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"Cutting effect" of organoclay platelets in compatibilizing immiscible polypropylene/polystyrene blends

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Abstract: In this work, polypropylene (PP)/polystyrene (PS) blends with different organoclay concentrations were prepared via melt compounding. Differing from the results of previous reports, the organoclay platelets are mostly located in the dispersed PS phase instead of the interface. The dimensions of the dispersed PS droplets are greatly reduced and apparent compatibilization effect still exists, which cannot be explained by the traditional compatibilization mechanism. A novel compatibilization mechanism, "cutting" to apparently compatibilize the immiscible PP/PS blends was proposed. The organoclay platelets tend to form a special "knife-like structure" in the PS domain under the shear stress of the continuous PP phase during compounding. The "clay knife" can split the dispersed PS domain apart and lead to the dramatic reduction of the dispersed domain size.

Key words: Compatibilization, Organoclay, Polymer blends, Polypropylene (PP), Polystyrene (PS)
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INTRODUCTION

Nanoscale fillers, especially organically modified clay (organoclay), have recently evoked intense research interests as a novel compatibilizer for several types of immiscible polymer blends by effectively reducing the domain size of the dispersed phases with very small concentration (Wang *et al.*, 2003; Khatua *et al.*, 2004; Sinha Ray and Bousmina, 2005a; Si *et al.*, 2006).

Researchers have proposed several explanations on the compatibilizing effect of organoclay to immiscible polymer blends. The generally accepted explanations are described as follows: (1) Suppression of phase coalescence and promotion of phase breakup. When the clay platelets disperse in the continuous phase of polymer blends, the high aspect ratio of the clay platelets can prevent the coalescence of the dispersed domains during melt compounding. Moreover, the addition of organoclay can increase the viscosity of the continuous phase, and then prevent the coagulation of the domains and the growth of the domain size (Khatua *et al.*, 2004; Li and Shimizu, 2004; Yoo *et al.*, 2005; Zou *et al.*, 2006; Lee *et al.*, 2006; Kontopoulou *et al.*, 2007). On the other hand, the viscosity ratio between the continuous phase and dispersed phase is dramatically changed due to the addition of clay. As a result, the change of the viscosity ratio mentioned above can significantly influence the deformability and then the breakup of the droplets (Dharaiya and Jana, 2005; Li and Shimizu, 2005; Hong *et al.*, 2006; Kontopoulou *et al.*, 2007); (2) Interfacial interaction. When the clay platelets are located in the interface of polymer blends, firstly, the polymer chains in the corresponding blends can be physically absorbed on the clay platelets due to their large specific surface areas during melt compounding (Nesterov and Lipatov, 1999; Nesterov *et al.*, 2001; Lipatov *et al.*, 2002). Thus, the clay platelets migrate to the interface and act as an effective graft copolymer

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which can reduce the interfacial tension (Wang *et al.*, 2003; Yoo *et al.*, 2005; Sinha Ray *et al.*, 2007); Secondly, the clay platelets locating at the interface can react and chemically bond with the components in polymer blends so as to act as an in-situ compatibilizer (Sinha Ray *et al.*, 2004; Sinha Ray and Bousmina, 2005a; 2005b; Chow *et al.*, 2005; Si *et al.*, 2006; Gonzalez *et al.*, 2006; Su *et al.*, 2007; Fang *et al.*, 2007).

This work aims to investigate the compatibilization mechanism of organoclay when it is located in the dispersed phase of immiscible polymer blends. For this purpose, polypropylene (PP)/polystyrene (PS) and PP/PS/organoclay blends were prepared via melt blending. The morphologies of PP/PS/organoclay immiscible blends are studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs.

EXPERIMENT

Materials

The PP (T300, isotactic homopolymer, M_w=333000 and M_n=80600) used in this study was purchased from Sinopec Shanghai Petrochemical Co., China. The PS (666 D, M_w=310000 and M_n=87000) was obtained from Yanshan Petrochemical Co., China. The commercial organoclay, provided by Zhejiang Huate Co., China, was obtained by a cation exchange reaction between Na-montmorillonite (110 meq/100 g cation exchange capacity) and dioctadecyl dimethyl ammonium bromide.

Specimen preparation

PP/PS (80/20, w/w) with different organoclay contents was prepared by melt mixing using an internal mixer (Haake Rheomix 600) at 180 °C with a rotor speed of 60 r/min, and the mixing time was 6 min for each sample. Then the specimens were compression-molded into different shapes required for further characterization.

Characterization

Rheological measurements were performed using an ARES© rotational rheometer (Rheometrics, Inc.) with a parallel plates geometry (plate diameter=25 mm, gap=1.14 mm). Dynamic frequency sweep tests were executed in the frequency range of 0.01~100 rad/s. The temperature for testing was 180 °C. The strain sweeps were first performed before dynamic testing to ensure that the frequency sweeps were within the linear viscoelastic and stable region.

Phase morphologies were investigated by SEM using a Hitachi S-570 electron microscope operated at 20 kV. The specimens were cryo-fractured from liquid nitrogen, and then etched with toluene for 24 h at about 40 °C in order to remove the PS component. The resulting fracture surfaces were coated with a layer of gold to avoid electrical charging and to increase image contrast.

The TEM were obtained with a JEM-1200EX electron microscope by examining the dispersion and intercalation of clay in PP/PS blends. The specimens were ultrathin-sectioned using a microtome equipped with a diamond knife. The sections (200~300 nm in thickness) were cut from a piece of about 1 mm×1 mm, and they were collected in a trough filled with water and placed on a 200 meshes copper grid.

RESULTS AND DISCUSSION

Fig.1 shows the phase morphologies of PP/PS (80/20, w/w) blends with different organoclay contents. The SEM typical morphology of the virgin PP/PS blend shown in Fig.1a clearly demonstrates a two-phase morphology, where hollow domains indicate the extracted PS phase. Compared to the virgin PP/PS blends, there is little change on the dispersed domain size when the concentration of organoclay is lower than 1 phr (per hundred parts of resin). However, a rapid and then gradual decrease of the dispersed domain size is observed with further increasing of the concentration of organoclay, as shown in Figs.1b~1e. To quantitatively analyze the morphology of different samples, the number-average domain diameter D_n and the volume-to-surface area average domain diameter D_{vs} are calculated with image analyzing software (Image-Pro, Media Cybernetics Inc.). The long and short axis diameters of each domain in the SEM micrographs are measured and the arithmetic value of these two values (D_i=(D_{1i}+D_{2i})/2) is determined. Then, D_n and D_{vs} are obtained by using the following equations,

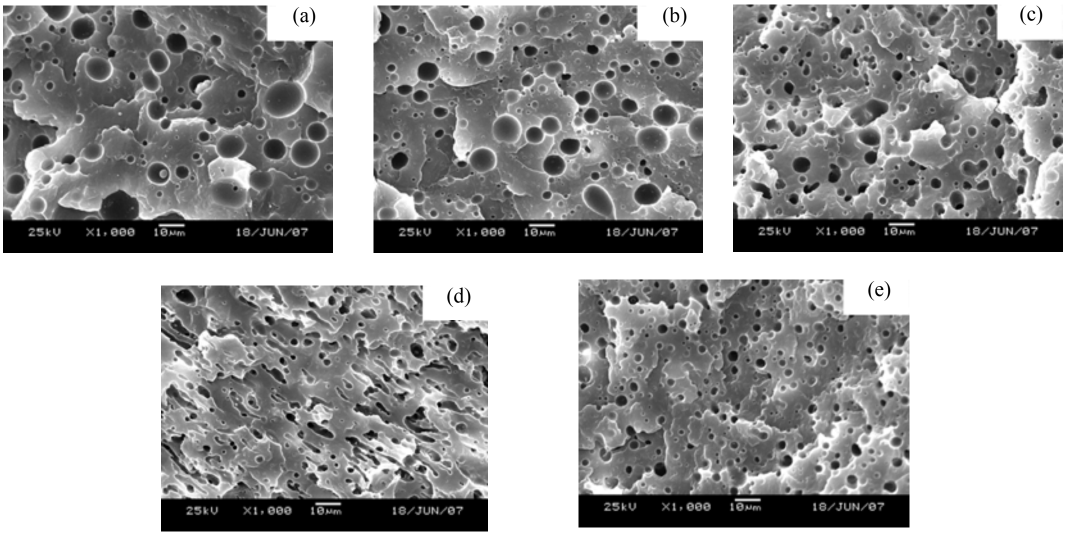

Fig.1 SEM micrographs of PP/PS (80/20, w/w) blends with various amounts of the organoclay. The concentration (phr) of the organoclay is (a) 0, (b) 1, (c) 2, (d) 4 and (e) 8, respectively

$$D_{\mathrm{n}}=\sum(D_i/N), \tag{1}$$

$$D_{\mathrm{vs}}=\sum D_i^3 \Big/ \sum D_i^2, \tag{2}$$

where N is the total number of disperse domains (over 200 droplets) observed in the SEM micrograph (Hong *et al*., 2006). On the basis of SEM micrograph, the plots of D_{n} and D_{vs} vs the concentration of the organoclay, are shown in Fig.2. From the results of Fig.2, at 1.0 phr organoclay loading D_{n} and D_{vs} are both slightly reduced, from 5.7, 9.2 μm to 5.5, 7.9 μm, respectively. However, D_{n} and D_{vs} are dramatically reduced when the clay content is higher than 1.0 phr and the rate of reduction becomes slow with further increasing of clay concentration. It is obvious that the organoclay does play a significant role in reducing the domain size of dispersed PS phase in the PP/PS blends. These phenomena are similar to what have been reported in the same immiscible blends system (Wang *et al*., 2003; Sinha Ray *et al*., 2004).

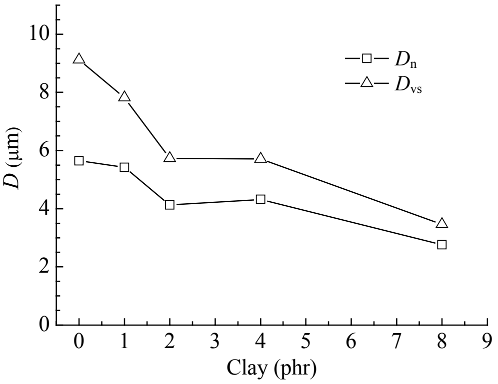

Fig.2 D_{n} and D_{vs} of the PP/PS (80/20, w/w) blends vs the amounts of the organoclay

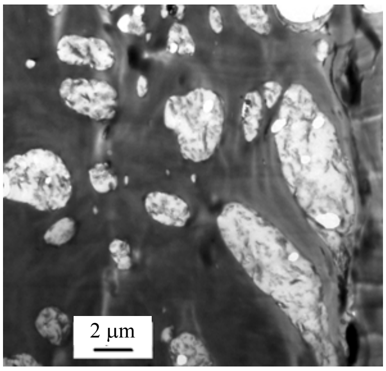

Fig.3 TEM micrograph of PP/PS (80/20, w/w) blends with 4 phr organoclay

The dispersion and location of organoclay in the polymer blends have a significant influence on the morphological development of the blends as well as the compatibilization mechanism. TEM is considered to be a routine and effective method to gain more insight into the dispersion and location of organoclay in the polymer blends. The TEM image is shown in Fig.3. As a result, the continuous PP matrix (dark region) and the dispersed PS domains (white region) in the immiscible PP/PS blends can be clearly observed without using a phase contrast-staining agent. The measured PS domain size is in good agreement with that obtained from the SEM observation. Besides, the organoclay platelets (dark lines or platelets) are easily visualized in the TEM micrograph and are seen to exclusively disperse in the PS domains. Possibly due to the higher viscosity and the higher surface energy under our processing condition, the PS component has a stronger affinity for clay surfaces than the PP component. This result is obviously different from what have been reported (Wang *et al.*, 2003; Sinha Ray *et al.*, 2004) in the same immiscible blends system in which most of the clay platelets are located at the interface. The clay platelets at the interface act as a graft copolymer which can efficiently reduce the interfacial tension and enhance the compatibilization of immiscible polymer blends. In our research, the absence of organoclay at the interface in the blends is experimental evidence against this possible compatibilization mechanism of interfacial interaction.

Another mechanism governing compatibilization effect of organoclay in immiscible polymer blends can be attributed to the alternation of viscosity ratio between the two components of polymer blends (Li and Shimizu, 2004; Hong *et al.*, 2006). Due to the different affinity between the organoclay and various components in polymer blends, the viscosity ratio of two components in the blends can be significantly changed with the addition of organoclay. It should be pointed out that the ultimate domain size in the blend is determined by the balance between two opposing factors: droplet breakup and coalescence. The preferential location of clay in continuous phase can significantly improve its viscosity and prevent the coalescence of the dispersed phase. Moreover, network structure can be formed with the increase of clay concentration due to the large specific area of clay platelets (Galgali *et al.*, 2001; Ren *et al.*, 2003). The network structure of clay has been proved to influence the deformability and breakup of the droplet.

To evaluate the effect of clay on the viscosity of PP/PS blends, the complex viscosities η^* of neat PP, PS and PS/organoclay were measured by ARES and the results were shown in Fig.4. It is seen that η^* of the PS matrix is slightly higher than that of the PP matrix during the whole frequency range. After introducing the organoclay (4 phr) into the PP/PS (80/20, w/w) blends, the organoclay platelets selectively locate in the dispersed PS domain, as shown in Fig.3. Therefore, it means that the modified domain is actually consisted of PS/organoclay (20/4, w/w). To investigate the actual influence of organoclay on the viscosity of the PS domain, the rheological property of PS/organoclay (100/20, w/w) is carried out. It is clear from the curves that the complex viscosity of the PS/organoclay (20/4, w/w) is much higher than that of PS matrix. The presence of organoclay in the dispersed phase results in the reduction of the ability to break up the dispersed domain and causes a higher tendency to coalescence.

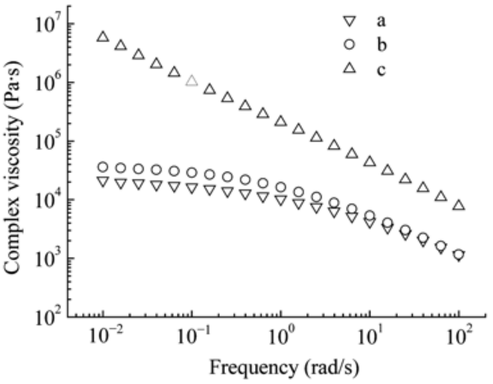

Fig.4 Complex viscosity (η^*) vs frequency (ω) at 180 °C. (a) PP; (b) PS; (c) PS/organoclay (20/4, w/w)

Other research groups attribute the compatibilization effect to the exfoliated or well-dispersed organoclay in the continuous polymer matrix, which may exert significant effects on the coalescence of dispersed domain during melt mixing. Unfortunately, almost all of the organoclay platelets disperse in the dispersed PS phase in our work. Under such situation, dispersed PS domain with high viscosity can easily be coalesced since there are no discernible organoclay platelets in the PP matrix. Therefore, we can conclude that the organoclay platelets locating inside the dispersed domains do not effectively act as a barrier to the coalescence of the dispersed domains.

From the results of TEM and rheological measurement, we can conclude that the apparent compatibilization effect of organoclay on the PP/PS blends in this study cannot be explained by traditional mechanisms. Therefore, another compatibilization mechanism must exist for PP/PS/organoclay systems.

Although many efforts have been made to explore the mechanism of the apparent compatibilization effect of the organoclay, the present mechanism cannot explain all the phenomena. Due to the appearance of irregular domain particles in the SEM micrograph of PP/PS/organoclay (80/20/4, w/w/w) system, a detailed TEM analysis is taken and the results are shown in Fig.5. Interestingly, a series of images are observed to illustrate the whole process of evolution and development for the dispersed PS phase with the presence of organoclay. It is observed that some organoclay platelets no longer homogenously disperse in the PS domain but migrate together forming a "clay knife" which "splits" the dispersed PS domains apart.

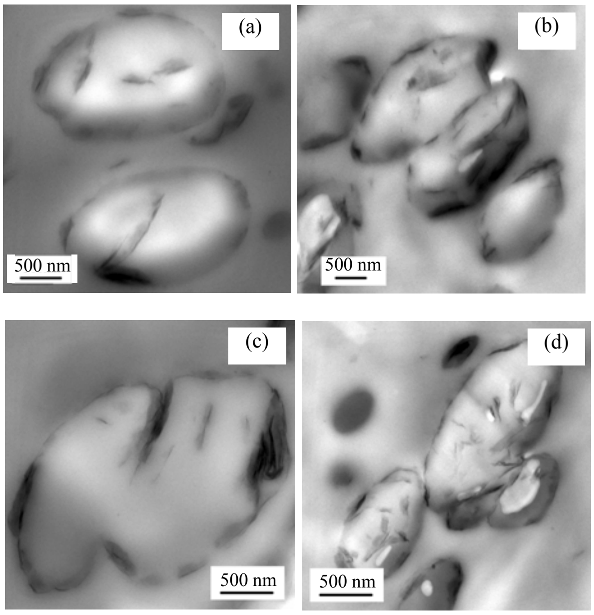

Fig.5 (a)~(d) showing a series of TEM micrographs of morphologies evolution of PP/PS blends (80/20, w/w) with 4 phr organoclay

Based on the TEM images, the "cutting" process of organoclay to apparently compatibilize the PP/PS blends can be schematically illustrated with Fig.6 and described as follows. During the first stage, when compounded with the immiscible PP/PS blends, the organoclay is exclusively and homogenously dispersed in the PS domain due to the higher polarity and viscosity of PS phase, as shown in Fig.6a. The amount of organoclay platelets dispersed in the PS domains exceeds the critical value with the increase of the concentration of organoclay and the extension of compounding time. It is well known that there is electrostatic interaction among clay platelets (Dijkstra *et al*., 1995; Haraguchi *et al*., 2005), because the boundary of clay is generally electronegative and the plane of clay is electropositive. If the amount of clay platelets per unit volume is higher than the critical value of physical cross-linking formation, clay platelets will link together through electrostatic attraction. In order to contain more clay platelets, clay platelets in PS domains aggregate together and form a special "knife-like" structure. As the "clay knife" grows, the location of "clay knife" is prone to focusing the shear stress, resulting in the reduction of the body destroyed energy of the dispersed phase. Thereby, the PS droplets are torn up along the "clay knife" as shown in Fig.6b. With further growing, the "clay knife" is strong enough to completely "split" the dispersed PS domain apart, and the morphology evolution of the domain develops as shown in Fig.6c. In this stage, more dispersed PS droplets are broken up, leading to the dramatically reduction of the domain size. Simultaneously, the boundaries of new forming PS droplets are rich in organoclay platelets. During the final stage, as shown in Fig.6d, the new forming PS droplets spontaneously turn into spherical shape and the organoclay also becomes uniformly dispersed in PS phase under the shear stress. Undergoing those four stages, a whole loop is formed and the dispersed domain size becomes smaller gradually after such loops.

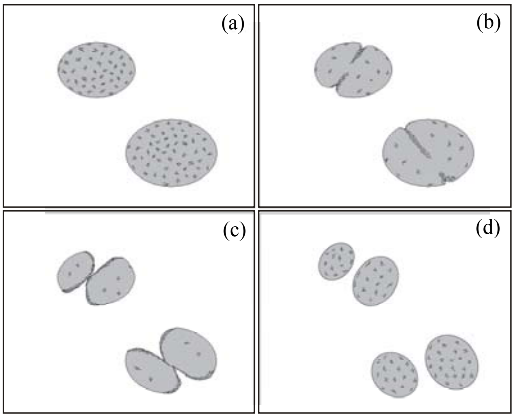

Fig.6 (a)~(d) showing the compatibilization mechanism of organoclay in PP/PS blends

Giving an overview of the entire morphological development of PP/PS/organoclay blends, the organoclay spontaneously arranges in the dispersed domain to form a "clay knife" structure which "splits" the domain apart and then results in the reduction of the disperse domain size. This novel compatibilization mechanism gives a reasonable explanation for the apparent compatibilization effect for the immiscible polymer blends of PP/PS system when the organoclay platelets are located in the dispersed phase. In fact, similar observations have been observed by other researchers (Lee *et al*., 2006), although their work do not involve the explanation of compatibilization mechanism. Their results give an additional proof to the "cutting mechanism" of this study.

CONCLUSION

The present work shows that organoclay plays a significant role in reducing the dispersed domain sizes in typical immiscible PP/PS blends. A novel compatibilization mechanism, "cutting" to apparently compatibilize the immiscible PP/PS blends is proposed when organoclay platelets are located in the dispersed PS phase. The organoclay platelets tend to form a special "knife-like" structure in the PS domain under the shear stress of the continuous PP phase during compounding. The "clay knife" can split the dispersed PS domain apart and leads to the dramatic reduction of the dispersed domain size.

References

Chow, W.S., Ishak, Z.A.M., Karger-Kocsis, J., 2005. Atomic force microscopy study on blend morphology and clay dispersion in polyamide-6/polypropylene/organoclay systems. *Journal of Polymer Science Part B: Polymer Physics*, **43**(10):1198-1204. [doi:10.1002/polb.20408]

Dharaiya, D.P., Jana, S.C., 2005. Nanoclay-induced morphology development in chaotic mixing of immiscible polymers. *Journal of Polymer Science Part B: Polymer Physics*, **43**(24):3638-3651. [doi:10.1002/polb.20657]

Dijkstra, M., Hansen, J.P., Madden, P.A., 1995. Gelation of a clay colloid suspension. *Physical Review Letters*, **75**(11): 2236-2239.

Fang, Z.P., Xu, Y.Z., Tong, L.F., 2007. Effect of clay on the morphology of binary blends of polyamide 6 with high density polyethylene and HDPE-graft-acrylic acid. *Polymer Engineering and Science*, **47**(5):551-559. [doi:10.1002/pen.20675]

Galgali, G., Ramesh, C., Lele, A., 2001. A rheological study on the kinetics of hybrid formation in polypropylene nanocomposites. *Macromolecules*, **34**(4):852-858. [doi:10.1021/ma000565f]

Gonzalez, I., Eguiazabal, J.I., Nazabal, J., 2006. Nanocomposites based on a polyamide 6/maleated styrene-butylene-co-ethylene-styrene blend: Effects of clay loading on morphology and mechanical properties. *European Polymer Journal*, **42**(11):2905-2913. [doi:10.1016/j.eurpolymj.2006.07.014]

Haraguchi, K., Li, H.J., Mastuda, K., Takehisa, T., Elliott. E., 2005. Mechanism of forming organoic/inorganic networking structures during in-situ free-radical polymerization in PNIPA-clay nanocomposite hydrogels. *Macromolecules*, **38**(8):3482-3490. [doi:10.1021/ma047431c]

Hong, J.S., Namkung, H., Ahn, K.H., Lee, S.J., Kim, C., 2006. The role of organically modified layered silicate in the breakup and coalescence of droplets in PBT/PE blends. *Polymer*, **47**(11):3967-3975. [doi:10.1016/j.polymer.2006.03.077]

Khatua, B.B., Lee, D.J., Kim, H.Y., Kim, J.K., 2004. Effect of organoclay platelets on morphology of nylon-6 and poly(ethylene-ran-propylene) rubber blends. *Macromolecules*, **37**(7):2454-2459. [doi:10.1021/ma0352072]

Kontopoulou, M., Liu, Y., Austin, J.R., Parent, J.S., 2007. The dynamics of montmorillonite clay dispersion and morphology development in immiscible ethylene-propylene rubber/polypropylene blends. *Polymer*, **48**(15):4520-4528. [doi:10.1016/j.polymer.2007.05.068]

Lee, M.H., Dan, C.H., Kim, J.H., Cha, J., Kim, S., Hwang, Y., Lee, C.H., 2006. Effect of clay on the morphology and properties of PMMA/poly(styrene-co-acrylonitrile)/clay nanocomposites prepared by melt mixing. *Polymer*, **47**(12):4359-4369. [doi:10.1016/j.polymer.2006.04.003]

Li, Y.J., Shimizu, H., 2004. Novel morphologies of poly(phenylene oxide) (PPO)/polyamide 6 (PA6) blend nanocomposites. *Polymer*, **45**(22):7381-7388. [doi:10.1016/j.polymer.2004.09.018]

Li, Y.J., Shimizu, H., 2005. Co-continuous polyamide 6 (PA6)/acrylonitrile-butadiene-styrene (ABS) nanocomposites. *Macromolecular Rapid Communications*, **26**(9):710-715. [doi:10.1002/marc.200400654]

Lipatov, Y.S., Nesterov, A.E., Ignatova, T.D., Nesterov, D.A., 2002. Effect of polymer-filler surface interactions on the phase separation in polymer blends. *Polymer*, **43**(3):875-880. [doi:10.1016/S0032-3861(01)00632-2]

Nesterov, A.E., Lipatov, Y.S., 1999. Compatibilizing effect of a filler in binary polymer mixtures. *Polymer*, **40**(5): 1347-1349. [doi:10.1016/S0032-3861(98)00277-8]

Nesterov, A.E., Lipatov, Y.S., Ignatova, T.D., 2001. Effect of an interface with solid on the component distribution in separated phases of binary polymer mixtures. *European Polymer Journal*, **37**(2):281-285. [doi:10.1016/S0014-3057(00)00065-3]

Ren, J.X., Casanueva, B.F., Mitchell, C.A., Krishnamoorti, R., 2003. Disorientation kinetics of aligned polymer layered silicate nanocomposites. *Macromolecules*, **36**(11):4188-4194. [doi:10.1021/ma025703a]

Si, M., Araki, T., Ade, H., Kilcoyne, A.L.D., Fisher, R., Sokolov, J.C., Rafailovich, M.H., 2006. Compatibilizing bulk polymer blends by using organoclays. *Macromolecules*, **39**(14):4793-4801. [doi:10.1021/ma060125+]

Sinha Ray, S., Bousmina, M., 2005a. Compatibilization efficiency of organoclay in an immiscible polycarbonate/poly(methyl methacrylate) blend. *Macromolecular Rapid Communications*, **26**(6):450-455. [doi:10.1002/marc.200400586]

Sinha Ray, S., Bousmina, M., 2005b. Effect of organic modification on the compatibilization efficiency of clay in an immiscible polymer blend. *Macromolecular Rapid Communications*, **26**(20):1639-1646. [doi:10.1002/marc.200500447]

Sinha Ray, S., Pouliot, S., Bousmina, M., Utracki, L.A., 2004. Role of organically modified layered silicate as an active interfacial modifier in immiscible polystyrene/polypropylene blends. *Polymer*, **45**(25):8403-8413. [doi:10.1016/j.polymer.2004.10.009]

Sinha Ray, S., Bandyopadhyay, J., Bousmina, M., 2007. Effect of organoclay on the morphology and properties of poly(propylene)/poly[(butylenes succinate)-co-adipate] blends. *Macromolecular Materials and Engineering*, **209**:729-747. [doi:10.1002/mame.200700029]

Su, Q.S., Feng, M., Zhang, S.M., Jiang, J.M., Yang, M.S., 2007. Melt blending of polypropylene-blend-polyamide 6-blend-organoclay systems. *Polymer International*, **56**(1):50-56. [doi:10.1002/pi.2109]

Wang, Y., Zhang, Q., Fu, Q., 2003. Compatibilization of immiscible poly(propylene)/polystyrene blends using clay. *Macromolecular Rapid Communications*, **24**(3):231-235. [doi:10.1002/marc.200390026]

Yoo, Y., Park, C., Lee, S.G., Choi, K.Y., Kim, D.S., Lee, J.H., 2005. Influence of addition of organoclays on morphologies in nylon 6/LLDPE blends. *Macromolecular Chemistry and Physics*, **206**(8):878-884. [doi:10.1002/macp.200400526]

Zou, H., Zhang, Q., Tan, H., Wang, K., Du, R.N., Fu, Q., 2006. Clay locked phase morphology in the PPS/PA66/clay blends during compounding in an internal mixer. *Polymer*, **47**(1):6-11. [doi:10.1016/j.polymer.2005.11.031]