

Fractionated Crystallization in Polyolefins–Nylon 6 Blends

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SYNOPSIS

The crystallization behavior of polyolefins–nylon 6 polymer blends was studied by differential scanning calorimetry (DSC) measurements. In these blends, the crystallization of the minor component often starts with distinctly deeper supercooling than that of the pure polymer, and proceeds in several separate steps. The origin of this phenomenon was studied and was related to the volume fraction of the dispersed phase and the compatibility between the dispersed phase and the matrix. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Blends of polyolefins–polar polymer are typical incompatible blends, whose properties depend to a large extent on the mutual dispersion of the components, the supermolecular structure within the phase of a single component, and the structure of the interface. These structural parameters, in turn, depend on the processing or mixing conditions as well as on the degree of the thermodynamic compatibility of the components. These boundary conditions, together with the cooling rate, also control the crystallization process of a melt.

Investigation of incompatible polymer blends can tell the origin of changes in crystallization, whether structural, equilibrium thermodynamic, or kinetic. Among other effects, there have been reported the induction of specific crystal modification,¹ the rejection, engulfing, and deformation of the dispersed component by the growing spherulites of the matrix material,^{2,3} and nucleation at the interface.^{2,4} Polymer blends containing one component as a suspension of finely dispersed droplets sometimes exhibit the phenomenon of “fractionated crystallization,” which originates in the primary nucleation of isolated melt particles by units of different nucleating species.^{5–7}

In this study, we report on a novel kind of fractionated crystallization of polyolefins–nylon 6 blends, on which the influence of composition and compatibility are studied.

EXPERIMENTAL

Materials

Isotactic polypropylene (PP) 2401 ($[\eta]_{\text{decalin}}^{135^\circ\text{C}} = 22$ dL/g) from Yanshan Petroleum Chemical Co. was used. The nylon 6 (PA 6) was B30S, $\bar{M}_n = 3.38 \times 10^4$, produced by Jinzhou Petrochemical Works. Ethylene-propylene-diene monomer (EPDM) had a $\bar{M}_n = 1.27 \times 10^5$, containing 36.8% propylene. Maleated PP (PP-MA) was synthesized in this laboratory.

Preparation of Samples

Blends of EPDM–PA 6 were prepared by mechanical blending in a single-screw extruder at 250°C. Blends of PP–PA 6 and PP-MA–PA 6 were prepared in a Brabender Plasticorder: PA 6 was melted at 250°C, then PP (or PP-MA) was added and the contents mixed for 10 min.

Testing and Observation

Differential scanning calorimetry (DSC) measurements were carried out under N₂ with a Perkin-Elmer DSC-2C. In order to destroy the self-seeding

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nuclei in the components, the samples were preheated for 7 min at 250°C; then the crystallization and reheating runs were performed at a standard rate of 10°C/min.

A polarizing microscope fitted with an automated hot stage was used with the following procedure: sandwiches of blend films in between a microscope slide and a glass cover were heated up to 250°C, and kept at this temperature for 7 min to eliminate any trace of crystallinity. The temperature was then slowly lowered to ambient at 5°C/min.

Wide-angle X-ray diffraction (WAXD) was performed by means of a Philips PW1700 diffractometer using Ni-filtered CuK α radiation.

THEORETICAL BACKGROUND OF FRACTIONATED CRYSTALLIZATION

In studying the kinetics of crystallinity formation in super-cooled liquid tin, Pound found that Poisson's distribution function could be applied to describe the fraction of droplets that contained exactly z heterogeneities of kind A that were to induce initial crystallization⁸:

$$f_z^{(A)} = [(M^{(A)}V_D)^z / Z!] \exp(-M^{(A)}V_D) \quad (1)$$

where $M^{(A)}$ is the concentration of the randomly suspended heterogeneities, V_D the volume of dispersed phase, and $M^{(A)}V_D$ their mean number per droplet. The fraction of droplets containing at least one heterogeneity of kind A is given by $f_{z>0}^{(A)} = 1 - f_0^{(A)}$ and amounts to

$$f_{z>0}^{(A)} = 1 - \exp(-M^{(A)}V_D) \quad (2)$$

Frensch and Jungnickel⁹ thought that Eq. (1) could also be applied to incompatible blends containing crystalline components. $f_{z>0}^{(A)}$ in Eq. (2) describes that part of the droplets of the polymer whose crystallization is induced by heterogeneity A . The remainder, induced by heterogeneity B , crystallizes at a deeper supercooling and so on. For these further crystallization steps the same considerations hold. Since $f_{z>0}^{(i)}$ depends on V_D , the influence of the degree of dispersion on the relative share of the different crystallization steps is obvious. For sufficiently large droplets, $f_{z>0}^{(A)}$ is near to one and no fractionated crystallization occurs. On the other hand, the crystallization induced by heterogeneity A at the usual temperature is completely suppressed if the relation

$$M^{(A)}V_D \ll 1 \quad (3)$$

holds. From the relative intensity of the different crystallization steps, conclusions can be drawn on the concentration of the respective heterogeneities, if the mean size of the droplets is known.

Suppose the dispersed particles are spherical, then their volume depends on the radius. In a given stress field, there is a continuous breaking down of the dispersed phases to smaller particles with simultaneous coalescence. The equilibrium particle size of the dispersed phase is reached when the rates of breaking down and coalescence are in balance. Tokita¹⁰ obtained the following equation:

$$R^* = \frac{(12/\pi)P\sigma\phi_d}{\eta\gamma - (4/\pi)P\phi_d E_{dk}} \quad (4)$$

where R^* is the equilibrium particle size, P the probability that a collision will result in a coalescence, σ the interfacial tension between the matrix and the dispersed phase, ϕ_d the volume fraction of the dispersed phase, η the matrix viscosity, γ the shear rate, and E_{dk} the macroscopic bulk breaking energy. Equation (4) indicates that the equilibrium particle size R^* becomes smaller when (a) the apparent stress field, which is mainly due to the matrix viscosity, becomes larger; (b) the macroscopic bulk breaking energy becomes smaller under the same stress field; (c) the interfacial tension becomes smaller; and (d) the volume fraction of the dispersed phase is smaller. Therefore, the above factors affect also the fractionated crystallization of materials.

RESULTS AND DISCUSSION

Relation between Fractionated Crystallization and Volume Fraction of the Dispersed Phase

From Eqs. (2) and (4), we infer that the less the volume fraction of the dispersed phase, the larger the probability of fractionated crystallization. There was fractionated crystallization of PA 6 in PA 6-EPDM blends when the content of PA 6 was less than some 15 wt %. Two crystallization peaks were observed at 155-165°C and 180-190°C (Fig. 1). The crystallization peak at the higher temperature was from the normal crystallization of PA 6 bulk, and the crystallization peak at 155-165°C was from the smaller droplets of PA 6 in the blends. WAXD showed that, in all samples, PA 6 crystallized at an almost constant α/γ ratio mainly in the α modifi-

cation; the existence of EPDM in the blends did not affect materially the crystalline forms of PA 6. Frensch and Jungnickel⁹ also obtained similar results in the PA 6-poly(vinylidene fluoride) (PVF₂) blends. This proved that the fractionated crystallization of PA 6 in the PA 6-EPDM blends did not result from the transformation in PA 6 crystalline form. In addition, variation in cooling rate (between 0.5 and 100°C/min)⁹ did not influence the number and relative intensities of the crystallization peaks.

According to Turnbull's approximate relation¹¹:

$$T_c^\circ - T_{ho} \doteq T_c^\circ / 5 \quad (5)$$

where T_c° is the melt/crystal equilibrium temperature and T_{ho} is the crystallization temperature induced by homogeneous nucleation. From Eq. (5), $T_{ho} = 4T_c^\circ/5$, T_c° of PA 6 being 500 K,¹² then T_{ho} (PA 6) = 400 K (127°C). Thus, the crystallization peak of PA 6 at 155–165°C resulted from heterogeneous nucleation. Under the same conditions, there was no fractionated crystallization of PA 6 when the content of PA 6 was above 15 wt % in the PA 6-EPDM blends.

Relation between Fractionated Crystallization and Compatibility of Components

Interfacial tension (σ) between the matrix and the dispersed phase decreases with an increase in their compatibility. The equilibrium particle size R^* is proportional to σ [Eq. (4)]. Therefore R^* decreases with the improvement of compatibility, facilitating an increase in fractionated crystallization.

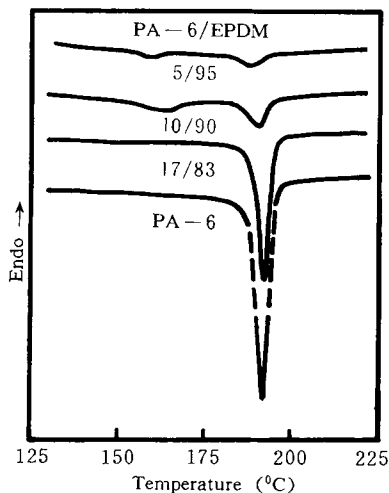


Figure 1 DSC cooling curves of PA 6-EPDM blends.

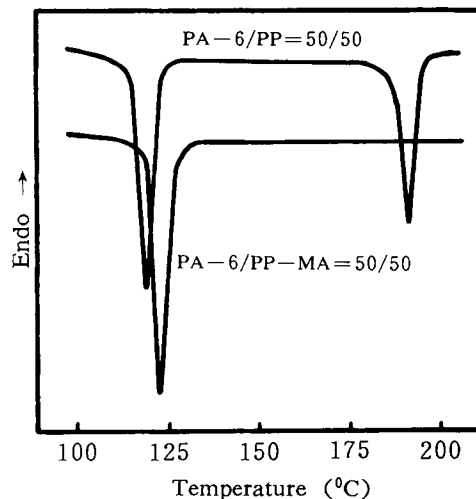


Figure 2 DSC cooling curves of PA 6-PP and PA 6-PP-MA blends prepared in a Brabender Plasticorder.

In order to prove the above inference, a series of PA 6-PP-MA blends were prepared with a Brabender Plasticorder, and their crystallization behavior was studied systematically. The crystallization behavior of the blend of PA 6-PP-MA = 50/50 was remarkable in that the crystallization of the dispersed phase (PA 6) was suppressed at its usual temperature and delayed to coincide with that of the PP matrix. In contrast, the blend of PA 6-PP of the same composition had two crystallization

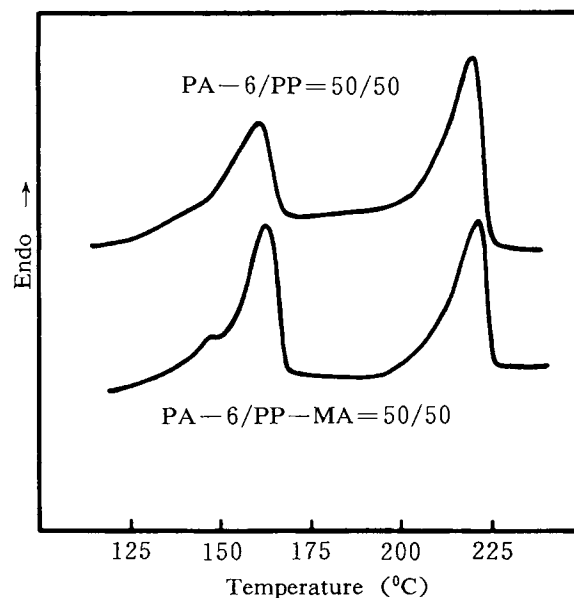
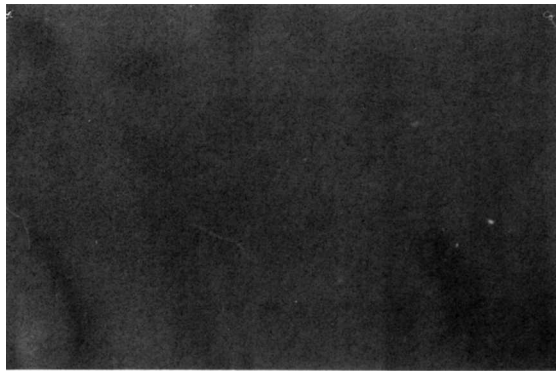
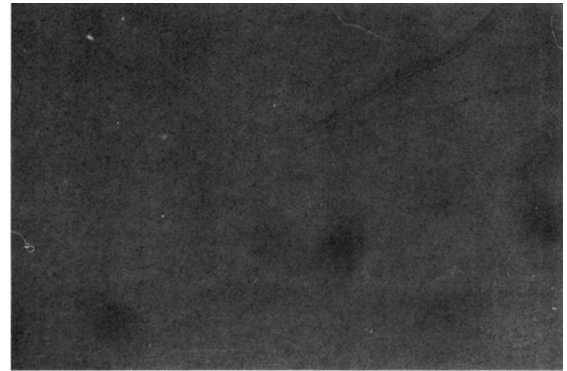


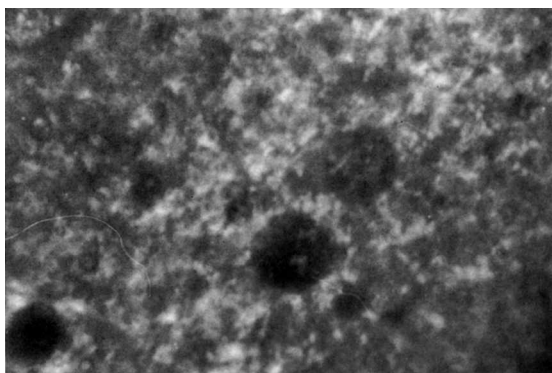
Figure 3 DSC heating curves of PA 6-PP and PA 6-PP-MA blends prepared in a Brabender Plasticorder.



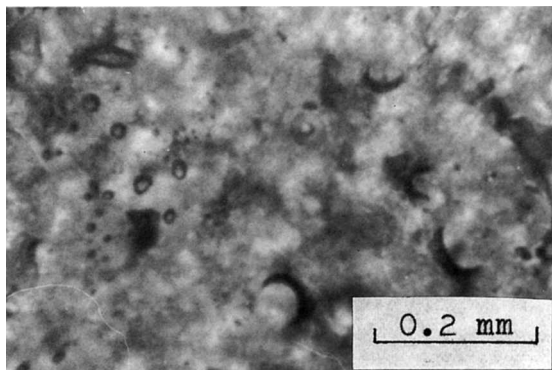
250—185°C



250—125°C

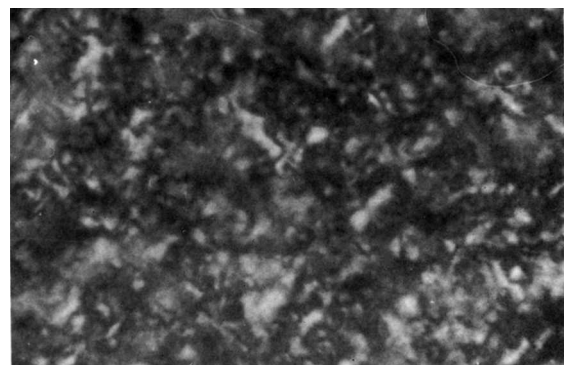


180—125°C



below 120°C

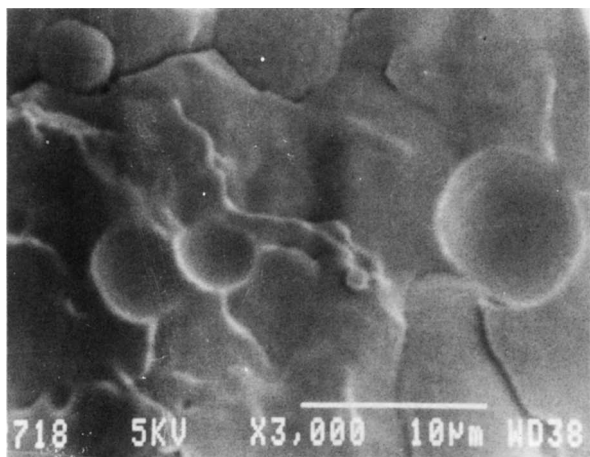
PA—6/PP=50/50



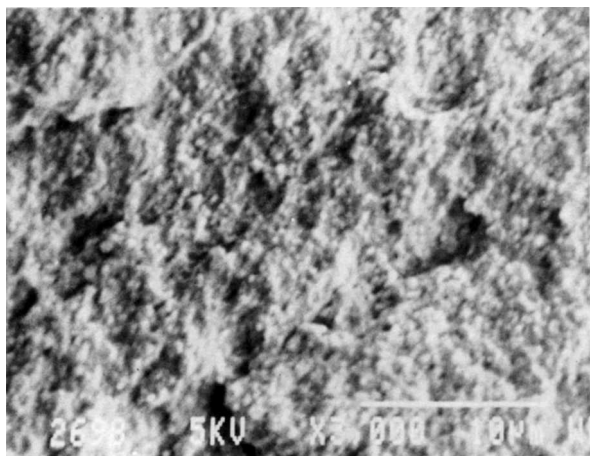
below 120°C

PA—6/PP—MA=50/50

Figure 4 Polarizing microscope micrographs of PA 6-PP and PA 6-PP-MA blends prepared in a Brabender Plasticorder.



PA-6/PP = 50/50



PA-6/PP-MA = 50/50

Figure 5 Fracture surface morphology of PA 6-PP and PA 6-PP-MA blends.

peaks, that of PP and PA 6, respectively (Fig. 2), although the melting behavior of two blends was similar (Fig. 3). The above two blends were heated to 250°C and kept at that temperature for a few minutes to allow the blends to melt completely, then cooled at 5°C/min, and observed with a polarizing microscope (Fig. 4).

At ~ 180°C, PA 6 started to crystallize in the PA 6-PP blend, but there was no crystallization in the PA 6-PP-MA blend. From 180 to 130°C, there was no difference in crystalline state of the two. From 130 to 120°C, PP in PA 6-PP started to crystallize, and PA 6-PP-MA crystallized completely at 122°C or so. Below 120°C, the two blends did not crystallize further. WAXD showed that PP crystal-

lized mainly in its α modification and PA 6 in its γ modification.

Scanning electron micrographs of fracture surfaces of 50/50 blends of PA 6-PP and PA 6-PP-MA revealed that PA 6 was the dispersed phase and PP the matrix (Fig. 5). During the process of blending, the MA of PP-MA reacted with NH_2 groups of PA 6 to form the graft copolymer (PP-MA)-*g*-PA-6, which is a good compatibilizer for PA 6-PP blends. Therefore, the particle size of PA 6 in the blend PA 6-PP-MA was much smaller than that in the PA 6-PP. Because the normal crystallization peak of PA 6 was completely suppressed, the relation $M^{(A)}V_D \ll 1$ held; then the droplet sizes of PA 6 were small enough to initiate crystallization by heterogeneity *B* at a deeper supercooling.

In blends of PVF₂-PA 6, Frensch and Jungnickel⁹ thought that PVF₂ crystallization induced the crystallization of PA 6, owing to the constant T_c of PVF₂ at 140°C under simultaneous crystallization of the finely dispersed PA 6 and the PVF₂ matrix. For the blend PA 6-PP-MA = 50/50, coincidence of crystallization temperature of the finely dispersed part of PA 6 with that of the PP-MA matrix at 122°C indicates a nucleation either of PP-MA crystals in the PA 6 melt or of PA 6 crystals in the PP-MA melt. Now T_m^0 for (γ -PA 6) is 500 K (227°C),¹² and one gets a $T_{ho} = 400$ K (127°C) for PA 6. Therefore the PA 6 in the PA 6-PP-MA = 50/50 blend (mixed

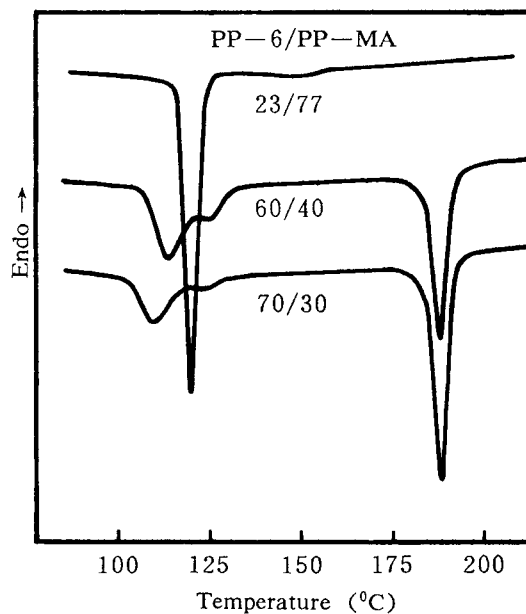


Figure 6 DSC cooling curves of PA 6-PP-MA blends prepared in a Brabender Plasticorder.

in a Brabender Plasticorder) must be homogeneously nucleated. In view of the above results, we think that PA 6 crystallization induced the crystallization of PP-MA rather than vice versa.

In changing the ratio of PA 6 to PP-MA, it was the dispersed phase, no matter what component it was, that always had the fractionated crystallization (Fig. 6). For example, the normal crystallization of PA 6 as the dispersed phase in PA 6-PP-MA = 23/77, was completely suppressed, and there were two fractionated crystallization peaks of PA 6 at 151 and 121°C (overlapping with the PP crystallization peak), respectively.

On the other hand, with blends of PA 6-PP-MA at 60/40 and 70/30, fractionated crystallization of the dispersed phase PP-MA occurred, and its peak height increased with the content of PA-6.

CONCLUSIONS

The work reported here shows that the phenomenon of fractionated crystallization is related to the volume fraction of the dispersed phase and the compatibility between the dispersed phase and the matrix. The connection between the degree of dispersion and the type (or strength) of the particular fractionated crystallization, via DSC measurements, permits a qualitative identification of the dispersion state. Sometimes, the dispersed phase was crystallized by homogeneous nucleation, and the coinci-

dence of the crystallization of both components occurred because of the higher degree of dispersion of the dispersed phase.

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