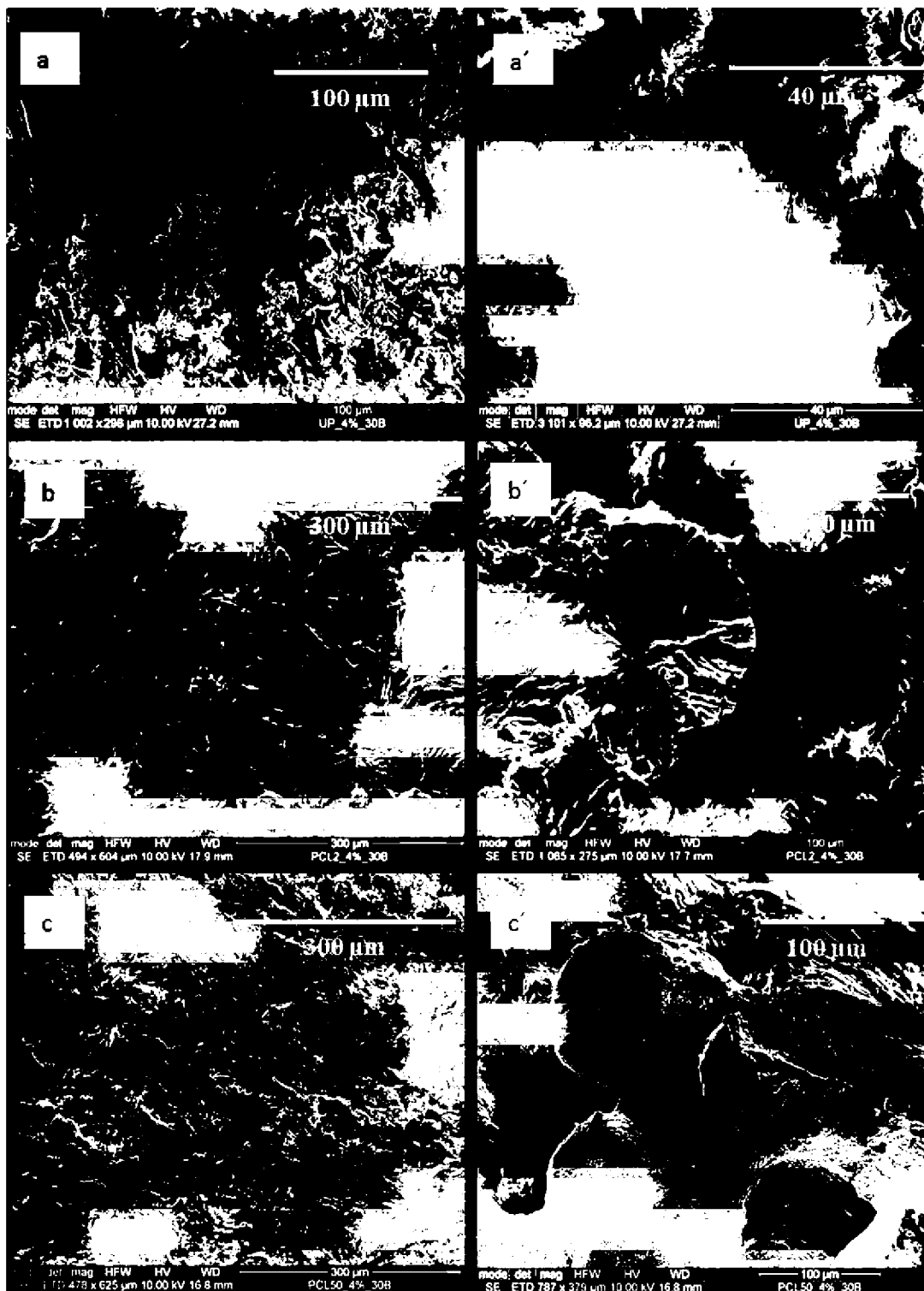


FIG. 2. SEM micrographs of fracture surface of binary nanocomposites: (a), (a') UP/4%30B; (b), (b') PCL2/4%30B; (c), (c') PCL50/4%30B, at different magnifications.

to consider is the limitation in mobility of polymer chains imposed by the presence of 30B nanoclay. For ternary nanocomposites with PCL50 the  $T_g$  values are similar to the corresponding one to UP/30B as a consequence of the immiscibility between UP and PCL50 [5]. However, for

nanocomposites containing PCL2 the reinforcing effect of 30B clay partially compensates the plasticizing effect due to the miscibility of PCL2 and UP matrix [5], and therefore the  $T_g$  values of UP/PCL2/4%30B are slightly lower than the corresponding one obtained for UP/30B.

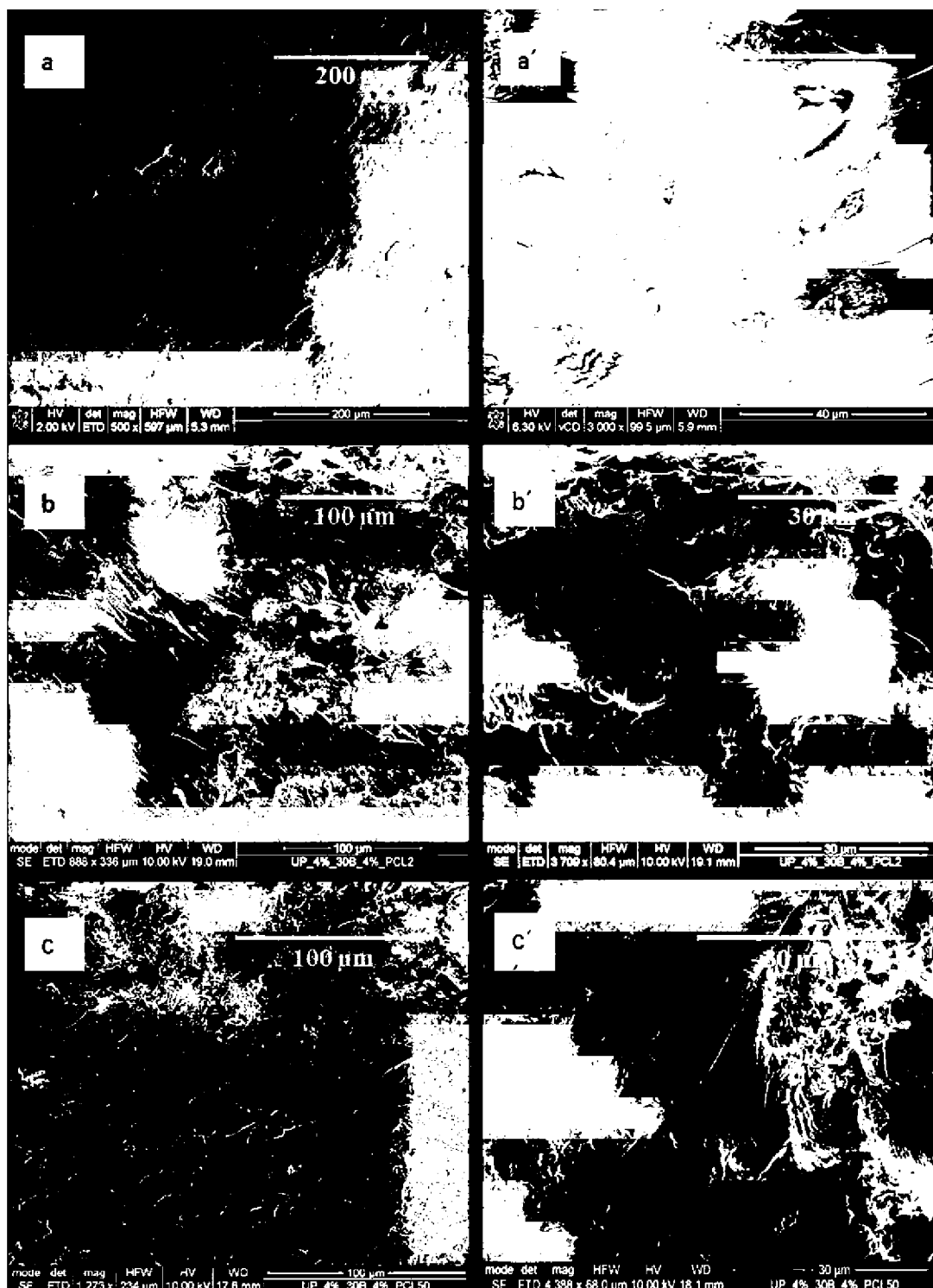


FIG. 3. SEM micrographs of fracture surface of ternary nanocomposites: (a), (a') UP/4%PCL2/4%30B(P1); (b), (b') UP/4%PCL2/4%30B(P2); (c), (c') UP/4%PCL50/4%30B (P2) at different magnifications.

Table 3 collects the crystallinity degree of pure components, PCL2, PCL50, the binary systems UP/PCL, PCL/4%30B, and the corresponding to ternary systems UP/PCL/4%30B obtained from protocol P2. Table 3 also includes the UP  $T_g$  and a composition of a ternary system obtained

according to protocol P1, as an example, to indicate that there are no significant differences between both protocols.

From the analysis of Table 3, it can be noticed that, in the binary systems UP/PCL, the crystallization of PCL is different depending on the molecular weight of PCL. For

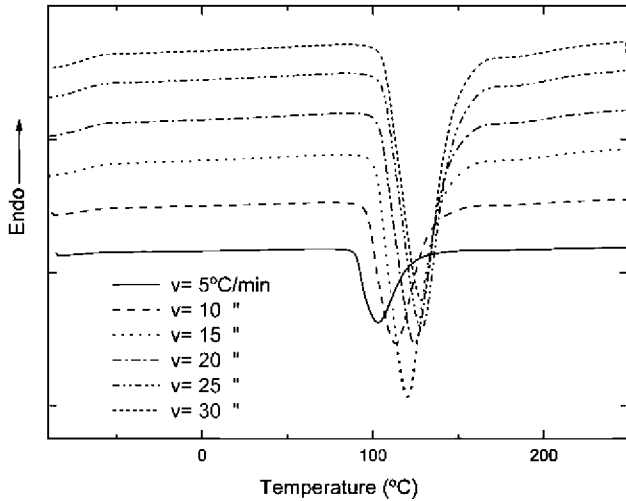


FIG. 4. Dynamic heating curves for UP/4%PCL2/4%30B (P1) at several heating rates.

(UP/PCL2) systems, PCL2 crystallizes only when its content is around 10%. For lower contents of PCL2, the binary blends do not present any evidence of crystallinity, showing only a single  $T_g$  intermediate between those of the pure polymers [5]. Focusing now on PCL2/30B nanocomposites, silicate layers could act as nucleating agents in the PCL2 crystallization and also as noncrystallizable barriers that disturb crystal growth [26, 27]; both effects compensate each other, and as a result the crystallinity degree is still similar to the corresponding one of pure PCL2  $\sim 70\%$ . For UP/PCL2/4%30B (P1) ternary nanocomposites the behavior is similar to UP/PCL2 binary systems; PCL2 does not crystallize when PCL2 content is lower than 10%, but when 4% of 30B is added to UP/10%PCL2 system the crystallinity degree falls to 4%. In

TABLE 2. Total reaction heat,  $\Delta H$ , apparent activation energy,  $E_a$ , and glass transition temperature,  $T_g$ , for neat UP, UP/PCL blends, and UP binary and ternary nanocomposites.

System	$\Delta H$ (Jg <sup>-1</sup> )	$E_a$ (kJ/mol UP)	$T_g$ cured (°C)
(Norsodyne 44233) UP	-352 ± 10	86 ± 1	108
UP/4%30B	-364 ± 8	83 ± 2	115
UP/4%PCL2	-350 ± 13	83 ± 2	105
UP/6%PCL2	-348 ± 11	82 ± 1	111
UP/10%PCL2	-346 ± 8	83 ± 1	107
UP/4%PCL2/4%30B (P1)	-359 ± 5	84 ± 2	113
UP/6%PCL2/4%30B (P1)	-347 ± 13	82 ± 2	113
UP/10%PCL2/4%30B (P1)	-358 ± 5	81 ± 1	108
UP/4%PCL2 /4%30B (P2)	-356 ± 10	81 ± 2	111
UP/6%PCL2/4%30B (P2)	-345 ± 9	79 ± 4	105
UP/10%PCL2/4%30B (P2)	-364 ± 5	79 ± 4	110
UP/4%PCL50	-354 ± 10	82 ± 2	111
UP/6%PCL50	-352 ± 14	83 ± 2	108
UP/10%PCL50	-346 ± 14	82 ± 1	110
UP/4%PCL50/4%30B (P2)	-346 ± 10	84 ± 2	115
UP/6%PCL50/4%30B (P2)	-347 ± 10	83 ± 2	116
UP/10%PCL50/4%30B (P2)	-349 ± 9	84 ± 2	118

TABLE 3. Crystallinity degree for PCL2, PCL50, UP/PCL binary blends, and PCL binary and ternary nanocomposites.

System	Crystallinity degree (%)
PCL2	70
PCL2/4%30B	71
UP/10% PCL2	11
UP/4%PCL2/4%30B (P2)	-
UP/6%PCL2/4%30B (P2)	-
UP/10%PCL2/4%30B(P2)	4
PCL50	80
PCL50/4%30B	71
UP/6%PCL50	16
UP/10%PCL50	50
UP/4%PCL50/4%30B (P2)	1
UP/6%PCL50/4%30B (P2)	11
UP/10%PCL50/4%30B(P2)	46
*UP/6%PCL50/4%30B (P1)	12

this case the effect of the silicate layers of the cloisite, acting as barriers that disturb crystals growth, prevails.

PCL50 is less miscible with UP than PCL2, as a consequence the systems, where PCL50 is involved, show crystallinity for compositions of PCL50 (wt% > 4) [5]. Nevertheless when 4 wt% of cloisite 30B is added to the systems UP+PCL50 to obtain ternary nanocomposites UP/PCL50/4%30B, the PCL50 crystallinity degree decreases as occurred in the ternary systems containing PCL2 previously discussed. The obtained results can be explained taking into account that the presence of 30B creates barriers that prevent the crystal growth, leading to a slight decrease of crystallinity degree concerning the corresponding binary systems. This effect is most apparent for ternary systems containing PCL2 due to the higher dispersion level of nanoclay in these systems, as shown in SEM micrographs.

## DMTA

The ratio of the loss modulus to the  $E'$  is measured as the mechanical loss factor or  $\tan \delta$ . The  $\tan \delta$ -temperature curves at 1 Hz, in the  $\alpha$ -relaxation region for neat UP and for ternary PCL2 systems, as a function of PCL2 concentration are presented in Fig. 5a and b according to protocols 1 and 2, respectively. The  $\tan \delta$ -temperature curve for the neat UP shows a maximum at 137°C associated with the  $T_g$  of the cross-linked polyester, and there is a shoulder at approximately 55°C as it was analyzed in a previous article [5]. It can be noticed that  $T_g$  values, for both ternary samples containing 4 wt% of PCL2, are the same as in neat UP; nevertheless  $T_g$  values are slightly lower when the systems contain more than 4 wt% of PCL2. These results are in accordance with DSC measurements and can be justified considering the same opposing effects as it was described above. These  $T_g$ 's results indicate on one hand that the presence of nanoclay in contact with UP resin prevents segmental motions of the polymer chains, but on the other hand the PCL2 would provoke a decrease

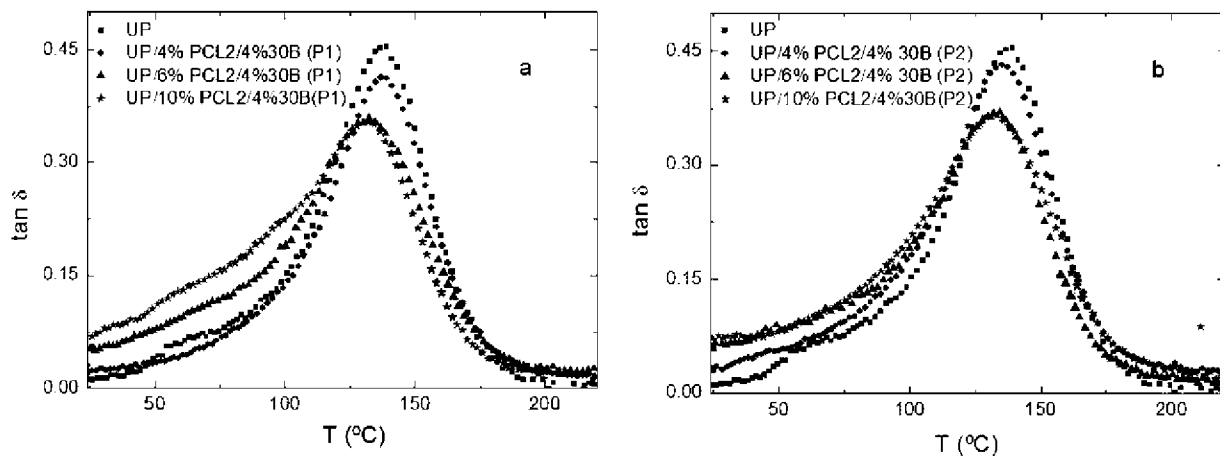


FIG. 5. Loss function ( $\tan \delta$ ) versus temperature for: (a) UP/PCL2/4%30B (P1); (b) UP/PCL2/4%30B (P2).

on  $T_g$  of the UP resin. Therefore as a consequence of both effects, the  $T_g$  of the nanocomposite UP/PCL2/30B remains almost as the  $T_g$  of UP/30B system.

In Fig. 6, different DMTA curves are shown for ternary nanocomposites obtained with P2 and P1 protocols containing PCL50 between 4 and 10 wt% together with neat UP and UP/30B system. It was mentioned before that UP is miscible with PCL2 but is not miscible with PCL50 [5]. As a consequence  $T_g$  values in all the ternary systems with PCL50 are practically identical to  $T_g$  values for nanocomposite UP/30B and higher than the corresponding one to neat UP.

The  $\tan \delta$ -peak height and peak width at half height are sensitive to the amplitude of the macromolecular chain motions and homogeneity of the sample, respectively [31]. A restrictive chain motion causes the reduction of damping capability and consequently an intensity decrease. This restriction in the chain motion can be detected in all the ternary systems with PCL2, independently of the protocol preparation of the nanocomposites. All the results concern-

ing  $\tan \delta$ -peak height and width are included in Table 4. In all the cases the peak heights are lower than for neat UP; however for systems with PCL50 the  $\tan \delta$ -peak heights are closer to the corresponding UP peak height. On the other hand, width at half height values for  $\tan \delta$  peaks for PCL2 ternary nanocomposites compared with pure UP and UP/C30B binary systems allow observing that there is an enlargement of the relaxation peak provoked by a higher level of heterogeneity in the local chain environments that increases with PCL2 content; However, in UP/PCL50/30B (P2) nanocomposites the width of the  $\alpha$ -relaxation peak remains practically constant with PCL50 composition, and is practically identical to that obtained for pure UP and UP/C30B systems reflecting again the immiscibility of PCL50 with UP thermosetting.

DMTA results confirm the results obtained from SEM micrographs and DSC measurements; the influence of PCL molecular weight is an important factor when the morphology of the nanocomposites is analyzed. It seems to be confirmed that 30B is dispersed with less difficulty

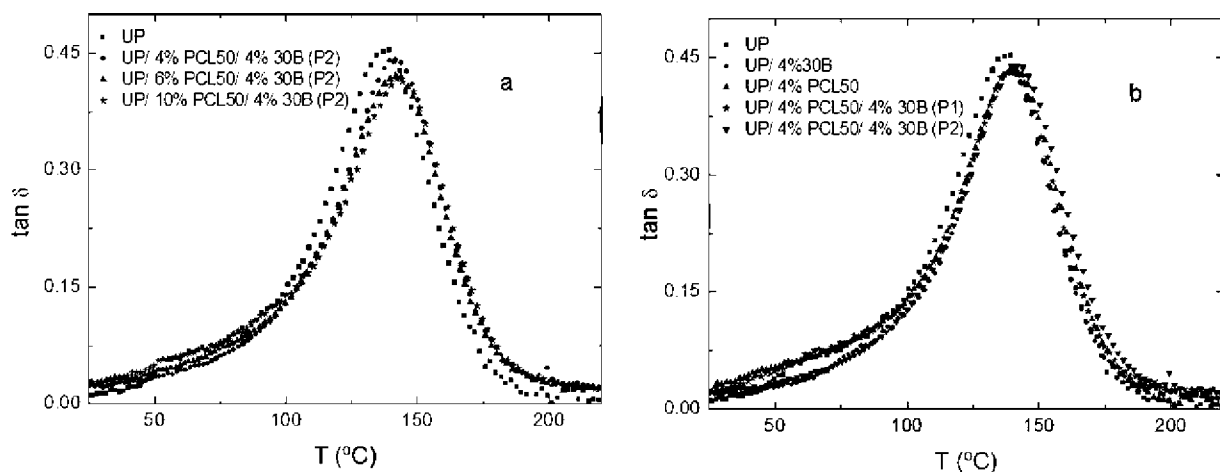


FIG. 6. Loss function ( $\tan \delta$ ) versus temperature for: (a) UP/PCL50/4%30B (P2); (b) ternary nanocomposites (P1) and (P2), neat UP and binary systems UP/4%30B and UP/4%PCL50.



TABLE 4.  $\tan \delta$  peak height, peak width at half height, and apparent activation energy,  $E_a$ , for the  $\alpha$ -relaxation of neat UP and UP binary and ternary nanocomposites.

System	Peak height	Peak width at half height	$E_{a(\alpha\text{-relaxation})}$ (J/mol UP)
UP	0.45	49	$350 \pm 7$
UP/C30B	0.44	46	$410 \pm 8$
UP/4% PCL2/4%30B (P1)	0.41	49	$360 \pm 19$
UP/6% PCL2/4%30B (P1)	0.35	71	$310 \pm 13$
UP/10%PCL2/4%30B (P1)	0.35	92	$380 \pm 16$
UP/4%PCL2/4% 30B (P2)	0.43	56	$370 \pm 11$
UP/6%PCL2/4% 30B (P2)	0.37	67	$370 \pm 9$
UP/10%PCL2/4% 30B (P2)	0.37	78	$330 \pm 14$
UP/4%PCL50/4% 30B (P2)	0.44	48	$380 \pm 4$
UP/4%PCL50/4% 30B (P2)	0.42	50	$390 \pm 6$
UP/4%PCL50/4% 30B (P2)	0.42	54	$410 \pm 6$

in the UP/PCL matrix when PCL molecular weight is low.

The level of dispersion of 30B reached in these ternary systems allows a compensation of the thermal deficiencies (lowering  $T_g$ ) observed in the corresponding binary UP/PCL binary systems. Fixing the attention in the systems that contain PCL2 and in the values of peak width at half height, it can be deduced that both nanocomposites prepared by protocols P1 and P2 present higher heterogeneity of chain motions than those that contain PCL50, which could indicate a higher level of interaction between the three components of PCL2 ternary systems. Therefore, it would confirm that the presence of PCL2 makes easier the dispersion of 30B in the UP/PCL matrix.

It is widely accepted an Arrhenius behavior for  $\beta$  and  $\gamma$ -relaxations, but Williams-Landel-Ferry equation is normally used for  $\alpha$ -relaxation, corresponding to the  $T_g$ . However in our case the Arrhenius law has been applied,

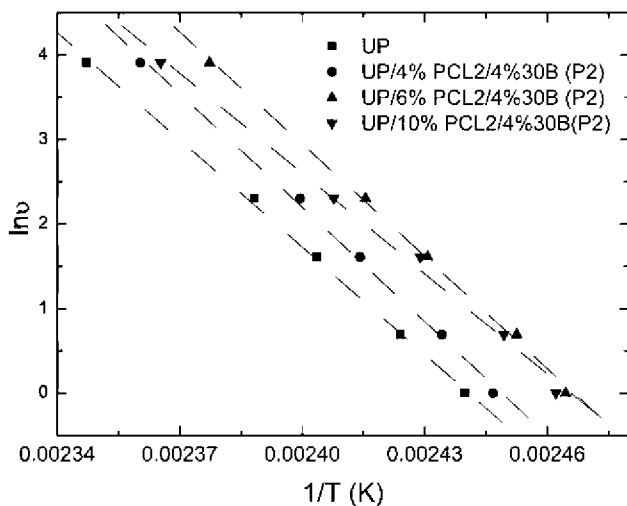


FIG. 7. Arrhenius plots for the dynamic mechanical  $\alpha$ -relaxation of neat UP and UP/PCL2/4%30B (P2) composites, with different PCL2 content.

for the  $\alpha$ -relaxation, because a linear behavior is observed for the logarithm of the frequency,  $\ln v$ , and the inverse of temperature corresponding to the maximum of the peak,  $1/T$ , in the temperature range selected. Accordingly, the apparent  $E_a$  of the individual samples was obtained from the slope of the plots presented, as an example, in Fig. 7 for ternary systems concerning PCL2 and obtained according to protocol 2. In Table 4, the  $E_a$  values are also summarized for all the ternary systems containing PCL2 and PCL50. This Table also includes the  $E_a$  values for binary system and neat UP. The analysis of these values shows that for all the nanocomposites studied the glass transition activation energy are in accordance with the observed  $T_g$  values.

Figure 8 shows the DMTA plots of  $E'$  versus temperature for neat UP and UP/PCL2/4%30B (P1) (Fig. 8a) and UP/ PCL2/4%30B (P2) (Fig. 8b) nanocomposites. The  $E'$  for the system UP/4%PCL2/4%30B (P1) in the low-temperature region (glassy region)  $\sim (30\text{--}50^\circ\text{C})$  has practically the same value than neat UP and UP/30B systems (see Fig. 8c), but for the other systems with higher PCL2 composition  $E'$  values are lower than those of UP, but higher than the corresponding ones to UP/PCL2 with the same concentration of PCL [5]. The same trend has been observed in UP/C30B/PCL50 (P2) nanocomposites as Fig. 8d shows.

In the high temperature region (rubbery plateau) ( $\sim 180^\circ\text{C}$ ), the differences in  $E'$  values are more significant making possible to observe that the presence of 30B equals or increases the  $E'$  values regarding the neat UP, independently of molecular weight and concentration of PCL present in the system. It can be observed that  $E'$  for the UP/4%PCL2/4%30B nanocomposite prepared by P1 protocol, coincides with the corresponding to UP/4%30B system ( $\sim 3,2$  MPa) in Fig. 8c. This value means an increase of 68% related to neat UP and it indicates that the incorporation of a 4% of cloisite 30B would cause the same reinforcing effect on the UP/4%PCL2 matrix than in neat UP and therefore clay modification is more effective in stiffening a flexible matrix than a stiff matrix [32].

### Tensile Properties

The tensile mechanical properties of neat polyester resin and all the binary (ductile, reinforced) and ternary nanocomposites systems are listed in Table 5. Tensile properties of UP thermoset are affected by the addition of PCL. In UP/PCL systems, when the PCL content is low (4%), independently of the molecular weight of PCL, Young's modulus decreases as a consequence of the plasticizing effect. Due to the fact that PCL is in the rubbery state at room temperature, it provokes an enhancement in the ultimate strain of the UP network and a more ductile material.

On the other hand mechanical properties of UP/30B nanocomposites were also analyzed previously with the clay content [15]. An increase in the Young's modulus is

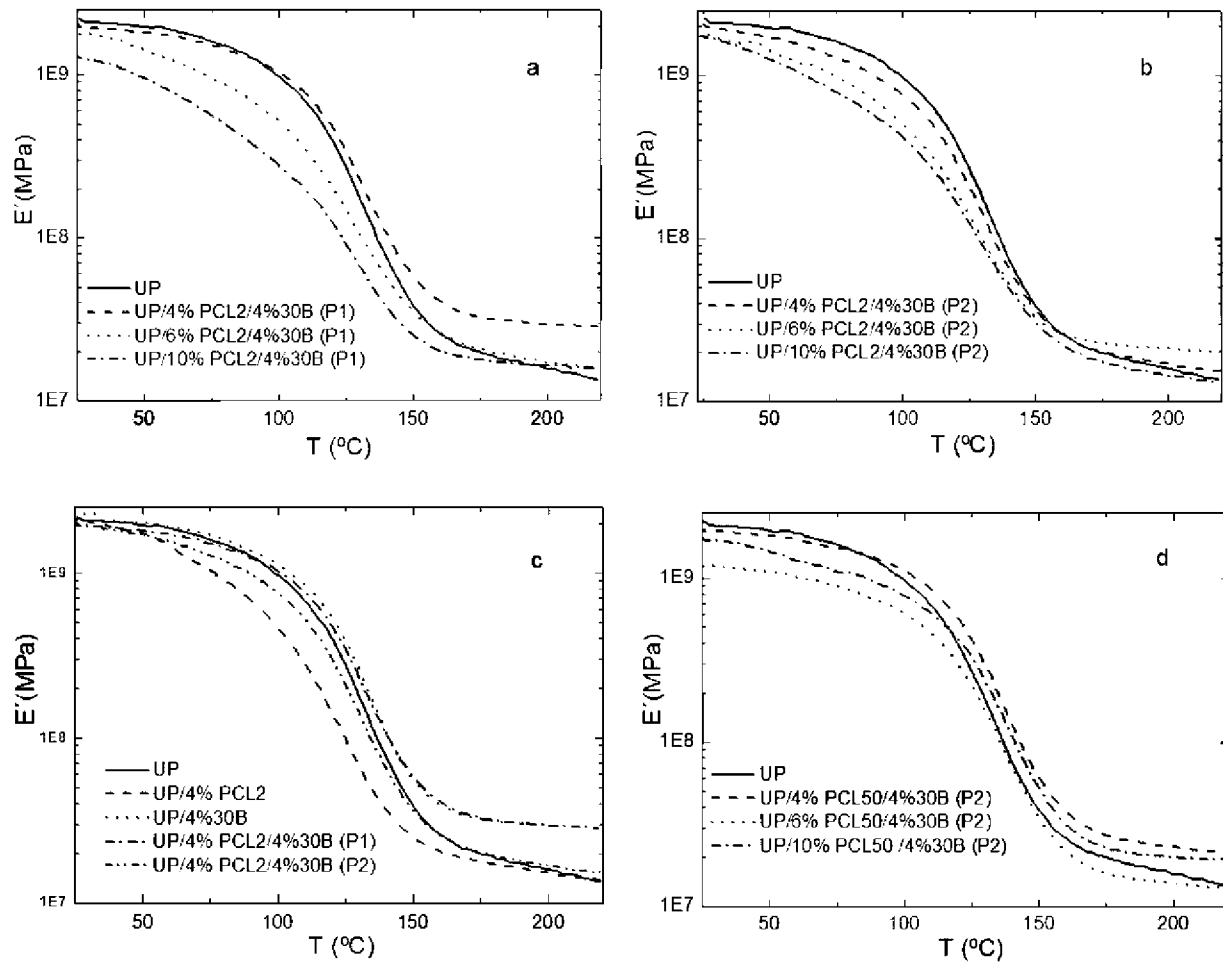


FIG. 8. Temperature dependence of storage modulus for neat UP and UP nanocomposites at 1 Hz.

observed for the UP/4%30B, as it was expected. It is known that the MMT 30B has high elastic modulus and high aspect ratio that contribute to the improvement of the UP mechanical properties [11, 33]. Similar effects on the UP Young modulus are obtained when UP is reinforced with other MMTs in a similar concentration tested (5 wt%) [34]. Also, taking into account the mismatch of

TABLE 5. Tensile properties of neat UP, UP/PCL blends, and UP binary and ternary nanocomposites.

System	$\sigma$ (MPa)	$\epsilon$ (% at fracture)	$E$ (GPa)
UP	$43 \pm 3$	$1.3 \pm 0.1$	$3.8 \pm 0.1$
UP/4%30B	$40 \pm 5$	$1.1 \pm 0.1$	$4.5 \pm 0.1$
UP/4%PCL2	$45 \pm 3$	$1.6 \pm 0.1$	$3.3 \pm 0.2$
UP/4%PCL50	$42 \pm 3$	$1.4 \pm 0.2$	$3.0 \pm 0.2$
UP/4%PCL2/4%30B (P1)	$47 \pm 2$	$1.60 \pm 0.01$	$3.80 \pm 0.02$
UP/6%PCL2/4%30B (P1)	$29 \pm 4$	$0.9 \pm 0.2$	$3.5 \pm 0.2$
UP/10%PCL2/4%30B (P1)	$33 \pm 6$	$1.4 \pm 0.2$	$2.8 \pm 0.3$
UP/4%PCL2/4%30B (P2)	$43 \pm 3$	$1.4 \pm 0.2$	$3.6 \pm 0.1$
UP/6%PCL2/4%30B (P2)	$26 \pm 6$	$0.9 \pm 0.2$	$3.3 \pm 0.2$
UP/10%PCL2/4%30B (P2)	$26 \pm 5$	$1.1 \pm 0.3$	$2.9 \pm 0.2$
UP/4%PCL50/4%30B (P2)	$30 \pm 6$	$1.0 \pm 0.2$	$3.3 \pm 0.2$
UP/6%PCL50/4%30B (P2)	$28 \pm 5$	$1.0 \pm 0.2$	$3.2 \pm 0.1$
UP/10%PCL50/4%30B (P2)	$18 \pm 5$	$0.6 \pm 0.2$	$3.20 \pm 0.08$

thermal expansion coefficient of the UP and 30B, a compression zone was created around the nanoparticles. These compression zones improve the stress transfer between the UP network and the nanoclay thereby improving the Young modulus.

From the analysis of the tensile properties concerning the ternary nanocomposites, differences are observed when PCL molecular weight is considered. Systems containing PCL50 do not show any improvement in the mechanical behavior compared with neat UP. However it can be deduced that the UP/4%PCL2/4%30B nanocomposite exhibits the best mechanical properties among all. The incorporation of 4% of 30B into the UP/4%PCL2 system increases the tensile strength and elongation at break values until 9 and 23% compared with that of neat UP while the Young modulus is still constant. These results indicate that a synergistic effect occurs when the UP hybrid nanocomposites contain 4 wt% of PCL2 and 4 wt% 30B, especially when the nanocomposites have been obtained according to protocol 1. This effect enhances mechanical properties such as strength and elongation at break. Presumably, a good adhesion and bonding between the nanoclay and UP/4%PCL2 matrix, and a good dispersion occurs as it was already seen in the SEM results. In

this case few particle aggregates act as defects, lowering the tensile strength of the reinforced systems. Analogous synergistic effects have been found in other UP ternary systems such as UP/C30B/CSR [25]. There is a slight difference in the mechanical behavior for nanocomposites obtained following protocol 2 and the PCL2 concentration still being 4 wt%. However an increase of PCL2 content (wt% > 4) at any concentration provokes a worsening in the mechanical behavior of the corresponding ternary systems as a consequence of the plasticizing effect of PCL2 that exceeds the reinforcing effect of 30B nanoclay, when PCL2 content is over 4 wt%. For ternary nanocomposites containing PCL50, microvoids caused by the segregation of PCL50 during the curing reaction and nanoclay aggregates would be the cause of the decrease observed in the tensile strength of UP/PCL50/4%30B nanocomposites.

## CONCLUSIONS

Polyester/PCL/cloisite30B nanocomposites were prepared by dissolving the thermoplastic and dispersing laminar nanoclay in the UP matrix, using two different preparation protocols, and two different molecular weights of PCL samples.

The combination of UP, PCL, and 4 wt% cloisite 30B gave intercalated nanocomposites as was confirmed by WAXD. The analysis of X-ray diffraction patterns shows that there is no significant difference in the intercalation level of the cloisite 30B in UP/PCL mixtures, independently of the molecular weight of the PCL and the preparation method of the ternary nanocomposites.

The fracture surface of specimens was examined through SEM. When the PCL2 content in ternary systems is 4 wt%, it favors a more homogeneous dispersion of intercalated aggregates of clay sheets in the polyester matrix of ternary systems, in comparison with UP/30B binary system as a consequence of the miscibility of PCL2.

For ternary nanocomposites containing PCL2, the reinforcing effect of 30B clay partially compensates the plasticizing effect due to the miscibility of PCL2 and UP matrix, and as a consequence the  $T_g$  values of UP/PCL2/4%30B are slightly lower than the corresponding one obtained for UP/30B. However, for UP/PCL50/4%30B nanocomposites,  $T_g$  values are similar to the corresponding one to UP/30B due to the immiscibility between UP and PCL50.

DMTA results indicate that in UP/PCL2/C30B nanocomposites there is an increase in the width of the relaxation peak, which suggests more heterogeneity in the local chain environments of these systems that increases with the PCL2 content; but for UP/30B/PCL50 nanocomposites the width of the  $\alpha$ -relaxation remains practically constant with the PCL50 composition, reaching the values of pure UP and UP/30B systems.

The analysis of the tensile properties concerning the ternary nanocomposites shows that the UP/4%PCL2/4%30B (P1) nanocomposite exhibits the best mechanical

properties among all studied in this work, although the differences with the properties of UP/4%PCL2/4%30B (P2) nanocomposite are not significant. The incorporation of 4 wt% of 30B into the UP/4% PCL2 system increases the tensile strength and elongation at break values until 9 and 23%, respectively, compared with that of neat UP while the Young modulus remains constant.

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