

KINETIC PARAMETERS OF UNSATURATED POLYESTER RESIN MODIFIED WITH POLY(ϵ -CAPROLACTONE)

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The curing of the neat unsaturated polyester resin (UP) with benzoyl peroxide (initiator) as well as the curing of UP modified with two poly(ϵ -caprolactone) PCL samples (PCL2 and PCL50) of different molecular masses ($M_n=2 \cdot 10^3$ and $M_n=5 \cdot 10^4$, respectively), were investigated by non-isothermal differential scanning calorimetry (DSC), at different heating rates. The activation energy was determined from the variation of the peak exotherm temperature, T_{peak} , upon heating rate. Besides, the degree of conversion (α) was obtained from isothermal DSC measurements at 80°C at different curing times for neat UP, UP+PCL2 and UP+PCL50. Kinetic parameters were deduced assuming the n^{th} order reaction kinetic model for neat UP, UP+PCL2 and UP+PCL50 systems.

Keywords: blends, cure kinetics, DSC, poly(ϵ -caprolactone), unsaturated polyester

Introduction

Commercial unsaturated polyester resins (UP) consist mainly of a linear polyester with different amount of unsaturated units, a cross-linking monomer (usually 33–45 mass% depending on the resin viscosity and processing conditions) and inhibitors that are used to prevent any cross-linking reaction before the resin is processed. The most frequently used cross-linking monomer is styrene. UP resins are used in polymeric composites because of their relatively low cost, good balance of properties and adaptability to many composite processes [1]. The principal problem of UP resins is their high polymerization shrinkage. The addition of thermoplastics as ‘low profile’ additive (LPA) to the UP resin can substantially reduce the shrinkage caused by the copolymerization between UP and styrene. LPA are thermoplastics generally serving as non reactive additives in UP resins. They are initially soluble or form stable dispersion in the resin mixture before curing, but they become incompatible with the cured resin during cure process. This two-phase structure is essential for shrinkage compensation. Poly(ϵ -caprolactone) (PCL) is a semicrystalline polymer considered as one effective LPA [2, 3]. In previous works [4, 5] we have studied blends of a linear unsaturated polyester, UP, with PCL. The analysis of those results indicated that the morphology of the amorphous phase was heterogeneous for UP+PCL blends and changed depending on the thermal treatment. PCL was found to be miscible with uncured polyester resin under specific thermal treatment. The next part of our in-

vestigations about these systems has been to study the influence of crosslinking of thermosetting polymers on the miscibility of their blends.

The purpose of this paper is to evaluate the influence of the PCL as LPA additive, on the curing reaction of UP [6–21]. The curing of the neat UP resin as well as the curing of UP modified with PCL samples (PCL2 and PCL50) of two different molecular masses were investigated by non-isothermal differential scanning calorimetry (DSC) [22], at different heating rates. The activation energy was determined from the variation of the peak exotherm temperature, T_{peak} , upon heating rate. Besides the degree of conversion (α) was obtained from isothermal DSC measurements at 80°C at different curing times for neat UP, UP+PCL2 and UP+PCL50. Kinetic parameters, k , n , were deduced assuming the n^{th} order reaction kinetic model for neat UP and UP+PCL systems.

Experimental

Materials

The UP (Estratil 6603) was provided by Plastiform (Spain) having a 38 mass% of styrene as a cross-linking agent. Nuclear magnetic resonance spectroscopy (¹H NMR) was used to characterize the linear polyester. UP6603 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 is included in

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Table 1 Characteristics of poly(ϵ -caprolactone) and UP6603

Polymer	M_n	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$	r
PCL50	50000	-62	59	1.6
PCL2	2000	-64	50	1.4
UP6603+ 38% styrene	3700	-69	-	-

Table 1. In curing the resin, benzoyl peroxide was used as initiator being supplied by Panreac. Poly(ϵ -caprolactone) (PCL) samples were provided by Polysciences Eppelheim (Germany). The M_n of PCL and polydispersity index, $r=M_w/M_n$, obtained by gel permeation chromatography are also shown in Table 1.

Differential scanning calorimetry

To determine glass transition temperatures and heats of reaction a Mettler Toledo differential scanning calorimeter 821e was used. The instrument was calibrated with indium and zinc. Samples of 10–20 mg were placed in aluminium pans. All the measurements were done under nitrogen atmosphere. The glass transition temperature was taken at the midpoint of the change in heat capacity.

The resin was mixed with the initiator (1.5 mass%) at room temperature and with the corresponding concentration of PCL in the modified UP samples. Non-isothermal curing measurements were carried out from -110 to 250°C at different heating rates (5, 10, 15, 20, 25, 30°C min⁻¹) for neat UP6603 resin and UP6603 modified with PCL2 and PCL50, to determine the total heat of reaction (ΔH_T). The activation energy was determined from the variation of the peak exotherm temperature, upon heating rate. For isothermal experiments the DSC was preheated to a curing temperature of 80°C. Samples were quickly

placed in the DSC cell and maintained at 80°C for different times, then quenched until -110°C and scanned to 250°C. The residual heat of reaction (ΔH_R) was calculated as the area of the exothermal peak of the corresponding scan. The degree of conversion, α , was obtained as:

$$\alpha = (\Delta H_T - \Delta H_R) / \Delta H_T \quad (1)$$

Results and discussion

Non-isothermal curing for neat UP6603 and UP6603+PCL blends with 1.5 mass% of benzoyl peroxide

The curing non-isothermal measurements were carried out at different heating rates for neat UP6603 resin and UP6603 modified with PCL2 and PCL50. Figure 1 includes the curves corresponding to dynamic scans for neat UP6603. For dynamic experiments the temperature at which the peak exothermal (T_p) occurs depends on the heating rate. The total heat of reaction, ΔH_T , was obtained from the area of the exothermal in the curves. An average value of 335 J g⁻¹ was assigned to the heat of crosslinking of the UP resin being independent of the content of the PCL in the blend (Table 2). This result is in accordance with those reported in [7, 21]. Other researchers [23, 24] have reported values of total heat of reaction from 293 to 426 J g⁻¹ for UP resins. This range may be due to the different types of UP resins and free-radical initiator systems employed in each study. Figure 2 shows the linear variation of the logarithm of heating rate with the inverse of temperature at the peak exothermal, for neat UP6603 resin and UP6603 modified with different contents (4, 6 and 10 mass%) of PCL2. The activation energy E was calculated from the slope of the straight line using the Ozawa calculation procedure [25]. As can be noticed, there is

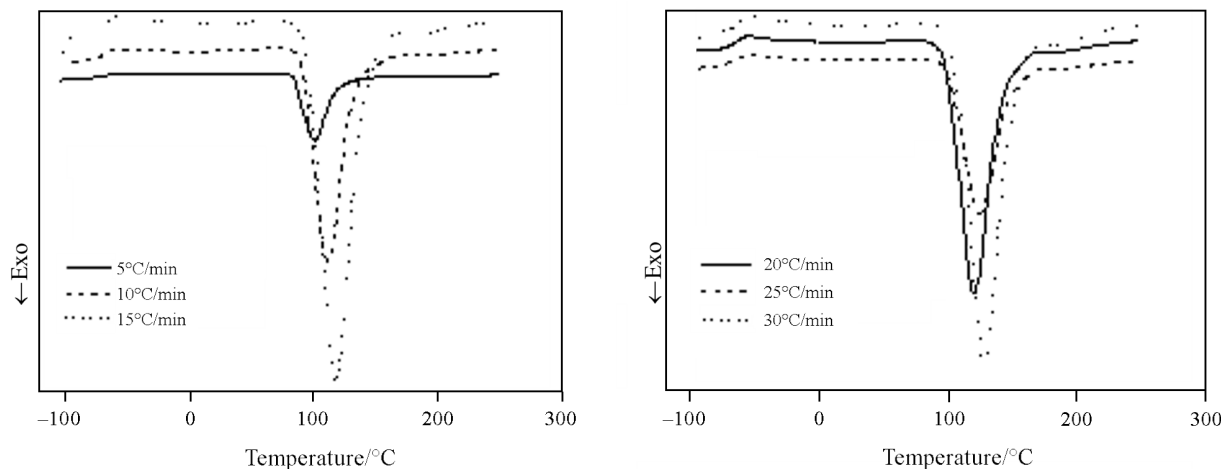
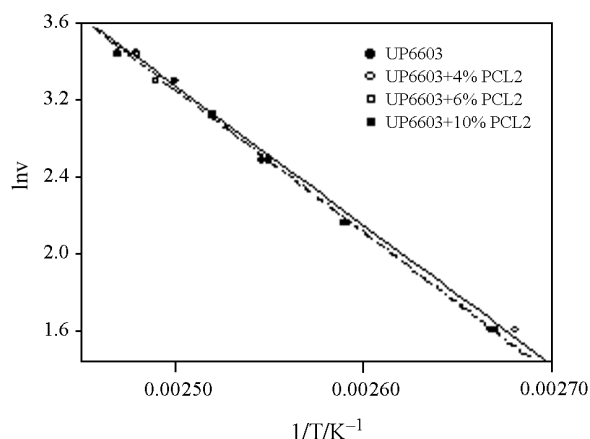


Fig. 1 DSC dynamic scans for neat UP6603 at different heating rates

Table 2 Total heat of reaction, ΔH_T , peak temperature T_p , at different heating rates β

$\beta/^\circ\text{C min}^{-1}$	$\Delta H/\text{J g}^{-1}$		$T_p/^\circ\text{C}$	
	Neat UP6603	UP6603+6% PCL2	Neat UP6603	UP6603+6% PCL2
5	-331.4	-335.8	101.7	101.9
10	-334.9	-338.3	112.5	112.1
15	-357.7	-334.4	119.5	118.1
20	-341.0	-333.7	123.8	124.1
25	-320.5	-348.6	126.3	128.5
30	-340.4	-321.3	131.3	128.2

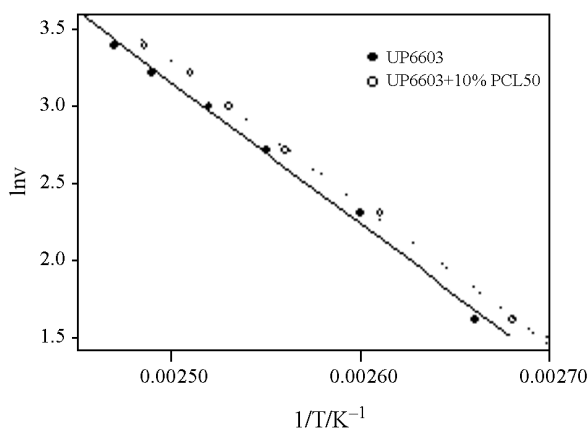

Fig. 2 Arrhenius plots for neat UP6603 and its blends with PCL2

no significant differences between pure UP6603 resin and its blends with PCL2 leading for all the cases to an average activation energy of 73 KJ mol^{-1} similar to that obtained by other authors for different unsaturated polyester resins [21]. PCL2 content seems not to affect to the dynamic curing of UP6603.

Figure 3 shows an analogous representation to Fig. 2 but for UP6603 modified with a 10 mass% of PCL50 in comparison with neat UP6603. Both linear variations are parallel (the same slope and consequently the same activation energy) indicating that the presence of PCL50 does not change the curing kinetic mechanism of the unsaturated polyester resin. However as can be deduced from Fig. 3, PCL50 as modifier of UP6603, behaves in a different way than PCL2, accelerating slightly the dynamical curing of UP6603.

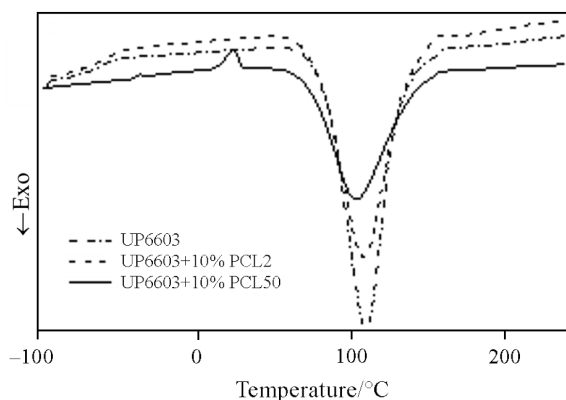
Isothermal curing for neat UP6603 and UP6603+PCL blends at 80°C with 1.5 mass% of benzoyl peroxide

Samples of neat UP6603 and blends of UP6603 with 10 mass% of PCL2 and 10 mass% of PCL50 were cured at 80°C for different times (t_c); after, were scanned at $10^\circ\text{C min}^{-1}$ to determine the glass transitions and the residual heats of reaction. Figure 4


Fig. 3 Arrhenius plots for neat UP6603 and its blends with PCL50

shows the curves of these blends cured at 80°C during 5 min. It is worth to notice the PCL50 melting during the scan. Conversion as a function of the curing time is calculated using the Eq. (1) from the curves of the cured blends at different times. In Fig. 5 the calculated degrees of conversions for all the systems above mentioned, vs. curing times are represented. As can be observed the behaviour of UP6603 and UP6603+10 mass% PCL2 is very similar, being difficult to detect some effect on the cure reaction due to the presence of PCL2, even taking into account the dilution of reactants. UP6603+10 mass% PCL50 behaves as if the presence of PCL50 provoked the kinetics to become slightly faster, in accordance with the dynamic results. In other UP modified systems the modifier can affect the overall curing reaction kinetics, increasing the rate of reaction [26].

The reaction rates have been calculated from the conversion curves included in Fig. 5. The reaction rate vs. curing time curves did not display a maximum indicating a non autocatalytic behaviour. As a consequence, assuming that the curing reaction follows n^{th} order kinetics and that the temperature-dependence of


Fig. 4 DSC curves for UP6603 resins cured at $T_c=80^\circ\text{C}$ at $t_c=5 \text{ min}$

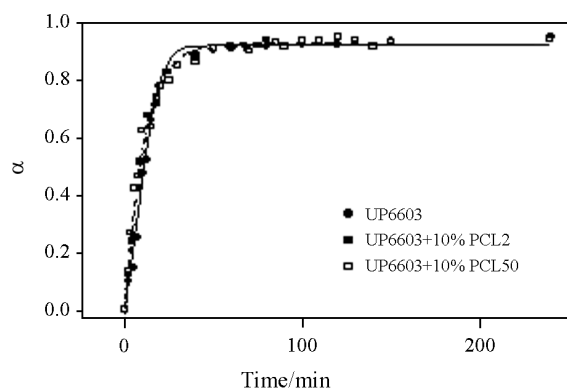


Fig. 5 Conversion–time curves for UP6603 resins cured at 80°C

the kinetic rate constant is consistent with the Arrhenius law, the following equation can be written:

$$d\alpha/dt = k(1 - \alpha)^n \quad (2)$$

For the UP6603 resin cured at 80°C total conversion is not reached, so the Eq. (2) has to be amended and expressed as:

$$d\alpha/dt = k(\alpha_m - \alpha)^n \quad (3)$$

where α_m is the maximum degree of cure reached at the test temperature used. Plots of reaction rate vs. $(\alpha_m - \alpha)$ for neat UP6603, and UP6603 modified with PCL are collected in Fig. 6. In all the cases data fit quite well when assuming the n^{th} order reaction kinetic model for these systems. It can be noticed from the plots of Fig. 6 that, for UP6603 modified with

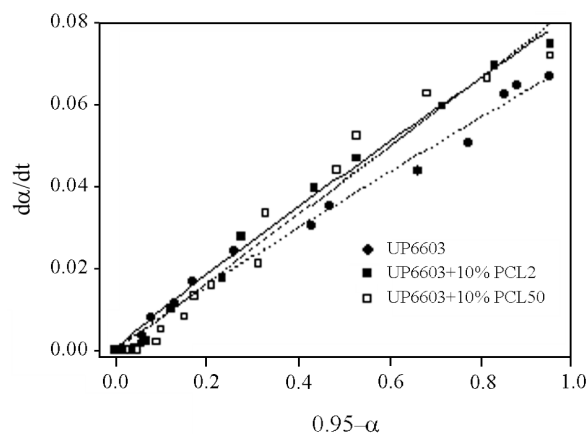


Fig. 6 Plots of reaction rate vs. conversion for UP6603 resins cured at 80°C

Table 3 Kinetic parameters for UP6603 and UP6603+PCL

System	<i>n</i>	<i>k</i> /min ⁻¹
UP6603	0.93	0.069
UP6603+10% PCL2	0.94	0.081
UP6603+10% PCL50	1.02	0.083

PCL, the kinetic parameters *k* and *n*, are slightly higher than the corresponding ones for neat UP6603. These results would indicate that the PCL slightly accelerates the kinetic of crosslinking reaction of UP6603. Kinetic parameters are included in Table 3.

Conclusions

The curing kinetics of unmodified polyester resin with benzoyl peroxide and blended with poly(ε-caprolactone) of different molecular masses were investigated by DSC.

The activation energy of the UP resins cure reaction was determined from non-isothermal measurements. The activation energy values obtained were found to be independent, not only from PCL content but also from PCL molecular mass.

Isothermal cure reactions of neat polyester and polyester modified with PCL of different molecular masses fit in kinetics order *n*. Kinetic parameters of UP6603+PCL systems increase slightly, in comparison with neat UP6603, revealing a PCL molecular mass effect in UP6603 kinetic.

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References

- 1 ASM International Handbook Engineering Plastics, Vol. 2 ASM International 1997.
- 2 Q. Guo, Polymer, 36 (1995) 4753.
- 3 Q. Guo and H. Zheng, Polymer, 40 (1999) 6377.
- 4 D. Nava, C. Salom, M. G. Prolongo and R. M. Masegosa, J. Mater. Process. Technol., 1 (2003) 6835.
- 5 R. M. Masegosa, D. Nava, M. G. Prolongo and C. Salom, Thermochim. Acta, 440 (2006) 93.
- 6 M. Avella, E. Martuscelli and M. Mazzola, J. Thermal Anal., 30 (1985) 1359.
- 7 K. de la Caba, P. Guerrero, A. Eceiza and I. Mondragón, Eur. Polym. J., 33 (1997) 19.
- 8 W. Li and J. Lee, Polymer, 39 (1998) 5677.
- 9 K. de la Caba, P. Guerrero, I. Mondragón and J. M. Kenny, Polym. Int., 45 (1998) 333.
- 10 N. Delahaye, S. Marais, J. M. Saiter and M. Metayer, J. Appl. Polym. Sci., 67 (1998) 695.
- 11 Y. M. Yun, S. J. Lee, K. J. Lee, Y. K. Lee and J. D. Nam, J. Polym. Sci. B., 35 (1997) 2447.
- 12 W. Li, L. J. Lee and K. H. Hsu, Polymer, 41 (2000) 711.
- 13 W. Li and L. J. Lee, Polymer, 41 (2000) 697.
- 14 M. Messori, M. Toselli, F. Pilati and C. Tonelli, Polymer, 42 (2001) 9877.
- 15 V. Kosar and Z. Gomzi, Eur. Polym. J., 40 (2004) 2793.

- 16 Y. J. Huang and J. S. Leu, *Polymer*, 34 (1993) 295.
17 E. M. S. Sanchez, C. A. C. Zavaglia and M. I. Felisberti, *Polymer*, 41 (2000) 765.
18 E. Bureau, K. Chebli, C. Cabot, J. M. Saiter, F. Dreux, S. Marais and M. Metayer, *Eur. Polym. J.*, 37 (2001) 2176.
19 J. C. Lucas, J. Borrajo and R. J. J. Williams, *Polymer*, 34 (1993) 1886.
20 Y. J. Huang and C. C. Su, *Polymer*, 35 (1994) 2397.
21 J. L. Martin, *Polymer*, 40 (1999) 3451.
22 J. M. Salla, A. Cadenato, X. Ramis and M. Morancho, *J. Therm. Anal. Cal.*, 56 (1999) 441.
23 T. R. Cuadrado, J. Borrajo, R. J. J. Williams and F. M. Clara, *J. Appl. Polym. Sci.*, 28 (1983) 485.
24 H. Ng and I. Mana-Zloczower, *Polym. Eng. Sci.*, 29 (1989) 1097.
25 T. Ozawa, *J. Thermal Anal.*, 2 (1970) 301.
26 M. Avella, E. Martuscelli and M. G. Volpe, *J. Thermal Anal.*, 34 (1988) 441.

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