Mutual Influence of LDPE and PP in Their Blends during Crystallization

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Summary: An indication for the mutual influence of LDPE and PP was the change of the morphology parameters of PE and PP at different ratios of the polymers in blends. That influence depends on the blend composition and is different for PE and PP. It is especially interesting in the blend PE75/PP25 where the influence between PE and PP shows dependence also on the sample geometry. Melting parameters, non-isothermal crystallization parameters - crystallization peak temperature T_c, crystallization begin temperature T_{onset} , half-width $w_{1/2}$ of the crystallization peak, degree of crystallinity α and crystallization rate coefficient *CRC*, as well as the isothermal kinetics parameters showed dependence on the blend composition. It was established that PE is more stable then PP concerning the mutual influence of both polymers on their crystallization. It was established that PE affects the crystal nucleation of PP and causes a decreasing of PP spherulite size.

Introduction

One of the most interesting and useful properties of the polymers is their behavior during melting and during the consequent crystallization. This is especially important in the case of molded polymer blends when the polymers are influenced by their mutual presence and by the specific processing conditions.

Basically PE and PP are incompatible.[1,2] But during crystallization in blends they show a behavior, which is different from that of the pure polymers. The aim of this study is to investigate the mutual influence of PP and LDPE in their blends depending on the blend composition, thermal conditions and sample morphology.

Materials and methods

Blends from isotactic PP "Buplen"6631 [MFI(230/2.16) = 1.1g/10min, M_w/M_n=6.8] and LDPE "Ropoten"FB-7-104 [MFI(190/2.16) = 5,8g/10min, M_w/M_n=20.5], supplied by Lukoil Neftochim Bulgaria, were prepared using a two-screw extruder "Brabender" DSE 17/25D. The ratio of the two components in the blends was LDPE/PP = 0/100, 25/75, 50/50, 75/25 and 100/0 wt. %. In all compositions the concentration of the chemical blowing agent (azodicarbonamide "Genitron" EPA) used was 0.5wt.%.

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The specimens were produced on an on-line injection molding machine KuASY 800/250 by the classical low pressure process in a pre-pressurized with nitrogen mold cavity at following processing conditions: melt temperature $T_m = 210^0$C, mold temperature $T_f = 20^0$C, cooling time $t = 5$ min, gas-counter pressure $P_G = 0.5$ MPa. The sample had a non-regular shape (Fig.1). It consisted of three co-axial cylinders with different diameters (10, 20, 30 mm) and it was injected through the smallest cross-section. The injection molding process used allows preparing of samples with an integral structure: an external stiff (unfoamed) skin and an internal foamed core. This fact together with the complex specimen geometry causes the formation of a defined microstructure in each of the three sections of the specimen.

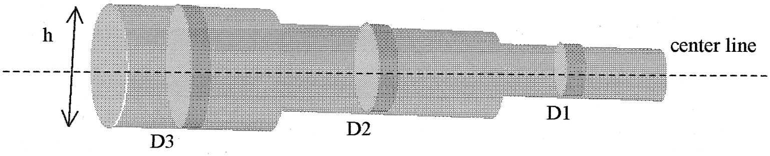


Figure 1. Sample geometry.

Differential Scanning Calorimetry (DSC) as a basic method in this study was used. The scans were made at heating rate of 10^0C/min. After heating, samples were hold for 5 min at 200^0C and then cooled to room temperature. The cooling rate was 5, 10 and 20^0C/min and the weight of the sample was about 5-6 mg. Isothermal crystallization was performed at crystallization temperatures between 96 and 125^0C.

Optical microscopy investigations were performed on a MIN8 polarized light microscope. The microscopic specimens were prepared using Canada balsam. The samples with thickness of 40μm were cut in direction perpendicular to the centerline by microtome from the middle of each of the three different parts of the specimens.

Results and discussion

Melting

From the results obtained for the melting temperature (Fig.2) of both polymers it can be seen that in blends PP melts at lower temperature than pure PP. This tendency is valid in the skin and in the foamed core for all sections of the sample. Probably PE causes a deterioration in the crystal perfection of PP. It seems that when PE is the disperse phase, in blends PE/PP=25/75wt% and PE/PP=50/50wt%, it helps PP in its crystal nucleation and the amount of the crystallized PP increases (Fig.3). But in the case when PE is the matrix in the blends it doesn't relieve the crystallization of PP. The higher degree of crystallinity of PE in the

PE75/PP25 blend could be combined well with the lower crystallinity of PP in this blend in order to confirm the assumption that in the case when PE is the matrix PE crystallizes without helping to PP in it's crystal nucleation.

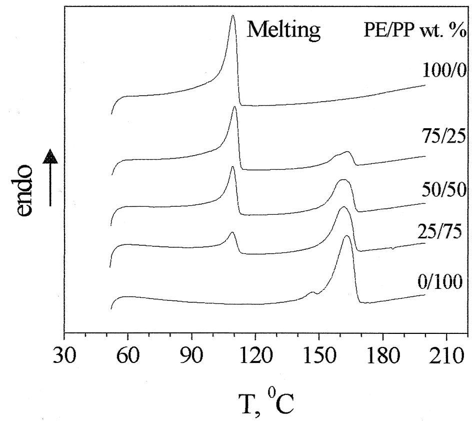


Figure 2. Melting thermograms of PE/PP blends obtained from the core of the middle section of the specimen.

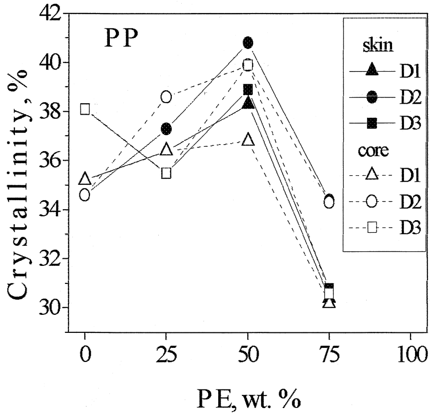


Figure 3. Crystallinity of PP in blends for the three sections of the specimen (small D1, middle D2 and large section D3) depending on the blend composition.

In contrast to PP, PE doesn't show any prominent changes in the melting temperature and crystallinity with variation of the blend composition.

It can be seen also, that the degree of crystallinity of PP in the middle section D2 has the highest value (Fig.3), especially in the blend PE75/PP25 where PP reaches the crystallinity of neat PP.

It should be pointed out that in the case of the PE75/PP25 blend the melting peak shape of PP in the core of the middle-sized section had some special features. A low temperature shoulder in the melting PP peak at temperature 158^{0}C was found, which probably is due to the melting of some "quasi-crystal" regions of PP or lamelae of PP with some PE conclusions.[1, 2] This shoulder of PP peaks could be caused also by the melting of lamellae with different thickness formed at the specific crystallization conditions in that section of the sample. Also a presence of a β-PP phase in the core was observed in the melting endotherms of pure PP.

Non-isothermal crystallization parameters

Figure 4 shows crystallization thermograms of the middle section of specimens made from different PE/PP blends. It can be seen that in the PE/PP=50/50 and 25/75 blends PE and PP show two well distinguished crystallization peaks, while in PE/PP=75/25 blend only one crystallization peak was observed.

The pure PP has highest values of the T_c and T_{onset} parameteres and in blends they decrease with increasing the amount of PE. In the blend PE75/PP25 these temperatures have exceptionally low values, close to those of PE, as it is shown in Figure 5. The very low values of T_c and T_{onset} in this blend is due to the fact that in this composition both polymers crystallize almost simultaneously, in conttrast to the other blends (Fig.4.). That retardation of the PP crystallization[2] in the PE/PP=75/25 blend is caused probably by the presence of PE, which, as a dominant component matrix in this system, imposes on PP its crystallization characteristics, including the lower temperature interval of cystallization and as a result – nucleation controlled crystallization with higher rate.

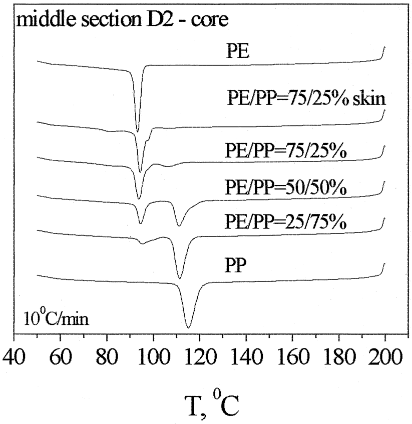


Figure 4. Crystallization peaks of PE/PP blends obtained from the middle section of the specimen at cooling rate 10^0C/min.

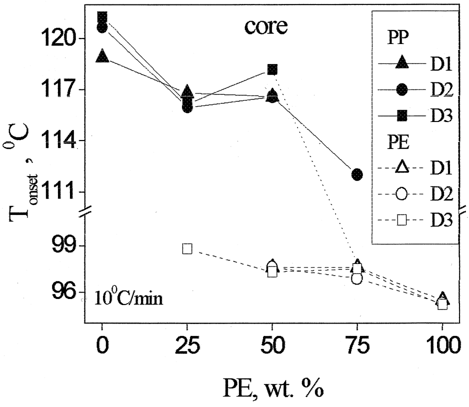


Figure 5. Temperature of crystallization beginning T_{onset} of PP and PE in the core of the three specimen sections (small-D1, middle-D2 and big-D3) as function of the blend composition.

This is confirmed also by the values of the other crystallization parameters of PP in this blend – low crystallinity, little half-width $w_{1/2}$ of the crystallization peak and high crystallization rate coefficient.[3] It has to be said that the values of the PP parameters in the 75/25 blend are rather uncertain, because it was impossible to distinguish precisely the crystallization peaks of PE and PP in this case.

As it was mentioned before, in blend PE/PP=75/25wt% PP appears only as a shoulder in the crystallization peak of PE. But in the core of the middle section of the same blend PP shows a separated small peak before the big PE peak (Fig. 4). This was observed at each rate of cooling. In this case T_{onset} is higher, indicating that nucleation is better, rate of crystallization is lower, because it occurs at higher temperature, crystallinity is better and close to that of pure PP. The reasons for that behavior of PP only in the core of the middle section of the sample are complex. They include the suitable conditions for such "self-crystallization" of PP exactly at this part of the specimen, the effect of thermal "history" that probably saves some of the nuclei after treatment at 200^0C, and the specific influence of PE in the composition PE75/PP25.

Isothermal kinetics

Isothermal kinetics was followed using the Avrami equation

$$X(t)=1-e^{Ktn} ,$$

where $X(t)$ is the volume fraction of the crystallized material at time t, K is the crystallization rate constant, n is the Avrami coefficient connected with the type of nucleation.

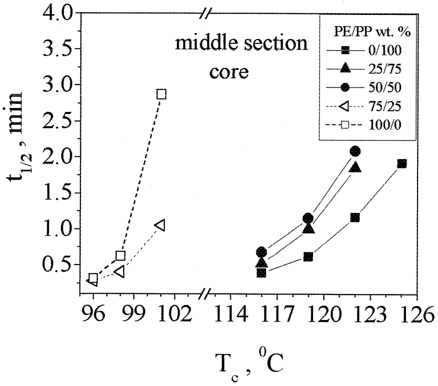


Figure 6. Half-crystallization time of PE/PP blends in the core of the middle section of the sample, depending on crystallization temperature and blend composition.

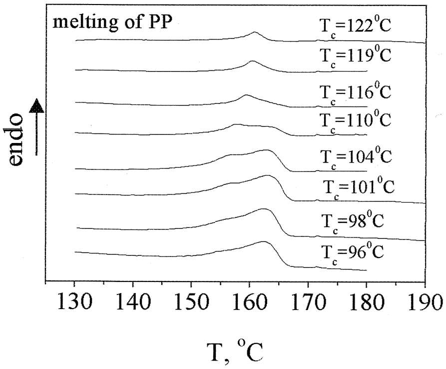


Figure 7. Melting peaks of PP in PE/PP=75/25 blend, received after isothermal crystallization at different crystallization temperatures T_c.

In the high-temperature area of isothermal crystallization (T_c=122-110^{0}C) only PP crystallizes, while PE is in the molten state during this process. But in the low-temperature regime of isothermal crystallization (T_c=104-96^{0}C) both polymers crystallize simultaneously. From Figure 6 it can be seen that at higher crystallization temperatures the half-crystallization time of PP increases with increasing T_c and the content of PE in the blends. The crystallization rate constant K has the opposite dependence on these factors. The Avrami coefficient n shows that there is no change in the type of crystal nucleation.

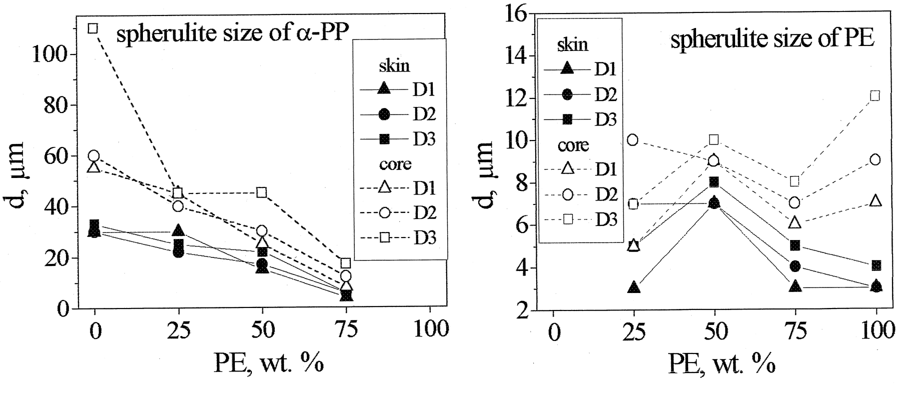
Table 1. Crystallization rate constant K and Avrami exponent n of PE/PP blends, depending on the temperature of isothermal crystallization T_C.

PE/PP wt. %	0/100		25/75		50/50		75/25		100/0	
T_C, °C	*K*	*n*	*K*	*n*	*K*	*n*	*K*	*n*	*K*	*n*
96							24	2.6	9.5	2.3
98							6.2	2.4	2.2	2.6
101							0.7	2.1	0.1	2.9
116	8.3	2.7	4.7	2.9	2.1	2.7				
119	2.2	2.6	0.7	2.8	0.5	2.7				
122	0.4	2.5	0.1	2.7	0.1	2.5				
124	0.1	2.4								

At lower crystallization temperatures a shoulder in the melting peak of PP in the 75/25 blend is observed after isothermal crystallization (Fig. 7). It is due probably to the influence of PE when both polymers crystallize simultaneously and PP forms some quasi- crystals containing also PE.

Morphology

Both polymers form spherulitic crystals. Figure 8 shows that for both poymers the spherulite size in the skin is smaller then in the foamed core. While for PP the difference in the crystal



8a

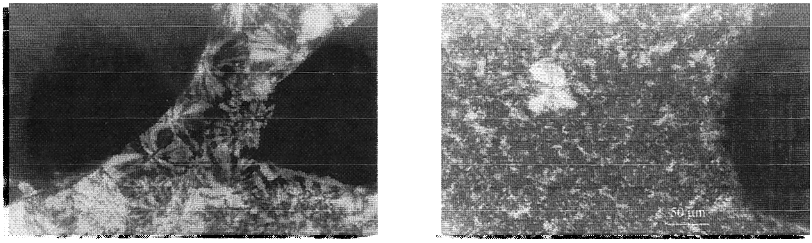
8b

Figure 8. Spherulite size of PP (8a) and PE (8b) in the skin and in the foamed core of the small section D1, middle section D2 and big section D3, as a function of the blend composition.

size in these parts of the specimens decreases with increasing PE in the blends, there is no such effect for PE.

It was observed that increasing of the PE content in the blends causes a reduction in the spherulite size of PP. A possible reason for this effect is that PE could exert influence on the nucleation of PP or/and impede its spherulitic growth rate. For PE there is no essential influence of PP on its spherulite size.

A presence of β-PP in the foamed core was indicated (Fig. 9). It was established that its amount decreases with increasing of the PE in the blends. The microscopic results are in a good agreement with the results obtained from DSC.



9a 9b

Figure 9. Microphotographs of pure PP (9a) and PE/PP=25/75wt% blend (9b), obtained from the foamed core of the biggest section of the specimen.

Conclusions

In general the influence between PP and LDPE in their blends during crystallization depends on the blend composition, on the sample geometry and on the thermal conditions

It was established that PP is more sensible than PE to their mutual influence during crystallization. PE influences the phase transition parameters of PP, affecting mainly its crystal nucleation. In some cases it was detected that PE could affect also crystal growth of PP, which as a result could give some quasi-crystals of PP with PE occlusions.

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[3] L. Minkova, P. L. Magagnini, *Polym. Degr. Stab.* **1993**, *42*, 107.