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Structural changes during cryogenic mechanical milling of iPP/sPS blends

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Recent investigations on Cryogenic Mechanical Milling (CMM) of thermoplastic polymers indicated that macromolecules undergo chain scission leading to the formation of free macro-radicals, crosslinking or amorphization. This makes CMM a promising strategy for the design of highly dispersed blends of thermodynamically immiscible polymers in order to obtain new materials with desirable properties. In this study, CMM is applied on immiscible syndiotactic polystyrene (sPS)/isotactic polypropylene (iPP) blends and compared to conventional melt blending. The resultant blends are characterized by their microstructure in particular their thermal properties. The domain size of iPP in the CMM blends was found to be markedly reduced compared to conventional melt blended samples, although the samples were recrystallized from the molten state. © *2004 Kluwer Academic Publishers*

1. Introduction

Blending polymers allows to design new materials exhibiting a combination of the desirable properties of each blend component. But even in the molten state most polymers are thermodynamically immiscible because of their positive heat of mixing and the negligible entropy contribution to the Gibbs free energy of mixing. Therefore, conventional melt-blending techniques (e.g., extrusion) are known to have serious limitations like coalescence of initially fine dispersed droplets during shear flow or a high viscosity ratio of the blend components [1] and it is generally known that the mechanical and optical properties of such multi-phase blends depend critically on the disperse phase morphology and the interfacial adhesion [2].

Recently, Cryogenic Mechanical Milling (CMM) attracted much attention with superior advantages compared to the conventional melt blending techniques. Smith *et al.* reported that CMM of blends of poly(methylmethacrylate) and poly(ethylene-*alt*-propylene) results in a nanoscale dispersion of on polymer within the matrix of another without the aid of compatibilizing agents [3]. Since these blends were prepared as solid powders by milling below the glass transition temperatures of the components, subsequent processing steps are necessary to gain materials of practical relevance. Prerequisite for stabilizing the blend morphology at elevated temperatures is the irreversible alteration of the initial polymer chain structure by the formation and recombination of different macro-radical species, thus promoting a kind of self-compatibilization [3–5]. Therefore (CMM) might be an alternative route to promote and retain intimate mixing. The aim of this paper is a systematic investigation on CMM of sPS/iPP blends.

2. Experimental

The sPS (melting temperature $T_m = 270°C$; glass transition temperature $T_g = 100°C$) was kindly supplied by Dow Chemical & Co.) iPP ($T_m = 164°C$; $T_g = 0°C$) by the BASF Ludwigshafen. Blends of sPS/iPP (50/50 wt%) were prepared by milling 1 g of the polymer pellets in a SPEX Freezer/Mill for 30 min at liquid nitrogen temperatures. A detailed description of the milling treatment is given elsewhere [6]. For comparison melt mixed blends were prepared in a DSM laboratory extruder at 60 rpm for 5 min. Melt blending was performed at 290°C under a continuous flow of nitrogen.

A TA-Instruments DSC-2910 was used for thermal analysis. Each sample was heated from 30 to 310°C at a heating rate of 10 K/min and kept isothermally for 5 min in order to erase the previous thermal and "mechanical" history before cooling to ambient temperature with a cooling rate of 5 K/min. For WAXS (Philips PW1140/90 goniometer; Ni-filtered Cu K_α-radiation) the samples were placed on a sapphire plate fixed in a custom made metal frame.

A Leitz DM RB equipped with a hot-stage was used for polarization microscopy. Thin films were prepared by melting the blends between two glass slides at 300°C for 5 min; afterwards the samples were slowly cooled to ambient temperature.

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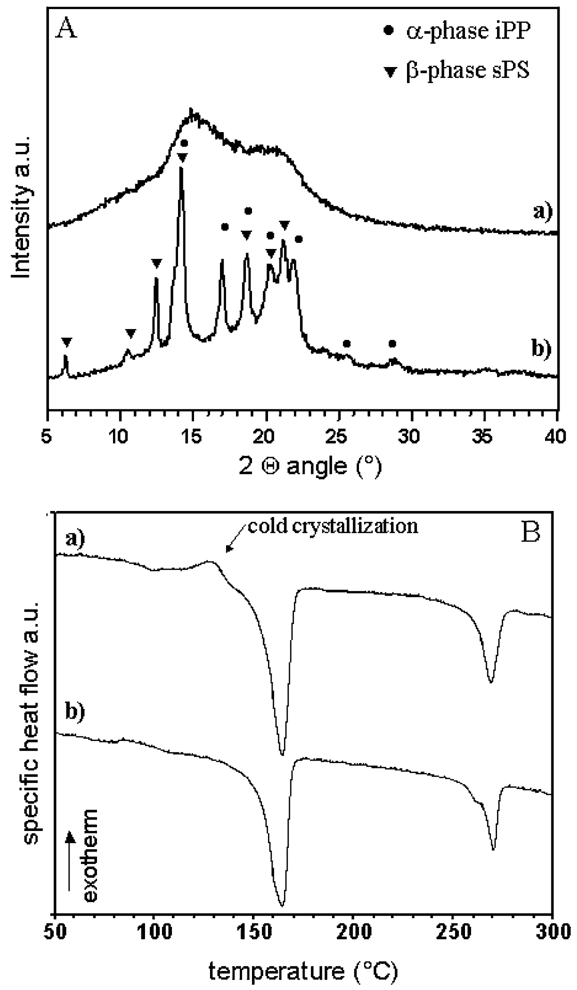

Figure 1 (A) WAXS of the sPS/iPP (50/50 wt%) blend after CMM for 30 min (a) and (b) extruded blend. (B) Corresponding DSC heating curves (10 K/min) of sPS/iPP blends after CMM (a) and after extrusion (b).

3. Results and discussion

Similar as previously reported for both single components [6, 7] CMM of sPS/iPP results in a progressive amorphization of the initially semi-crystalline material. In Fig. 1A the WAXS obtained for the milled blend and—as a reference—for the extruded blend are presented. The reference sample is showing distinct peaks near the diffraction peaks for the sPS β-form and for the iPP α-form. After 30 min of cryogenic mechanical milling there is no evidence for a phase transformation as observed in milled polyethylene by Castricum *et al.* [8]. Moreover, no distinguishable diffraction peaks can be observed. According to the corresponding DSC results presented in Fig. 1B there is strong evidence that this milling treatment far below the T_g of both blend components results in an amorphous or highly metastable state.

It can be seen that the DSC trace of the milled blend shows an exothermic transition above the T_g of sPS. This exothermic process is attributed to the cold crystallization of sPS in the blend. Therefore, one can conclude that the degree of crystallinity was markedly reduced by CMM.

Two possible explanations for the absence of any distinct diffraction peaks are reasonable: (i) the initial crystal size in the reference sample is markedly reduced during CMM, (ii) prolonged milling is leading to a remarkable amorphization at least of the initially semi-crystalline sPS as indicated by the observed cold crystallization. Comparing CMM of the sPS/iPP blend to the results of our previous studies on the single components we can conclude that simultaneously milling of sPS and iPP is leading to similar structural changes.

In order to reveal, whether alterations of the initial polymer chain structure during CMM has taken place which should lead to *irreversible* structural changes, non-isothermal crystallization experiments were conducted. Fig. 2 shows the DSC cooling curves and the corresponding WAXS of sPS/iPP. The X-ray diffraction of the milled and extruded sPS/iPP blends after melt-crystallization (Fig. 2A) exhibits no differences between the two preparation techniques, but significant changes in the non-isothermal crystallization behavior are noticeable (see Fig. 2B).

For the sPS in the CMM blend the onset of crystallization is shifted to higher temperatures: the maximum of the crystallization peak (T_c) increases by about 10°C. This shows clearly that CMM indeed leads to irreversible structural changes. The occurrence of well defined crystallization and melting peaks, however, indicate that noticeable crosslinking of the

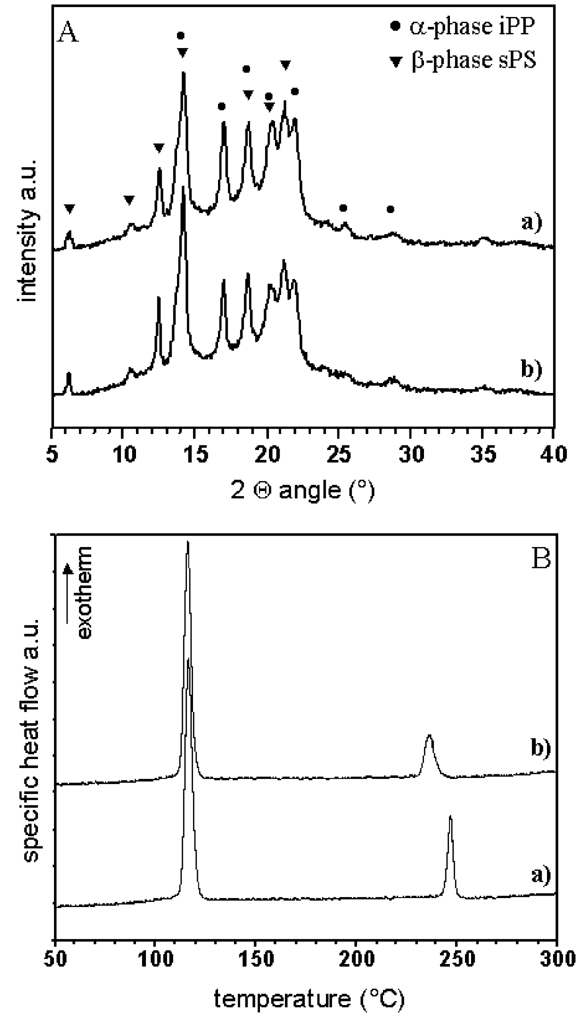

Figure 2 (A) WAXS of the sPS/iPP (50/50 wt%) CMM blend after crystallization from the melt (a) and of the extruded blend (b). (B) Corresponding DSC cooling curves (5 K/min) of the sPS/iPP blends prepared by CMM (a) and prepared by extrusion (b).

blend components can be excluded. An explanation for the changed crystallization behavior is a decrease of the molecular weight (M_w) and/or a change of the M_w-distribution by milling as observed in polypropylene/polyamide 6 blends by Chen *et al.* [8, 9]. Nucleation and crystal growth is known to be very sensitive to the M_w and M_w-distribution [10–12]. In contrast to our reported result [6] on the influence of CMM in single iPP no effect on the onset of crystallization of iPP in the blend can be seen. During melt crystallization, iPP ($T_c = 116°C$) crystallizes in the presence of already formed sPS ($T_c = 246°C$) crystals. Therefore we assume that the surfaces of the sPS crystals will act as heterogeneous nucleation sites thus concealing the influence of CMM on this component.

The morphology of the sPS/iPP blends prepared by CMM a well as by melt blending after the melt crystallization is shown in Fig. 3. Although the blends were crystallized from the melt there still exist an influence of the previous milling treatment. Whereas the CMM blend shows spherical iPP-domains dispersed in a sPS matrix (Fig. 3B).

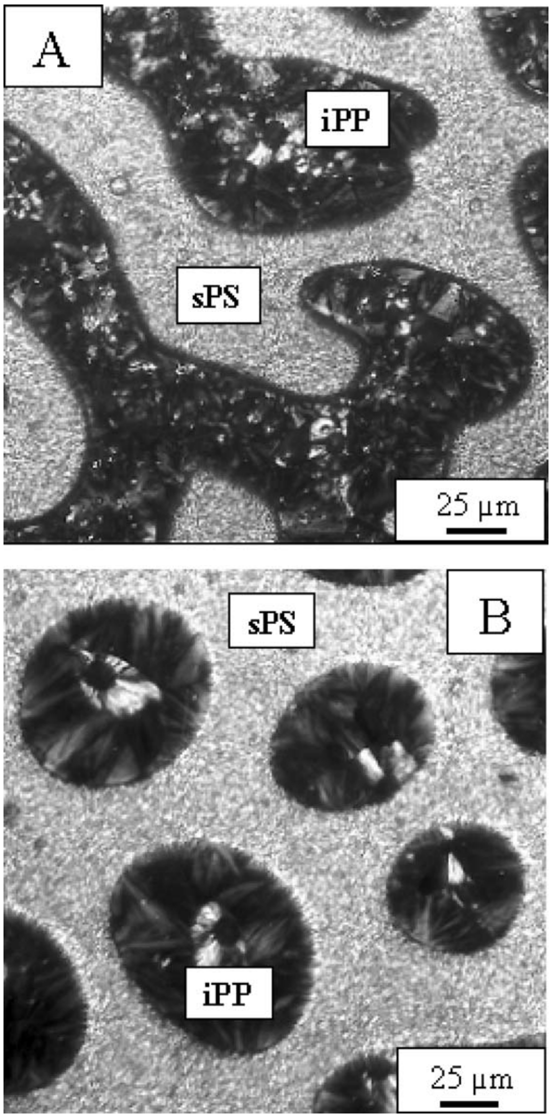

Figure 3 (A) Morphology of the sPS/iPP (50/50 wt%) extruded blend and (B) of the sPS/iPP (50/50 wt%) prepared by CMM after both were crystallized from the melt.

In contrast to that, a coarse co-continuous morphology can be seen in Fig. 3A resulting from liquid-liquid phase separation during extrusion. This is the most important result with regard to the design of polymer blends, thus confirming our expectations on the beneficial use of CMM.

4. Conclusion

A strong influence on the structure, thermal behavior and morphology was observed during Cryogenic Mechanical Milling (CMM) of sPS/iPP blends. Similar as observed in our previous studies on the single components CMM causes a distinct broadening of all X-ray diffraction peaks. The formation of a distinct cold crystallization peak in sPS can be attributed to partial amorphization. Whereas this change is reversible as proved by the recrystallization experiments, CMM also leads to irreversible structural changes, resulting in a significantly altered crystallization behavior. Comparing the morphologies of the CMM blends to that of the extruded blends a higher degree of dispersion can be observed, although the samples were recrystallized from the molten state. This result demonstrates that CMM may yield polymer blends with unexpected morphologies, even after processing from the molten state.

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References

1. D. R. PAUL and S. NEWMAN, "Polymer Blends" (Academic Press, 1978), Vol. 2, p. 35.
2. A. J. RAMIC, S. D. HUDSON, A. M. JAMIESON and I. MANAS-ZLOCZOWER, *Polymer* **41** (2002) 1155.
3. A. P. SMITH, H. ADE, S. D. SMITH, C. C. KOCH and R. J. SPONTAK, *Macromolecules* **34** (2001) 1536.
4. Y. LIU and Q. WANG, *Polym. Journal* **34** (2002) 132.
5. A. R. NESARIKAR, S. H. CARR, K. KHAIT and F. M. MIRABELLA, *J. Appl. Polym. Sci.* **63** (1997) 1179.
6. M. STRANZ and U. KÖSTER, *Coll. Polym. Sci.* **282** (2004) 381.
7. *Idem.*, *J. Metast. Nanocryst. Mater.* **20/21** (2003) 281.
8. Z. CHEN and Q. WANG, *Polym. Int.* **50** (2001) 966.
9. M. RÄTZSCH, M. ARNOLD, E. BORSIG, H. BUCKA and N. REICHELT, *Progr. Polym. Sci.* **27** (2002) 1195.
10. S. Z. D. CHENG, J. J. JANIMAK and A. ZHANG, *Macromolecules* **23** (1990) 298.
11. B. DE CARVALHO and R. E. S. BRETAS, *J. Appl. Polym. Sci.* **68** (1998) 1159.
12. P. J. PHILIPS and N. VATANSEVER, *Macromolecules* **20** (1987) 2138.

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