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THERMOANALYTICAL STUDY OF NUCLEATING EFFECTS IN POLYPROPYLENE COMPOSITES

I. Liquid crystal polymer containing polypropylene

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Abstract

Nucleating and transcrystallization behaviour of additives in engineering PP composites and the effect of modified interfacial structure is the subject of this series of papers. The first part concentrates on polypropylene/liquid crystalline polyester blends. Increased crystallisation temperature and degree of crystallinity of polypropylene is characteristic to the blends containing different amount of LCP additive. Transcrystallization process governs the formation of crystalline structure in these systems in course of isothermal crystallisation at 132°C. The nucleating effect of LCP gives rise to more uniform crystalline structure in the polypropylene phase.

Keywords: DSC studies, engineering polypropylene, nucleating effect, polypropylene/liquid crystalline polyester blends, transcrystallization

Introduction

Modified types of isotactic polypropylene (PP) play an increasing role among materials currently developed for widening the choice of engineering thermoplastics. The reinforcement and flame retarding of PP required in engineering application fields are generally accomplished through formation of multicomponent composites. Thermodinamically incompatible polymers, elastomers, fillers, reinforcements and low molecular weight or particulate form of flame retardants are the main components in these systems. The studies for determining the effect of these additives on the crystallization and melting behaviour of PP has not completed yet. Great effort is made especially in the area of fillers [1–7]. The earlier experiments concentrated, however, mainly on the effect of pure components, while composite structures of modified interphase were much less studied. Several reinforcing fillers and fibres has been found to be active in effecting the supermolecular (i.e. spherulitic) structure of PP, like talc, mica, carbon fibre and others [8–11]. Some artificial nucleating agents may promote the formation of hexagonal β spherulite form [12, 13], in

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presence of fillers and reinforcements, however, the crystalline phase is in most cases rich in the thermodinamically more stable α spherulites [14]. Other components of engineering PP composites like polymer additives and flame retardants are not so widely studied. Certain types, such as EPM, EPDM, PA-6, HDPE, halogenated aromatic flame retardants of high melting point may contribute to the heterogeneous nucleation process [15–20], while others are inactive or decrease the nucleation density in PP [19, 20].

In these papers the thermoanalytical investigation of the nucleating activity of liquid crystal polyester (first part), talc and $CaCO_3$ fillers (second part) and intumescent flame retarding additives (third part), as well as the effect of modified interphases is presented.

Experimental

Materials

The polymer grades used in this study were:

Polypropylene (PP): Moplen T 30 S homopolymer, product of Montedison (Italy), density: 0.9 g cm^{-3}, melt index: 3.5 g $(10 min)^{-1}$ (21.6 N, 230°C).

Liquid Crystalline Polymer (LCP): Vectra A 950, product of Hoechst (Germany), standard aromatic copolyester type, density: 1.40 g cm^{-3}, water take up 0.02% (after 24 hour, 23°C). LCP was dried in oven, under vacuum, at 120°C in order to avoid the hydrolytic chain scission during processing.

Test methods

The PP/LCP blends of different LCP content were prepared using the mixing chamber of Brabender Plasti-Corder PL2000 equipment. Mixing parameters: Temperature: 270°C, rotor speed: 120 rpm, duration of mixing: 8 min. 2 mg of N-phenyl-naphthylamine were added to each mixture in order to avoid the degradation of PP.

Differential Scanning Calorimetry (DSC) measurements were performed using Setaram DSC 92, sample weight: 10 mg, heating rate: 10°C min^{-1}, atmosphere: air. The samples were heated up to 230°C in order to remove their thermal history (melting memory effect) (14) and then the crystallization and second heating curves were determined. Heat of fusion of polypropylene 207.1 J g^{-1} was assumed in calculation of degree of crystallinity [21].

Optical microscopic images were taken at different stages of isotherm crystallization using Zeiss polarizing microscope equipped with Chinotherm 10A temperature controller. Thin films (10–20 μm) were prepared and annealed first at 230°C and then cooled to the crystallization temperature. The temperature has been set with accuracy of 0.5°C and maintained within the interval 0.05°C.

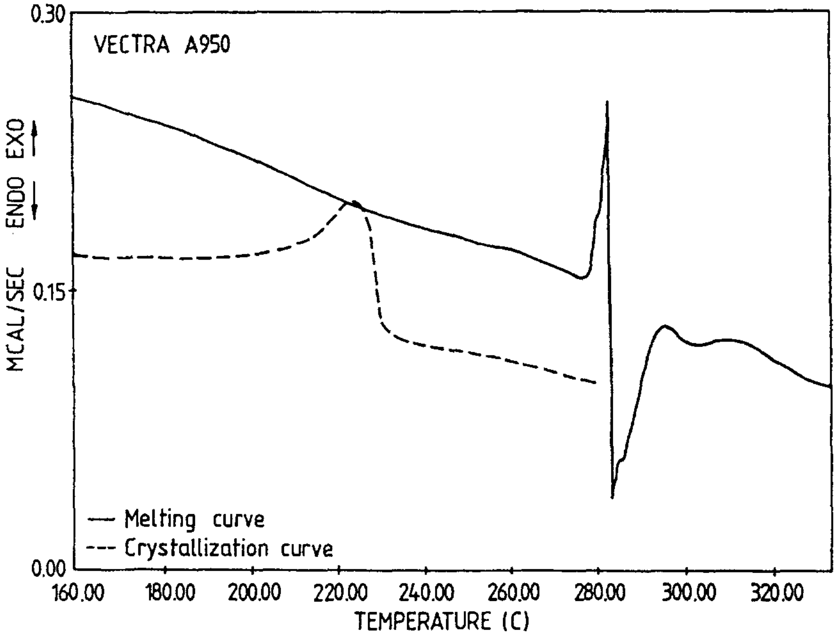

Fig. 1 DSC curve of Vectra 950

Results and discussion

The chance of forming a self-reinforcing blend through the orientation of LCP phase in PP matrix, especially after compatibilisation, gives the importance of PP/LCP blends [22, 23]. The starting efforts in this area have not clarified and explained the effect of LCP on crystalline structure of PP yet [24].

The anisotherm DSC curve of pure LCP in Fig. 1 suggests the presence of significant frozen stress in the material originating from its processing history. This stress is released just before melting of the crystalline phase, resulting in a sharp exothermic peak. Although the crystalline-nematic transition of LCP is at ~283°C, homogeneous blend with PP could be prepared at ~270°C due to the plastic behaviour of LCP below its transition. Blends of 2, 5, 10 and 20% LCP content have been prepared this way.

Table 1 gives the DSC data of crystallization and second melting (first melting was used for removing the memory effect) of pure polymers and blends of different LCP content.

The crystallization enthalpy of PP phase in PP/LCP blends ($\Delta H_{C,\ PP}$) were calculated considering the PP content of the blends. These values were found to be higher in presence of LCP than that of pure PP.

Table 1 DSC results of LCP, PP and PP+LCP blends

Materials	Crystallization temp./°C		$\Delta H_{C,\ PP}$	Second melting temp./°C		Peak width*/
	onset	peak	J g^{-1}	onset	peak	°C
LCP	230.9	225.3	3.56	282.1	283.3	
PP	113.0	107.8	107.7	145.5	162.5	1.8
PP+2%LCP	115.5	110.8	112.2	149.5	161.0	0.8
PP+5%LCP	117.6	113.6	123.8	149.8	160.8	0.8
PP+10%LCP	117.1	113.1	123.2	152.5	160.6	0.6
PP+20%LCP	117.0	113.1	121.1	150.2	160.8	0.7

* at half value of total peak height

The degree of crystallinity (X_c%, calculated from the crystallization enthalpy data) and heat of fusion ($\Delta H_{f,\ PP}$) of PP phase in PP/LCP blends, is plotted in Fig. 2 against the LCP content. Low level of LCP content (2–5%) is enough to increase the degree of crystallinity in PP phase, at higher LCP content (>10%), however, the achieved value does not change further significantly. The slight decrease at higher LCP content is a consequence of increased size of LCP particles in that blends.

A shift of crystallization DSC peak towards higher temperature is shown in Fig. 3, that is considered generally as a sign of nucleating effect. This effect is increasing up to 5% of LCP and does not change further at higher concentration (Table 1). The higher crystallization temperature (lower supercooling) of the blends suggest, that the enhanced crystallinity shown in Fig. 2 can be explained

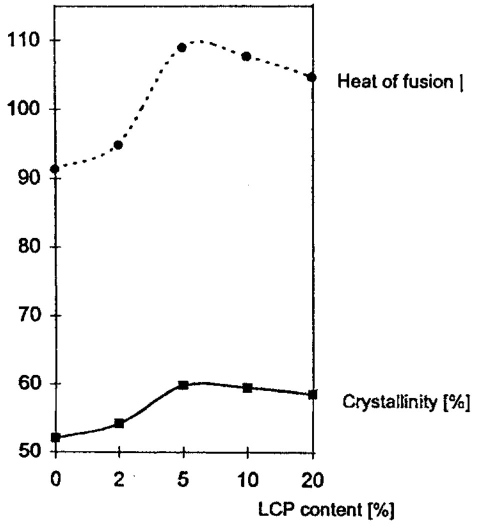

Fig. 2 Crystallinity and heat of fusion (at second heating up) of PP phase in PP/LCP blend

by higher mobility of PP macromolecules, ensuring more perfect crystallization process at higher temperature.

Polarizing microscopic image of the spherulitic structure in pure PP crystallized isothermally at 132°C, show the relatively high content of β spherulites (vivid, bright crystal agglomerates), in this grade (Fig. 4). The micrograph of 5% and 10% LCP containing PP blends are shown in Figs 5–6.

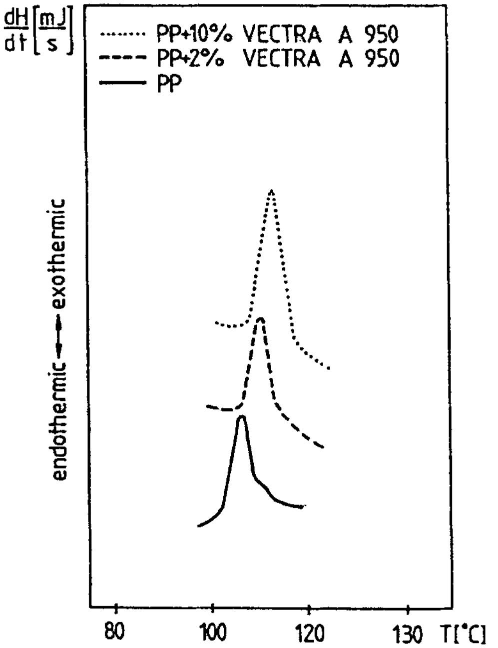

Fig. 3 Crystallization curves of PP and PP/LCP blends

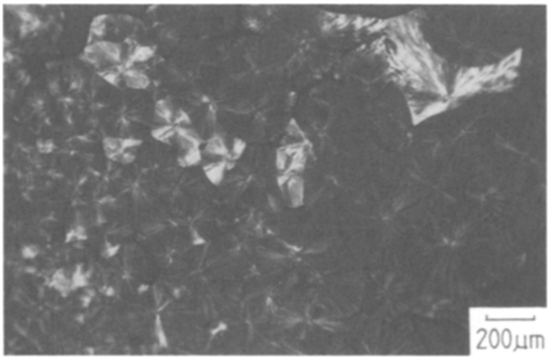

Fig. 4 Spherulitic structure of Moplen T 30 S polypropylene homopolymer type (result of isothermal crystallization at 132°C)

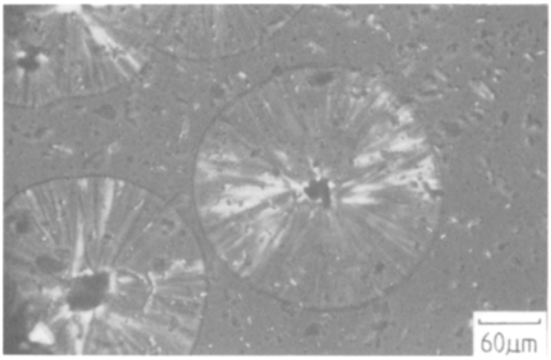

Fig. 5 Development of transcrystalline layer around LCP particles in 2% LCP containing PP (during isothermal crystallization at 132°C)

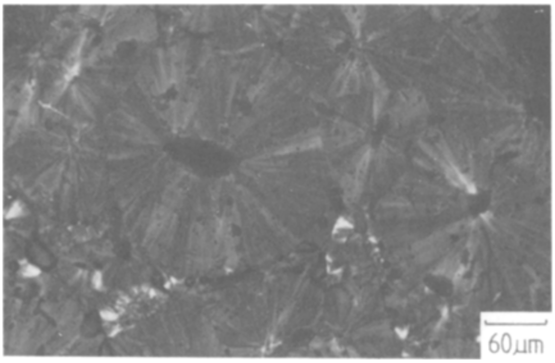

Fig. 6 Spherulitic structure of 10% LCP containing PP (result of isothermal crystallization at 132°C)

A transcrystallization front is starting from the surface of some LCP particles of the blends earlier than the homonucleation starts in the bulk, so the growing of spherulites is initiated by LCP (Fig. 4). In the final crystalline structure almost all the spherulite contain an LCP particle in the centre (Fig. 5). The photos suggest that mainly the larger particles are active in nucleation. The transcrystallization around the LCP particles leads to the higher crystallization temperature and enthalpies determined by DSC. Comparing the spherulitic structure of PP (Fig. 4) and 10% LCP containing blend (Fig. 6) conclusion can be drawn that the heteronucleation initiated by LCP promotes the formation of α spherulites. The more than 5% of β spherulites characteristic to pure PP, disappeared completely in PP/LCP blends. This observation correlates with the DSC results in Table 1, where the width of melting peaks is decreasing with the LCP content. Both result indicate more homogeneous crystalline structure.

Conclusion

Blend of PP and Vectra A 950 type LCP can be formed below the crystalline-nematic transition of the LCP due to its plastic behaviour below the transition. LCP acts as nucleating additive in PP, increasing the crystallization temperature and the degree of crystallinity as well. An optimum of nucleating activity was found at 5% LCP. Transcrystallization around LCP particles leads to crystalline structure containing LCP particle at the centre of the spherulites. Vectra A 950 suppresses the development of β phase in PP and thus promotes the formation of more homogeneous crystalline structure.

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References

1 K. Friedrich and U. A. Karsch, Fibre Sci. Techn., 18 (1983) 37.
2 A. Garton, S. W. Kim and D. M. Wiles, J. Polym. Sci. Polym. Letters, 20 (1982) 273.
3 S. F. Xavier and Y. N. Sharma, Angew. Makromol. Chem., 145 (1984) 127.
4 H. Domininghaus, Gummi, Asbest, Kunststoffe, 37 (1984) 326.
5 T. Kowalewsky and A. Galeski, J. Appl. Polym. Sci. 32 (1986) 2919.
6 J. L. Acosta, M. C. Ojeda, E. Morales and A. Linares, J. Appl. Polym. Sci. 32 (1986) 4119.
7 J. Varga, J. Therm. Anal. 35 (1989) 1891.
8 F. Rybnikar, J. Appl. Polym. Sci. 27 (1982) 1479.
9 A. Garton, S.W. Kim and D. M. Wiles, J. Appl. Polym. Sci., 27 (1982) 4179.
10 J. L. Thomason and A.A. Van Rooyen, J. Mater. Sci., 27 (1992) 889.
11 M. Avella, E. Martuscelli, B. Pasucci and M. Ramino, Polym. Eng. Sci. 32 (1992) 383.
12 J. Varga, J. Therm. Anal., 31 (1986) 165.
13 L. Jingjang, W. Xiufen and G. Qipeng, J. Appl. Polym. Sci., 41 (1990) 2829.
14 J. Varga, in Polypropylene Structure, Blends and Composites, Vol. 1, Ed. J. Karger-Kocsis, Chapman and Hall London 1995 pp. 56.
15 Z. Bartzak, A. Galeski, E. Martuscelli and H. Janik, Polymer, 26 (1985) 1843.
16 B. Z. Jang, D. R. Uhlmann and J. B. Van der Sande, J. Appl. Polym. Sci., 29 (1984) 4377.
17 B. Pukánszky, F. Tüdős, D. Kalló and G. Bodor, Polymer, 30 (1989) 1399.
18 E. Martuscelli, F. Riva, C. Selliti and C. Silvestre, Polymer, 26 (1985) 270.
19 Z. Bartzak, E. Martuscelli and A.Galeski, in Polypropylene Structure, Blends and Composites Vol. 2, Ed. J. Karger-Kocsis, Chapman and Hall London 1995, pp. 25.
20 E. P. Chang, J. Appl. Polym. Sci., 21 (1977) 937.
21 H. S. Bu, S. Z. Cheng and B. Wunderlich, Makromol. Chem. Rapid Commun., 9 (1988) 76.
22 A. M. Sukhadina, A. Datta and D.G. Baird, SPE Technical Papers, 37 (1991) 1008.
23 H. O'Donnell, A. Datta and D.G. Baird, SPE Technical Papers, 38 (1992) 2248.
24 Ye Yongcheng, F. P. La Mantia, A. Valenza, V. Citta, U. Pedretti and A. Roggero, Eur. Polym. J., 27 (1991) 723.