

Thermal behaviour of the PET/Rodrun 3000 system

L. Incarnato^{a,*}, O. Motta^b and D. Acierno^a

^aDepartment of Chemical and Food Engineering, University of Salerno, Via Ponte Don Melillo, 84084 Fisciano, Salerno, Italy

^bChemical Institute, Faculty of Engineering, University of Catania, Viale A. Doria 6, 95125 Catania, Italy

(Revised 24 July 1997)

The crystallization behaviour of poly(ethylene terephthalate) (PET) and its blends with a liquid crystal polymer (Rodrun 3000) was studied by differential scanning calorimetry (d.s.c.), under both non-isothermal and isothermal conditions. The theories of Ozawa and Avrami were applied to study the kinetics of non-isothermal and isothermal crystallization respectively. In both cases it was found that a very low percentage of a thermotropic liquid crystal polymer (TLCP) determines an increase in the overall crystallization rate, while increasing the amount of TLCP results in a progressive decrease in the crystallization rate and the melting temperature. However, the crystallinity of PET in the blends was found to increase on increasing the TLCP content. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene terephthalate); thermotropic liquid crystal polymers; crystallization)

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a well-known semi-crystalline polymer with important applications and, therefore, is of high commercial interest. In order to enhance the mechanical, rheological and physical properties of PET, it has been studied in blends with many polymers and, more recently, with several thermotropic liquid crystal polymers (TLCPs)^{1–7}.

The presence of rigid TLCP chain in blends with semicrystalline polymers also influences the thermal properties of the matrix, such as crystallization kinetics, crystallinity and melting of the crystallizable component.

Studies reported in the literature have shown that blending a semicrystalline polymer with a TLCP results in an enhancement of the crystallization of the polymer^{1,7–11}.

In our previous work we studied the mechanical, rheological and morphological behaviour of PET/Rodrun 3000 blends^{4,12} and investigated how this TLCP influences the mechanical and barrier properties of PET films^{13,14}.

Since the crystalline phase plays an important role in determining the ultimate solid-state properties of these materials, we considered it of interest to study the influence of different amounts of Rodrun 3000 on the thermal properties of PET more accurately. In the following work the crystallization behaviour of PET in both non-isothermal and isothermal conditions was investigated by differential scanning calorimetry (d.s.c.) and data obtained were analysed adopting Ozawa and Avrami equations.

EXPERIMENTAL

Materials

The thermoplastic polymer used in this work is the poly(ethylene terephthalate) (PET) of 0.6 dl g⁻¹ intrinsic viscosity, produced by Montefibre. The thermotropic liquid

crystalline polymer (TLCP) is a copolyester composed of 60 mol% of *para*-hydroxybenzoic acid and 40 mol% of PET reported as Rodrun 3000 and produced by Unitika. The materials were vacuum dried at $T = 110^\circ\text{C}$ for 16 h prior to use.

Blends with composition ranging from 2 to 90% w/w of Rodrun 3000 in PET were prepared by means of a Brabender equipped with a mixing chamber. The mixing was performed under nitrogen at a temperature of 290°C, at 40 rev min⁻¹, for 40 min. The PET sample used for comparison was also subjected to the same treatment.

D.s.c. measurements

The calorimetric measurements were carried out on a Mettler TC 11 differential scanning calorimeter operating under nitrogen flow.

The samples were first heated at a rate of 10°C min from 30 to 300°C and held at this temperature for 10 min to allow the complete melting of the crystallites. The non-isothermal crystallization experiments were performed at four different cooling rates: 2, 5, 8, 20°C min⁻¹ on samples of PET and blends at 2, 10, 30, 50, 70 and 90% of Rodrun 3000. The values of crystallization temperature T_c and enthalpy of crystallization ΔH_c were calculated during these cooling runs. The samples were then heated up to 300°C at 10°C min⁻¹ and the results of the glass transition temperature T_g , melting temperature T_m and enthalpy of melting ΔH_m referred to these traces are reported.

For isothermal crystallization measurements the samples were preheated with the same procedure described above for non-isothermal measurements, then rapidly cooled to 210°C and the exothermic crystallization peak at this temperature was recorded for PET and the blends at 2, 10 and 30% of Rodrun 3000.

RESULTS AND DISCUSSION

From a technological point of view, the non-isothermal crystallization behaviour of polymers is of great importance

* To whom correspondence should be addressed

Table 1 D.s.c. data of PET/Rodrun 3000 system obtained at: (a) cooling run at 5°C min⁻¹, second heating run at 10°C min⁻¹; (b) cooling run at 20°C min⁻¹, second heating run at 10°C min⁻¹

TLCP (%)	T_g (°C)	T_c (°C)	ΔH_c (J g ⁻¹ PET)	T_m (°C)	ΔH_m (J g ⁻¹ PET)
(a)					
0	86.7	191.0	39.2	256.3	38.2
2	85.7	196.5	43.5	255.5	39.0
10	85.7	192.3	45.0	253.0	40.6
30	85.0	186.0	48.2	245.0	45.5
50	85.0	174.5	49.0	237.0	46.0
70	83.3	174.0	50.1	223.0	48.0
90	-	174.0	31.6	211.4	37.0
100	-	146.5	2.60	200.0	2.00
(b)					
0	86.0	172.0	35.3	257.0	40.8
2	85.5	176.3	38.5	257.2	40.0
10	85.5	170.0	40.6	254.0	41.4
30	85.0	167.0	43.0	247.8	43.0
50	84.3	165.4	45.4	238.9	48.0
70	82.0	165.2	49.0	224.9	52.0
90	-	165.0	37.0	217.0	38.0
100	-	142.0	3.00	200.8	3.00

because most of the processing techniques occur under non-isothermal conditions.

Non-isothermal crystallization measurements were performed on the pure components and on the blends of PET and Rodrun 3000 at different cooling rates.

In order to erase all previous thermal history, the samples were heated up to 300°C and held at this temperature for 10 min to allow complete destruction of the crystals. In Table 1 the numerical data obtained from dynamic d.s.c. experiments, at cooling rates of 5 and 20°C min⁻¹, for PET and blends with compositions ranging from 2 to 90% are reported. The values of T_g , T_m and ΔH_m are referred to the heating traces obtained after the cooling runs.

The enthalpies of melting and crystallization, normalized to the PET content, appear strictly dependent on the TLCP content showing an increase on increasing the amount of

TLCP in the blend. The area under the crystallization exotherm is a measure of the amount of PET crystallinity, so this suggests that a higher amount of PET crystallinity is present in the blends. For the blend with 90% of Rodrun 3000 the ΔH_c calculated on the basis of PET weight decreases. It should be noted, however, that this value could not be calculated correctly, since the quantity of PET in the PET/Rodrun 3000 10/90 sample is too small to allow an accurate normalization calculation.

The glass transition temperature of PET is not significantly affected by the presence of the liquid crystal polymer. The system analysed, in fact, is a mainly incompatible blend, as was pointed out in previous work^{4,12}. As can be seen from the tables the melting temperature values show a progressive decrease on increasing the amount of TLCP in the blend. Similar results on the same system were found by

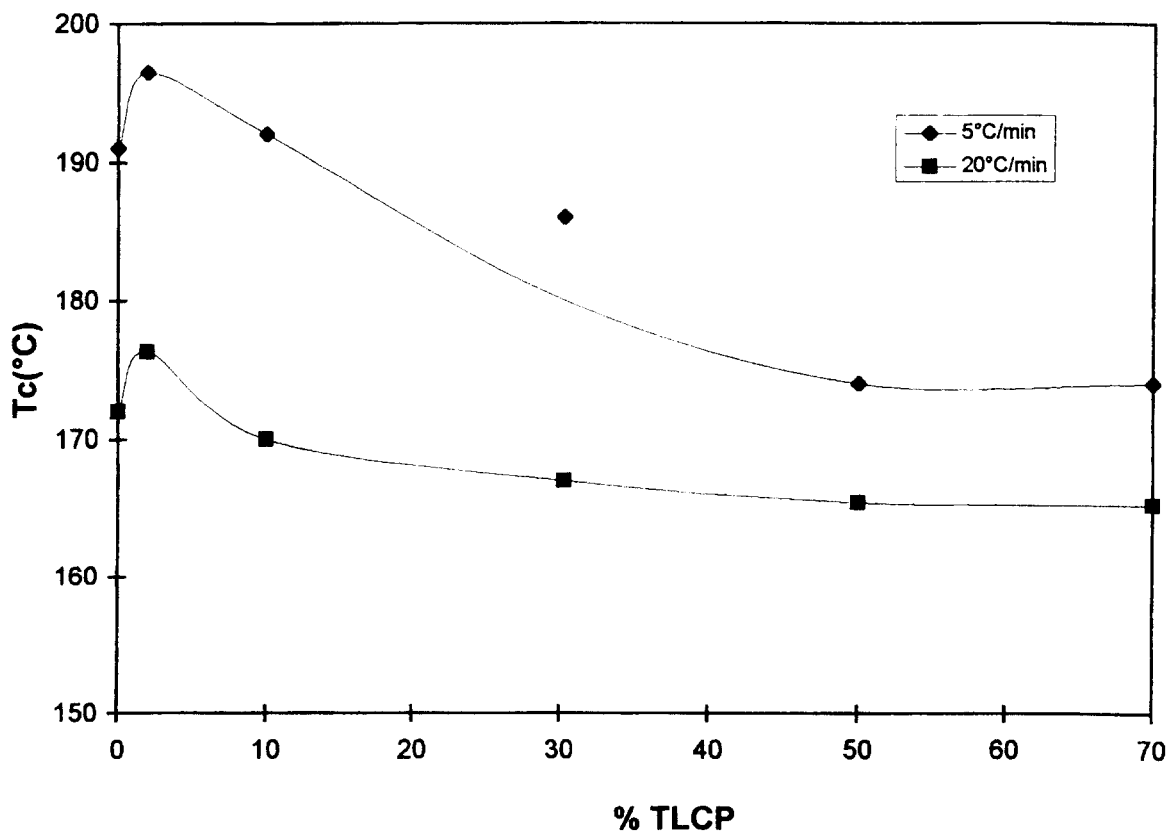


Figure 1 Crystallization peak temperature versus TLCP content at different cooling rates

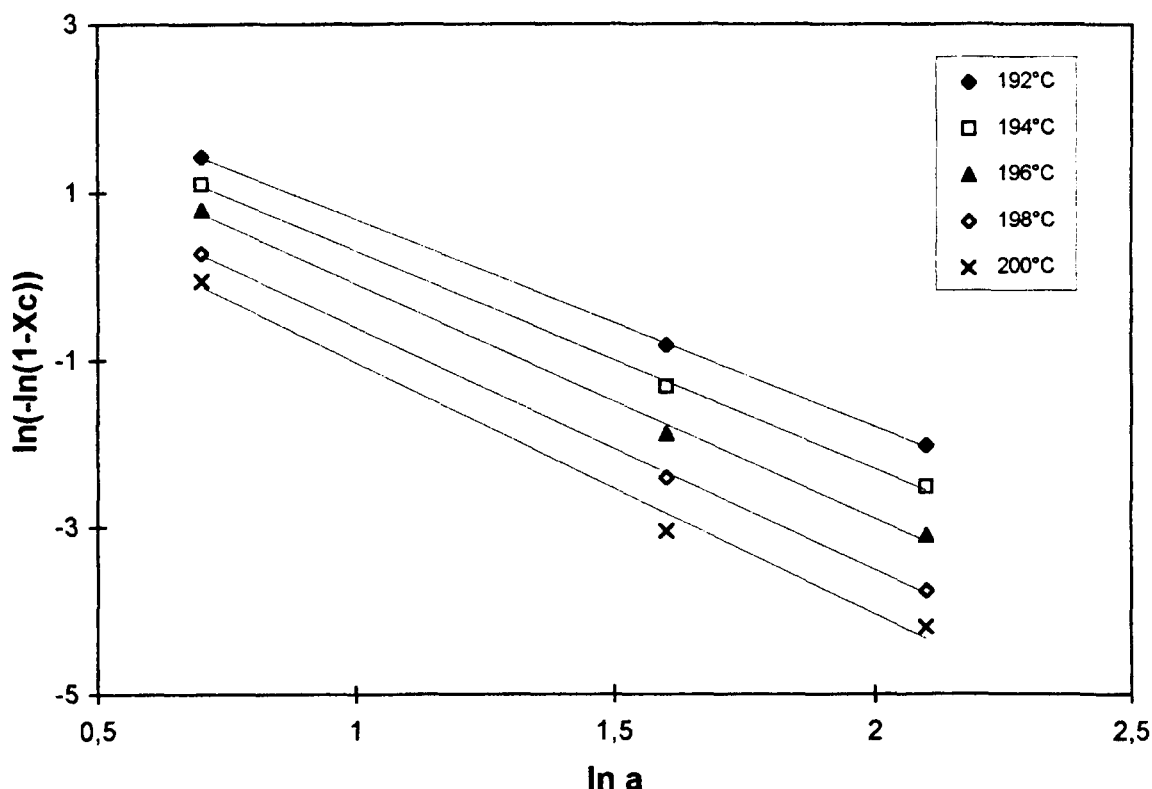


Figure 2 Ozawa plot of non-isothermal crystallization for PET

Joseph *et al.*¹ on both solution-cast blends and mechanically mixed blends.

The crystallization temperature obtained during the cooling runs reaches a maximum for the blend at 2% of TLCP. On increasing the TLCP content a decrease in T_c values of the blends is observed as reported in Figure 1. At a TLCP content of 50 wt% a 'plateau' is reached and upon further addition of TLCP no significant difference in the T_c value is observed. Moreover, as can be expected, the lower the cooling rate the higher the temperature range at which the crystallization occurs. In fact, at slow cooling rates, there is sufficient time to activate nuclei at a higher temperature.

The effect of TLCP amount on crystallization temperature during cooling runs has been analysed by Sharma *et al.*⁷ They studied two different systems, PET/VECTRA and PET/PET-PHB80, and in both cases found that the T_c value is maximum for the blend at 5% of TLCP providing that TLCP acts as an effective nucleating agent only at very low levels (0–5%). In particular, for the system PET/PET-PHB80 only the blend at 5% of TLCP shows a T_c higher than PET and then decreases on increasing the TLCP content, as observed in our system.

The kinetics of PET and blends at 2, 10 and 30% in non-isothermal crystallization conditions has been studied by the application of Ozawa theory¹⁵. Only these three blends have been analysed because the temperature range of crystallization for the blends with TLCP content higher than 30% and PET do not overlap. Ozawa theory is based on the acceptance of the simplifying assumption that crystallization occurs under constant cooling rate and proceeds by nuclei being formed randomly and growing in three-dimensions. In this case the parameters determining the crystallization kinetics are the Avrami exponent n and the cooling crystallization function χ . These parameters can be determined from the Ozawa equation:

$$\ln[-\ln(1-X_c)] = \chi - n \ln a \quad (1)$$

where X_c is the volume fraction of material crystallized at a given temperature T and a is the cooling rate. The Avrami exponent n and the cooling crystallization function χ can be estimated from the slope and the intercept of the straight line obtained by plotting $\ln[-\ln(1-X_c)]$ against $\ln a$.

Ozawa applied this equation to study the non-isothermal crystallization of PET obtaining good agreement with the results of isothermal crystallization.

The d.s.c. data obtained in the dynamic cooling crystallization of PET at 2, 5 and 8°C min⁻¹ were analysed according to equation (1). As expected, the diagrams in Figure 2 show a clear linear dependence of the double logarithm of the amorphous fraction $\ln[-\ln(1-X_c(t))]$ on the cooling rate, $\ln a$. The Ozawa plots for PET and for the blends at 2, 10 and 30% of Rodrun 3000 obtained at $T = 198^\circ\text{C}$ are reported in Figure 3. It shows that the Ozawa equation can also be applied satisfactorily to analyse the non-isothermal crystallization behaviour of the blends.

The value of the Avrami exponent n for pure PET and the blends is almost equal to 3, in good agreement with the results reported by Ozawa, and does not change appreciably with blend composition. This indicates that the nucleation mechanism does not change with TLCP addition. In general, an Avrami exponent $n = 3$ can be related to crystallization processes involving heterogeneous nucleation and three-dimensional crystal growth.

The cooling crystallization function of PET calculated at different temperatures decreases with increasing temperature, in agreement with data on PET presented by Ozawa¹⁵. Furthermore, as can be seen from Figure 3, the cooling crystallization function χ , obtained from the intercept of the lines at $T = 198^\circ\text{C}$, is found to have the highest value for the blend with the lowest amount of TLCP (2%).

To better understand the influence of the TLCP on the thermal behaviour of PET, isothermal measurements were performed on PET and some of the blends of PET and Rodrun 3000.

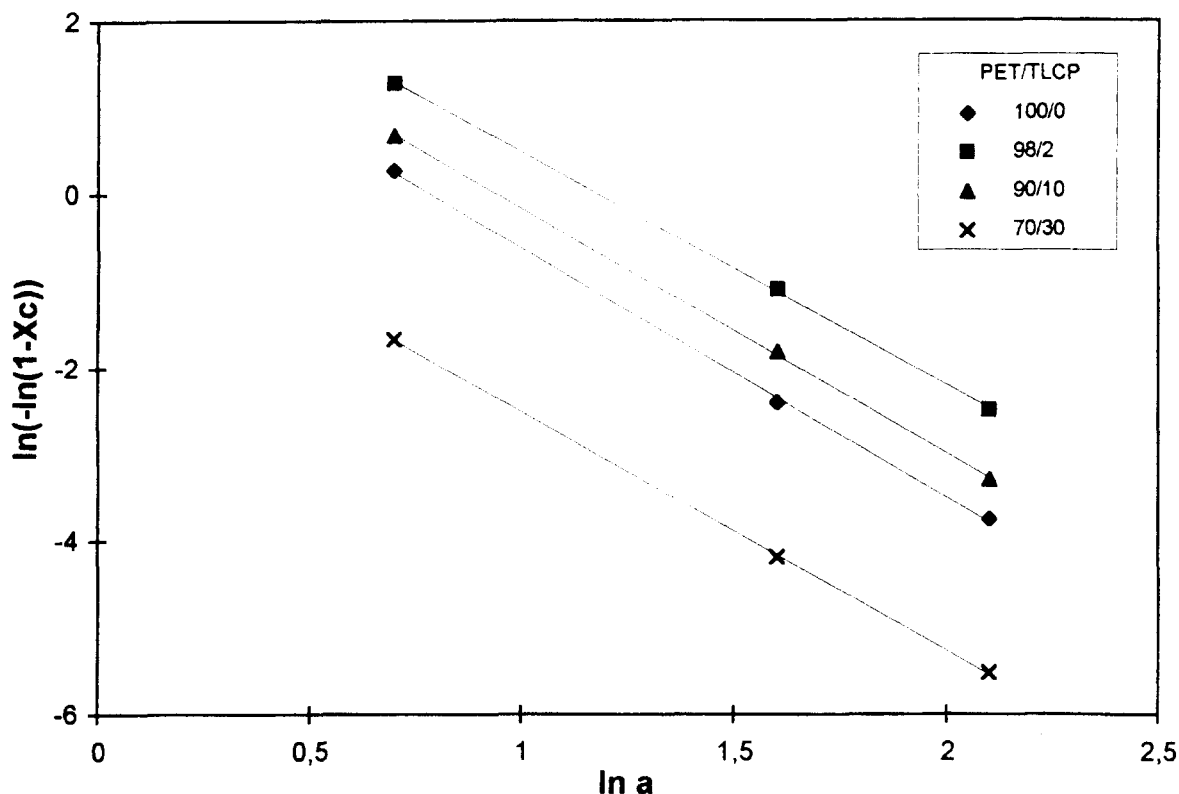


Figure 3 Ozawa plot of non-isothermal crystallization for PET/Rodrun 3000 blends

Isothermal crystallization measurements were performed as described in the experimental section for pure PET and the blends at 2, 10 and 30% of Rodrun 3000. In Figure 4 the crystallization isotherms of PET and the blends at 2 and 30% of TLCP obtained at $T = 210^{\circ}\text{C}$ are reported. From the

crystallization curves, the fraction of polymer crystallized at time t , $X_c(t)$, has been calculated by the usual point to point method, as the ratio of the area under the isotherm at time t to the total area.

The kinetics data of isothermal crystallization of PET and

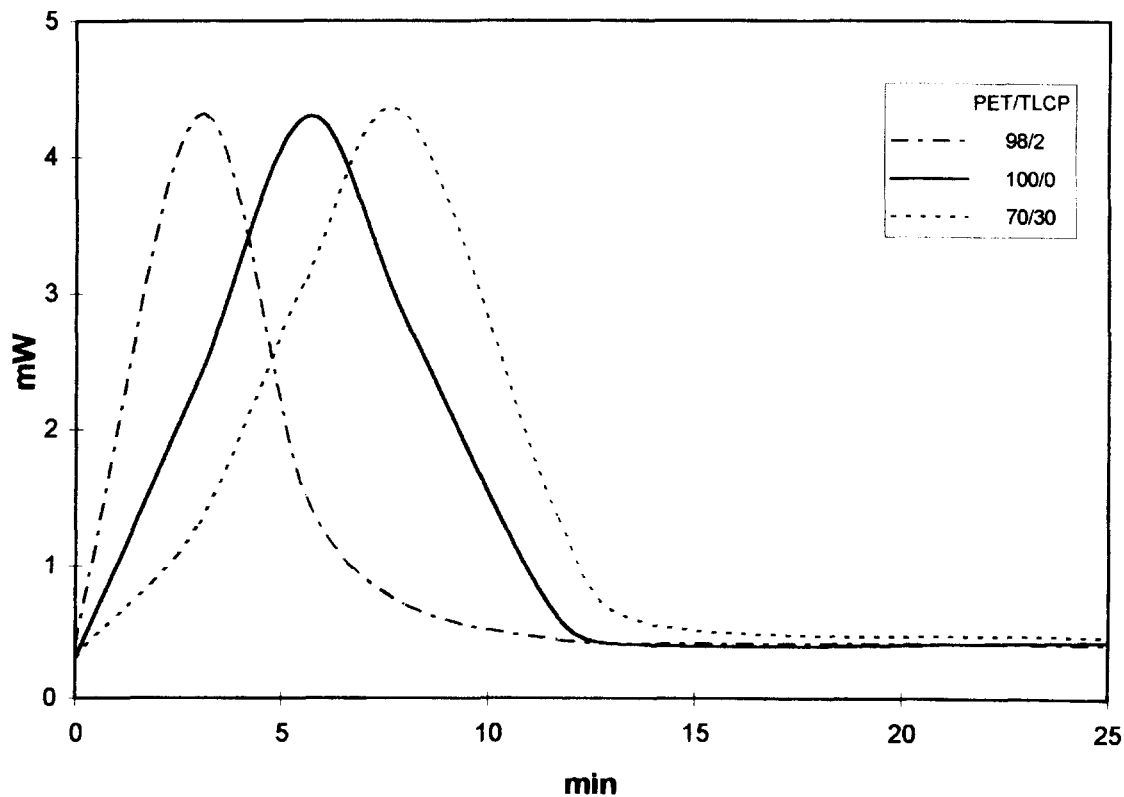


Figure 4 D.s.c. thermograms of isothermal crystallization of PET/Rodrun blends at $T = 210^{\circ}\text{C}$

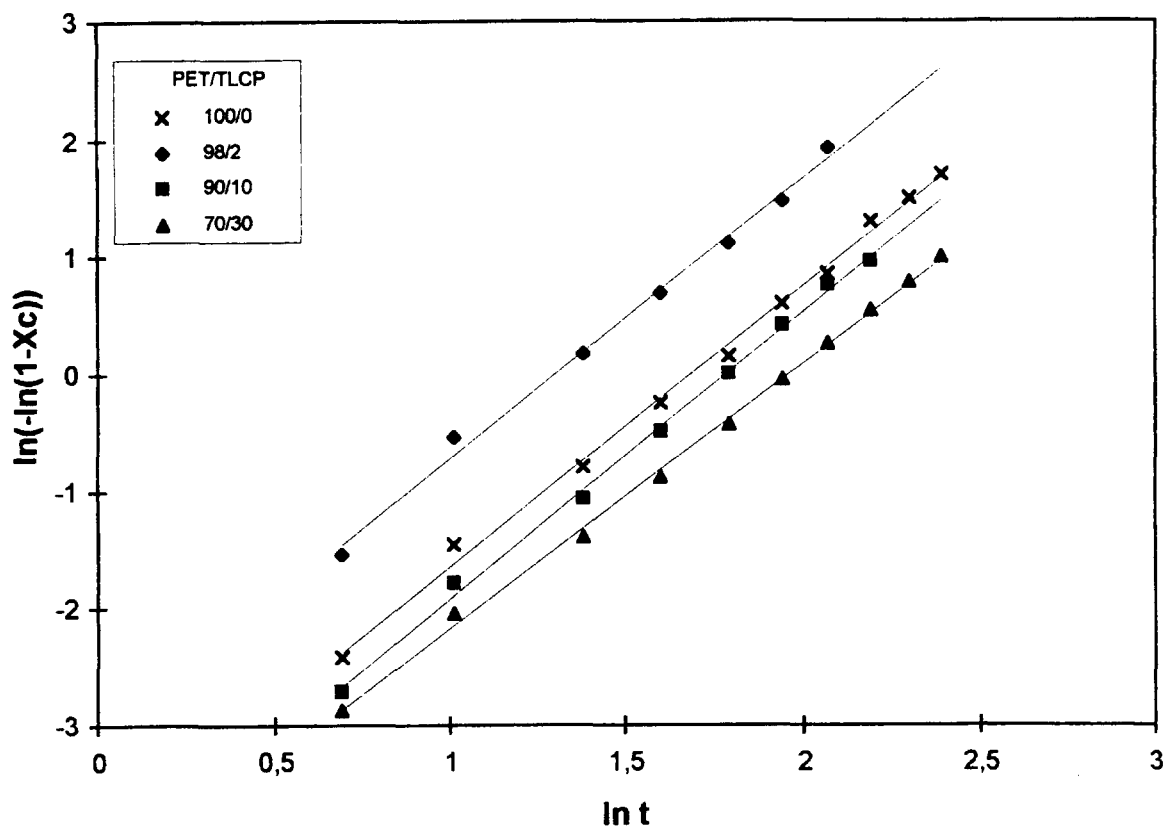


Figure 5 Avrami plot of isothermal crystallization for PET/Rodrun 3000 blends at $T = 210^{\circ}\text{C}$

the blends with Rodrun 3000 have been analysed in terms of the well-known Avrami equation¹⁶:

$$X_c(t) = 1 - \exp(-Kt^n) \quad (2)$$

where $X_c(t)$ is the volume fraction of crystals at time t , K is a rate constant of crystallization that includes the temperature dependent terms and contains information regarding diffusion and nucleation rates, and n is the Avrami exponent, which can be related to the type of nucleation and to the geometry of crystal growth.

The parameters K and n can be determined by taking the double logarithm of equation (2):

$$\ln[-\ln(1 - X_c(t))] = \ln K + n \ln t$$

Consequently, K is the intercept and n the slope of the straight line obtained in the plot of the double logarithm of the amorphous content as a function of the logarithm of time (Avrami plot).

In Figure 5 the Avrami plot for PET and the blends at 2, 10 and 30% of TLCP is reported. From the diagram it is evident that the presence of 10% of TLCP does not appreciably influence the rate of crystallization of PET while a very low content (2%) of TLCP determines an increase in the crystallization rate. By increasing the TLCP content to 30% a decrease in the rate of crystallization is observed.

Crystallization rates of polymers can be expressed in terms of the half-times of crystallization $t_{1/2}$ obtained from the crystallization isotherms as the times for which $X_c(t) = 0.5$. The shorter the half-time, the faster the crystallization rate, and vice versa.

The half-time of crystallization of PET and PET/TLCP blends is plotted as a function of TLCP content in Figure 6. The figure clearly shows that at a TLCP level of 2% a minimum in the curve is obtained, while increasing the

amount of TLCP results in an increase in the half-time of crystallization at constant T_c .

In the literature different types of behaviour are reported depending on the system and the conditions analysed. Hong *et al.*¹⁰ have found that for the system PPS/Vectra B950 the half-time of crystallization decreases monotonically with the increasing of TLCP in the blend and they suggested that the TLCP behaves as a nucleating agent for the crystallization of PPS for all the blend compositions investigated. On the other hand, Zhong *et al.*⁹ have found a minimum in the crystallization half-time for the blend containing about 20 wt% of TLCP for the system PEEK/LCP-111.

From the data above reported we can point out that in our system, on increasing the amount of Rodrun 3000 in the PET matrix a higher degree of crystallinity is obtained. However, we must emphasize that the increase in the bulk crystallization peak temperature (Figure 1), as well as the increase in the isothermal crystallization rate of the samples (Figure 6), shows that the incorporation of a very low amount of Rodrun 3000 (2%) resulted in a significant improvement in the overall crystallization of the PET homopolymer. A reduction in the rate and temperature of crystallization occurred as a result of the higher level of TLCP in the blend.

Since the polymer crystallization is controlled essentially by the nucleation rate and polymer mobility, in the discussion of the results our attention will be concentrated on the influence of TLCP on these two factors. The molten polymer mobility accounts for the effect of viscosity on the transport of polymer molecules from the amorphous phase to the crystal phase. In particular, for the system analysed we have to consider that at the heating conditions used (10 min at 300°C) the PET matrix is in an isotropic melting state while Rodrun 3000 is in its nematic liquid crystal phase. The presence of nematic domains provides

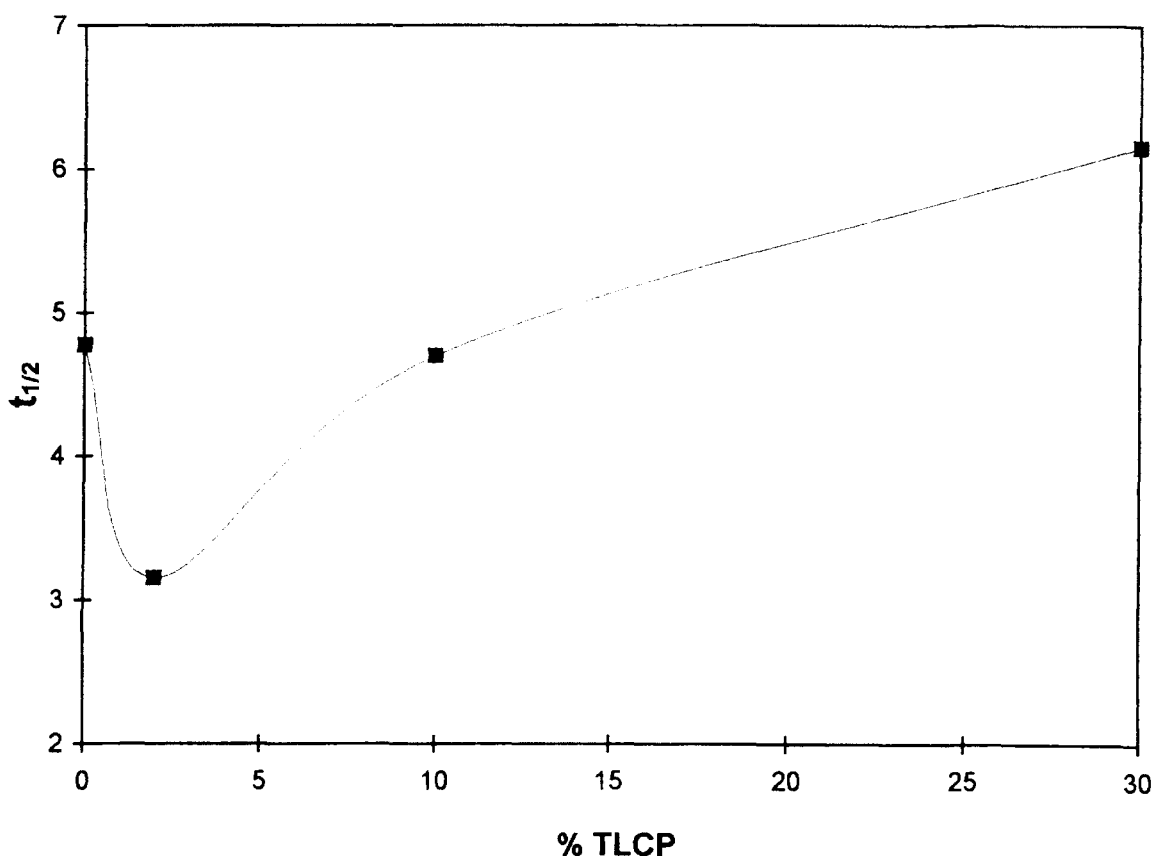


Figure 6 Half-time of crystallization versus TLCP content

nucleating sites and reduces the melt viscosity of PET^{4,12} especially at a high content of TLCP. The lower melting viscosity suggests that the TLCP component in the blend may possibly be acting as a 'diluent' agent¹⁷ for the crystallization of PET.

Another important feature that should be considered when treating with TLCPs is that under some thermal conditions TLCPs may remain fluid below their melting point temperature^{18,19}, indicating that the nematic phase can supercool. In particular, Wissbrun¹⁸ found a strong supercooling effect in the case of 60/40 HBA-PET (which has the same chemical composition as Rodrun 3000) preheated to 300°C. He shows that on cooling from 300°C the viscosity of the TLCP drops dramatically. This thermal history presumably also influences the rheological behaviour of the blends, so the viscosity values of the blends preheated to 300°C are expected to be lower than those measured in rheological tests, where the samples are heated directly to the test temperature. Moreover, it is reasonable to believe that the solidification of the system is relatively lowered by the supercooled nematic state, especially at high TLCP content.

From the above considerations an initial conclusion that can be drawn is that the Rodrun 3000 behaves as a heterogeneous nucleating agent for the PET matrix by providing nucleation sites, as well as a diluent by enhancing the polymer mobility. At a very low percentage of TLCP the nucleating and diluent effects are responsible for the higher crystallinity and rate of crystallization of PET observed.

On increasing the TLCP concentration the number of nucleation sites increases but the size distribution of the TLCP domains varies. At a low percentage the TLCP phase is finely dispersed in the matrix in the form of small droplets with an average diameter of 0.4 μm ; at a higher content the TLCP phase segregates to form larger domains, as observed

in previous work¹². In this connection, studies reported in literature have found that the crystallization of PET depends upon concentration, size distribution and nucleation ability of the nucleating agent²⁰. Moreover, the increased presence of Rodrun 3000 decreases the supply of PET at the crystallization front and consequently the diffusion of PET to the growth front could become the rate-controlling step in the crystallization process. The magnitude of this effect increases with increasing initial TLCP concentration. Thus the observed T_m depression with increasing TLCP content in such incompatible blends can be attributed to morphological effects of the polymer diluent on reducing crystal sizes or inducing crystal defects in the crystalline structure, as was also observed by Zhong *et al.*⁹. Furthermore, on increasing the amount of Rodrun 3000, the TLCP supercooling effect contributes to produce a depression of the crystallization temperature range of the PET/Rodrun 3000 system. However, this does not imply a decrease in crystallinity of the PET/Rodrun 3000 blends.

CONCLUSIONS

The theories of Ozawa and Avrami have been applied to analyse data corresponding to non-isothermal and isothermal crystallization of PET and its blends with a liquid crystalline polymer (Rodrun 3000). The results have indicated that the thermal behaviour of the system is strongly influenced by blend composition, viscosity ratio and conditions used to treat the samples. It was found that a very low amount (2%) of TLCP determines an increase in the overall crystallization rate, while increasing the amount of TLCP results in a progressive decrease of the crystallization rate and melting temperature. However, the crystallinity of PET in the blends was found to increase on increasing the TLCP content.

REFERENCES

1. Joseph, E. G., Wilkes, G. L. and Baird, D. G., in *Polymeric Liquid Crystal*, ed. A. Blumstein. Plenum Press, New York, 1984, p. 197.
2. Zhuang, P., Kyu, T. and White, J. L., *Polym. Eng. Sci.*, 1988, **28**, 1095.
3. Sukhadia, A. M., Done, D. and Baird, D. G., *Polym. Eng. Sci.*, 1990, **30**(9), 519.
4. Incarnato, L., Nobile, M. R., Frigione, M., Motta, O. and Acierno, D., *Int. Polym. Process.*, 1993, **8**(3), 191.
5. La Mantia, F. P., *Thermotropic Liquid Crystal Polymer Blends*. Techomic Publishing, 1993.
6. Handlos, A. A. and Baird, D. G., *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, 1995, **C35**(2), 183.
7. Sharma, S. K., Tendolkar, A. and Misra, A., *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.*, 1988, **157**, 597.
8. Minkova, L. I., Paci, M., Pracella, M. and Magagnini, P. L., *Polym. Eng. Sci.*, 1992, **32**, 57.
9. Zhong, Y., Xu, J. and Zeng, H., *Polymer Journal*, 1992, **24**(10), 999.
10. Hong, S. M., Kim, B. C., Kim, K. U. and Chung, I. J., *Polymer Journal*, 1992, **24**(8), 727.
11. Minkova, L. I. and Magagnini, P. L., *Polymer*, 1995, **36**, 2059.
12. Incarnato, L., Motta, O. and Acierno, D., in *Liquid Crystalline Polymers*, ed. C. Carfagna. Pergamon, 1993, p. 211.
13. Motta, O., Incarnato, L., Di Maio, L. and Acierno, D., *Polymer*, 1996, **37**, 2373.
14. Gorrasi, G., Incarnato, L., Di Maio, L., Acierno, D. and Vittoria, V., *Journal of Macromolecular Science, Physics*, 1997, **B36**(5), 643.
15. Ozawa, T., *Polymer*, 1971, **12**, 150.
16. Wunderlich, B., *Macromolecular Physics*, Vol. 2. Academic Press, New York, 1976, Chapter 6.
17. Wang, Y. F. and Lloyd, D. R., *Polymer*, 1993, **34**, 4740.
18. Wissbrun, K. F., *The British Polymer Journal*, 1980, **12**, 163.
19. Done, D. and Bird, D. G., *Polym. Eng. Sci.*, 1987, **27**(11), 816.
20. Groeninckx, G., Berghmans, H., Overbergh, N. and Smets, G., *J. Polym. Sci. Polym. Phys.*, 1974, **12**, 303.