Chinese Journal of Polymer Science Vol. 24, No. 6, (2006), 569–573

Chinese Journal of Polymer Science
©2006 World Scientific

PRELIMINARY INVESTIGATION ON THE MISCIBILITY OF ISOTACTIC POLYPROPYLENE (*i*PP) AND SYNDIOTACTIC POLYPROPYLENE (*s*PP) BLENDS*

Chun-xiao Zheng[a,c], Xiu-qin Zhang[a,c], Joerg Rottstegge[a,c], Xia Dong[b], Ying Zhao[b], Du-jin Wang[a,b**], Shan-nong Zhu[a], Zhi-gang Wang[a], Charles C. Han[a,b] and Duan-fu Xu[b]
[a]*Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
[b]*State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*
[c]*Graduate School of Chinese Academy of Sciences, Beijing 100080, China*

Abstract Experimental miscibility studies were performed on different compositions of *i*PP/*s*PP blends, where *s*PP has a low syndiotacticity ([rrrr] = 81%). Combining optical microscopy, rheology, and solid state NMR spectroscopy, the miscibility of the blends was investigated at different scales in the traditionally thought to be "immiscible" *i*PP/*s*PP blends. For the composition of *i*PP/*s*PP (90/10) blend, it shows to be miscible in the melt, and furthermore, the existence of intermolecular chain interactions between *s*PP and *i*PP components was detected in the solid state.

Keywords: *i*PP/*s*PP blends; Miscibility; Optical microscopy; Rheology; Solid state NMR spectroscopy.

INTRODUCTION

Due to its crucial influence on both processing conditions and ultimate chemical and physical properties of polymer materials, investigation on the miscibility of polymer blends has attracted much attention over the last several decades[1–4]. Among the polymer blends, that of isotactic polypropylene (*i*PP) and syndiotactic polypropylene (*s*PP), both showing the same chemical repeating units but only differing in tacticity, has provoked particular interests. Blending of *i*PP with *s*PP will either promote the potential application of *s*PP or compensate the disadvantages of *i*PP as a high crystalline polymer. According to earlier investigations[5–12], *s*PP has been found to be immiscible with *i*PP over the whole composition range, and one of the direct proofs to which is that the liquid-liquid phase separation has always been observed in the melt of *i*PP/*s*PP blends. Kressler *et al.*[5] observed neither an *s*PP nor an *i*PP melting temperature depression in the *i*PP/*s*PP blends, indicating that *s*PP and *i*PP are completely immiscible in melt. Thermodynamic incompatibility of the *i*PP/*s*PP blends has also been claimed[6, 7]. Wang *et al.* [12] reported that there is a possibility of partial mixing in the *i*PP/*s*PP blends, which may occur simultaneously during the course of phase separation. The authors supported their hypothesis only by isothermal crystallization study; however, neither other evidences have been provided nor followed work reported.

Despite lots of work being done on phase behavior of the *i*PP/*s*PP blends, their research objectives were mainly concentrated on the *s*PP samples with relatively high syndiotacticity ([rrrr] > 85%). The *i*PP/*s*PP blends with low syndiotacticity of *s*PP have seldom been investigated. The syndiotacticity, however, plays an

---

* This work was supported by the National Natural Science Foundation of China (NSFC) (Nos. 50290090, 20490220 and 10590355). ZW acknowledges the financial support from "One Hundred Young Talents" of the Chinese Academy of Sciences.

**Corresponding author: Du-jin Wang (王笃金), E-mail: djwang@iccas.ac.cn.

Received December 13, 2005; Revised January 20, 2006; Accepted January 26, 2006

important role in the thermodynamic behavior of *i*PP/*s*PP blends. Our previous work has shown that there should be some miscibility in the sample of *i*PP/*s*PP (90/10), based on the measurements of mechanical properties[13]. Here we report an experimental study of the miscibility performed on the *i*PP/*s*PP blends. The *s*PP sample used in this study is of lower syndiotacticity, compared with that of *s*PP samples in previously reported *i*PP/*s*PP blending systems[5−10]. The particular objective of this communication is to characterize the miscibility of *i*PP/*s*PP blends by using different techniques at different scales, and to re-evaluate the miscibility of this "immiscible" *i*PP/*s*PP blend.

EXPERIMENTAL

Materials and Sample Preparation

In order to guarantee that the *i*PP used in this work has the same melt flow index as *s*PP sample (10.0 g/min), the *i*PP pellets (PP2401, Yansan Petrochemical Company, China) were chemically degraded by using peroxide[14]. The average molecular weight of the degraded *i*PP was determined to be $M_w = 1.77 \times 10^5$ g/mol with a polydispersity of $M_w/M_n = 3.86$. The *s*PP sample was supplied by Atofina Company with $M_w = 8.59 \times 10^4$ g/mol and a polydispersity of $M_w/M_n = 4.10$. The microstructure of the *s*PP chains, determined by ^{13}C-NMR spectroscopy, was characterized to be a fraction of the fully syndiotactic pentads [rrrr] of 81%. The detailed ^{13}C-NMR assignment was performed by using the Suter and Flory rotational isomeric state model of polypropylene[15]. The defects are mainly isotactic defects, *i.e.*, *mm* triads with [rmmr] = 11% and *m* dyads with [rrmr] = 9%. From the practical point of view, the *i*PP/*s*PP blends (90/10, 85/15, 70/30, 50/50, 30/70, 10/90, *W/W*) were prepared using a Haake-RC90 twin-screw extruder with four temperature zones, ranging from 150°C to 190°C along the extruder barrel. For comparison, *i*PP/*s*PP blends were also prepared by precipitation from 1.5 wt% xylene solutions and were also characterized with optical microscope.

Hot-Stage Optical Microscopy

An Olympus optical microscope equipped with phase contrast optics was used to observe the melt morphology of *i*PP/*s*PP blends at 180°C, 190°C and 200°C, respectively, and similar results were observed. In this report, only the experimental results at 200°C were displayed.

Rheology

The storage modulus, G', and loss modulus, G'', were measured as functions of angular frequency (ω) on an Advanced Rheometric Expansion System (2ARES-9A) with the parallel plate geometry of 25 mm in diameter covering the frequency range ω from 0.05 to 100 rad/s. Three experimental temperatures were chosen, *i.e.*, 180°C, 190°C and 200°C. All blends were compressed at 10 MPa and 200°C to form films with a diameter of 25 mm and a thickness of 1.5 mm. The strain amplitude (γ_0) was kept at 0.1 to ensure linear viscoelastic behavior for the blends. Similar results were obtained for different experimental temperatures, so only the representative results at 180°C are shown in this report.

Solid-State NMR Spectroscopy

NMR measurements with cross polarization (^{13}C-CP MAS) were performed on a Bruker DSX 300 spectrometer operating at a magnetic field of 7.05 T and spinning speed of 4 kHz[16, 17]. The sample of *s*PP, *i*PP and *i*PP/*s*PP blends were first melted at 200°C for 5 min and then compressed into films with a thickness of 0.5 mm, followed by quenching to room temperature. The 90° pulse length is 5 μs for both ^{1}H- and ^{13}C-NMR spectra, and the contact time for the cross-polarization process is 1 ms at a recycle delay time of 2 s. All spectra were referenced to adamantane ($\delta = 38.5$) as the chemical shift reference.

RESULTS AND DISCUSSION

Miscibility of the Melt

The basic concept of miscibility for polymer blends under optical microscope is that once phase separation occurs, the phase domain sizes will become larger and larger with extension of time. Therefore, for immiscible polymer blends even with a very small amount of one component (generally less than 10 wt%), phase separation will eventually be observable under optical microscope after long time annealing. Figure 1 shows the micromorphology of *i*PP/*s*PP (90/10) and *i*PP/*s*PP (50/50) blends in the molten state at 200°C. The *i*PP/*s*PP (50/50) blend shows bicontinuous structures, characteristic of phase separation after heating for 5 min, while the *i*PP/*s*PP (90/10) blend does not show obvious phase-separated domains even after 30 h, indicating the characteristic of miscibility. The *i*PP/*s*PP (70/30) and *i*PP/*s*PP (30/70) blends also show typical bicontinuous structure (not shown here), resulting from the spinodal decomposition within several minutes. The *i*PP/*s*PP (10/90) blend, which has the symmetrical composition as *i*PP/*s*PP (90/10), shows evident phenomenon of phase separation after annealed 5 h. So, we can say that, for *i*PP/*s*PP (90/10) blend, the time scale of 30 h is long enough for the occurrence of phase separation, supposing the *i*PP/*s*PP blend of this composition is immiscible. Our experimental results indicate that the *i*PP/*s*PP blends show an upper critical solution temperature behavior, *i.e.*, with temperature increasing, the occurrence of phase separation requires longer induction time. Similar results were obtained from the solution mixing system for *i*PP/*s*PP blends, except that relative slow phase separation occurs in the melt. For *i*PP/*s*PP (90/10), phase separation phenomenon still could not be observed.

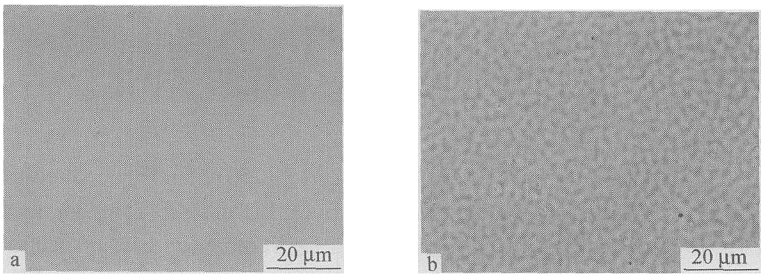

Fig. 1 Micromorphology of *i*PP/*s*PP melts keeping at 200°C for 5 min and 30 h, respectively
(a) *i*PP/*s*PP (90/10), 30 h; (b) *i*PP/*s*PP (50/50), 5 min

Since phase separation could not be observed for *i*PP/*s*PP (90/10) blend in the experimental temperature range, therefore, an intermediate composition between 90/10 and 80/20, *i.e.*, *i*PP/*s*PP (85/15) was chosen to clarify the phase separation boundary by means of remixing experiment. After annealing at a relatively low temperature (220°C) for 370 min to get a phase separation structure, it was subsequently heated to a higher temperature (240°C), for 620 min, and remixing phenomenon was observed. This means that the phase boundary of *i*PP/*s*PP (85/15) only exists between 220 and 240°C. In this case, the phase separation should be neither deep nor coarse, so that it is not very difficult to observe this remixing phenomenon. However, if the phase separation is very fast and deep, it becomes very difficult to observe this remixing process in a reasonable period of time. Furthermore, as *s*PP content exceeds 20 wt%, the remixing temperature becomes too high to be used for detecting the phase separation boundary.

To reconfirm the miscibility in *i*PP/*s*PP blends, the rheological measurement was performed, because rheological parameters are believed to be sensitive to the morphological changes during the phase separation[18]. It has been found that oscillatory shear at small amplitude in the terminal region has little effect on the morphological development, and thus avoids the shear-induced mixing[19]. This makes the rheological measurement comparable to other effective static techniques for studying liquid-liquid phase separation, such as small-angle neutron scattering and turbidity observations[20]. Oscillatory measurements at small amplitude can commonly be applied to probe the miscibility in the polymer blends. Many rules have been used in rheological studies to determine miscibility of the polymer blends, such as time-temperature superposition principle, Han curve, Cole-Cole plot, *etc*. Among them, Cole-Cole plot or plot of *Eta″* versus *Eta′*, *i.e.*, plot of η'' versus η' is thought to be a useful tool, which shows more sensitivity than the classical frequency dependence of the material functions relating to miscibility and phase separation in polymer blends[20–26]. Smooth, semicircular shaped Cole-Cole plots imply miscibility, while the appearance of tailing in the plot indicates the formation of new phases, or the occurrence of phase separation[26]. The rheological results obtained during dynamic shear for the *i*PP/*s*PP blends are presented in Fig. 2. All the blends except the *i*PP/*s*PP (90/10) system show obvious tailing on the Cole-Cole plots, suggesting that there might truly exist miscibility in the *i*PP/*s*PP (90/10) blend.

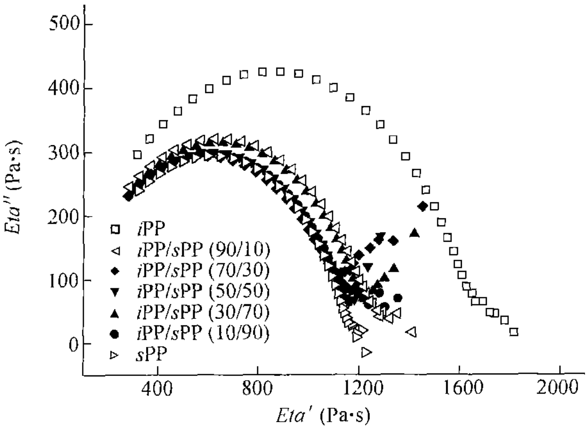

Fig. 2 Cole-Cole plots for the *i*PP/*s*PP blends at test temperature of 180°C
The angular frequency was 0.05–100 rad/s, and the strain amplitude was 10%

Miscibility in the Solid State

Figure 3 shows the ^{13}C-CP MAS spectra of *i*PP/*s*PP (90/10) and (50/50) blends quenched from melt, and they are compared with that of superposition of individual spectra of pure *i*PP and *s*PP components. A frequency shift can be found for the spectra of the *i*PP/*s*PP (90/10) blend in Fig. 3. Subtraction of the spectra of pure *i*PP and *s*PP from the *i*PP/*s*PP (90/10) blend spectrum results in three minor signals, which are similar to that of *i*PP but the remaining signals show frequency shifts from those of pure *i*PP, *i.e.*, the frequency shift for methylene resonance is about $\delta = 0.4$. On the contrary, in the case of the *i*PP/*s*PP (50/50) blend showing strong phase-separation, the ^{13}C-CP MAS spectrum is almost the same as that of superposition of the individual spectra of the pure *i*PP and *s*PP components. However, subtraction of the spectrum of pure *s*PP from that of the *i*PP/*s*PP (50/50) blend also results in additional contributions beside the *i*PP and *s*PP signals. The chemical shifts of

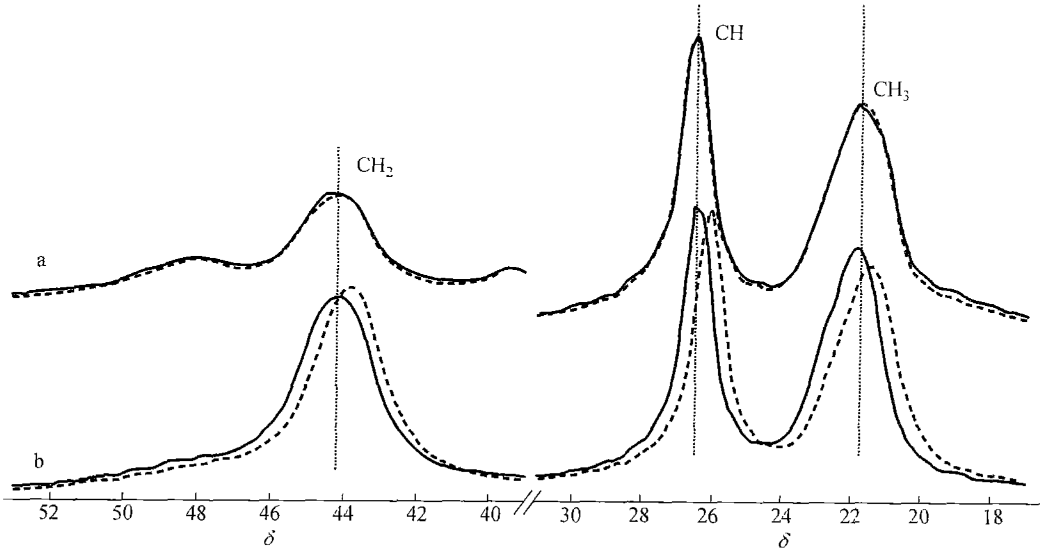

Fig. 3 ^{13}C-CP MAS NMR spectra of the resonances of CH, CH$_2$ and CH$_3$ groups in the *i*PP/*s*PP blends or simple mixtures: (a) 50/50 and (b) 90/10
The solid line is the superposition of measured spectra of pure *i*PP and *s*PP components, and the dotted line corresponds to the measured spectra of the *i*PP/*s*PP blends.

*i*PP/*s*PP (50/50) are consistent with those of the *i*PP/*s*PP (90/10) blend, though with weak intensities. All the above results indicate that an intermolecular chain interaction exists between *s*PP and *i*PP components at solid state after quenching from the melt. Such an interaction becomes more evident as *i*PP quickly crystallizes from the blended melt, with the minor *s*PP component still uniformly dispersing in *i*PP domains. Therefore, a big interface between *i*PP and *s*PP components is obtained, providing strong intermolecular interactions. This interaction is helpful to improve the miscibility between *i*PP and *s*PP in the blends, especially in the blend with small amount of *s*PP component, *e.g.*, the *i*PP/*s*PP (90/10) blend.

CONCLUSIONS

Miscibility in the *i*PP/*s*PP blends with different compositions has been investigated by combinational studies of optical microscopy, rheological character, as well as solid state NMR spectroscopy. It was found that most of the blends with different compositions are immiscible, *i.e.*, phase separation occurred in the melt. However, for the *i*PP/*s*PP (90/10) blend, no phase separation in melt was observed even after 30 h annealing at 200°C. Furthermore, the miscibility of *i*PP/*s*PP (90/10) blend at solid state was confirmed by the result of solid state NMR spectroscopy. The existence of intermolecular interactions between *s*PP and *i*PP components is helpful to improve the miscibility of the *i*PP/*s*PP blends, especially with less amount of *s*PP.

REFERENCES

1 Lee, S.C. and Woo, E.M., Macromol. Rapid. Commun., 2000, 21: 1196

2 Larson, R.G., Rheol. Acta, 1992, 31: 497

3 Huang, C.I., Chang, C.P., Shimizu, K. and Han, C.C., J. Polym. Sci., Part B: Polym. Phys., 2004, 42: 2995

4 Fukai, T., Yang, J.C., Kyu, T., Cheng, S.Z.D., Lee, S.K., Hsu, S.L.C. and Harris, F.W., Polymer, 1992, 33: 3621

5 Thomann, R., Kressler, J., Setz, S., Wang, C. and Mülhaupt, R., Polymer, 1996, 37: 2627

6 Thomann, R., Kressler, J., Sets, S., Wang, C. and Mülhaupt, R., Polymer, 1996, 37: 2635

7 Phillips, R.A., J. Polym. Sci., Part B: Polym. Phys., 2000, 38: 1947

8 Silvestri, R. and Sgarzi, P., Polymer, 1998, 39: 5871

9 Clancy, T.C., Pütz, M., Weinhold, J.D., Curro, J.G. and Mattice, W.L., Macromolecules, 2000, 33: 9452

10 Xu, G.Q., Clancy, T.C. and Mattice, W.L., Macromolecules, 2000, 35: 3309

11 Eckstein, A., Suhm, J., Friedrich, C., Maier, R.D., Sassmannshausen, J., Bochmann, M. and Mülhaupt, R., Macromolecules, 1998, 31: 1335

12 Wang, Z.G., Phillips, R.A. and Hsiao, B.S., J. Polym. Sci., Part B: Polym. Phys., 2001, 39: 1876

13 Zhang, X.Q., Zhao, Y., Wang, Z.G., Zheng, C.X., Dong, X., Su, Z.Q., Sun, P.Y., Wang, D.J., Han, C.C. and Xu, D.F., Polymer, 2005, 46: 5956

14 Machado, A.V., Maia, J.M., Canevarolo, S.V. and Covas, J.A., J. Appl. Polym. Sci., 2004, 91: 2711

15 Suter, U.W. and Flory, P.J., Macromolecules, 1975, 8: 765

16 Komorowski, R.A., "High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk", VCH Publishers Inc., New York, 1986, p.177

17 Schmidt-Rohr, K. and Spiess, H.W., "Multidimensional Solid-State NMR and Polymers", Academic Press, London, 1994, p.58

18 Polios, I.S., Soliman, M., Lee, C., Gido, S.P., Schmidt-Rohr, K. and Winter, H.H., Macromolecules, 1997, 30: 4470

19 Larson, R.G., Rheol. Acta, 1992; 31: 497

20 Nesarikar, A.R., Macromolecules, 1995, 28: 7202

21 Chaung, C.I. and Han, C.D., J. Appl. Polym. Sci., 1984, 29: 2205

22 Scholz, P., Froelich, C. and Muller, R., J. Rheol., 1989, 33: 481

23 Cho, K., Lee, B.H., Hwang, K.M., Lee, S. and Choe, S., Polym. Eng. Sci., 1989, 29: 1969

24 Muñoz-Escalona, A., Lafuente, P., Vega, J.F., Munoz, M.E. and Santamaria, A., Polymer, 1997, 38: 589

25 Chopra, D., Kontopoulou, M., Vlassopoulos, D. and Hatzikiriakos, S.G., Rheol. Acta, 2002, 41: 10

26 Ajji, A., Choplin, L. and Prudhomme, R.E., J. Polym. Sci., Part B: Polym. Phys., 1991, 29: 1573