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LETTER

The thermodynamic behavior and morphology of PP/POE blends prepared by melt- and solution-mixing methods

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Polypropylene (PP) is one of the three general plastics of considerable commercial importance. It is a semi-crystalline polymer, with good mechanical and thermal properties, corrosion resistance, low cost, easy processing, and low density. It has been used to make a variety of products. However, one of the drawbacks of PP is its poor impact performance, which limits its application in some fields. The investigation for improving the property of PP for industry production is important.

Polymer blends provide an effective way for improving the property of materials. To overcome the drawback of PP aforementioned, several elastomeric materials such as ethylene–propylene rubber (EPR), ethylene–propylene diene monomer (EPDM), low-density polyethylene (LDPE), ethylene vinyl acetate (EVA), and polystyrene–butadiene–styrene (SBS) are used as impact modifiers to compound with PP to enhance the impact resistance of PP [1–3]. Polyethylene-1-octene (POE) is one of the most effective impact modifiers commonly used for PP. It is the newest member of the PE family, produced by ethylene and octane, using metallocene technology by Dow Elastomers Company [4]. Metallocene catalysts for olefin polymerization have allowed the control of molecular weight distribution, proportion, and distribution of comonomer incorporation. Therefore, mixing POE with PP might be a good option for enhancing the characteristics of PP. The success of blending depends upon the miscibility between the polymers. Investigations on the mechanical properties, rheological properties, and morphology of PP/POE blends have been developed in order to testify the miscibility of PP and POE. For example, Da Silva and co-workers explored the rheological properties and miscibility of PP/POE blends [5, 6], which showed that PP and POE have partial miscibility. Yang et al. [7] researched the brittleness transition behavior of PP/POE blends by carrying out impact resistance and high-speed tensile test. McNally et al. [8] discussed the time-dependence and shear rate-dependence of viscosity property of PP/POE blends, and showed that PP and POE are miscible even when the content of POE attained 15 wt%. Kontopoulou et al. [9] explored the miscibility of PP/POE blends and found that PP and POE are not miscible. Cerrada et al. [10] used Differential Scanning Calorimetry (DSC) and X-ray diffraction (XRD) methods to study PP/POE blends; he obtained the same result as Kontopoulou. Although there have been a number of investigations on the miscibility of PP/POE blends, the results are not always consistent with each other. The blend miscibility is quite dependent on the method of preparation [11]: solution and melt blending are the two procedures widely applied in mixing the PP and other impact modifiers. Feng et al. [12] have used both melt and solution mixing methods to investigate the miscibility of PP/HDPE blend. To offer more information for industry application, we studied the miscibility of PP/POE blends with melt- and solution-mixing method and the further influence of the microscopic morphology on the change of crystallization exhibited.

PP (commercial grade (PP1300) ($\rho \sim 0.900$ g/cm^3) (Mw = 224000, Mw/Mn = 4.2) Yanshan Chemical Industries, Beijing) and POE (commercial grade (Engage 8150) ($\rho \sim 0.868$ g/cm^{-3}) (Mw = 178000, Mw/Mn = 2.45)

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Dow Chemical Company, metallocene-catalyzed copolymer of ethylene and 1-octene with 25 wt% 1-octene comonomer) were mixed in a XSM-1/20-80 rubber mixer to obtain melt-mixing blends with different compositions. The blends were prepared at 210 °C for 10 min, and the mixing rotor speed is set at 64 rpm. The solution-mixing blends were obtained by the following methods.

1. PP and POE pellets were cleaned by tap water and distilled water, then PP were kept under vacuum oven at 80 °C, and POE was kept under vacuum oven at 50 °C for 18–24 h to remove water.
2. Desired composition of PP and POE were dissolved in dimethylbenzene (the total weight of PP and POE is 1 *g*, the weight ratios of PP/POE are 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 0/100), the volume of dimethylbenzene is 50 mL, and solution temperature is 130 °C. Stir the solution for 1 h after dissolving to make sure the blends dissolved completely.
3. After agitation, the solution was poured into the vessel, the solvent was evaporated above 130 °C for half an hour to ensure total elimination of the solvent, and then the blends were placed under vacuum at 30 °C for 72 h to completely remove the residue solvent.

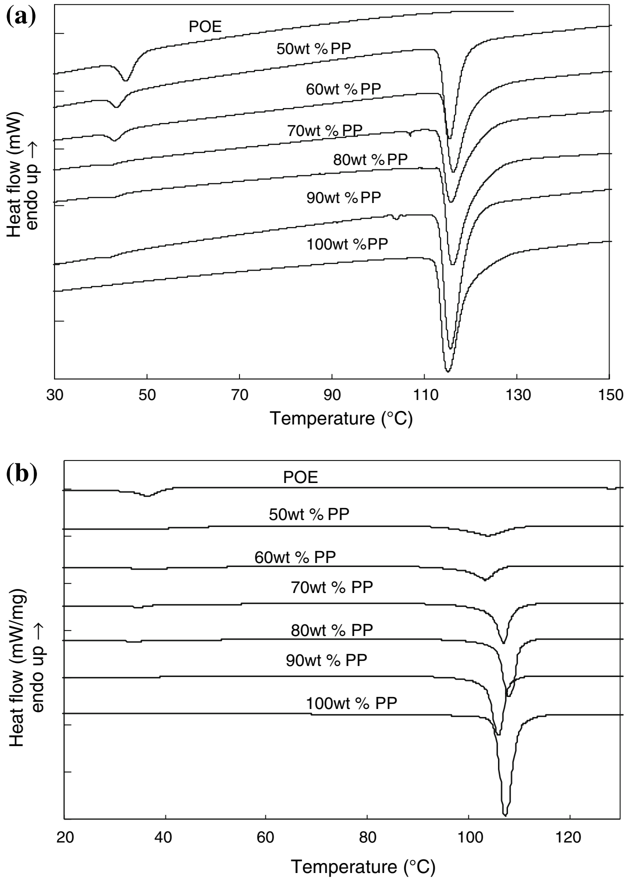

Fig. 1 Cooling DSC curves of PP/POE blends prepared by solution-mixing (**a**) and melt-mixing method (**b**). The DSC curves for different components have been shifted vertically for the sake of clarity

The thermal analysis measurements were performed using Perkin-Elmer energy compensation Diamond Differential scanning calorimetry (DSC). The DSC measurements reported in this study are recorded during the second heating/cooling cycle at the rate of 10 °C/min. This procedure ensures that previous thermal history is erased and provides comparable conditions for all the samples. The sample weights for DSC measurement were about 5–10 mg. The temperature was calibrated using standard Hg and Indium materials while C_p was calibrated using standard sapphire. Figure 1a, b showed the cooling crystallization curves for PP/POE blends prepared by melt and solution mixing, respectively. All the DSC curves for the blends in Fig. 1a show two crystallization peaks corresponding to the crystallization of PP and POE, while the pure samples show only one peak. With change of composition in PP/POE blends, the temperature of the crystallization peaks of PP and POE components has almost no change compared to that of pure samples (around 115 °C for PP and 45 °C for POE); this result is in accordance with reference9, indicating that there exists two crystallizable components [13], and there is no interaction between PP and POE in the melting blends. It may be because of intense exclusion between PP and POE crystal region, which would not affect the crystal behavior of the other composition. However, in the solution-mixing blends, the crystallization temperatures of PP decrease as well as the crystallization peaks broaden with the increase of POE content, while the crystallization temperature of POE decrease with the increase of PP content, as shown in Fig. 1b, indicating that the two components are partially miscible [14], and there are some interactions occurring between PP and POE components. Crystallization enthalpy (ΔH_c) and melting enthalpy (ΔH_m) of PP are calculated by analysis of the miscibility of the blends, and the variation in the values of crystallization and melting enthalpy with the content of PP experimental values of both melt- and solution-mixing blends and the calculated values are plotted in Figs. 2 and 4, respectively. The calculation methods for ΔH_c and ΔH_m are as follows:

$$\Delta H_c = x\Delta H_c^1 \tag{1}$$

$$\Delta H_m = x\Delta H_m^1 \tag{2}$$

x is the weight percentage of the PP component, ΔH_c^1 and ΔH_m^1 are the crystallization and melting enthalpies of pure PP obtained in the same experimental condition.

The crystallinity (X_c) was calculated using the following equation [12]:

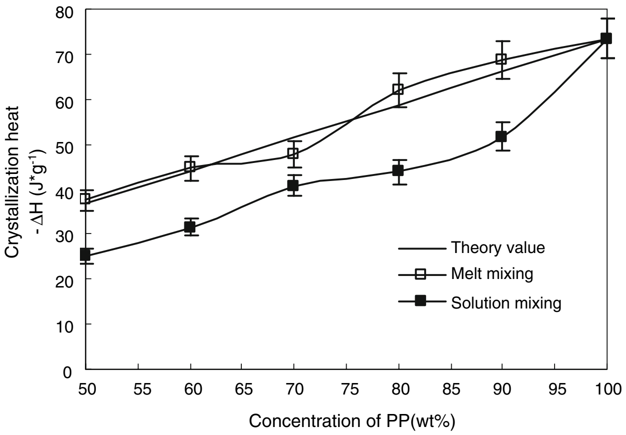

Fig. 2 Variation of crystallization heat with concentration of PP

$$\%\text{Crystallinity} = (\Delta H_{\text{m}}/\Delta H_{\text{m}}^{0}) \times 100\% \qquad (3)$$

Here ΔH_{m} is the melting enthalpy, ΔH_{m}^{0} is the 100% melting enthalpy of pure PP.

Figure 2 describes the variation of crystallization enthalpy with the content of PP. From this figure, we can find that the experimental values of the melt-mixing blends are very close to the theoretically predicted values based on linear additive theorem, suggesting that the addition of POE components in the melting blends will not affect the crystallization behavior of PP. However, in the solution-mixing blends, the values of crystallization enthalpy are lower than the calculated values, which may be because the addition of POE destroyed the perfect crystal of PP; in other words, the existence of POE restrained the crystallization behavior of PP, which suggests that some POE dispersed into the PP phase, the two components are partial miscible.

The DSC melting thermograms of blends and pure samples are shown in Fig. 3a, b. From Fig. 3a, we can find the melting temperature of pure PP is near 165 °C, while the pure POE is near 60 °C. The melting temperatures of the components in the melt-mixing blends are not affected by blending, which suggests that both PP and POE components in the melt-mixing blends can crystallize and melt without being affected. The DSC thermograms in Fig. 3b are the melting curves of PP/POE blends made by solution-mixing method. There are still two peaks in the DSC curves of the blends, corresponding to the PP and POE components, respectively. But with the increase of PP concentration, the melting peak around 60 °C of POE shifts to lower temperature, accompanied by the decrease of the peak area; and with the increase of POE concentration, the melting peak around 165 °C of PP also shifts to lower temperature, accompanied by the decrease of the peak area. These peak areas represent the melting enthalpy, which are corresponding to the crystallinity of the samples according to Eq. 3, and the decrease of the melting enthalpy of PP with the increase of POE content is lower than the calculated values which can be observed from Fig. 4. It is

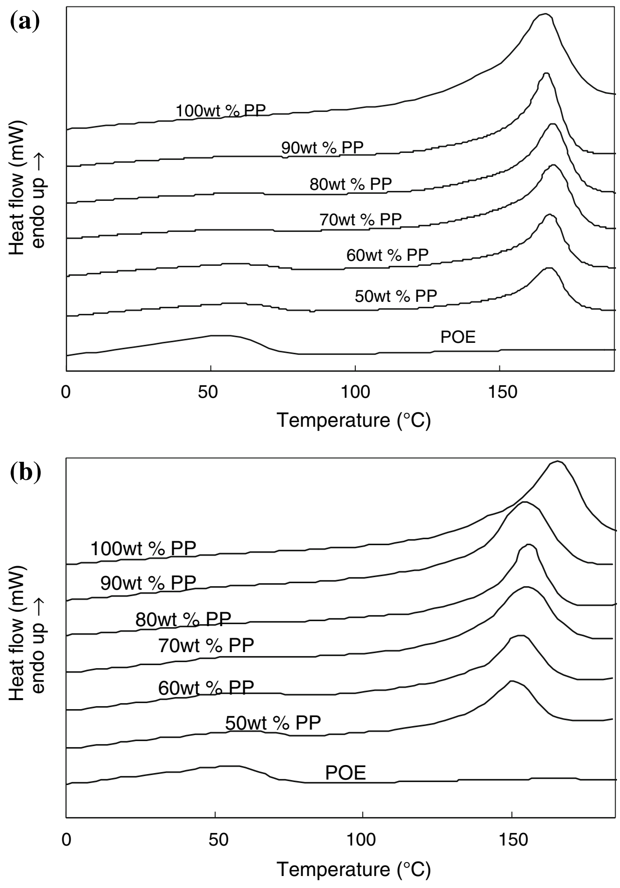

Fig. 3 The heating melt DSC curves of PP/POE blends prepared by solution- (**a**) and melt-mixing methods (**b**). The DSC curves for different components have been shifted vertically for the sake of clarity

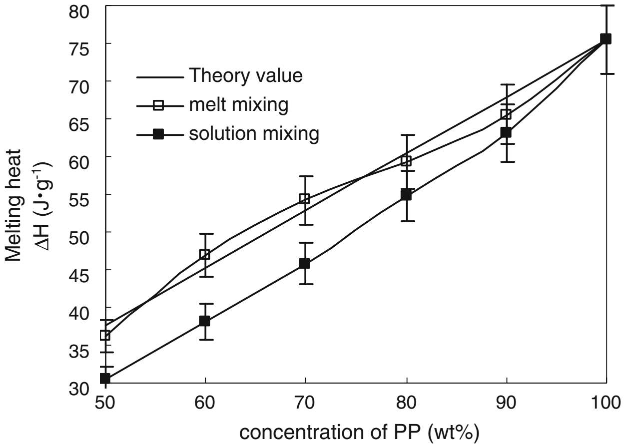

Fig. 4 The variation of melting heat of PP with the concentration of PP in the PP/POE blends prepared by melt- and solution-mixing methods

suggested that the presence of POE restrains the crystal behavior of PP, and there exist some interactions between PP and POE in the solution-mixing blends.

Figure 4 shows the variation of melting enthalpy of PP with the change of PP and POE compositions. It is well known that in the heating melt process, the more prefect the crystals, the higher the melting point [12]. From Fig. 4, we can find the melting enthalpy of PP in melt-mixing blends is around the calculated value. It is suggested that the addition of POE has no effect on the crystallization behavior of PP in the melt-mixing blends. However, in the solution-mixing blends, the presence of POE restrained the crystallization behavior of PP, with the increase of POE concentration, and the degree of crystallinity of PP becomes lower, which can be obtained from the variety of the melting enthalpies observed in Fig. 4.

From the above normal DSC analysis, PP/POE blends made by solution-mixing method are partially miscible. With the addition of PP, the melting peak of POE becomes weaker gradually, and the position of the peak shifts to lower temperature. At the same time, the melting interval of POE becomes wider, and so, melting phenomenon of POE is too faint to be observed by normal DSC. The normal DSC analysis was not performed under thermodynamic equilibrium. In order to enable observe the melting behavior of POE clearly. Step-Scan DSC technique was used to analyze the melting behavior of POE in the PP/POE blends made by solution-mixing method, which consists of a periodic succession of short heating segments and isothermal segments to make the sample undergo a thermodynamic equilibrium process during heating. It can accurately reflect the thermodynamic properties of polymers. Before the start of the Step-Scan DSC method, the samples were heated from −50 to 200 °C at 10 °C/min, and then held at isothermal condition for 3 min in order to erase the thermal history; thereafter, the samples were cooled from 200 to −50 °C at 10 °C/min, and held for 60 min at −50 °C in order to ensure the heat flow reached equilibrium, then heated from −50 to 100 °C at every 1 °C jump of 5 °C/min heating rate and 2 min isothermal. The empty crucible, and the crucible having the same weight as that of the sample crucible containing sapphire are scanned with the same procedure, and the data computed in order to obtain curves for thermal capacity versus temperature. The relationship between thermal capacity (C_p) and temperature is plotted in Fig. 5.

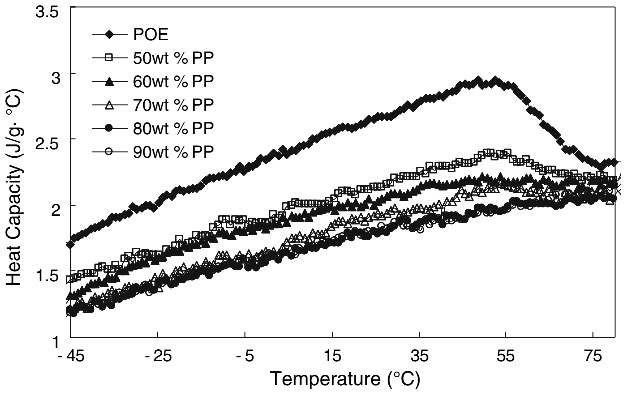

Fig. 5 Plots of C_p vs. temperature for PP/POE solution blends as measured by Step-Scan DSC method

These curves of C_p versus temperature for PP/POE solution-mixing blends in Fig. 5 were obtained by Step-Scan DSC technique. From these plots, we learn that the melting range of the blends become wider with the increase of PP content, the melting point become inconspicuous, which indicates that the addition of PP restrained the crystal, and the crystallinity of POE becomes less perfect. When the content of PP reaches 80 or 90 wt% as shown in Fig. 5, there is almost no melting peak of POE, which result is in accordance with normal DSC testing result and indicates that the PP/POE blends made by solution mixing are partially miscible. The heat capacity of solid macromolecules can be described fully based on a vibrational behavior of atoms, while that of the liquid polymers is commonly described as the sum of vibrational, conformational, and external contributions [15–17]. Figure 5 indicates that the heat capacity of 80 wt% PP and 90 wt% PP are almost the same; it may be because there is a strong intermolecular interaction between PP and POE, and the vibration of POE was restricted by PP when the concentration of PP attained 80 wt%.

The solubility parameter of the polymer repeat chemical units in PP (propylene) and in POE (ethylene) is 8.022 and 7.665, respectively [18]. According to the theoretical prediction of Krause [19], when the absolute difference in solubility parameter is 0.1, the critical molecular weight will be 120,000, when the difference is 1.0, the critical molecular weight will be less than 1,200. In this study, the molecular weights of both PP and POE are higher than the critical value, and so the mixing systems prepared by both melt- and solution-mixing methods show some immiscibility, although the solution-mixing system shows better miscibility than the melt-mixing system.

The analysis of the morphology was also used to investigate the miscibility of PP/POE blends prepared by both melt- and solution-mixing methods. According to the DSC and Step-Scan DSC results, when the concentration of PP is more than 80 wt%, the miscibility of PP and POE blends made by solution-mixing method will be obvious. To observe the difference between miscibility and incompatible PP/POE blends through microstructure, morphologies were observed using an Olympus DP-12-polarized optical microscope, 90 wt% PP was selected because of its obvious crystal behavior by solution-mixing method. The samples were melted at 200 °C and squeezed to films. The samples were put on hot stage and heated to 200 °C at 10 °C/min and held at isothermal temperature for 5 min to allow complete melting. Then the samples were cooled to room temperature at 10 °C/min before the morphology observation. The nitrogen gas was purged through the hot stage during the heating and cooling of samples. The crystalline morphologies of the blends investigated by the polarized optical microscope (POM) are shown in Fig. 6a, b. Figure 6a is the PP/POE blend with 90 wt% of PP prepared by the melt-mixing method. It can be clearly observed that the PP component formed perfect spherulites, and the POE component dispersed in the PP matrix. Because during the crystallization process from molten state the formation of PP crystalloid occurs earlier than when compared with POE, the POE was trapped into the interlamellar region during the crystallization process. Phaseseparation was formed between the two components; PP/POE blends are not miscible. Figure 6b is the POM picture of PP/POE blend with 90 wt% of PP prepared by solution-mixing method. It can be seen that the morphology of the crystal grain becomes dendrite from spherulite, which is a more complicated crystal form. The perfect level of dendrite is lower than Spherulitic [20]. It can be explained that the addition of POE restrained the crystallization process of PP. With the POE concentration increasing further in the blends, the difference in the morphology for the different mixing methods is not so significant and the morphology is similar to that as in Fig. 6b.

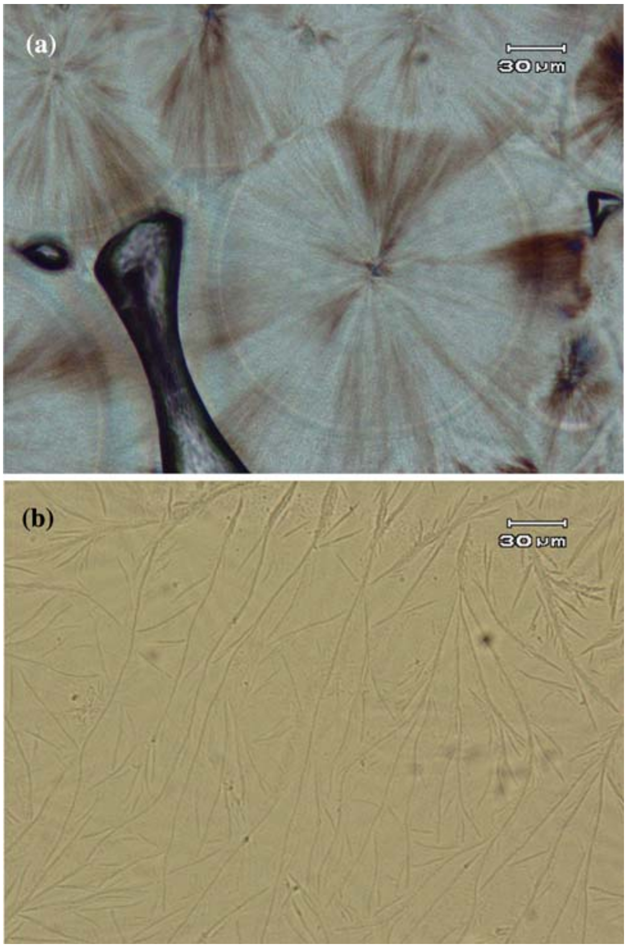

Fig. 6 The POM Pictures of 90 wt% PP prepared using two blending methods

In conclusion, the DSC technique was used to analyze the miscibility of PP/POE blends made by melt- and solution-mixing methods. The crystallization, melting behavior, and morphology of PP/POE blends were studied. The experimental results show that the PP/POE blends made by solution-mixing method have partial miscibility. With the increase of POE content, the crystallization and melting temperatures of PP shift to low temperature. However, the melt-mixing ones are incompatible, which result can be found from the perfect morphology of spherulite of PP, and the invariableness of the crystallization and melting points of PP and POE with the ratio change of PP/POE.

References

1. Huang L, Pei QW, Yuan Q, Li HD, Cheng FM, Ma JC, Jiang SX, An LJ, Jiang W (2003) Polymer 44:3125
2. Jiang W, Yu DH, An LJ, Jiang BZ (2004) J Polym Sci, Part B: Polym Phys 42:1433
3. Ying JR, Liu SP, Guo F, Zhou XP, Xie XL (2008) J Therm Anal Cal 91:723
4. Song N, Zhu L, Yan XL, Xu YB, Xu XH (2008) J Mater Sci 43:3218. doi:10.1007/s10853-008-2554-9
5. Da Silva ALN, Tavares MIB, Politano DP, Coutinho FMB, Rocha MCG (1997) J Appl Polym Sci 66:2005
6. Da Silva ALN, Rocha MCG, Coutinho FMB, Bretas RES, Farah M (2002) Polym Test 21:647
7. Yang JH, Zhang Y, Zhang YX (2003) Polymer 44:5047
8. McNally T, McShane P, Nally GM, Murphy WR, Cook M, Miller A (2002) Polymer 43:3785
9. Kontopoulou M, Wang W, Gopakumar TG, Cheung C (2003) Polymer 44:7495
10. Cerrada ML, Prieto O, Perena JM, Benavente R, Perez E (2003) Macromol Symp 198:91
11. Liau WB, Chang CF (1999) J Appl Polym Sci 76:1627
12. Feng Y, Jin X, Hay JN (1998) J Appl Polym Sci 69:2469
13. Qin JL, Gao JG, Li ZT, Run MT (2008) J Appl Polym Sci 107:1235. doi:10.1002/app.27157
14. Chiu FC, Lau CS (2006) J Polym Sci, Part B: Polym Phys 44:2798. doi:10.1002/polb.20942
15. Pyda M, Wunderlich B (1999) Macromolecules 32:2044
16. Pyda M, Wunderlich B (2002) J Polym Sci, Part B: Polym Phys 40:1245
17. Wunderlich B (1995) Pure Appl Chem 67:1019
18. David DJ (1996) Adv Polym Technol 15:315
19. Krause SJ (1978) In: Paul DR, Newman S (eds) Polymer blends, chapter 2, vol 1. Academic Press, London
20. Shieh YT, Lee MS, Chen SA (2001) Polymer 42:4439