

# Thermomechanical properties of cured isophthalic polyester resin modified with poly( $\epsilon$ -caprolactone)

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**Abstract** The effect of a low profile additive, poly( $\epsilon$ -caprolactone) (PCL), on the thermal and mechanical properties of unsaturated polyester resins (UP) was investigated by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and tensile tests. The morphology of the systems has been studied by scanning electronic microscopy (SEM). Two PCL molecular mass were selected (PCL2:  $M_n = 2000 \text{ g mol}^{-1}$  and PCL50:  $M_n = 50000 \text{ g mol}^{-1}$ ) to analyze the influence of the molecular mass and the content of PCL on the UP resins and to establish the relation between thermomechanical behavior and morphology. DSC and DMTA glass transition temperatures ( $T_g$ ) of the UP cured samples containing PCL indicate that PCL2 is miscible with UP whereas for UP + PCL50 system,  $T_g$  values are very close to the ones corresponding to neat UP. Besides in UP + PCL2 systems, one phase morphology is observed in which PCL2 would act as solvent of the reacting mixture along curing process; however, UP + PCL50 systems present phase-separated morphology. The presence of PCL2 and PCL50 in UP resin leads to a decrease of the tensile strength and the Young's modulus as much notorious as the PCL concentration increases. For UP + PCL2 system the elongation at fracture increases in relation to neat UP, increasing as well with the PCL content.

**Keywords** Unsaturated polyester resin · DSC · DMTA · Glass transition · Poly( $\epsilon$ -caprolactone) · Miscibility · Mechanical properties

## Introduction

Adding specific thermoplastic polymers as low profile additives (LPAs) in the unsaturated polyester resins (UP) is a well-known industrial technology. Such modified thermosetting polymers, essentially made from UP, styrene monomer and LPA enhance the polymerization shrinkage during the cure process [1–5]. Depending on the difference in polarity between LPA and linear UP, some LPAs such as thermoplastic polyurethane (PU) are usually compatible with UP, while others such as poly(methyl methacrylate) (PMMA) and polystyrene (PS) are not [6, 7]. When a vinyl monomer, like styrene, is added to form a ternary styrene/UP/LPA system, the LPA and UP usually can not coexist in a homogeneous phase, especially for systems containing PMMA and PS [6, 7]. The ternary phase characteristics before reaction depend on the chemical nature and the molecular mass of the UP and LPA chosen. Irrespective of the miscibility behavior of the reacting mixture before curing reaction, the final morphology of UP/LPA cured systems is quite complex. During curing reaction, two competing processes take place simultaneously, on one hand, the crosslinking reaction between UP resin and the vinyl monomer styrene, and, on the other hand, the phase separation of the LPA provoked by the increase in the molecular mass of the reacting species (decrease in entropy of mixing). The final morphology obtained is dependent on the molecular mass of the components of the reacting mixture, the content of LPA selected, the degree of

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crosslinking reached, and the reaction conditions (temperature, viscosity of the mixture).

The most common methods to investigate the morphological characteristics of UP/LPA cured systems are the determination of the glass transition temperature,  $T_g$ , and the determination of morphology by electron microscopy. By means  $T_g$  it is possible to distinguish between immiscible or partial miscible systems, and miscible systems. In the first case, the microheterogeneity caused by the immiscibility provokes the existence of two well distinguished  $T_g$ , or a broad  $T_g$ , depending on the level of interaction between polymers. For miscible polymers, a single  $T_g$  is detected. Electron microscopy supplies information about the fracture surfaces of the systems which depend on the morphological characteristics of the coexisting phases.

There are many articles in the literature concerning amorphous LPAs (PMMA, PVAc, PU) [1–8], but there are very few about polymer blends containing one crystallizable component and a thermosetting component [9]. In previous articles, the miscibility of the systems formed by linear UP resin and poly( $\epsilon$ -caprolactone) (PCL) [10–13] were studied. For the corresponding cured UP/PCL systems, the curing and kinetic parameters were also studied [14, 15]. The aim of this study is to determine the thermo-mechanical properties of cured systems, analyzing the influence of the molecular mass and PCL content on the miscibility of the systems and the resulting morphology of the cured blends. The differences in the overall compatibility of the polyester resin and both PCL samples (very different molecular mass) explain the mechanical behavior of these systems.

## Experimental

### Materials

The UP, (Estratil 6603), UP, was provided by Plastiform (Spain) having a mass/38% of styrene as a crosslinking agent. Nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) was used to characterize the linear polyester. UP consists of isophthalic anhydride (IA), maleic anhydride (MA), and 1,2-propylene glycol (PG). The relative composition calculated was IA:MA:PG = 3:2:5. The number average molecular mass,  $M_n$  calculated from the acid value was  $3700 \text{ g mol}^{-1}$ . The molar ratio (MR) of styrene to polyester C=C bonds were  $\text{MR} = 3/1$  and constant in all the cases. In the curing process, benzoyl peroxide was used as initiator being supplied by Panreac. PCL samples were provided by Aldrich Chemical Company and Polysciences Eppelheim. The  $M_n$  and polydispersity index were obtained by gel permeation chromatography. The  $M_n$  values found

for PCL2 and PCL50 were  $2000$  and  $50000 \text{ g mol}^{-1}$  with a polydispersity 1.4 and 1.6, respectively. PCL is a semi-crystalline thermoplastic polymer with glass transition temperature,  $T_g$  between  $-64$ ,  $-62 \text{ }^\circ\text{C}$ , melting temperature,  $T_m$  between  $50$ ,  $59 \text{ }^\circ\text{C}$  depending on the molecular mass, and crystallinity degree,  $X_c = 60\%$  [13].

### Techniques

Calorimetric measurements reported were carried out at  $20 \text{ }^\circ\text{C min}^{-1}$  heating rate, in a Mettler Toledo mod. 821e DSC instrument. The temperature scale was calibrated using Indium, and the measurements were conducted under nitrogen atmosphere. Glass transition temperature,  $T_g$  was obtained from the inflection point of the curves corresponding to the second scan. In all the cases, pans of aluminum of  $40 \mu\text{L}$  were used, and the mass of the samples was kept in the range  $10$ – $20 \text{ mg}$ .

Dynamic mechanical thermal analysis (DMTA) was performed with a DMTA V Rheometrics Scientific Instrument. These samples were submitted at frequencies of 1, 10, and 50 Hz in the temperature range from  $-110$  to  $180 \text{ }^\circ\text{C}$  in the double cantilever mode. The heating rate was  $3 \text{ }^\circ\text{C min}^{-1}$ . The maximum of the tan-temperature curves was associated with  $\alpha$ -relaxation corresponding to the glass transition.

Infrared (IR) spectra were obtained on a Nicolet 5700 spectrometer from Thermo electron. The samples were collected using the ATR method (MCT/A detector,  $4000$ – $400 \text{ cm}^{-1}$  spectral range and resolution of  $8 \text{ cm}^{-1}$ ). The baseline spectra were normalized to the spectra to be comparable.

Scanning electron microscopy (SEM) has been used to study the morphology of UP + PCL cured samples. 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  $1500$  to  $3500\times$ . The fracture surfaces were observed.

Tensile mechanical properties of rectangular specimens were measured using a MTS machine QTest 2L model and a MTS extensometer, model number 63411F-54. The samples were loaded at constant rate of  $1 \text{ mm min}^{-1}$  until fracture. At least five specimens of each sample were measured to obtain the average value of the mechanical properties.

### Preparation of cured specimens

Crosslinking reaction was initiated by adding mass/1.5% of benzoyl peroxide to UP + PCL mixtures prepared with different contents of PCL (mass/4, 6, and 10%). The mass of benzoyl peroxide was calculated with respect to the UP

content. The mixture was achieved by stirring at 400 rpm, at room temperature. The sample solutions were slowly poured into aluminum rectangular moulds and cured in an oven at 80 °C for 40 min followed by a post-cure at 110 °C for 2.5 h, and then the samples were cooled until room temperature. The mould dimensions were 75 × 35 × 1.5 and 140 × 10 × 2 mm<sup>3</sup> for DMTA measurements and tensile tests, respectively.

## Results and Discussion

### Differential scanning calorimetry measurements

Cured samples for calorimetric measurements were obtained following the protocol described before. For differential scanning calorimetry (DSC) measurements, the specimens were first cooled in nitrogen atmosphere at -110 °C and scanned at 20 °C min<sup>-1</sup> to 180 °C. The obtained thermograms corresponding to the different composition of UP + PCL2 and UP + PCL50 systems are presented in Fig. 1, those corresponding to pure components, PCL2, PCL50, and UP are also included. For UP + mass/4% PCL2 cured blends, the thermograms present a single glass transition temperature,  $T_g \approx 70$  °C, intermediate between those of the pure polymers indicating miscibility; furthermore, the melting endotherm of the crystalline phase PCL2 is only very slightly detected for UP + mass/6% PCL2 and UP + mass/10% PCL2 resins. In these cases, this small endotherm overlaps with the glass transition temperature of the network, being difficult to define exactly the  $T_g$  value of the resin. The arrows placed on the thermograms indicate approximately the  $T_g$  location of the systems. These  $T_g$  values are in accordance with the miscibility of the UP + PCL2 system, in the mass composition range 4–10% PCL2. For these compositions the polymer network in UP + PCL2 systems would be formed mainly by the integration of PCL2 amorphous polymer chains in the crosslinked structure of UP network giving rise to a unique amorphous phase.

The thermograms presented in Fig. 1 also illustrate the behavior of UP + PCL50 for the same blend mass compositions 4–10% PCL50. It can be seen in these systems that the melting endotherm of the crystalline phase PCL50 is more defined in UP + PCL2 systems and does not overlap with the  $T_g$  of the resin. The  $T_g$  values obtained for UP + PCL50 cured blends remain practically constants, regardless of the PCL content, reaching values ( $\approx 100$  °C) very close to the  $T_g$  value of neat UP ( $\approx 105$  °C); this confirms that the segregation of PCL50 occurs along the curing reaction, giving rise to a biphasic microstructure.

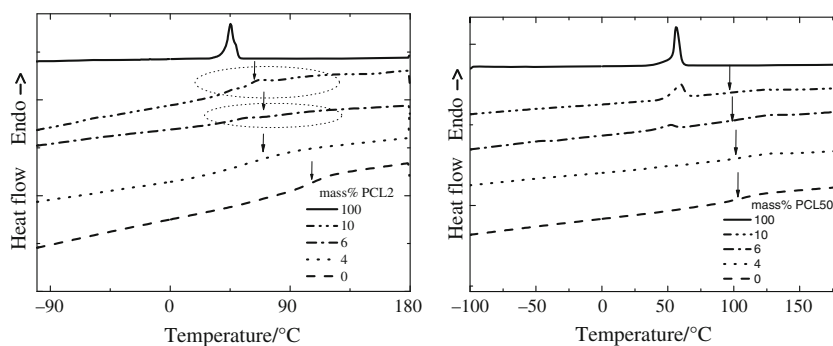
### Fourier transform infrared spectroscopy

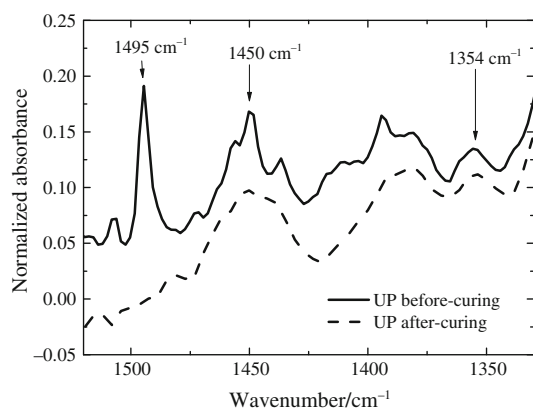
The whole IR spectrum obtained for commercial UP resins before and after curing is well known [16–19]. The variation of the different components in the curing UP resin allows the identification of the relevant IR bands, the changes of which can be used for both qualitative and quantitative determination of the composition of the resin. In Fig. 2, an expanded view of the UP resin IR spectra before and after curing is shown to emphasize the band at 1354 cm<sup>-1</sup> corresponding to the C=C polymerized MA. From this spectrum it can be noticed that after the UP curing, the band at 1354 cm<sup>-1</sup> still remains, representing the polymerized MA residue. The presence of styrene can be detected by its numerous bands. In the presented spectra are marked the frequency of a styrene characteristic band at 1495 cm<sup>-1</sup> assigned to free styrene. The absence of the band at 1495 cm<sup>-1</sup> and the presence of the band at 1354 cm<sup>-1</sup> band, in the cured UP spectrum, confirms the PS homopolymerization formation during the UP curing.

### Morphology of cured UP resins

SEM micrographs in Fig. 3 show the fracture surface morphologies of modified and unmodified UP resin. The appearance of fracture surfaces was in good agreement with the macroscopic visual inspection. In neat UP, the fracture surface was found homogeneous and uniform

**Fig. 1** DSC curves of UP + PCL2 and UP + PCL50 networks for several compositions





**Fig. 2** Expanded view of IR spectra 1525→1325  $\text{cm}^{-1}$

according to the transparency observed by visual inspection of the samples. In neat UP, slim lines appear uniformly distributed on the fracture surface [20]. UP + PCL2 cured systems were found to be transparent (at least for the three compositions reported) as well; it can be seen from SEM micrographs that the fracture surface of those systems is very similar to neat UP with uniform slim lines, morphology compatible with a miscibility behavior. The PCL50 effect on the morphology of UP cured samples is different from the one obtained for PCL2. The fracture surface observed from the micrographs appears rough in UP + PCL50 samples, in agreement with the opacity observed by visual inspection of the samples and  $T_g$  results. SEM micrographs in Fig. 3c evidence also, how the roughness of the fracture surface increases with the PCL50 content in the sample. This microstructure is compatible with a phase-separated behavior. In them it can be noticed the domains of a PCL50-enriched phase. These behaviors can be explained taking into account that the miscibility of UP + PCL resins is affected by the molecular mass of PCL as it was previously found for linear UP + PCL systems [12, 13].

#### Dynamic mechanical thermal properties

The ratio of the loss modulus to the storage modulus 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 UP + PCL systems, as a function of PCL concentration are presented in Fig. 4.

The position and height of  $\tan\delta$  peak are indicative of the structure and properties of the material. The  $\tan$ -temperature curve for the neat UP shows a maximum at 125 °C associated with the glass transition temperature of the crosslinked polyester, and a shoulder at approximately 48 °C (not detected by DSC measurements). This is a consequence of the UP crosslinking which is mainly a result of styrene

homopolymerization and its copolymerization reaction with the C=C double bonds of the UP chain [21, 22]. Table 1 shows the  $T_g$  values associated to the maximum temperatures of  $\tan\delta$  for neat UP, UP + PCL2, and UP + PCL50 for PCL compositions (mass/4, 6, and 10%); the data named as  $T_g$  shoulder correspond to the  $\alpha$ -relaxation of the styrene homopolymerization.

From Table 1 and Fig. 4a it can be noticed that  $T_g$  values of the UP + PCL2 networks are lower than the  $T_g$  of the neat UP. The lowering of UP network  $T_g$  could be assigned to a plasticization effect of PCL2 on the cross-linked polyester network caused by the miscibility of PCL2 chains with UP.

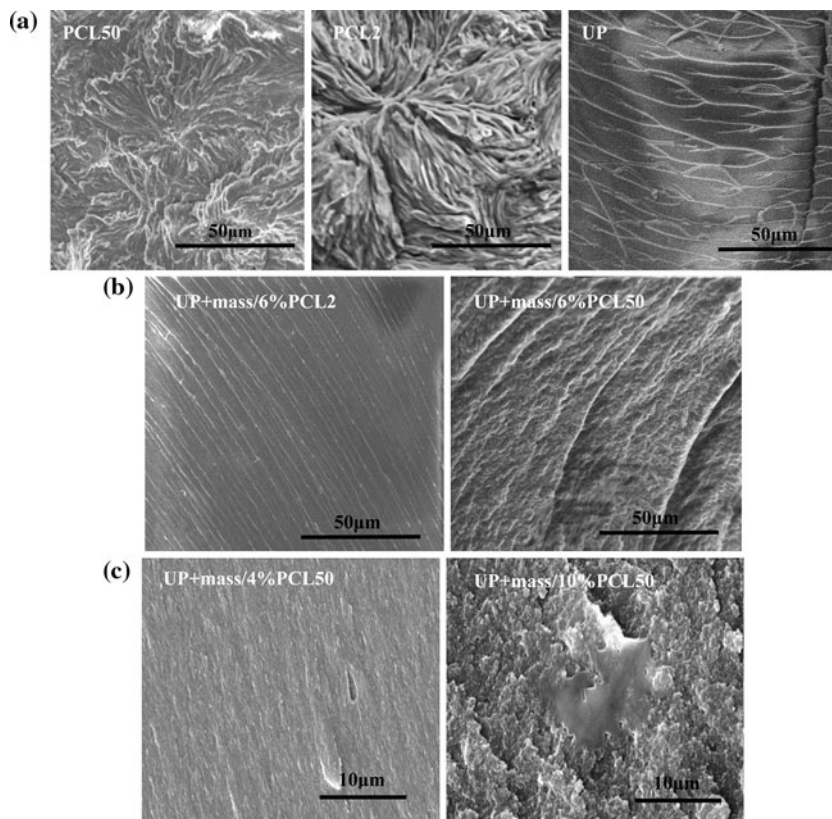
The  $\tan\delta$  peak height and peak width at half height are summarized in Table 2. These magnitudes are sensitive to the amplitude and homogeneity of the macromolecular chain motions, respectively [23]. A restrictive chain motion causes the reduction of damping capability and consequently an intensity decrease. It can be seen that the neat UP  $\alpha$ -relaxation is narrower than the UP + PCL2 ones. The heterogeneity of the chain local environment leads to wider relaxation spectra [24–27]; as a consequence, the enlargement of the relaxation peak indicates the existence of more heterogeneity in the local chain environments of UP + PCL2 samples with respect to pure UP.

Figure 4b shows the  $\tan\delta$ -temperature curves at 1 Hz for the UP + PCL50 systems. In all the cases,  $\tan\delta$ -temperature curves show two transition peaks according to UP network topology, like in the UP + PCL2 systems. It can be noticed that in  $\tan\delta$ -temperature curves the  $T_g$  values of the UP + PCL50 networks are very close to the  $T_g$  of the neat UP (125 °C). These  $T_g$  results are also in accordance with the glass transition temperatures obtained through DSC experiments. The small variation in the  $T_g$  values of UP + PCL50 systems, comparatively to the  $T_g$  of neat UP, indicates that PCL50 is not miscible with UP resin. Besides, the broadness of the  $\alpha$ -relaxation for UP + PCL50 system is similar to the neat UP, indicating that these blends are more homogeneous than the corresponding ones UP + PCL2 networks. The differences in broadness values of the  $\alpha$ -transitions for UP + PCL50 and UP + PCL2 are compared in Table 2. The peak width and height values similar for the UP + PCL50 and UP systems are explained considering that the segregation of the thermoplastic phase provokes the coexistence of domains with composition close to neat UP network and neat PCL50, and therefore, it confirms the lack of miscibility observed by DSC measurements.

Figure 5 shows  $\tan\delta$ -temperature curves at 50 Hz for UP + mass/4% PCL2 and UP + mass/4% PCL50, emphasizing the temperature range corresponding to the PCL glass transition temperature. In the UP + PCL50 system it can be appreciated that the  $T_g$  of the PCL



**Fig. 3** SEM micrographs of fracture surface of **a** pure components **b** UP + mass/6% PCL2 and UP + mass/6% PCL50, and **c** UP + mass/4% PCL50 and UP + mass/10% PCL50

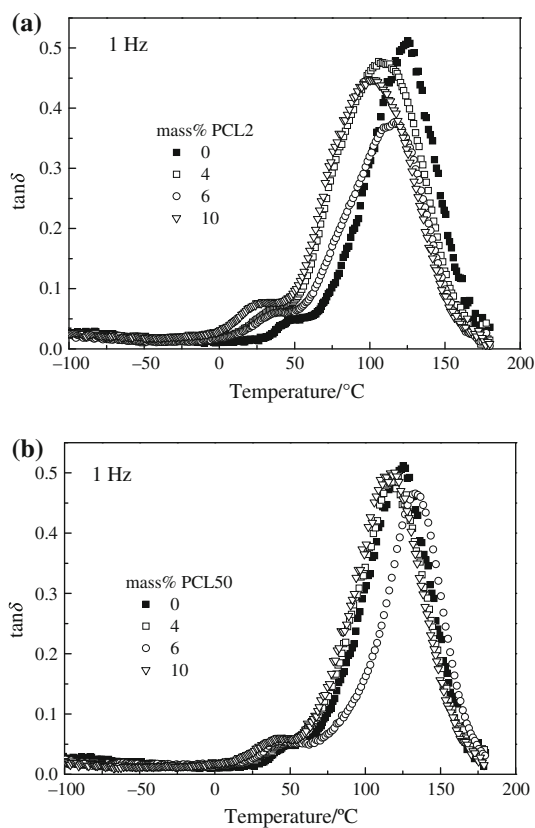


associated to the maximum of  $\tan\delta$  located between  $-60$  and  $-65$  °C; however, for UP + mass/4% PCL2 system this  $T_g$  can not be detected. This result assesses that UP is miscible with PCL2 amorphous phase but is not miscible with PCL50. The behavior found is the same in both systems for all the compositions and frequencies measured.

Storage modulus and  $\tan\delta$  measurements performed at high frequencies result in higher values than those at low frequencies. The effect of frequency on  $T_g$  of the UP + PCL systems can be well explained by Arrhenius relationship because for the present systems a linear behavior between the logarithm of the frequency,  $\ln\nu$ , and the inverse of temperature corresponding to the maximum of  $\tan\delta$ ,  $1/T$ , in the temperature range selected, it was observed. Particularly in the UP + PCL50 system five measurement frequencies instead of three were selected to confirm the Arrhenius behavior as can be seen in Fig. 6.

In Table 3 are summarized the apparent activation energy values for the relaxation processes for all the UP + PCL systems. The analysis of these values reveals that for UP + PCL2 resins, the activation energy,  $E_a$ , decreases significantly in all the cases, respect to  $E_a$  for neat UP, but in the UP + PCL50 systems the corresponding  $E_a$  varies slightly respect to the neat UP, in accordance with the immiscible behavior discussed above [28].

Figure 7a and b shows the temperature dependence of storage modulus,  $E'$ , at frequency of 1 Hz, of fully cured polyester UP containing different amounts of PCL2 and PCL50, respectively. In both UP + PCL systems it can be observed a slightly decrease in the storage modulus with regard to the corresponding one to neat UP in the glassy state indicating a decrease in the stiffness of these systems. It is interesting to note that, for both UP + PCL systems, the rubber elastic modulus,  $E_r$ , ( $T_g + 40$  °C) decreases in a significant way when PCL content is increased up to mass/10%. For a single phase polymer, the rubbery modulus is proportional to the concentration of crosslinks in the network structure [29–32]. The decrease in  $E_r$  denotes an increase in the molecular mass between crosslinking junctions,  $M_c$ , and therefore, a decrease in the crosslinking degree, which would indicate that the presence of thermoplastic obstructs the interaction between reactive groups during curing reaction, giving rise to a more open structure of polyester network. This effect occurs regardless of final morphology reached after curing process. In UP + PCL2 system, a one phase morphology is observed. In this case, PCL2 acts as a solvent of the reacting mixture along curing process. In UP + PCL50 system, a separated phase morphology is observed, in which the thermoplastic phase would turn into an obstacle for reacting groups, reducing the connectivity of thermoset phase and lowering the



**Fig. 4** Loss function ( $\tan\delta$ ) versus temperature for **a** UP + PCL2 and **b** UP + PCL50 networks

modulus. It has been suggested for other polyester/additive systems [6] that during cure the additive is pushed to the surface of the growing microgel particles which reduce the tendency of the polyester gel particles to coalesce, favoring the formation of a continuous additive phase. If PCL content is lower (mass/6%), the thinner effect of PCL2 diminishes and the size of the PCL50-enriched domains diminishes too, and consequently,  $E_r$  values for both systems would be closer to the corresponding neat UP network.

**Table 2** The  $\tan\delta$  peak height, peak width at half height of UP + PCL networks

Sample	Peak height	Peak width at half height
UP	0.51	55
UP + mass/4% PCL2	0.48	74
UP + mass/6% PCL2	0.38	67
UP + mass/10% PCL2	0.45	75
UP + mass/4% PCL50	0.49	59
UP + mass/6% PCL50	0.47	48
UP + mass/10% PCL50	0.50	61

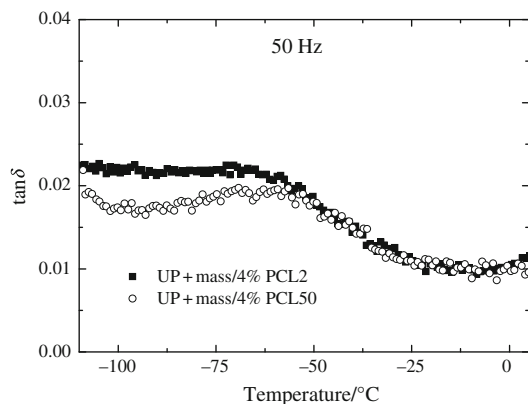
### Tensile properties

Tensile properties of UP thermoset are affected by the addition of PCL. The effects of varying PCL2 and PCL50 concentration on the resin are shown in the typical stress-strain curves of Fig. 8, and the corresponding data are collected in Table 4. For all the three UP + PCL2 systems, the tensile strength,  $\sigma$ , and Young's modulus,  $E$ , decrease when PCL concentration rises. The decrease of  $E$  is a consequence of the sample morphology described above, in which PCL2 acts as plasticizer of cured UP network. This behavior is according to the bibliographical results obtained for other UP/thermoplastic systems [6, 33], in which the thermoplastic exhibits a  $T_g$  lower than room temperature, like PCL2. A polymeric plasticizer provides flexibility to the thermoset and improves the workability. The effect of PCL2 concentration on the ultimate strain,  $\varepsilon$ , shows the opposite trend as that observed for  $\sigma$  and  $E$  values. Since PCL2 is in the rubbery state at room temperature, the increase in PCL2 concentration in the network enhances the ultimate strain of the UP resin, and a more ductile material is obtained.

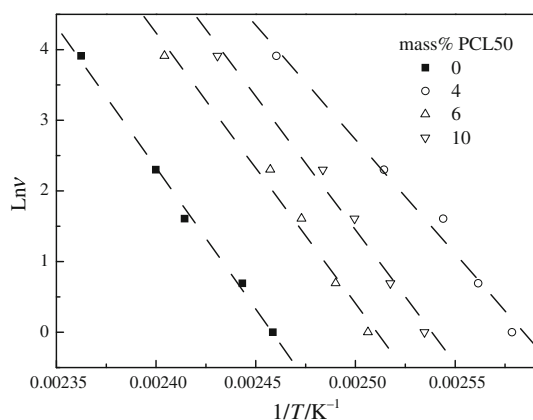
The influence of the PCL molecular mass on the mechanical properties of UP + PCL crosslinked systems depends on the system miscibility. The tensile strength of the UP + PCL50 networks decreases by increasing the PCL50 concentration, as well as in UP + PCL2 cured

**Table 1** DMTA glass transitions temperatures,  $T_g$ , for UP + PCL networks

Sample	Frequency/Hz		
	1 $T_g$ shoulder/ $T_g$ cured resin/ $^{\circ}\text{C}$	5 $T_g$ shoulder/ $T_g$ cured resin/ $^{\circ}\text{C}$	10 $T_g$ shoulder/ $T_g$ cured resin/ $^{\circ}\text{C}$
UP	48/125	58/133	68/140
UP + mass/4% PCL2	38/106	42/121	45/132
UP + mass/6% PCL2	38/116	44/126	46/133
UP + mass/10% PCL2	33/99	38/113	41/122
UP + mass/4% PCL50	47/117	51/127	58/136
UP + mass/6% PCL50	45/133	48/142	56/149
UP + mass/10% PCL50	43/117	45/127	49/134



**Fig. 5** Loss function ( $\tan\delta$ ) versus temperature for UP + mass/4% PCL networks. Temperature range corresponding to the glass transition zone of PCL

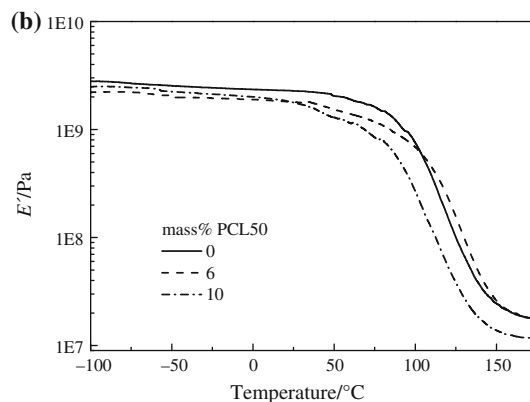
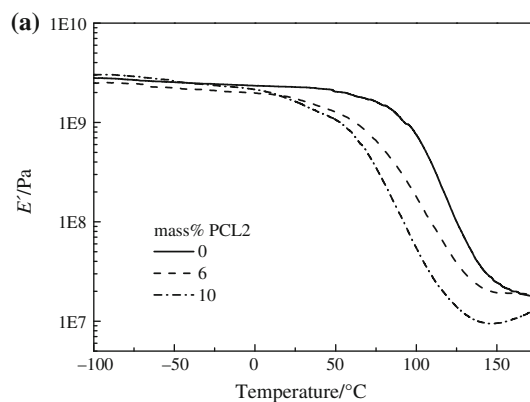


**Fig. 6** Arrhenius plots of the  $\ln v$  versus  $1/T$

**Table 3** Apparent activation energy,  $E_a$ , for the  $\alpha$  relaxation of UP + PCL networks

Sample	$E_a/\text{kJ mol}^{-1}$
UP	$330 \pm 15$
UP + mass/4% PCL2	$210 \pm 10$
UP + mass/6% PCL2	$310 \pm 15$
UP + mass/10% PCL2	$240 \pm 12$
UP + mass/4% PCL50	$300 \pm 15$
UP + mass/6% PCL50	$350 \pm 15$
UP + mass/10% PCL50	$300 \pm 15$

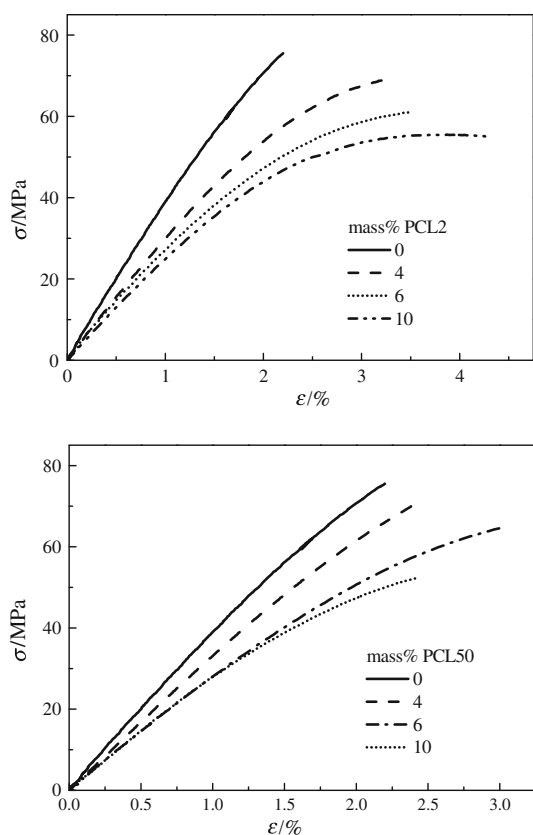
blends. The fall in  $\sigma$  observed in UP + PCL50 systems has been also detected for cured samples of polyester resins containing other LPA additives like PS or poly(methyl-methacrylate) (PMMA) [6]. The tensile strength depends on several factors as are, the crosslinking density of the UP network, the final morphology of the samples, and the percentage of microvoids in the cured samples. These



**Fig. 7** Temperature dependence of storage modulus,  $E'$ , for UP with mass/0, 6, and 10% PCL2 (a) and PCL50 (b) at 1 Hz frequency

microvoids are caused by the segregation of the thermo-plastic phase during the curing reaction and the subsequent cooling at room temperature, being responsible of the reduction or even elimination of the polymerization shrinkage that takes place during the cure process [1–5]. As a consequence, the existence of microvoids in UP + PCL50 cured samples with respect to neat UP cured resin and the lacking interfacial adhesion between coexisting phases (UP rich phase and PCL crystalline rich phase) would be the cause of the decrease observed in  $\sigma$  values of UP + PCL50 samples (see Table 4).

Table 4 also shows the effect of PCL50 content on  $E$ , for UP + PCL50 cured samples. The behavior is similar to that obtained for tensile strength, although the reason, to justify it, is different. Based on the iso-strain model [6] the Young's modulus of the UP + PCL50 systems would be dominated by the modulus of the UP and its volume fraction in the blend, both higher than the corresponding ones to PCL50 (Young's modulus of PCL  $\approx 500$  MPa) consequently, Young's modulus decreases by increasing the PCL50 concentration. Finally, the ultimate tensile strain values for UP + PCL50 systems reveal that PCL50 does not affect significantly the ultimate tensile strain of the system due to its phase-separated morphology.



**Fig. 8** The effects of PCL content on tensile properties of UP + PCL networks

**Table 4** Tensile properties of UP + PCL networks

Sample	$E/\text{GPa}$	$\sigma/\text{MPa}$	$\epsilon/\%$ at fracture
UP	4.0	76	2.7
UP + mass/4% PCL2	3.3	68	3.4
UP + mass/6% PCL2	3.0	54	3.3
UP + mass/10% PCL2	2.5	53	3.7
UP + mass/4% PCL50	3.3	72	2.5
UP + mass/6% PCL50	3.1	66	3.3
UP + mass/10% PCL50	2.9	54	2.5

## Conclusions

$T_g$  values determined by DSC for UP + PCL2 systems, in the mass composition range 4–10% PCL2, are in accordance with the miscibility of these systems. On the other hand,  $T_g$  calorimetric values for UP + PCL50 systems are very close to the corresponding value for neat UP, which reveals that PCL50 is not miscible with UP network leading to a system of separated phases.

The DMTA  $T_g$  results are in accordance with the corresponding ones obtained by DSC. Neat UP  $\alpha$ -relaxation is narrower than the UP + PCL2 ones; the higher the content

of PCL2, the broader gets the peak associated to  $\alpha$ -relaxation too. The enlargement of the  $\alpha$ -relaxation peak indicates the existence of some heterogeneity in the local chain environments of UP + PCL2 samples with respect to the pure UP. The intensity and the broadness of the  $\alpha$ -transitions for UP + PCL50 system are similar to the neat UP, independently of the percentage of PCL50 in the network, indicating that these resins are more homogeneous than the corresponding ones to the UP + PCL2.

SEM micrographs of UP + PCL2 show that the fracture surface is similar to the morphology of the neat UP: uniform with slim lines and compatible with a miscibility behavior and the transparency of the samples. The PCL50 effect, on the morphology of UP cured samples is different from the one obtained for PCL2. In UP + PCL50 systems SEM micrographs show a microstructure compatible with a phase-separated behavior. The fracture surface observed from the micrographs appears rough compared to the neat UP, in agreement with the opacity observed by visual inspection.

For UP + PCL2 systems, the tensile strength and Young's modulus decrease by increasing the PCL concentration as a consequence of the PCL2 plasticizer effect leads to a polymer network formed by PCL2 polymer chains enclosed in the crosslinked structure of the UP network. The increase in PCL2 concentration in the network enhances the ultimate strain, obtaining a more ductile material.

The tensile strength and Young's modulus of UP + PCL50 cured samples decrease also with the content of PCL50. The existence of microvoids in UP + PCL50 cured samples with respect to the neat UP cured resin and the lacking interfacial adhesion between coexisting phases provoke that the tensile strength of these systems decreased by increasing the PCL50 concentration.

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