

# Influence of the Compounding Route on the Properties of Polypropylene/Nano-CaCO<sub>3</sub>/Ethylene–Propylene–Diene Terpolymer Tercomponent Composites

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**ABSTRACT:** The influence of the compounding route of polypropylene (PP)/ethylene–propylene–diene terpolymer (EPDM)/nano-CaCO<sub>3</sub> composites on their properties, including their mechanical properties, the dispersion degree of nano-CaCO<sub>3</sub>, and the morphology of EPDM, was studied. The results showed that the toughness of the composites and the morphology of the EPDM particles were markedly influenced by the compounding route, whereas the dispersion degree of nano-CaCO<sub>3</sub> in the matrix was little influenced by the compounding route. The impact strength of composites prepared by one route was about 60 kJ/m<sup>2</sup> with 20 wt % nano-CaCO<sub>3</sub>. The results indicated that a sandbag of nano-

CaCO<sub>3</sub> embedded in EPDM could effectively improve the toughness of the composites. A sandbag composed of EPDM and nano-CaCO<sub>3</sub> eliminated the deterioration effect of the nano-CaCO<sub>3</sub> agglomerate on the toughness of the composites, whereas the nano-CaCO<sub>3</sub> agglomerate separately dispersed in PP decreased the toughness of the tercomponent composite © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2268–2272, 2006

**Key words:** elastomers; modification; nanocomposites; poly(propylene) (PP); toughness

## INTRODUCTION

Although polypropylene (PP) is extensively used in many applications, its poor low-temperature impact strength significantly hinders its even wider utilization. The typical method for overcoming this drawback is PP toughened with an elastomer; however, the inclusion of an elastomer lowers its stiffness and heat resistance. To compensate for the effect of the elastomer, a rigid filler is usually added to the blend. PP/elastomer/filler composites are attracting increasing industrial and academic interest because of their balance of mechanical properties. The relationships of the properties and phase structure, the distribution of the components, and the compounding route have been widely investigated.<sup>1–4</sup> Kurauchi and Ohta<sup>5</sup> proposed a “cool drawing concept”, in which the impact energy is absorbed by the large plastic deformation of a brittle particle dispersed in a ductile matrix.

Nanoparticles have been commercially manufactured with the development of the manufacturing technology of nanopowders, such as nano-calcium carbonate (nano-CaCO<sub>3</sub>), nano-titanium dioxide, and

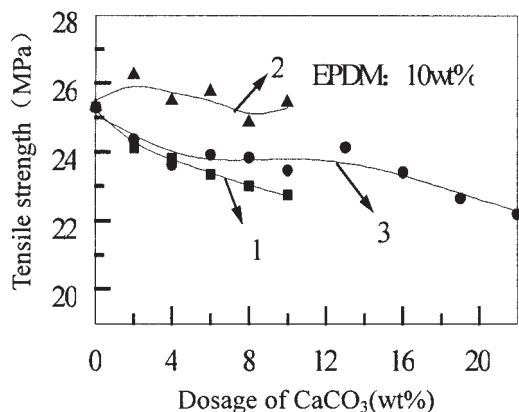
zinc oxide. The higher free energy of adsorption and larger specific surface of nanoparticle have inspired the recent interest in polymer modification with nanoparticles. Composite behavior is influenced by a number of parameters, such as the nature of the matrix structure and the morphology of the filler as well as the characteristics of the phase interaction between the particle and polymer matrix. Rui Huang<sup>6</sup> studied the compounding technology and properties of high-density polyethylene toughened with nano-CaCO<sub>3</sub> and poly(vinyl chloride) modified with carborundum.

We studied the influence of the compounding route of PP/ethylene–propylene–diene terpolymer (EPDM)/nano-CaCO<sub>3</sub> composites on their properties; the composites were prepared through melt mixing in a twin-screw extruder. The results showed that the toughness of PP was markedly enhanced when nano-CaCO<sub>3</sub> was embedded in EPDM. The structure of nano-CaCO<sub>3</sub> embedded in EPDM is called a sandbag and consists of nano-calcium as sand and a flexible shell of EPDM as a bag, like a sandbag for boxing.

## EXPERIMENTAL

Isotactic PP homopolymer (melt flow rate = 1.0 g/10 min; Beijing Yanshan Petrochemical, Ltd., Co., Beijing, China) was used as the matrix. EPDM (4725P, DuPont, Wilmington, DE) was used as the elastomer. Nano-

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**Figure 1** Effect of the compounding route on the tensile strength of PP/EPDM/nano-CaCO<sub>3</sub>: (1) route A, (2) route B, and (3) route C.

CaCO<sub>3</sub> (CCR, 40 nm), coated with a fatty acid, was manufactured by Guangping Chemical, Ltd., Co. (Guangdong, China).

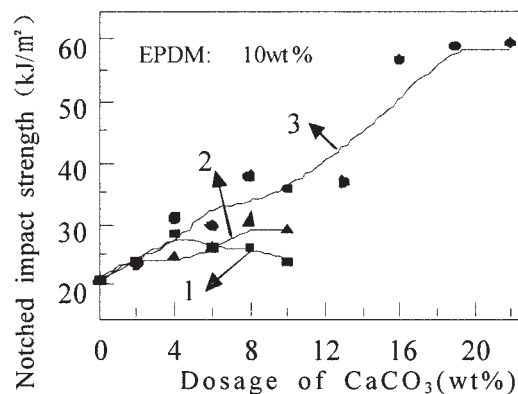
Three routes were used to prepare the PP/EPDM/nano-CaCO<sub>3</sub> tercomponent composites:

1. PP, EPDM, and nano-CaCO<sub>3</sub> were mixed in a twin-screw extruder with a length/diameter ratio of 32 and a screw diameter of 30 mm. The extruding temperature was 200°C.
2. At first, PP and nano-CaCO<sub>3</sub> were mixed in a twin-screw extruder, and then the compound and EPDM were mixed again in the same twin-screw extruder. The extruding temperature was 200°C.
3. At first, nano-CaCO<sub>3</sub> and EPDM were mixed in a twin-roll mill, and then the compound and PP were mixed in the twin-screw extruder. The temperature of the roller surface was 135°C, and the extruding temperature was 200°C.

The final pellets of the composites were molded in a reciprocating-screw injection-molding machine into dog-bone-shaped tensile specimens and rectangular impact specimens.

Tensile tests were carried on a GMT-5140 tester (Shenzhen, China) at a speed of 50 mm/min. An XJ-300A impact tester (Gansu, China) was used for measuring the Charpy impact strength.

The morphology of the sandbag structure and EPDM particles dispersed in the matrix was investigated with scanning electron microscopy (SEM; XL30, Philips, Hillsboro, OR). The samples used for investigating the sandbag structure were taken from rectangular impact specimens cryofractured in liquid nitrogen, and the fractured sections were immersed in pentane for 30 min to remove the EPDM shell of the sandbag. The samples for investigating the morphol-



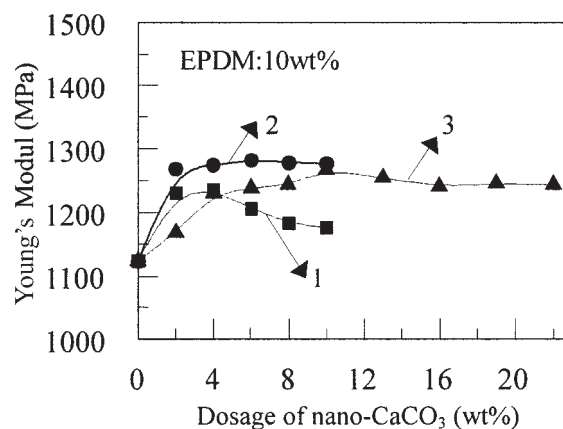
**Figure 2** Effect of the compounding route on the impact strength of PP/EPDM/nano-CaCO<sub>3</sub>: (1) route A, (2) route B, and (3) route C.

ogy of EPDM were also taken from rectangular impact specimens parallel to the flow direction of the melt and perpendicularly to the flow direction of the melt via cryofracturing in liquid nitrogen, and the fractured sections were immersed in pentane for 2 h before ultrasonic action for 5 min to etch the EPDM phase from the composites. The SEM samples were dried before being coated with platinum. The distribution of nano-CaCO<sub>3</sub> was investigated with transmission electron microscopy (TEM; JEM 1200, JEOL, Tokyo, Japan); the sample for investigating the distribution of nano-CaCO<sub>3</sub> was cut into ultrathin flakes with a thickness of 100–120 nm from rectangular impact specimens.

## RESULTS AND DISCUSSION

### Influence of nano-CaCO<sub>3</sub> on the properties of the PP/EPDM/nano-CaCO<sub>3</sub> composites

The influence of the dosage of nano-CaCO<sub>3</sub> on the tensile strength of the composites prepared by various



**Figure 3** Effect of the compounding route on the Young's modulus of PP/EPDM/nano-CaCO<sub>3</sub>: (1) route A, (2) route B, and (3) route C.

TABLE I  
Mechanical Properties of the Tercomponent Composites

PP/EPDM/nano-CaCO <sub>3</sub>	Route A			Route B			Route C		
	Tensile strength (MPa)	Young's modulus (MPa)	Impact strength (kJ/m <sup>2</sup> )	Tensile strength (MPa)	Young's modulus (MPa)	Impact strength (kJ/m <sup>2</sup> )	Tensile strength (MPa)	Young's modulus (MPa)	Impact strength (kJ/m <sup>2</sup> )
90/10/0	25.2	1123	21.1	25.2	1123	21.1	25.2	1123	21.1
88/10/2	24.1	1230	24.3	26.9	1268	24.0	24.3	1168	23.9
86/10/4	23.8	1235	28.8	25.4	1274	24.9	23.6	1229	31.4
84/10/6	23.3	1206	26.6	25.7	1282	26.6	23.9	1238	30.2
82/10/8	23.0	1183	26.6	24.8	1278	31.0	23.8	1243	38.2
80/10/10	22.7	1176	24.4	25.4	1276	29.7	23.4	1267	36.2
77/10/13							24.1	1254	37.4
74/10/16							23.4	1240	57.0
71/10/19							22.6	1245	59.2
68/10/22							22.2	1243	59.7

routes is shown in Figure 1. Nano-CaCO<sub>3</sub> slightly increased the tensile strength of the composites prepared by route B at breakup to 4 wt %. The tensile strength of the composites prepared by route A and route C decreased with the addition of nano-CaCO<sub>3</sub>.

Figure 2 compares the Charpy impact strength of the composites prepared by the various routes. The addition of nano-CaCO<sub>3</sub> improved the toughness of the composites to different degrees. Curves 1 and 2 indicate that the Charpy impact strength of the tercomponent composites prepared by route A and route B was improved at a lower dosage of nano-CaCO<sub>3</sub>. Curve 3 shows that the Charpy impact strength of the tercomponent composite prepared by route C was markedly improved with an increasing dosage of nano-CaCO<sub>3</sub> and reached approximately 60 kJ/m<sup>2</sup> at 20 wt % nano-CaCO<sub>3</sub>. Figure 3 shows that the modulus of the tercomponent composite was slightly increased at a lower dosage of nano-CaCO<sub>3</sub>. The data for the mechanical properties of the tercomponent composites prepared by the various routes are listed in Table I.

According to the differences of the compounding routes, the distribution of nano-CaCO<sub>3</sub> dispersed in the polymer matrix is illustrated in Figure 4. In the

composites prepared by route A, nano-CaCO<sub>3</sub> was randomly distributed in the PP matrix and EPDM particles. In the composites prepared by route B, nano-CaCO<sub>3</sub> particles and EPDM particles were separately distributed in the PP matrix. In the composites prepared by route C, nano-CaCO<sub>3</sub> particles and their agglomerates were embedded in EPDM particles to form a sandbag structure like a sandbag for boxing. Figure 5 shows a sandbag structure composed of nano-CaCO<sub>3</sub> agglomerates and EPDM rubber existing in a composite prepared with route C.

Figure 6 shows the morphology of nano-CaCO<sub>3</sub> particles and their agglomerates dispersed in the polymer matrix. The TEM photographs illustrate that some nano-CaCO<sub>3</sub> was dispersed in the matrix on a nanoscale ( $\leq 100$  nm), whereas the rest was dispersed in the agglomerates. The dispersion degrees of nano-CaCO<sub>3</sub> in the composites prepared with the three routes were very similar.

Figures 2, 4, and 5 reveal the influence of the distribution of nano-CaCO<sub>3</sub> in the matrix on the toughness of the tercomponent composites. In the composites prepared by route A and route B, the relation of the toughness of the composite and the nano-CaCO<sub>3</sub> dosage was in good agreement with the results obtained

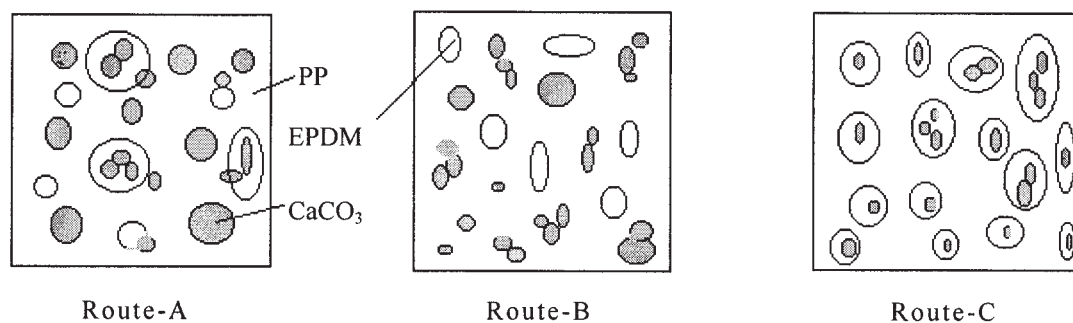
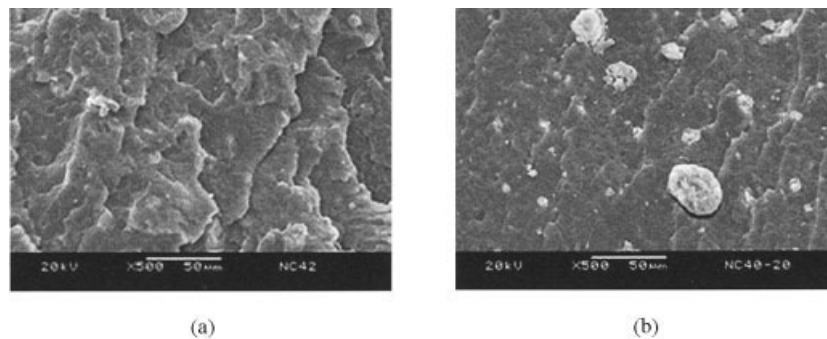


Figure 4 Sketch of the distribution of nano-CaCO<sub>3</sub> and EPDM in PP.



**Figure 5** SEM photographs of the sandbag structure dispersed in composites prepared with route C: (A) unetched and (B) etched.

in the previous research. In the composites prepared by route C, the toughness of the composites was continually improved up to 20 wt % nano- $\text{CaCO}_3$ . When the nano- $\text{CaCO}_3$  particles and their agglomerates were embedded in the EPDM shell, cavitation on interface and deformation of nano- $\text{CaCO}_3$  agglomerates led to the deformation of the sandbag when the sample was impacted, and then the deformation of the sandbag could dissipate impact energy.

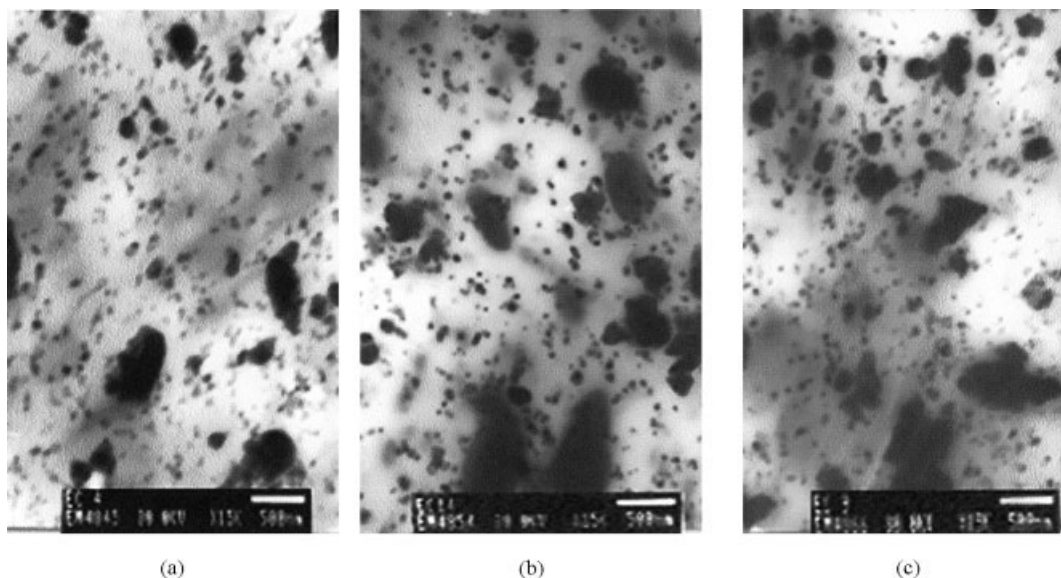
#### Morphology of the EPDM particles dispersed in the PP matrix

Figure 7 and Table II show that the morphology of the EPDM particles dispersed in the matrix was markedly influenced by the compounding route of the composites. The EPDM particles dispersed in the composites prepared by route C were smaller and more uniform than the EPDM particles dispersed in the composites

prepared by route A and route B. The EPDM particles dispersed in the composites prepared by route B were oriented to the melt flow direction, whereas the EPDM particles dispersed in the composites prepared by route A and route C were more spherical. The reason for the difference in the morphology of the EPDM particles was that the viscosity ratio of EPDM to PP was significantly changed by the distribution of nano- $\text{CaCO}_3$  in the matrix.

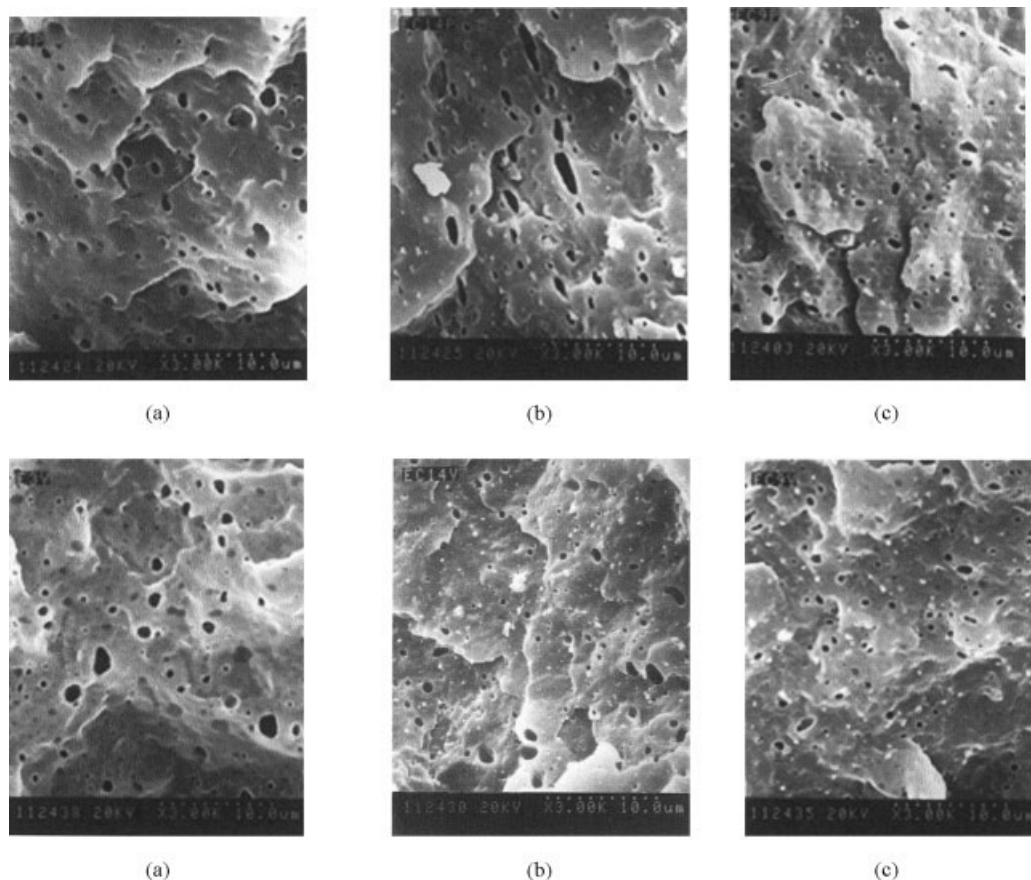
#### CONCLUSIONS

The distribution of nano- $\text{CaCO}_3$  in a component of PP/EPDM/nano- $\text{CaCO}_3$  was a crucial factor influencing the morphology of the EPDM particles and the toughness of the composites. In the composites prepared by route C, EPDM and nano- $\text{CaCO}_3$  formed a sandbag structure, whereas nano- $\text{CaCO}_3$



**Figure 6** TEM photographs of the dispersion of nano- $\text{CaCO}_3$  (15,000 $\times$ , PP/EPDM/nano- $\text{CaCO}_3$  = 82/10/8): (A) route A, (B) route B, and (C) route C.





**Figure 7** SEM photographs of EPDM dispersed in PP/EPDM/nano-CaCO<sub>3</sub> composites (3000 $\times$ , PP/EPDM/nano-CaCO<sub>3</sub> = 82/10/8): (A) route A, (B) route B, and (C) route C. The top three images are parallel to the flow direction of the melt; the bottom three images are perpendicular to the flow direction of the melt.

**TABLE II**  
Characteristics of the EPDM Particles in the Composites

		Route A	Route B	Route C
Mean diameter of EPDM particle (nm)	Parallel to flow direction of melt	530	600	452
	Perpendicular to flow direction of melt	496	526	438
Mean elliptic degree of EPDM particle	Parallel to flow direction of melt	1.99	2.66	2.06
	Perpendicular to flow direction of melt	2.06	2.28	1.83

and its agglomerate were embedded in the EPDM particles. The toughness of the composites was improved markedly by the presence of the sandbag, whereas the toughness of the composites was reduced by the nano-CaCO<sub>3</sub> agglomerate when EPDM and nano-CaCO<sub>3</sub> were separately dispersed in the matrix. The sandbag could dissipate the impact energy with deformation led by the debonding of the interface of nano-CaCO<sub>3</sub> and EPDM and with deformation of nano-CaCO<sub>3</sub> agglomerates in the sandbag. Because the sandbag could eliminate the deterioration effect of nano-CaCO<sub>3</sub> agglomerates on the toughness of the composites, composites with excel-

lent toughness and lower cost could be prepared by a convenient melt compounding route for many applications.

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