# Study on Isotactic Polypropylene/Zinc-Neutralized Sulfonated Ethylene Propylene Diene Monomer Rubber/CaCO$_3$ Ternary Blends

**Mingjia Zheng, Huilin Li**

*The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu, 610065, China*

**ABSTRACT:** The morphological structure and mechanical properties of isotactic polypropylene (PP)/zinc-neutralized sulfonated ethylene propylene diene monomer rubber (Zn–SEPDM)/CaCO$_3$ blends were studied. PP/Zn–SEPDM/CaCO$_3$ blends were prepared through two different sequences. A: Blending PP with Zn–SEPDM, then adding CaCO$_3$; B: Blending Zn–SEPDM with CaCO$_3$, then adding PP. The blending sequence has substantial influence on the mechanical properties. SEM micrographs and X-ray photo- electron spectrometry indicate that the CaCO$_3$ filler is encapsulated by Zn–SEPDM in those blends prepared through sequence B, which caused an extra increase of impact strength. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1635–1640, 2004

**Key words:** polypropylene; elastomers; fillers; blends; morphology

## INTRODUCTION

It is generally believed that in a polymer/filler composite, if the filler is encapsulated by an elastic outer layer, the elastic outer layer would act like pure rubber particles to toughen the polymers, yet the modulus and the yield strength can also be improved to some extent because of the enhanced rigidity of the dispersed phase and better adhesion of the filler with the matrix.[1–6] Coupling agents are the main choice for treating fillers at present. They have functional groups on one end that can react with the filler to form a chemical bond, whereas the long flexible chains on the other end are compatible with the polymer.

Zinc-neutralized sulfonated ethylene propylene diene monomer rubber (Zn–SEPDM) is one kind of thermoplastic elastomer. In this study it was employed to encapsulate CaCO$_3$ filler mechanically before being blended with isotactic polypropylene (PP). The blends were carefully investigated to decide whether it is an effective way to obtain some materials that have both good stiffness and toughness.

## EXPERIMENTAL

### Materials

EPDM: EP24 (Japan), propylene content 43%; iodine value 15 g/100 g rubber; light CaCO$_3$: 300 mesh (China); PP: 1300 (China), MI 1.5 g/10 min.

### Sample preparation

#### Preparation of Zn–SEPDM

Acetyl sulfonate was added to a 5 wt % EPDM solution of cyclohexane at room temperature. The sulfonating reaction was terminated by ethyl alcohol after 30 min, then the ageing-resistant agent was added. The zinc acetate was added to neutralize H–SEPDM and Zn–SEPDM was produced. Finally, the product was dried by evaporation of solvent, then vacuum dried and plasticated on a two-roll mill.

The acetyl sulfonate was synthesized by reaction of equimolar amounts of acetic anhydride and concentrated sulfuric acid in ethylene dichloride solutions below 5°C for 10 min.

#### Preparation of PP/Zn–SEPDM/CaCO$_3$

Blend A: Zn–SEPDM was blended with PP on a two-roll mill at 155–160°C for 5 min and then with CaCO$_3$ for a period of 10 min.

Blend B: Zn–SEPDM was blended with CaCO$_3$ on a two-roll mill at 155–160°C for 5 min and then with PP for a period of 10 min.
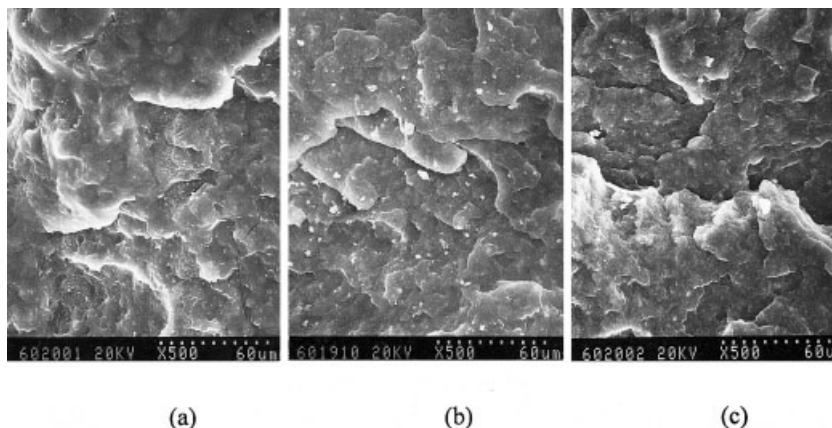
**Figure 1** SEM micrographs of surface fractured in liquid nitrogen: (a) PP/Zn–SEPDM (70/30); (b) PP/Zn–SEPDM/CaCO$_3$ (70/30/10, A); (c) PP/Zn–SEPDM/CaCO$_3$ (70/30/10, B).

All blends were molded into sheets (1 and 4 mm thick) at 180°C using a pressure of 10 MPa in a plate vulcanizer, for scanning electron microscopy (SEM), X-ray photoelectron spectrometry (XPS) analysis, and mechanical properties tests.

**Measurement and characterization**

Tensile strength: measured with an XL-60 tensile testing machine (Changsha, China) according to GB1040—79 (China national standards).

Impact strength: measured according to GB1843-80 (China National Standards) with XJ-40 (Wuzhong, China) impact strength testing machine. A few selected samples were also measured with a Ceast (Italy) impact strength testing machine to record force–time and energy–time curves during the fracture.

SEM observation: the specimens was vacuum coated with gold, then observed through SEM (X650,

Japan). The distribution of calcium on the surface was measured by XPS (PV9100, Japan) attached with SEM.

**RESULTS AND DISCUSSION**

**Morphology of PP/Zn–SEPDM/CaCO$_3$**

As shown in Figure 1, when fractured in liquid nitrogen, many of the CaCO$_3$ particles are exposed in blend A on the fractured surface, whereas there is rather less in blend B. Similar results were obtained through XPS (Fig. 2). Compared with blend A, the signal of calcium is very weak (the well-distributed white dots are noise; only the concentrated white dots represent one CaCO$_3$ particle) on the frozen fractured surface of blend B, implying that CaCO$_3$ particles are embedded beneath the surface. When the specimens were fractured in liquid nitrogen, the fracture surface would spread mainly in the brittle PP matrix and weakly
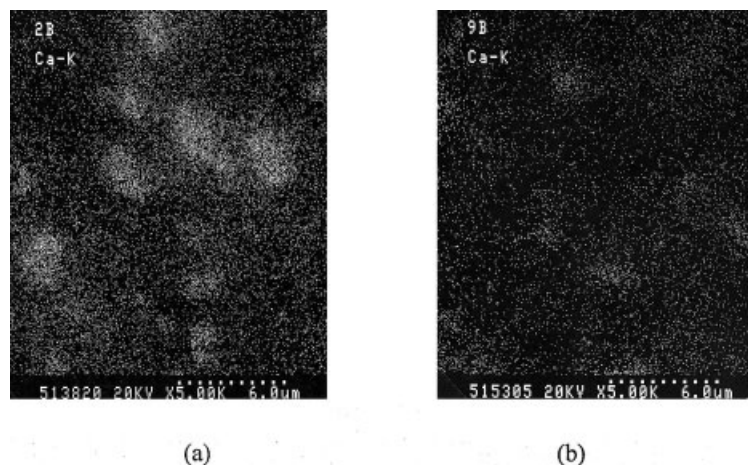


**Figure 2** Calcium distribution on the frozen fractured surfaces: (a) PP/Zn–SEPDM/CaCO$_3$ (70/30/10, A); (b) PP/Zn–SEPDM/CaCO$_3$ (70/30/10, B).
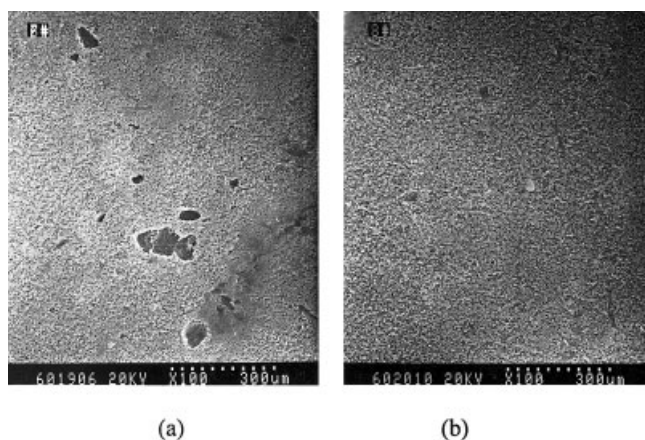
**Figure 3** SEM micrographs of surfaces etched by hydrochloric acid: (a) PP/Zn–SEPDM/CaCO₃ (70/30/10, A); (b) PP/Zn–SEPDM/CaCO₃ (70/30/10, B).

**TABLE II**
**Tensile Properties of PP/EPDM**

| Property | PP/EPDM | | |
|---|---|---|---|
| | 90/10 | 80/20 | 70/30 |
| Yield strength (MPa) | 31.7 | 25.0 | 19.2 |
| Break strength (MPa) | 21.3 | 19.2 | 17.5 |
| Elongation (%) | 15–270 | 80–340 | 420 |

ride acid. A few holes may be observed in specimen A, indicating that CaCO₃ particles were etched from the surface. Few holes, however, could be found in specimen B because of the encapsulation of the Zn–SEPDM outer layer on the CaCO₃ particles.

## Mechanical properties

As the Zn–SEPDM content of PP/Zn–SEPDM increases to 25 wt %, the impact strength changed abruptly and finally became more than 18 times as high as that of PP at 30 wt % Zn–SEPDM (Table I). Yield strength decreases continuously with increasing Zn–SEPDM, whereas the break strength remained at 19.8–23.5 MPa followed by a sharp rise to 30.8 MPa when Zn–SEPDM reached 30 wt %. The specimens of

bonded PP/CaCO₃ surfaces. The exposure of many CaCO₃ particles on the fracture surface of blend A reveals that the CaCO₃ and Zn–SEPDM were segregated in the PP matrix.[7–9]

Figure 3 shows the micrographs of the specimens whose thin PP layer on the surfaces was removed by fine sandpaper before they were etched by hydrochlo-

**TABLE I**
**Mechanical Properties of PP/Zn–SEPDM**

| Property | PP/Zn–SEPDM | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100/0 | 0/100 | 90/10 | 85/15 | 80/20 | 75/25 | 70/30 |
| Impact strength (J/m) | 45.0 | — | 125 | 167 | 304 | 655 | >800 |
| Yield strength (MPa) | 36.5 | — | 32.8 | 29.4 | 24.8 | 21.9 | 19.1 |
| Break strength (MPa) | 23.5 | 25.4 | 21.3 | 19.8 | 20.8 | 20.4 | 30.8 |
| Elongation (%) | 20–380 | 490 | 20–380 | 20–460 | 490 | 510 | 518 |

**TABLE III**
**Mechanical Properties of PP/Zn–SEPDM/CaCO₃ (A)**

| Property | PP/Zn–SEPDM/CaCO₃ | | | | | |
|---|---|---|---|---|---|---|
| | PP | 90/10/3.3 | 85/15/5 | 80/20/6.7 | 75/25/8.3 | 70/30/10 |
| Impact strength (J/m) | 45.0 | 60.6 | 71.7 | 160 | 291 | 690 |
| Yield strength (MPa) | 36.5 | 35.8 | 29.8 | 28.9 | 25.5 | 18.8 |
| Break strength (MPa) | 23.5 | 35.8 | 28.0 | 27.7 | 23.0 | 27.2 |
| Elongation (%) | 20–380 | 20 | 30 | 35 | 57 | 450 |

**TABLE IV**
**Mechanical Properties of PP/Zn–SEPDM/CaCO₃ (B)**

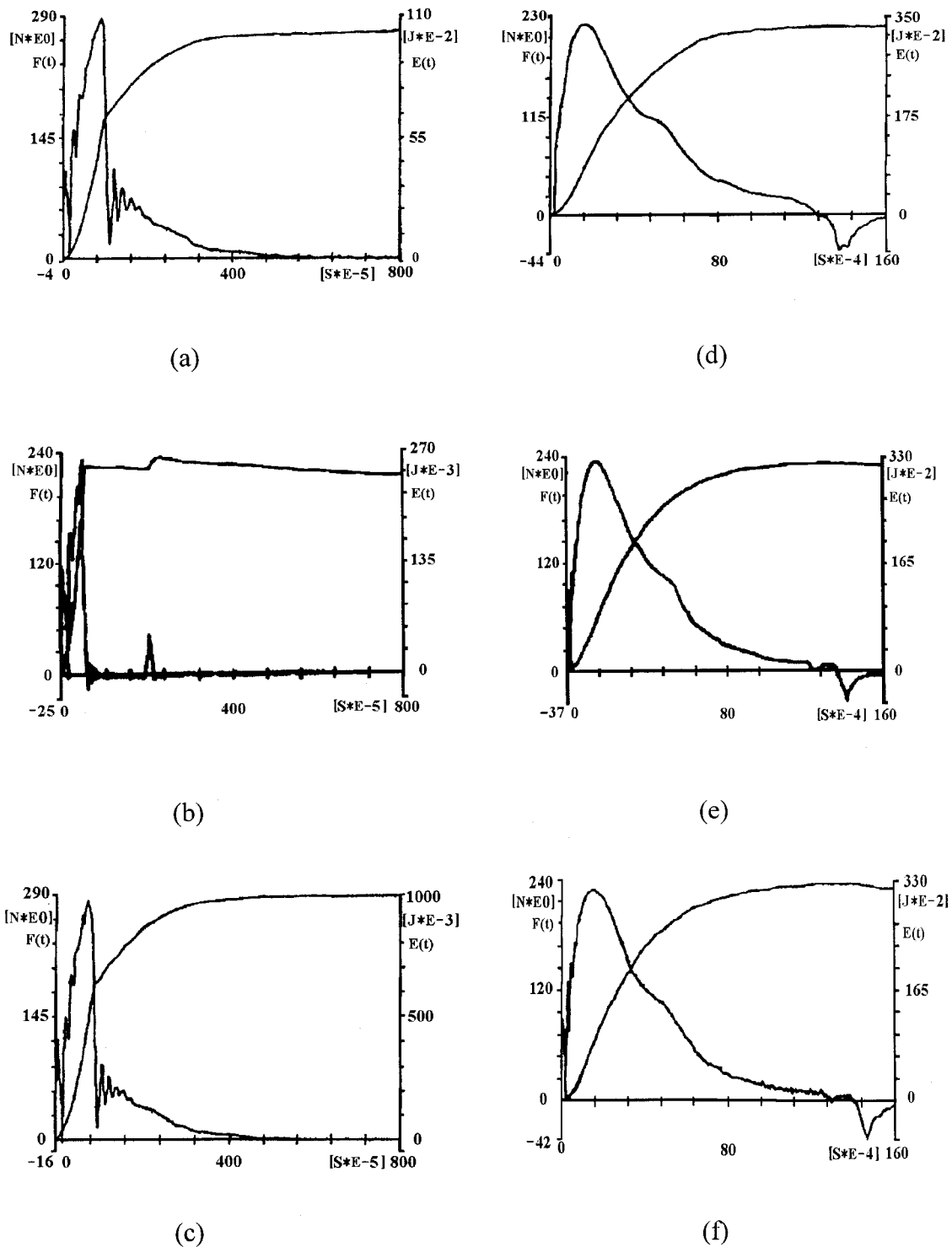| Property | PP/Zn–SEPDM/CaCO₃ | | | | | |
|---|---|---|---|---|---|---|
| | PP | 90/10/3.3 | 85/15/5 | 80/20/6.7 | 75/25/8.3 | 70/30/10 |
| Impact strength (J/m) | 45.0 | 108 | 181 | 248 | 460 | >800 |
| Yield strength (MPa) | 36.5 | 32.7 | 28.3 | 25.0 | 22.1 | 19.5 |
| Break strength (MPa) | 23.5 | 21.5 | 20.4 | 20.6 | 20.9 | 31.5 |
| Elongation (%) | 20–380 | 20–200 | 36–236 | 338 | 473 | 508 |

Figure 4 Force–time [*F*(*t*)] and energy–time [*E*(*t*)] during the impact fracture. PP/Zn–SEPDM/CaCO$_3$: (a) 85/15/0; (b) 85/15/5 (A); (c) 85/15/5 (B); (d) 70/30/0; (e) 70/30/10 (A); (f) 70/30/10 (B).

PP/Zn–SEPDM (100/0, 90/10, 85/15) break occasionally over a wide elongation range of 20–460%. When the Zn–SEPDM content was 20 wt %, all specimens had a long elongation before the final break. Dispersed rubber phases and the shear bands caused by them may be responsible for the high

elongations because of their ability to prevent cracks from expanding. Table II shows the tensile properties of PP/EPDM that present a tendency similar to that of PP/Zn–SEPDM, except that the break strength decreases continuously over the whole range. The reason for this is discussed later.
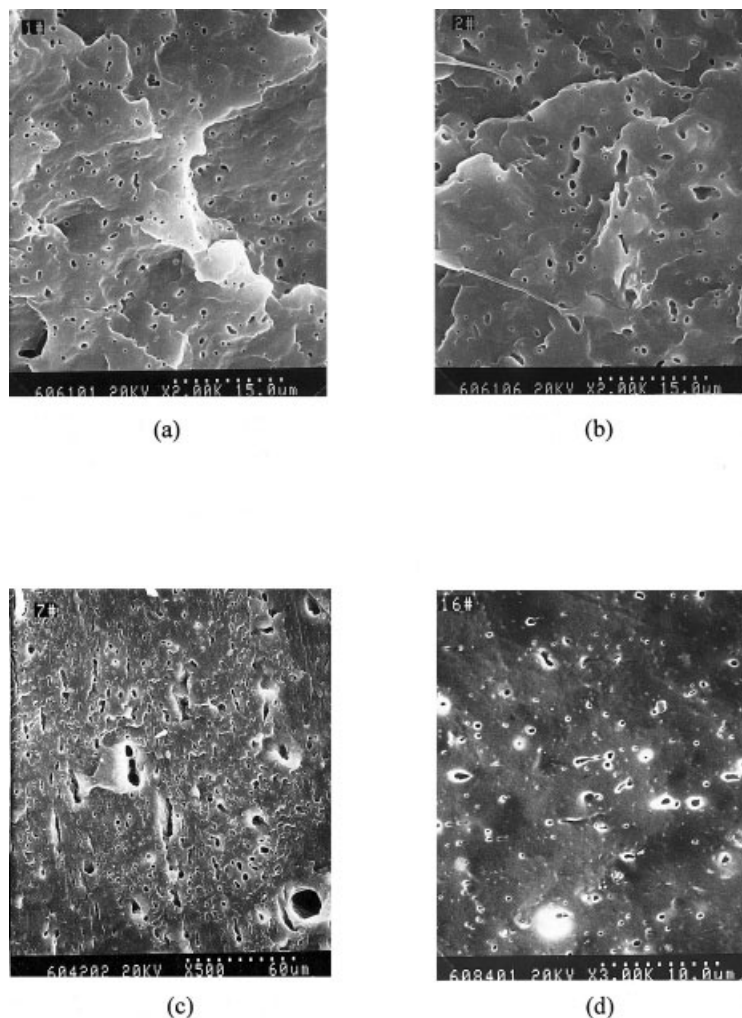
**Figure 5** SEM micrographs of frozen fractured surfaces (Zn–SEPDM was etched from the surface by solvents). PP/Zn–SEPDM: (a) 90/10; (b) 80/20; (c) 70/30; (d) PP/EPDM: 70/30.

The mechanical properties of PP/Zn–SEPDM/CaCO₃ prepared through the A sequence and the B sequence are listed in Table III and Table IV, respectively. The proportions of Zn–SEPDM/CaCO₃ are fixed at 3/1. PP/Zn–SEPDM/CaCO₃ A blends exhibit some high yield strengths, but the impact strength as well as elongation at break decreased significantly compared with that of PP/Zn–SEPDM. For B blends, every aspect of mechanical properties was close to that of PP/Zn–SEPDM, although some low-cost fillers were added in.[10–13]

Figure 4 records the curves of force–time [$F(t)$] and (absorbing) energy–time [$E(t)$] during the very short time of impact fracture. PP/Zn–SEPDM/CaCO₃ (85/15/5, B) [Fig. 4(c)] and PP/Zn–SEPDM/CaCO₃ (70/30/10, B) [Fig. 4(f)] have nearly the same $F(t)$ and $E(t)$ curves as those of PP/Zn–SEPDM (85/15) [Fig. 4(a)] and PP/Zn–SEPDM (70/30) [Fig. 4(d)], respectively, indicating that the CaCO₃ in the B blends has little effect on the fracture mechanism. Figure 4(b) shows

the $F(t)$ and $E(t)$ curves of PP/Zn–SEPDM/CaCO₃ (85/15/5, A). Not only is the maximum force, which corresponds to the emergence of cracks, about 50 N less than that of PP/Zn–SEPDM(85/15) [Fig. 4(a)] and (PP/Zn–SEPDM/CaCO₃ (85/15/5, B) [Fig. 4(c)], but also the force needed for crack propagation is far less than that of the other two blends. As a result, the energy for crack emergence is 60% less than that of the other two blends and the energy for crack propagation is even less. The great loss of impact strength could be attributed to the CaCO₃ filler scattered within the PP matrix, which causes cracks to emerge rather easily through stress concentration; moreover, this cannot effectively prevent the propagation of cracks.[7–9,11]

As the proportion of Zn–SEPDM/PP in the A blends increases to 30/70, the CaCO₃ does not show serious damage to impact stress [Fig. 4(e)], implying that the phase structure is different from the other morphologies or compositions.

Figure 5 shows the frozen fractured surface of PP/

**TABLE V**
**Mechanical Properties of PP/Zn–SEPDM/CaCO$_3$ (70/30/X, B)**

| Property | X | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| Impact strength (J/m) | >800 | >800 | >800 | 566 | 424 | 328 | 316 |
| Yield strength (MPa) | 19.1 | 19.3 | 19.5 | 19.8 | 19.6 | 19.1 | 19.6 |
| Break strength (MPa) | 30.8 | 34.0 | 31.5 | 25.3 | 21.1 | 20.4 | 18.5 |
| Elongation (%) | 518 | 510 | 508 | 460 | 453 | 344 | 106 |

Zn–SEPDM, where the Zn–SEPDM was previously etched from the surface using cyclohexane. At first, Zn–SEPDM was scattered within the PP matrix as isolated phases [Fig. 5(a), (b)]. When the Zn–SEPDM/PP proportion reached 30/70, some Zn–SEPDM networks began to form [Fig. 5(c)]. Because the Zn–SEPDM has both higher tensile break strength and elongation than that of PP (Table I), its dispersed phases or networks could bear stress as well as the PP matrix, which leads to a high break strength of PP/Zn–SEPDM (70/30) (Table I). In comparison, EPDM does not have chemical or physical crosslinks and could not be stretched long. When blended with PP, although the EPDM/PP amounts to 30/70, EPDM will be dispersed in the PP matrix and thus the break strength is rather lower than that of PP/Zn–SEPDM (Table II).

The mechanical properties of PP/Zn–SEPDM/ CaCO$_3$ (70/30/X, B) are listed in Table V. The proportion of PP/Zn–SEPDM was fixed at 70/30, and the CaCO$_3$ amount varied from 0 to 30 portions. When the CaCO$_3$ content was less than 15 portions, there were no great differences in mechanical properties, indicating that the networks of Zn–SEPDM basically remained unchanged.

## CONCLUSIONS

Zn–SEPDM has both higher tensile break strength and elongation than that of PP. When the content of Zn–SEPDM in composites with PP was increased to high

enough levels, some Zn–SEPDM networks began to form in the PP matrix and thus the break strength of their blend was enhanced.

In the PP/Zn–SEPDM/CaCO$_3$ composite prepared through the A sequence, the CaCO$_3$ and Zn–SEPDM were segregated in PP, which caused cracks to emerge rather easily through stress concentration; moreover, this could not effectively prevent the propagation of cracks. In the PP/Zn–SEPDM/CaCO$_3$ prepared through the B sequence, CaCO$_3$ was encapsulated by Zn–SEPDM. PP/Zn–SEPDM/CaCO$_3$ (B) was thus found to have better impact strength than that of PP/Zn–SEPDM/CaCO$_3$ (A).

## References

1. Daocheng, P.; Qinai, P.; Tongying, Y. Gaojuwu jiqi Gonghunwu de Lixue Xingneng; Shanghai Science Publishing House: Shanghai, 1988 (in Chinese).
2. Jinsong, Z.; Chixing, Z.; Jun, W. Plastics 1989, 3, 3 (in Chinese).
3. Tiejun, S.; Xiaoxia, T. Synth Rubber Ind 1994, 17, 228 (in Chinese).
4. Matonis, V. A.; Small, N. C. Polym Eng Sci 1969, 9, 99.
5. Matonis, V. A.; Small, N. C. Polym Eng Sci 1969, 9, 100.
6. Xinian, L.; Rui, Z. Fuhe Cailiao Xuebao 1995, 4, 48 (in Chinese).
7. Jancar, J.; Dibenedetto, A. T. J Mater Sci 1995, 30, 2438.
8. Sahnoune, F.; Lopez-Cuesta, J. M.; Crespy, A. J Mater Sci 1999, 34, 535.
9. Molnar, S.; Pukanszky, B.; Hammer, C. O. Polymer 2000, 41, 1529.
10. Kolank, J.; Jancar, J. Polymer 1992, 33, 4961.
11. Long, Y. U.; Shanks, R. A. J Appl Polym Sci 1996, 62, 639.
12. Long, Y. U.; Shanks, R. A. J Appl Polym Sci 1996, 61, 1877.
13. Prephet, K.; Horanont, P. Polymer 2000, 41, 9283.