

THERMOANALYTICAL STUDY OF NUCLEATING EFFECTS IN POLYPROPYLENE COMPOSITES

II. Filler and elastomer containing polypropylene

Gy. Marosi, R. Lágner, Gy. Bertalan, P. Anna and A. Tohl

Organic Chemical Technology Department of Technical University of Budapest, Hungary

Abstract

Interfacial structure plays an important role in the performance of polypropylene composites. Transcrystalline interfacial layer were determined in talc filled polypropylene. The crystallization and melting behaviour of talc and CaCO₃ filled polypropylene could be modified with smaller amount of additives like elastomer and surfactants. Through the effect of these additives the structure of interface and the degree of crystallinity could be controlled in filled polypropylene.

Keywords: DSC studies, elastomer containing polypropylene, filler, modified interfacial layer, nucleating effect, transcrystallization

Introduction

The effect of fillers and reinforcements on the crystallization and melting behaviour of PP has been a subject of intensive studies since the 80's [1-8]. Transcrystalline structure at the phase border was detected in case of talc, mica, C fibre and several polymer fibres [3, 4, 9-11]. Talc and CaCO₃ were among the first fillers used in PP and now these composites with modified interphase are extensively used in automotive industry. Although earlier works determined the existence of nucleation and transcrystallization effect of talc [12], experimental results on the development of transcrystalline zone in PP has not been published yet. The role of modified interphase in this process has not been clarified as well. Studies on the effect of interface modification concentrated mainly on mica and CaCO₃ filled PP and applied only lower molecular mass modifiers or oligomers [3, 7, 8]. Both of liquid ethylene-oxide oligomer and alkyl-dihydrogen phosphate interfacial layer decreases the degree of crystallinity of CaCO₃ filled PP composites [7, 8]. Presence of CaCO₃ in PP causes considerable increase in degree of crystallinity only at higher (30-40 wt%) filler content and lower particle size [7, 8].

The formation of thick (~0.15 μm) interphase around filler particles like talc and CaCO₃ using elastomers and surfactants or stearic acid has been studied

thoroughly [13–18]. Further works determined the conditions for ‘in situ’ encapsulation of the filler particles and clarified that an appropriate elastomer type up to a determined elastomer: filler ratio is present mainly in the interphase (this ratio in case of types of additives used in this paper is 1:6), while further amount of the elastomer forms independent disperse phase [19–21]. This structure explained the dynamic mechanical, and dielectric properties, as well as stiffness/toughness balance of these composites [19, 20, 22]. Thermoanalytical investigations for determining the crystalline morphology of these multicomponent PP systems have not been published yet.

In this work we compare the melting and crystallization behaviour of these filled PP systems without and with modification of the interphase.

Experimental

Materials

The polymer grades used in this study were:

Polypropylene (PP): Tipplen H 536F propylene homopolymer, product of Tisza Chemical Works (Hungary) density: 0.9 g cm^{-3} , melt index: $4 \text{ g (10 min)}^{-1}$ (21.6 N, 230°C) Termoplastic blend of HDPE (high density polyethylene) and EPDM (ethylene-propylene-diene terpolymer elastomer (TPEPDM): Vestopren FB 10000 (Hüls, Germany), density: 0.9 g cm^{-3} , melt index: $0.68 \text{ g (10 min)}^{-1}$ (21.6 N, 230°C).

Fillers:

Talc (T): Fintalc P40, average particle size: $40 \mu\text{m}$, specific surface: $4.1 \text{ m}^2 \text{ g}^{-1}$, Mohs hardness: 1, product of Suomen Takki (Finland).

CaCO_3 (C): Millicarb, average particle size: $2.5 \mu\text{m}$, specific surface: $2.95 \text{ m}^2 \text{ g}^{-1}$, Mohs hardness: 3, product of Omya S.A. (France).

Surfactant:

Nonionic surfactant: Tegin 4100, glycerol palmitic stearic acid ester, melting point: 56°C, product of Th. Goldschmidt AG. (Germany).

Test methods

The components of PP composites were compounded using a batch mixing chamber ($\sim 350 \text{ cm}^3$ internal volume) of Brabender Plasti-Corder PL2000, at 210°C, the rotor speed was 50 rpm. The samples were injection moulded at 220°C, pressure: 5.5 MPa. The processing conditions were strictly the same for all samples in order to ensure the same thermal history.

Differential Scanning Calorimetry (DSC) measurements were performed using Setaram DSC 92, sample weight: 10 mg, heating rate: $10^\circ\text{C min}^{-1}$,

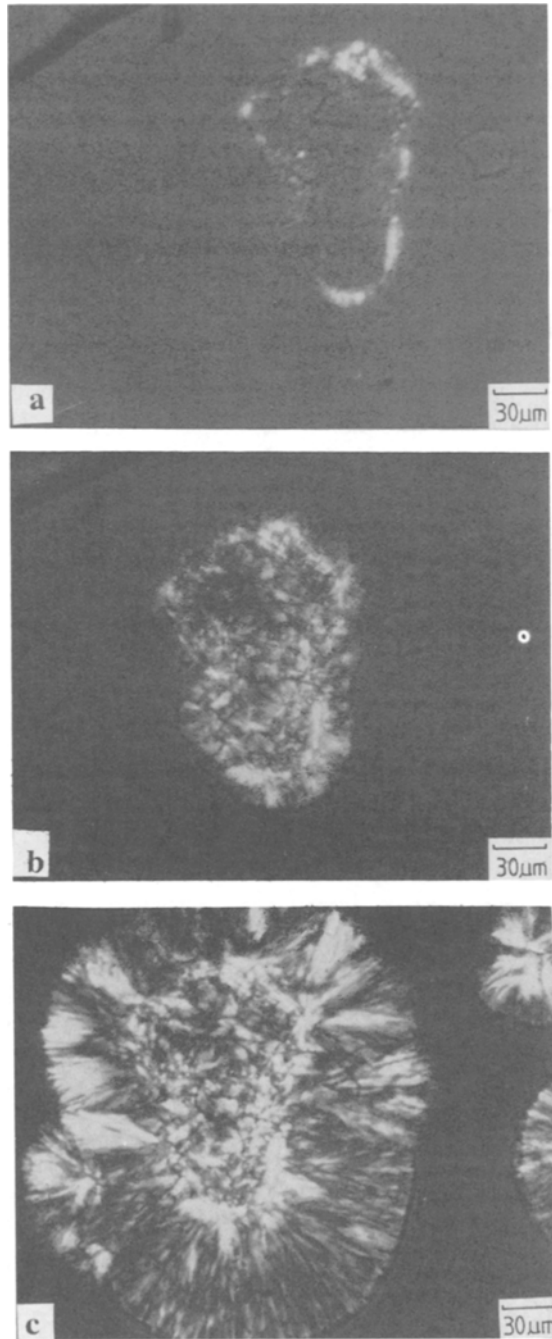


Fig. 1 Development of transcrystalline zone around talc particle in PP (isothermal crystallization at 134°C) (a: 1st min., b: 3rd min., c: 5th min of crystallization)

atmosphere: air. The samples were heated up to 230°C in order to remove their thermal history. Heat of fusion of polypropylene 207.1 J g⁻¹ was assumed in calculation of degree of crystallinity [23].

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.

Results and discussion

The growth of crystallites perpendicular to a heterogeneous (i.e. filler) surface by means of transcrystallization is generally followed under polarizing microscope [3, 7, 20, 24]. In this work the effect of modified interphase on crystallization of filled PP were studied, using hot stage microscope under isothermal conditions and anisotherm DSC method.

We followed first the growing transcrystalline zone around pure talc particles in order to get reference for the systems of modified interphase. Isothermal crystallization, under temperature controlled polarizing microscope, at 134°C were performed for studying the growing of spherulites. The development of this process in presence of pure talc can be seen in the Figs 1a–c. The crystallization starts on the surface of talc much earlier than in the bulk. A relatively thick transcrystalline interfacial structure is gradually growing around a talc particle, till the spherulites formed through homogeneous nucleation in the bulk stop the further enhancement.

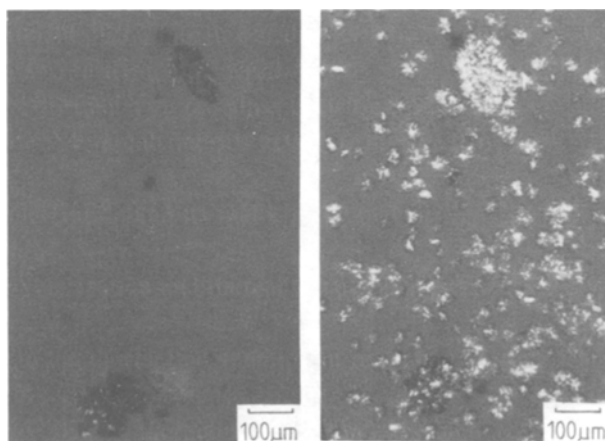


Fig. 2 Crystallization process of PP in presence of pure (top of figures) and elastomer coated (bottom of figures) talc particles (a: before and b: during the crystallization)

Significant improvement of stress distribution can be ensured in filled PP by a relatively thick interlayer. Elastomer interphase can be formed for this purpose around filler particles with appropriate elastomer, like TPEPDM, up to a thickness limit of $\sim 0.1\text{--}0.2\ \mu\text{m}$. This method has been described earlier [19–21]. The formation of elastomer interphase around talc particles causes a significant change in crystallization behaviour: in Figs 2a and 2b talc particles of different interface are included into PP matrix. Figures 2a and 2b show the case before and during the isothermal crystallization respectively. The particle on the top of figures is pure talc without any modification, while the talc particles on the bottom of figures are covered with TPEPDM elastomer. In the later case the interlayer diminishes the direct contact between talc and PP. Figure 2b shows the transcrystallization process of talc (top of figure). On the lower part however, the transcrystallization on the surface of talc is hindered by the encapsulating elastomer.

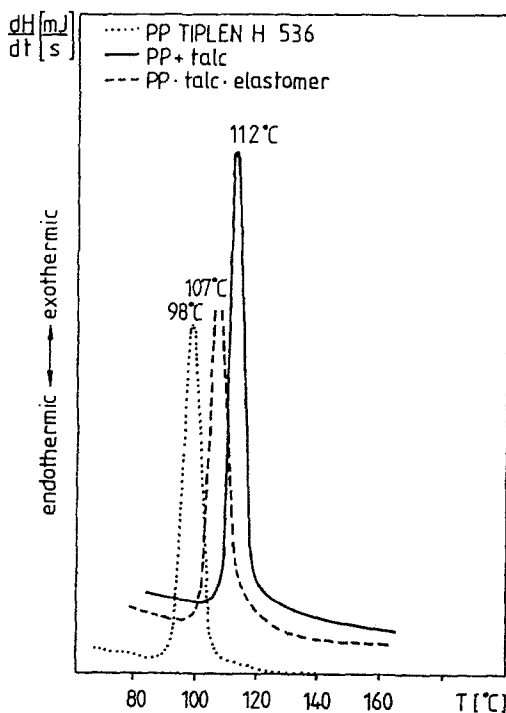


Fig. 3 DSC crystallization curves of PP, 30% unmodified talc containing PP and PP + 30% talc + 5% TPEPDM system

We studied the same process using DSC method as well. In Fig. 3 the crystallization curves of pure PP, unmodified talc filled PP (30% talc content) and the PP containing 30% talc and 5% TPEPDM is compared. The nucleating effect of talc increases the temperature of crystallization with 14 $^{\circ}\text{C}$, while the

introduction of TPEPDM reduces this nucleating effect substantially due to partial encapsulation of the heterogeneous nuclei.

In Table 1 the effect of TPEPDM elastomer (E) and surfactant (S) interfacial layers on the degree of crystallinity are compared in case of talc (T) and CaCO_3 (C) fillers.

Table 1 Comparison of crystallization data of pure PP and filled PP-s without and with interphase modification (T_{∞} =temperature of starting of crystallization, T_c =temperature of crystallization peak, X_c =degree of crystallinity)

Materials	T_{∞} °C	T_c °C	X_c %
PP	103	98	42.9
PP+10%T	117	112	47.5
PP+10%T+1.66%E	113	107	45.2
PP+30%T	117	113	48.0
PP+30%T+5%E	111	107	45.0
PP+10%C	103	98	43.0
PP+30%C	105	100	44.4
PP+30%C+5%E	105	99	43.0
PP+30%C+10%E	105	99	43.0
PP+30%C+25%E	106	100	43.5
PP+30%C+5%E+1%S	105	100	45.2
PP+30%C+10%E+1%S	103	100	46.0

The DSC data in Table 1 suggest, that higher degree of crystallinity of PP in presence of talc is a result of its nucleation effect. The higher crystallization temperature ensures higher mobility of segments of macromolecules, resulting in a spherulitic structure more perfect than in case of lower crystallization temperature. The crystallization temperature in case of CaCO_3 , however, increases only slightly even at higher loading level (30%), so the increased degree of crystallinity in presence of 30% CaCO_3 can not be explained on this basis. For the interpretation of this result, the heat of fusion in function of additive content has to be taken into account as well. The ΔH_m curves in Fig. 4 relate to the first melting of the samples. The enhancement of heat of fusion due to presence of 30% CaCO_3 is much higher than one can expect it considering the increase of degree of crystallinity of the same sample (in Table 1). The presence of elastomer reduces this effect only slightly. The considerably increased heat of fusion in presence of higher amount of filler can be explained by the orientation effect of the filler on the macromolecules in melt during processing. This increased orientation caused by the filler particles has been determined earlier using WAXD method [25]. Due to the interactions at the interfaces a part of this orientation does not disappear after melting and the residual orientation is the reason for the slightly increased degree of crystallization in presence of CaCO_3 .

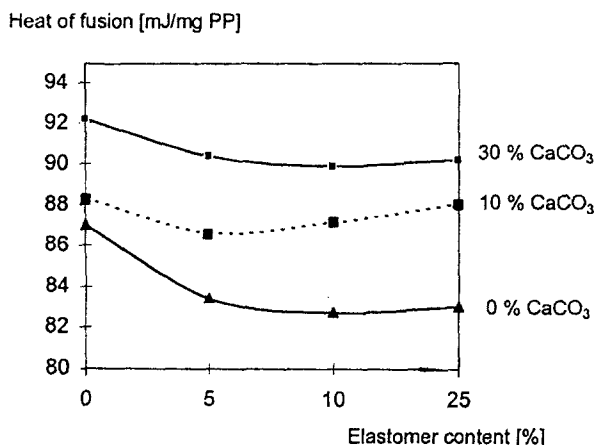


Fig. 4 Heat of fusion of PP phase containing different amount of CaCO₃ filler and TPEPDM elastomer, determined during the first melting of composites

It's worth to mention that the application of 1% of surfactant (S) in the filled and elastomer modified PP system increased the degree of crystallinity significantly (Table 1). The surfactant decreases the viscosity of the PP composite melt and increases the mobility of macromolecules [20], so the effect is similar to the enhancement of crystallization temperature. A systematic analysis of the effect of surfactant on the crystallization and other properties of PP composites is a subject of an other paper [26].

Conclusion

Development of thick transcrystalline layer of PP around talc particles during isothermal crystallization at 134°C could be demonstrated using a temperature controlled polarizing microscope. Modification of the interfacial layer around talc particles by means of elastomer reduces this effect and so the nucleating behaviour of talc as well. This nucleating effect explains the higher degree of crystallinity in presence of talc. CaCO₃ does not increase the temperature of crystallization significantly, we found that the reason for the enhanced degree of crystallinity in this case can be the orientation of the macromolecules at the interfaces. CaCO₃ increases the heat of fusion of PP phase due to its orientation effect during processing. This increased value is much less reduced by the presence of elastomer than that of pure PP. Application of surfactant in the multicomponent PP system leads to higher crystallinity, probably due to increased mobility of macromolecules.

* * *

The financial support of the OTKA 014194 is acknowledged with gratitude.

References

- 1 V. P. Chacko, F. E. Karasz and R. J. Farris, *Org. Coat. Plast. Chem.*, **45** (1981) 767.
- 2 V. P. Chacko, F. E. Karasz, R. J. Farris and E. L. Thomas, *J. Polym. Sci. Polym. Phys.*, **20** (1982) 2177.
- 3 A. Garton, *Polymer Composites* **3** (1982) 189.
- 4 J. Menczel and J. Varga, *J. Thermal Anal.*, **28** (1983) 161.
- 5 K. Friedrich and U. A. Karsch, *Fibre Sci. Techn.*, **18**, (1983) 37.
- 6 T. J. Hutley and M. W. Darlington, *Polym. Commun.*, **26** (1985) 264.
- 7 T. Kowalewsky and A. Galeski, *J. Appl. Polym. Sci.*, **32** (1986) 2919.
- 8 K. Mitsuishi, S. Ueno, S. Kodama and H. Kawasaki, *J. Appl. Polym. Sci.*, **43** (1991) 2043.
- 9 D. Campbell and M. M. Qayyum, *J. Polym. Sci. Polym. Phys.*, **18** (1980) 83.
- 10 M. G. Huson and W. J. McGill, *J. Polym. Sci. Polym. Chem.*, **22** (1984) 2571.
- 11 J. L. Thomason and A. A. Van Rooyen, *J. Mater. Sci.*, **27** (1992) 889.
- 12 F. J. Rybnikar, *J. Appl. Polym. Sci.*, **27** (1982) 1479.
- 13 Gy. Bertalan, I. Rusznák, A. Huszár, G. Székely, L. Trézli, V. Horváth, Z. Kalmár and A. Jancsó, *Plaste u. Kautsch.*, **25** (1978) 340.
- 14 Gy. Bertalan, I. Rusznák, P. Anna, Gy. Marosi, I. Molnár and L. Nagy, in *Verstärkte Plaste '84*, p. T3/4, Berlin, 1984.
- 15 I. Rusznák, Gy. Bertalan, P. Anna, Gy. Marosi and I. Molnár, *Plaste u. Kautsch.*, **32** (1985) 254, 258.
- 16 Gy. Marosi, Gy. Bertalan, I. Rusznák, P. Anna and I. Molnár, in *Polymer Composites Ed. B. Sedlacek, Walter de Gruyter, Berlin-New York 1986*, p. 457.
- 17 J. Kolarik, B. Pukánszky and F. Ledniczy, in *Interfaces in Polymer, Ceramic and Metal Matrix Composites* (ed. Ishida H.) Elsevier New York, London 1988.
- 18 B. Pukánszky, F. Tüdös, J. Kolarik and F. Ledniczy, *Polym. Comp.*, **11** (1990) 98.
- 19 Gy. Marosi, Gy. Bertalan, I. Rusznák and P. Anna, *Colloids and Surfaces*, **23** (1986) 185.
- 20 Gy. Marosi, *Effect of Additives in Filled Polypropylene Systems PhD Thesis*, Hungarian Academy of Sciences, Budapest 1989.
- 21 Gy. Marosi, Gy. Bertalan, P. Anna and I. Rusznák, *J. Polymer Eng.*, **12** (1993) 34.
- 22 Gy. Bánhegyi, Gy. Marosi, Gy. Bertalan and F. E. Karasz, *Colloid and Polymer Science*, **270** (1992) 113.
- 23 H. S. Bu, S. Z. Cheng and B. Wunderlich, *Makromol. Chem. Rapid Commun.*, **9** (1988) 76.
- 24 J. Varga, in *Polypropylene Structure, Blends and Composites vol. 1*, ed. J. Karger-Kocsis, Chapman and Hall London 1995, pp. 56.
- 25 I. Rusznák, A. Huszár, G. Székely, L. Trézli, G. Serfőző and I. Serfőző, *Periodica Polytechnica*, **19** (1975) 201.
- 26 Gy. Marosi, Gy. Bertalan, P. Anna and A. Tohl, in preparation.