

Study of the effects of the phase distribution change of a neat unsaturated polyester resin due to curing process variation on the properties of thermoset

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A commercial unsaturated polyester resin cured at several conditions was investigated. A relationship between phase distribution of cured resins and both thermal stability and dynamical mechanical properties measured by TGA and DMA, respectively, was observed. Morphology of the internal surfaces was analyzed by AFM showing that more homogeneous nanostructures with smaller domains resulted in an increase of storage modulus and glass transition temperature. Results of $\tan \delta$ peaks showed that differences between unsaturated polyester rich phase and polystyrene rich phase tended to decrease at higher curing temperature. Interaction parameters between unsaturated polyester and styrene were calculated and used to explain some of the achieved results.

Introduction

With over seventy years of commercial development, unsaturated polyester resin (UPR) applications continue growing due to their both low cost compared to other thermosets, and versatility of use in different applications such as compression molding, resin transfer molding, pultrusion, etc. (Johnson, and Yang, 2004). In the case of composite materials of reinforced plastics, the UPR constitute 39 % of the total of resins used (Lucintel, 2016).

A common UPR is composed of polyester with reactive unsaturation in its chain (UP), which is dissolved in a reactive solvent with a vinyl group such as styrene (ST) (Thomas *et al.*, 2019). Due to miscibility properties between UP and ST, liquid UPR generally present only one phase (Jones, 2016). However, during the curing process it is formed a heterogeneous system (Cao, and Lee, 2003). Some researchers consider that the curing mechanism of an UPR occurs generating microgels rich in UP (UP_{rich}) which are surrounded by a phase rich in ST (ST_{rich}) (Hashemi, and Shojaei, 2017; Yang, and Suspene, 1991). Moreover, literature shows that size of microgels depends on variation of intramicrogel reaction between UP and ST (Stuck *et al.*, 2020).

Many of the studies about UPR have been focused to understand the relationship between structure-property of the composite materials (Gao *et al.*, 2019), whereas for neat resins the studies are very limited (Sánchez *et al.*, 2000). Zheng *et al.* (1988) studied some effects of thermal treatment on phase separation. They observed that morphology of gelled UPR can be modified with the variation of curing temperature. Hsu and Lee (1991), proposed a phase separation mechanism during the curing of an UPR and demonstrated how curing temperature variation modifies the morphology of both microgels and structure of the fully cured UPR.

Notwithstanding, it has not been completely clarified the effect of phase distribution of cured neat UPR on its final properties when no changes in chemical composition were made to the liquid UPR. Yang and Lee (1988) studied the effects of ST content and UP composition on shape of three-dimensional UPR network. On the

other hand, Sanchez *et al.* (2000) presented that there is a direct relationship between both phase separation and crosslinking density, and ST concentration in cured UPR. Considering the above, the aim of this work was to investigate the relationship between phase distribution of a fully cured neat UPR and its dynamical mechanical and thermal properties.

Experimental section

A commercial orthophthalic unsaturated polyester resin (UPR) with trade name Cristalan® 860, manufactured by Andercol S.A.S was used. This resin used 30 wt % of styrene (ST) as reactive solvent and 70 wt % of unsaturated polyester (UP). Cobalt octoate solution to 6 wt % in ST and methyl ethyl ketone peroxide solution (MEKP) were used as curing agents. Samples were isothermally cured in a stove at 40, 60, and 80 °C. A post-curing process in stove from 35 to 200 °C, at a heating rate of 2 °C/min was carried out for all samples.

Morphology of internal surface of fully cured UPR was analyzed in tapping mode using an atomic force microscopy (AFM) Nanoscope V Multimode 8 from Bruker, equipped with an integrated silicon tip/cantilever. The resonance frequency was ~ 300 kHz. The tip radius was 5-10 nm, and cantilever was 125 µm long. Internal surface of each investigated sample was prepared using an ultramicrotome Leica Ultracut R with a diamond blade.

Dynamic mechanical analysis (DMA) was carried out in a Q800 of TA Instruments with a three point-bending device. The thermal scan started at 35 °C and went up to 200 °C at a rate of 2 °C/min, with a frequency of 1 Hz, and deformation of 0.1 %. Rectangular specimens having a size of 60 × 10 × 1 mm³ were used.

Thermogravimetric analysis (TGA) was performed in a Mettler Toledo SDTA851e equipment. The samples were heated from 35 to 550 °C at a heating rate of 5 °C/min with a nitrogen flow of 40 mL/min.

Results and discussion

Miscibility changes with temperature of UP and ST in a liquid UPR were analyzed by means of interaction parameter χ (see Figure 1). Corrected solubility parameters were calculated using Hildebrand-Scott equation (see Equations 1 to 3) (Hansen, 2007).

$$\delta_{DT} = \delta_D \times (1 - \Delta T \times \alpha \times 1,25) \text{ Eq (1),}$$

$$\delta_{PT} = \delta_P \times \left(1 - \Delta T \times \frac{\alpha}{2}\right) \text{ Eq (2), and}$$

$$\delta_{HT} = \delta_H \times \left[1 - \Delta T \times \left(0,00122 + \frac{\alpha}{2}\right)\right] \text{ Eq (3),}$$

where α is the expansion thermal coefficient, and ΔT is the change of temperature with reference in 25 °C.

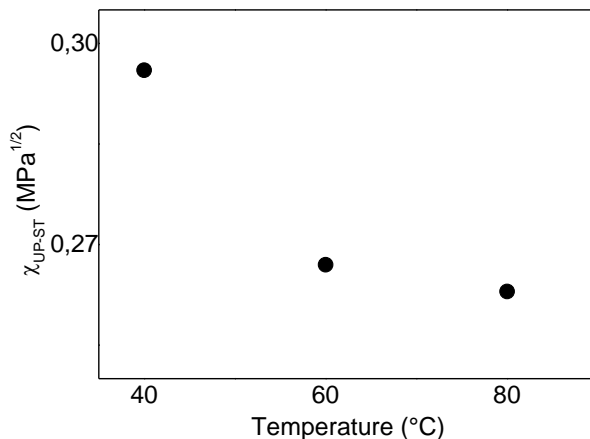


Figure 1. χ_{UP-ST} calculated at 40, 60 and 80 °C.

As can be observed, χ_{UP-ST} decrease as temperature increases indicating an improvement in UP and ST solubility. Considering the last, it is reasonable to think that UP chains are more extended in ST at higher temperature, *i.e.* the increase of temperature generated more UP-ST interactions.

To obtain thermosetting samples, UPR were mixed with MEKP and cured at 40, 60, and 80 °C and the samples were named UPR40, UPR60, and UPR80, respectively. The morphology of the internal surfaces of the fully cured samples was analyzed by mean of AFM (see Figure 2).

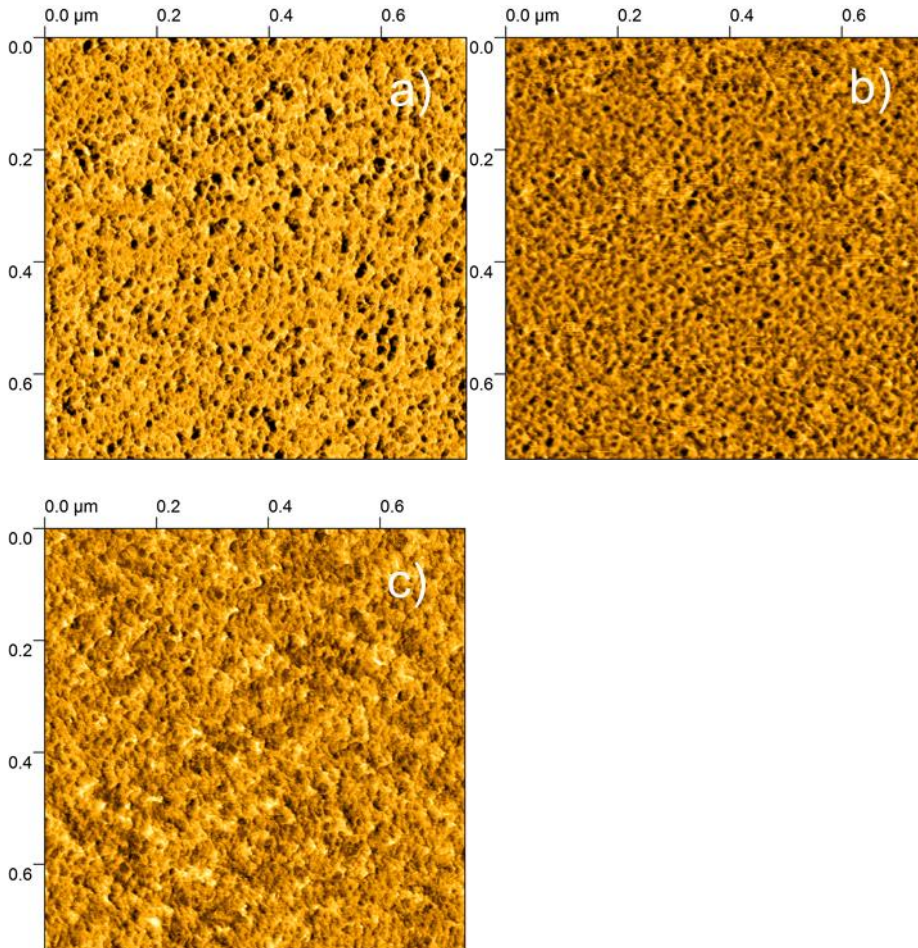


Figure 2. AFM images (750 nm x 750 nm) of internal surface of the fully cured UPR for a) UPR40, b) UPR60 and c) UPR80.

Morphologies were heterogeneous, composed by a phase rich in UP highly crosslinked (UP_{rich}) embedded in a less crosslinked phase rich in PS (ST_{rich}) (Builes *et al.*, 2012). It was possible to observe that curing temperature changed morphology of the final thermoset, and that the increase of curing temperature decreases domains size and become more homogeneous and compact phase distribution. These results could be explained taking into account both that domains are consequence of the microgelation during curing process (Builes *et al.*, 2012), and that higher curing temperatures generate smaller microgels (Stuck *et al.*, 2020). Furthermore, as was shown above in the analysis of interaction parameter, the rise of curing temperature increased miscibility. Consequently, it could be expected a delay of microphase separation during curing at higher curing temperatures. Indeed, due to the better UP-ST interactions, it could be also expected more UP-ST covalent bonds instead ST-ST or UP-UP linkages.

To further obtain more information on phases behavior, DMA measurements of fully cured samples were carried out. Figure 3 displays damping factor ($\tan \delta$) as a function of temperature. As can be seen, each $\tan \delta$ curve exhibits a high peak and a shoulder.

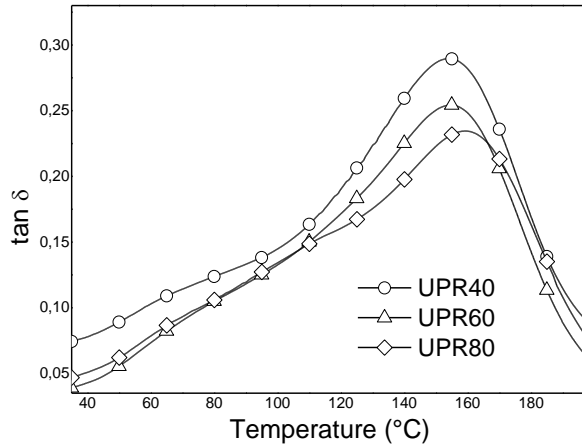


Figure 3. Variation of $\tan \delta$ with temperature for: UPR40, UPR60, and UPR80 samples.

These results suggest that there are at least two immiscible phases (Builes *et al.*, 2012). The peaks can be associated with UP_{rich} , whereas the shoulders correspond to ST_{rich} (Qazvini, and Mohammadi, 1969; Sousa *et al.*, 2016). Table 1 reports the temperatures of maximum of peaks and shoulders, which can be ascribed to glass transition temperatures of UP_{rich} and ST_{rich} phases, named as $T_{gUP_{rich}}$ and $T_{gST_{rich}}$, respectively.

Table 1. Temperature of maximum peaks and shoulders of $\tan \delta$ for UPR40, UPR60, UPR80 samples.

Sample	$T_{gUP_{rich}}$ (°C)	$T_{gST_{rich}}$ (°C)	$T_{gUP_{rich}} - T_{gST_{rich}}$
UPR40	156	109	47
UPR60	158	116	42
UPR80	163	122	41

It was noted that the increase of curing temperature decreased the difference between $T_{gUP_{rich}}$ and $T_{gST_{rich}}$. The last suggest that curing UPR at higher temperature promoted a similitude between UP_{rich} and ST_{rich} phases. These results agree with morphology results, where was observed that the rise of curing temperature decreased the phase separation.

Regarding storage modulus (E'), it was observed that in the rubbery plateau of UPR80 achieved the highest values and UPR40 the lowest one. In order to understand the changes in the tridimensional polymer network, crosslinking density (ρ) was calculated considering the theory of rubber elasticity (Nebioglu, and Soucek, 2007). Table 2 summarized the values of E' and ρ .

Table 2. Values of E' and ρ for the UPR40, UPR60 and UPR80 samples

Sample	E' (MPa)	ρ (cmol/m ³)
UPR40	115	1080
UPR60	124	1171
UPR80	143	1353

Taking into account that ρ is inversely proportional to the molecular weight of the chains between the cross-link junctions (M_c) (Liu *et al.*, 2015), the obtained values of ρ indicate a reduction of molecular weight of PS segments in the polymer network. The last could be understood as a furthering of UP-ST copolymerization instead of ST-ST homopolymerization. Furthermore, it could be the reason of the increase of restriction of chains motion observed due to the rise of $T_{gUP_{rich}}$ and $T_{gST_{rich}}$ and the decrease of heights of peaks after the increase of curing temperature.

To understand differences between UPR phases, TGA measurements were carried out (see Figure 4).

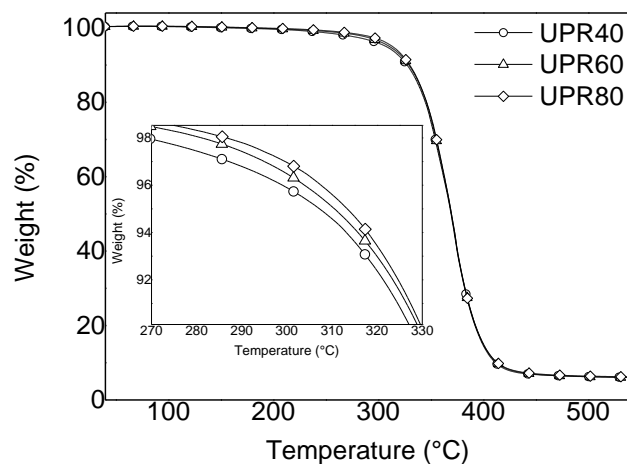


Figure 4. TGA curves of UPR40, UPR60 and UPR80. The inset corresponds to a magnification of the zone between 270 °C and 330 °C.

As can be seen, the increase of curing temperature improved the thermal stability of thermosetting samples. Taking into account that thermal decomposition of UPR begins with the PS chains (Manfredi *et al.*, 2006), the samples that presented less thermal stability could content longer PS chains. Consequently, the increase of thermal stability could be due to the increase of both ρ and UP-ST copolymerization.

Conclusions

It was shown that miscibility changes in liquid UPR have a strong effect on phase distribution and on properties of final thermoset. Theoretical calculations of interaction parameter between UP and ST, χ_{UP-ST} at different temperatures, showed that the increasing of curing temperature generates higher miscibility between UP and ST. Morphological analysis showed that higher curing temperatures generate more homogeneous phase distribution and less phase separation. It was found a relationship between DMA and phase distribution. It was observed that more homogeneity of phases distribution decreased the difference between the T_g of the phase rich in UP and the phase rich in polystyrene. Additionally, it was demonstrated through crosslinking density calculations and TGA measurements that an increase of curing temperature generated lower molecular weight between the crosslink points. Consequently, it could be considered that higher curing temperature favored UP-ST reaction instead of UP-UP and ST-ST.

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