Toughening of Polypropylene–Ethylene Copolymer with Nanosized CaCO$_3$ and Styrene–Butadiene–Styrene

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ABSTRACT: Nanocomposites of nanosized CaCO$_3$/polypropylene–ethylene copolymer (PPE) and nanosized CaCO$_3$/PPE/styrene–butadiene–styrene (SBS) were prepared by using a two-roll mill and a single-screw extruder. By adding CaCO$_3$ nanoparticles into the PPE matrix, the toughness of the matrix substantially improved. At a nanosized CaCO$_3$ content of 12 phr (parts per hundred PPE resin by weight), the impact strength of CaCO$_3$/PPE at room temperature reached 61.6 kJ/m^2, which is 3.02 times that of unfilled PPE matrix. In the nanosized CaCO$_3$/PPE/SBS system, the rubbery phase and filler phase are independently dispersed in the PPE matrix. As a result of the addition of nanosized CaCO$_3$, the viscosity of PPE matrix significantly increased. The increased shear force during compounding continuously breaks down SBS particles, resulting in the reduction of the SBS particle size and improving the dispersion of SBS in the polymer matrix. Thus the toughening effect of SBS on matrix was improved. Simultaneously, the existence of SBS provides the matrix with a good intrinsic toughness, satisfying the condition that nanosized inorganic particles of CaCO$_3$ efficiently toughen the polymer matrix. The synergistic toughening function of nanosized CaCO$_3$ and SBS on PPE matrix was exhibited. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 796–802, 2004

Key words: polypropylene (PP); nanocomposites; mechanical properties; toughness; matrix

INTRODUCTION

The challenge of increasing the impact toughness of polymer has provoked considerable interest. Among various successful toughening methods, rubber and inorganic particles as fillers are the most popular. It is commonly known that use of rubber toughens the polypropylene (PP) matrix. Considerable research has been carried out in the past ten years.[1–6] The main mechanism is that rubber particles can play the role of a craze-inducing agent, and cause shear yielding of the surrounding matrix and terminate the propagation of cracks. Bassani and Pessan[2] studied the toughening effect of styrene–butadiene–styrene (SBS) particles on PP matrix, and achieved some good toughening results of the PP matrix. Yokoyama and Ricco[3] investigated the efficiency of a series of blends aimed at toughening the PP matrix.

It is generally true in rubber toughening that the increase in toughness is achieved at the expense of elastic modulus/stiffness. In inorganic particle toughening, however, the modulus can also be slightly improved. Thus many researchers have studied the toughening of PP with CaCO$_3$[7–13] and other inorganic rigid particles.[14–17] Results indicate that CaCO$_3$ significantly improves the impact strength of PP. The toughening mechanism of PP with CaCO$_3$ and other inorganic rigid particles was also widely reported.[7–17]

Chan et al.[9] used 44 nm diameter CaCO$_3$ particles to noticeably increase the impact toughness of PP matrix because CaCO$_3$ nanoparticles can act as stress concentration sites, which promote cavitation at the particle–polymer interface during loading. Thio et al.[7] studied the toughening of isotactic PP with CaCO$_3$ particles. They found that particle size has a key effect on improvement of impact strength of the PP matrix. In their research, only 0.7 μm diameter particles improved Izod impact energy of the matrix, whereas 0.07 and 3.5 μm diameter particles had either an adverse or no effect on the impact toughness. Zuiderduin et al.[8] also observed that 0.7 μm diameter CaCO$_3$ particles impart a good toughening efficiency for PP matrix. At higher strain the particles debond and this leads to a

change in stress state, and also prevents crazing of the matrix polymer and allows extensive plastic deformation, resulting in large quantities of fracture energy. This finding is the same as that reported by Zhu and Qi.[5] Zhu and Qi used the J-integral method to investigate the notched fracture toughness of $CaCO_3$/PP nanocomposites. Under large stress, matrix and filler will increase the interface debonding at the two poles of the particle, thus forming a cavity. Therefore, the addition of nanosized $CaCO_3$ is advantageous for the shear yielding of PP matrix. Both the shear yielding and interface debonding caused by stress consume a lot of energy, thus substantially improving the impact strength.

The required condition of using a rigid filler to toughen a polymer is that the polymer matrix should have sufficient intrinsic toughness. If a rigid filler is used to toughen a brittle polymer, the rubbery component (SBS) should be added in advance, so that the resulting matrix has ample intrinsic toughness. The method mentioned above activates the synergistic toughening function of the rigid filler and SBS within the polymer matrix.[18–22] Li et al.[18] and Ou et al.[20] found that the incorporation of both inorganic fillers and rubber particles improves both stiffness and toughness of the PP matrix. In the study by Ou et al.,[20] because of the dispersion of the rigid filler in the rubbery phase, a core–shell-structured filler was formed, which improved the compatibility between the filler and the matrix. Wang et al.[21] also found that the rigid filler and rubber particles can synergistically toughen PP. Wu and Xu[22] studied the PP/nano-SiO_2/ethylene propylene diene monomer rubber (EPDM) system and found that SiO_2 and EPDM synergistically improve the toughness, strength, and elastic modulus of PP. When the ratio of PP/nano-SiO2/EPDM is 80/3/20, the apparent synergistic toughening takes effect.

Based on the preceding studies, if inorganic and rubber particles were simultaneously used in the PP, the toughness of the filled PP would be greatly improved, and its modulus would also experience a slight increase. As a result, in this work, we investigate the synergistic toughening by SBS and nanosized $CaCO_3$ in the PPE matrix.

EXPERIMENTAL

Materials

Modified nanosized $CaCO_3$ particles (size 30 nm) were prepared by our research center as reported previously.[23] PPE, the polypropylene copolymer containing some ethylene monomer, was supplied from Ji-Lu Petro. Chem. Co. (Shanghai, China) (Type EPF30R, with melt index of 2–4 g/10 min). SBS, the thermoplastic block copolymer of styrene–butadiene–styrene, was purchased from Yue-yang Petro. Chem. Co.

(Hunan, China) (Type 801; the weight ratio of styrene/butadiene is 30/70).

Preparation of nanocomposites

The PPE/SBS/$CaCO_3$ nanocomposite specimens were prepared by a two-roll mill and a single-screw extruder. First, materials were fed into the two-roll mill at $T = 175°C$. Then, the prepared sample was crushed and fed into the single-screw extruder. The specimen was obtained by injection molding. For comparison, the sample of PPE/$CaCO_3$ was also prepared according to the method above.

Characterization of the nanocomposites

The impact strength of the PPE/SBS/$CaCO_3$ nanocomposite was measured by Charpy pendulum impact testing machines. Tensile and flexural properties were recorded by an Instron (Cantun, OH) universal testing machine. TEM analysis of the nanocomposite was done on a Hitachi (Osaka, Japan) H-800 apparatus after the specimen was dyed by using osmium tetraoxide.

RESULTS AND DISCUSSION

Mechanical properties of $CaCO_3$/PPE/SBS nanocomposites

First, the Charpy impact strength of the $CaCO_3$/PPE nanocomposites, without SBS, at 23°C is shown in Figure 1. It can be observed that the impact toughness of PPE/$CaCO_3$ nanocomposites increases with nanosized $CaCO_3$ content up to 12 phr. When the content of nanosized $CaCO_3$ exceeds 12 phr, the impact strength of the nanocomposites decreases. Generally, if the particles are well dispersed in the polymer matrix, the interparticle distance will be reduced, leading to improved impact strength. Therefore, the decreasing impact strength at nanosized $CaCO_3$ content > 12 phr was probably a result of flocculation of these nanoparticles at high $CaCO_3$ content. At 12 phr nanosized $CaCO_3$ content, the Charpy impact strength of the nanocomposites is 61.6 kJ/m^2, which is 3.02 times that of unfilled matrix. It is apparent that the toughness of PPE was substantially improved by the addition of nanosized $CaCO_3$. The microstructure of dispersed calcium carbonate nanoparticles in the composites matrix is discussed in the next section.

Next, the toughness of the PPE/SBS/$CaCO_3$ nanocomposites was investigated. The results are displayed in Figure 2, where the ratio of PPE/SBS is fixed at 100 : 10. It can be seen that impact strength of PPE/SBS/$CaCO_3$ with nanosized $CaCO_3$ content exhibits the same behavior as that of the PPE/$CaCO_3$
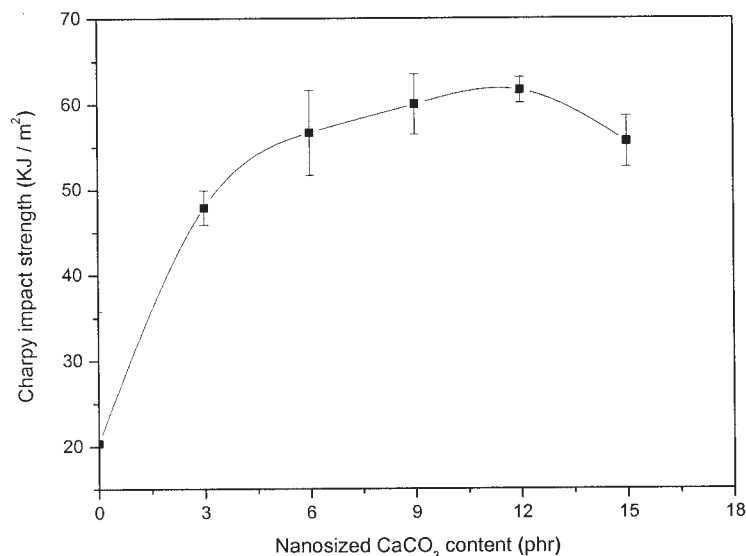
Figure 1 Charpy impact strength of PPE/CaCO$_3$ nanocomposite with nanosized CaCO$_3$ content (phr, parts per hundred of PPE resin by weight).

system, and also reaches a maximum at 12 phr CaCO$_3$ content.

In addition, the Izod impact strength of PPE/SBS/CaCO$_3$ nanocomposites was also measured by an Izod testing machine at room temperature (23°C) and low temperature (−20°C). The results are shown in Table I. One can observe that the PPE/SBS/CaCO$_3$ nanocomposites exhibit similar Izod and Charpy impact strength behavior. At room temperature, the Izod impact strength of CaCO$_3$/PPE nanocomposites, without SBS, can also reach 51.1 kJ/m^2, which is 3.06 times that of unfilled PPE (16.7 kJ/m^2). However, at low temperature (−20°C), both SBS and CaCO$_3$ must be present in PPE for increased toughness. As seen from Table I, the

Izod impact strength of PPE/SBS/CaCO$_3$ nanocomposites reaches 35.0 kJ/m^2, which is 3.43 times that of PPE/SBS nanocomposites, without CaCO$_3$ (10.2 kJ/m^2), at this temperature. Clearly, nanosized CaCO$_3$ has an effective toughening effect on the PPE/SBS system. In fact, there is a synergistic toughening effect of nanosized CaCO$_3$ and SBS on PPE matrix.

The tensile strength of PPE/SBS/CaCO$_3$ nanocomposites was measured, and results are summarized in Figure 3. It can be seen that with the addition of CaCO$_3$, the tensile strength of the nanocomposites undergoes a slight reduction. When the CaCO$_3$ content is at 12 phr, the tensile strength slightly decreases from 20.4 to 19.8 MPa. Moreover, the tensile strength
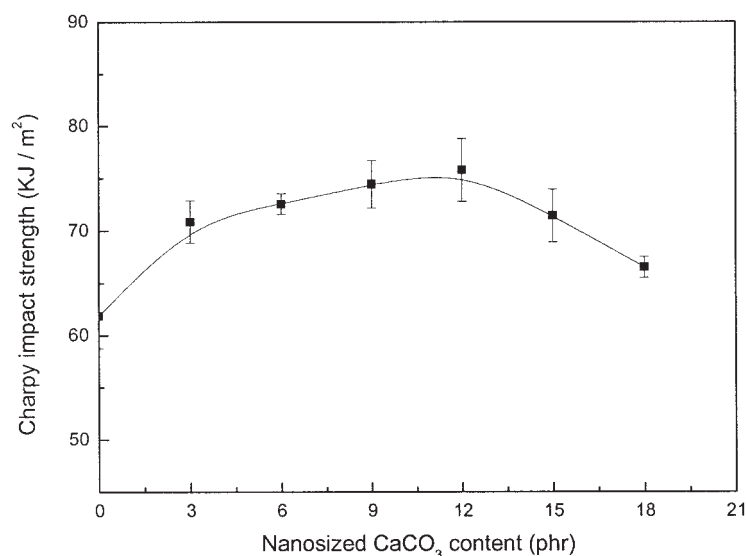

Figure 2 Charpy impact strength of PPE/SBS/CaCO$_3$ nanocomposite with nanosized CaCO$_3$ content (phr).

TABLE I
Izod Impact Strength of PPE/SBS/CaCO₃
Nanocomposites

Main composition			Izod impact strength (kJ/m²)	
PPE	SBS	Nanosized CaCO₃	23°C	−20°C
100	0	0	16.7 ± 0.9	7.6 ± 0.3
100	10	0	47.6 ± 2.4	10.2 ± 0.8
100	0	12	51.1 ± 3.1	8.3 ± 0.6
100	10	12	61.1 ± 3.5	35.0 ± 1.7

of neat PPE is 34 MPa. As is shown in Figure 3, without nanoparticles, the tensile strength of the composite with 8 phr SBS is 20.4 MPa. SBS induces a remarkable decrease in tensile strength by 40%. The strength of plastics obviously decreases by the addition of rubber particles. Theoretically, the nanoparticles should improve the tensile strength of composites; however, the strength is also reduced by the addition of CaCO₃ particles. The major reason is that the interfacial adhesion between matrix and filler is poor because surface treatment on CaCO₃ particles does not improve adhesion but merely serves the purpose of random dispersal of particles.

Figure 4 shows the flexural modulus of PPE/SBS/CaCO₃ nanocomposites with CaCO₃ content. With increasing CaCO₃ content, the flexural modulus of the nanocomposites increases monotonically. At 12 phr CaCO₃ content, the flexural modulus of the nanocomposites is 807 MPa, which is 1.24 times that of PPE/SBS nanocomposites without the addition of CaCO₃. Moreover, its rigidity was also slightly increased. This result meets theoretical expectation.

Micrographs of nanocomposites

For the CaCO₃/PPE nanocomposites, the sample corresponding to the largest Izod impact strength (i.e., 12 phr CaCO₃ contents) was used to observe the degree of dispersion of nanosized CaCO₃ in the polymer matrix. The TEM micrograph is shown in Figure 5, from which it can be seen that the degree of dispersion of nanosized CaCO₃ in the matrix is very good.

Micrographs of the PPE/SBS/CaCO₃ nanocomposites are shown in Figure 6. In Figure 6(a), the large particles with irregular shape are SBS particles. The particles with regular shape and size < 100 nm are nanosized CaCO₃. It can be seen that SBS particles in the PPE/SBS/CaCO₃ nanocomposites are obviously smaller than those in the PPE/SBS system without the addition of CaCO₃ [Fig. 6(b)]. Using the photoanalyzer, we calculated the SBS particle size distribution in the PPE/SBS/CaCO₃ nanocomposites and PPE/SBS system. Figure 7 shows the result. The average size of SBS particles in PPE/SBS/CaCO₃ nanocomposites is 96 nm, whereas that of PPE/SBS system, without the addition of CaCO₃, is 196 nm. Apparently, the addition of CaCO₃ causes the reduction of particle size of the SBS dispersed phase. In the blend process of polymer, because of the sizable specific surface area of nanoparticles, the viscosity of blending becomes larger when extra force was transferred into the rubbery phase by the matrix phase. The increased shear force continuously breaks down SBS particles, leading to a reduction in the size of SBS particles.

As shown in Figure 8, the oval bigger particles are SBS particles and the cubical smaller particles are CaCO₃ particles. It can be observed from Figure 8 that nanosized CaCO₃ particles are mainly distributed in
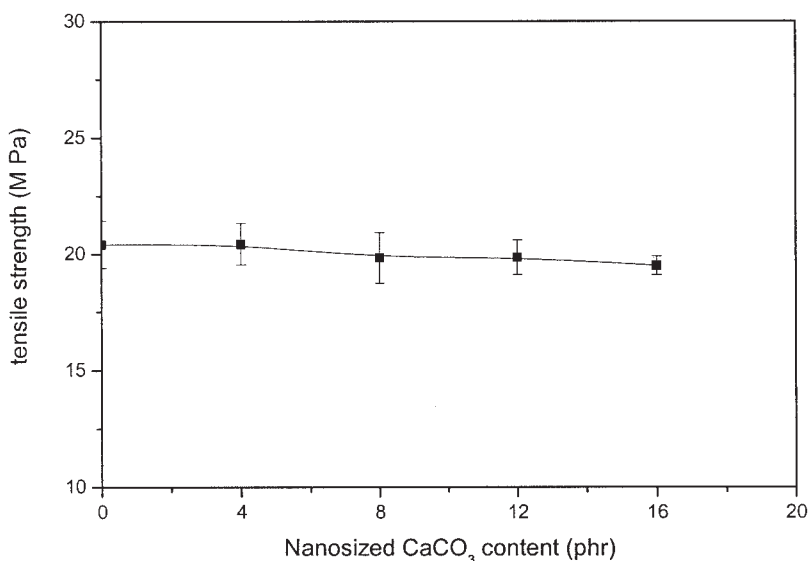

Figure 3 Tensile strength of PPE/SBS/CaCO₃ nanocomposite with nanosized CaCO₃ content (phr).
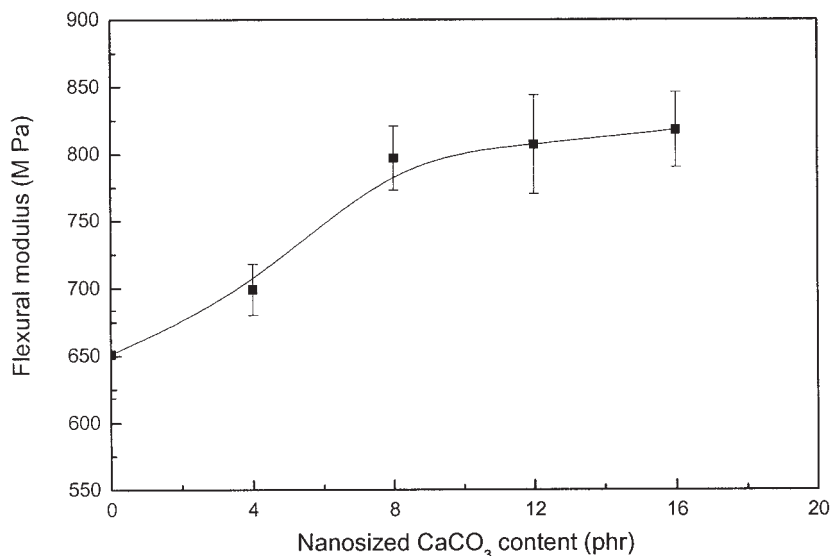
Figure 4 Flexural modulus of PPE/SBS/CaCO₃ nanocomposite with nanosized CaCO₃ content (phr).

the PPE phase and a few CaCO₃ particles are in the rubber phase, thus improving the viscosity of PPE melt phase in the blending process, which satisfactorily explains why nanosized CaCO₃ particles cause a reduction of particle size of the SBS phase.

Synergistic toughening mechanism of nanosized CaCO₃ and SBS on PPE

The well-dispersed nanoparticles and rubber particles also can improve the impact resistance of composites. As mentioned, the dispersion of nanosized CaCO₃ particles in the PPE phase causes an improvement in the degree of dispersion of SBS in the PPE matrix and the reduction of particle size of SBS. The decrease of SBS particle size improves its toughening effect of PPE matrix.[19] The average thickness of matrix ligaments between elastomer particles decreases, which further

improves the toughness of nanocomposites. In turn, the rigid filler effectively toughens the polymer matrix because the matrix is characterized by a good intrinsic toughness. In this study, PPE toughened by SBS provides the appropriate condition of toughness, enabling nanosized CaCO₃ to act as an effective agent. The above analysis elucidates the synergistic toughening mechanism of nanosized CaCO₃ and SBS on the PPE matrix.

As observed at room temperature, nanosized CaCO₃ has a significant toughening effect on PPE without the presence of SBS. This is because PPE has good intrinsic toughness at room temperature. At the lower temperature investigated, however, nanosized CaCO₃ has a more pronounced toughening effect on the PPE/SBS system than on the PPE matrix because impact toughness of PPE is relatively low at this temperature, compared to that of the PPE/SBS system.
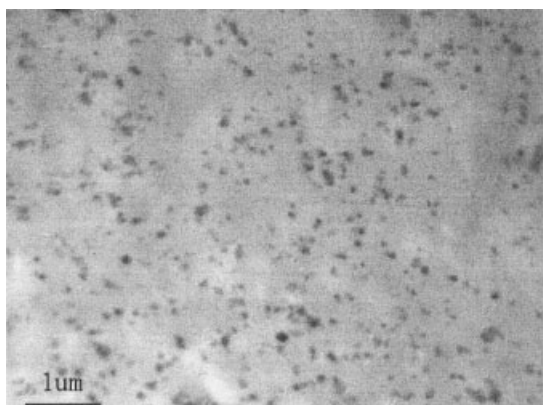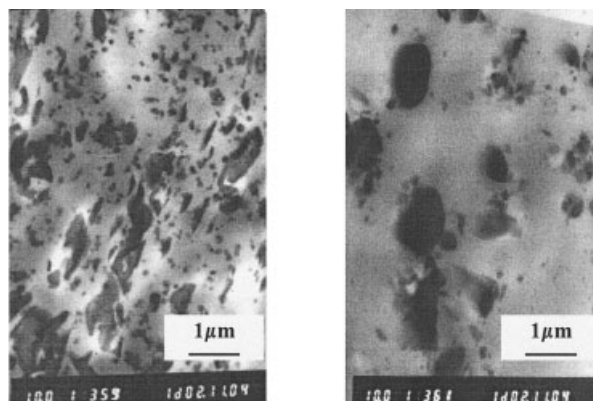

Figure 5 TEM micrograph of CaCO₃/PPE system at nanosized CaCO₃ content of 12 phr.

(a) PPE /SBS/CaCO₃ nanocomposite

(b) PPE /SBS nanocomposite

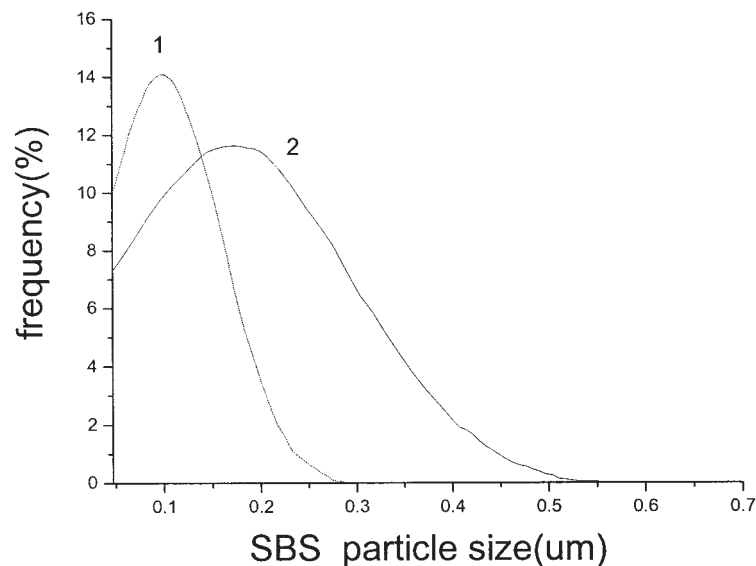**Figure 6** Micrographs of nanocomposites.

Figure 7 Particle size distribution of SBS.

CONCLUSIONS

PPE/CaCO$_3$ and PPE/SBS/CaCO$_3$ nanocomposites were prepared by using a two-roll mill and a single-screw extruder. In this study, nanosized CaCO$_3$ was observed to have considerable dispersion in the PPE matrix. At nanosized CaCO$_3$ content of 12 phr, the impact strength of PPE/CaCO$_3$ composites at room temperature reaches 61.6 kJ/m^2, which is 3.02 times that of the unfilled PPE matrix. Apparently, with the addition of nanosized CaCO$_3$ the toughness of PPE substantially improved. For CaCO$_3$/PPE/SBS nanocomposites, the impact strength at room temperature is 75.8 kJ/m^2, which is 1.23 times that of the clean PPE/SBS system. At a lower temperature of −20°C, the impact strength of nanosized CaCO$_3$/PPE/SBS composites is 35.0 kJ/m^2, which is 3.43 times that of the clean PPE/SBS system. Moreover, although the nanoparticles are well dispersed in the matrix, there is a poor interfacial adhesion between matrix and particles; thus the tensile strength of nanocomposites decreases slightly.
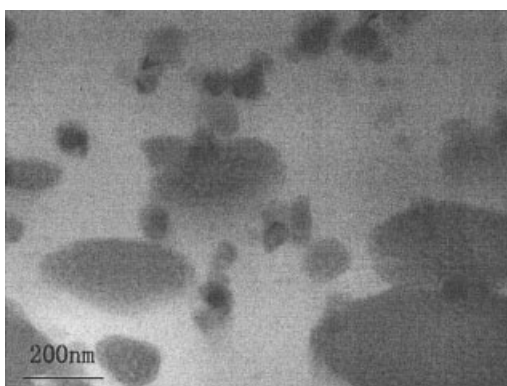
For the PPE/SBS/CaCO$_3$ system, the particle size of SBS is clearly smaller than that of PPE/SBS without nanosized CaCO$_3$. This is because the addition of nanosized CaCO$_3$ particles increases the viscosity of PP melt in the compounding process. The resultant increased shear force continuously shears SBS particles, thus reducing their size. Nanosized CaCO$_3$ has a toughening effect on PPE under the condition that the matrix must have adequate intrinsic toughness. The matrix toughened by SBS can provide the required toughness. In turn, nanosized CaCO$_3$ improves the dispersion of SBS in the matrix and reduces the size of SBS particles, both of which improve the toughening effect of SBS on the polymer matrix: this constitutes the synergistic toughening mechanism of SBS and nanosized CaCO$_3$ on the PPE matrix.

References

1. Liang, J. Z.; Li, R. K. Y. J Appl Polym Sci 2000, 77, 409.
2. Bassani, A.; Pessan, L. A. J Appl Polym Sci 2002, 86, 3466.
3. Yokoyama, Y.; Ricco, T. Polymer 1998, 39, 3675.
4. Chiu, H. T.; Chiu, W. M. Mater Chem Phys 1998, 56, 108.
5. Zhu, X. G.; Qi, Z. N. J Mater Res 1997, 11, 623 (in Chinese).
6. Zhang, M. L.; Liu, Y. Q.; Zhang, X. H.; Gao, J. M.; Huang, F.; Song, Z. H.; Wei, G. S.; Qiao, J. L. Polymer 2002, 43, 5133.
7. Thio, Y. S.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 2002, 43, 3661.

Figure 8 Micrograph of PPE/SBS/CaCO$_3$ nanocomposite.

8. Zuiderduin, W. C.; Westzaan, C.; Huétink, J.; Gaymans, R. J. Polymer 2003, 44, 261.

9. Chan, C. M.; Wu, J. S.; Li, J. X.; Cheung, Y. K. Polymer 2002, 43, 2981.

10. (a) Bartczak, Z.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 1999, 40, 2331; (b) Ibid. 1999, 40, 2347.

11. Wilbrink, M. W.; Argon, A. S.; Cohen, R. E.; Weinberg, M. Polymer 2001, 42, 10155.

12. Wang, X.; Huang, R. China Plast 1999, 13, 22 (in Chinese).

13. Khare, A.; Mitra, A.; Radhakrishnan, S. J Mater Sci 1996, 31, 5691.

14. (a) Lee, J.; Yee, A. F. Polymer 2001, 42, 577; (b) Ibid. 2001, 42, 589.

15. Rong, M. Z.; Zhang, M. Q.; Zheng, Y. X.; Zeng, H. M.; Walter, R.; Friedrich, K. Polymer 2001, 42, 167.

16. Wei, G. X.; Sue, H. J.; Chu, J.; Huang, C. Y.; Gong, K. C. J Mater Sci 2000, 35, 555.

17. Wei, G. X.; Sue, H. J.; Chu, J.; Huang, C.; Gong, K. Polymer 2000, 41, 2947.

18. Li, Y. M.; Wei, G. X.; Sue, H. J. J Mater Sci 2002, 37, 2447.

19. Kim, G. M.; Michler, G. H.; Gahleitner, M.; Mülhaupt, R. Polym Adv Technol 1998, 9, 709.

20. Ou, Y. C.; Guo, T. T.; Fang, X. P.; Yu, Z. Z. J Appl Polym Sci 1999, 74, 2397.

21. Wang, X.; Huang, R.; Jin, C. H.; Chen, H. T.; Pu, Y. N. China Plast 2000, 14, 34 (in Chinese).

22. Wu, W.; Xu, Z. D. Acta Polym Sinica 2000, 1, 99 (in Chinese).

23. Chen, J. F.; Wang, Y. H.; Guo, F.; Wang, X. M.; Zheng, C. Ind Eng Chem Res 2000, 39, 948.