

# Preparation and Properties of EPDM/TiO<sub>2</sub> Composites

Shan Haitao,<sup>1</sup> Cui Juqing,<sup>1</sup> Zhang Qiang,<sup>1</sup> Zhuang Wei,<sup>1</sup> He Qihui,<sup>1</sup> Hu Baixing,<sup>1</sup> Shen Jian<sup>1,2</sup>

<sup>1</sup>School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

<sup>2</sup>College of Chemistry and Environment Science, Nanjing Normal University, Nanjing 210097, People's Republic of China

Received 17 July 2006; accepted 2 April 2007

DOI 10.1002/app.26614

Published online 15 June 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Composites of EPDM/TiO<sub>2</sub> in which TiO<sub>2</sub> particles were surface modified with  $\gamma$ -methacryloxypropyl trimethoxysilane (MPS) and preultrasonically dispersed, and EPDM was grafted with maleic anhydride (MA) were successfully prepared. FTIR analysis showed that the modification of TiO<sub>2</sub> and the grafting of EPDM had taken place. The uniform dispersion of TiO<sub>2</sub> particles in EPDM matrix as well as good interfacial compatibility was observed from scanning electron microscopy (SEM) images. The tensile strength and elongation at break were greatly improved and reached the maximum as the con-

tent of TiO<sub>2</sub> in the composite reached 7.5% wt. The result of swell and solution test indicated that the composites were evidently crosslinked. Thermogravimetric analysis (TGA) indicated that the decomposition temperature of the composite was increased about 20°C. This work provides a potential way for crosslinking EPDM matrix with inorganic filler in a convenient method. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 314–319, 2007

**Key words:** EPDM; TiO<sub>2</sub>; dispersion; interfacial compatibility; reinforcement

## INTRODUCTION

Pristine rubbers should be enhanced before practical application because of their poor mechanical performances. The conventional vulcanization by sulfur or carbon black to form crosslinking network proved to be successful in rubber reinforcement. EPDM developed by DuPont in the 1960s is a low unsaturated synthetic rubber that shows remarkable properties such as ozone and heat resistance, good flexibility at low temperature and chemical resistance, but poor mechanical performance, poor wettability, and covulcanization ability because of its fewer double bonds that limits its industrial application.

Reinforcing rubber with inorganic fillers has generated tremendous interest in the rubber industry owing to decreased industrial cost and enhancements in a variety of mechanical and thermal performances.<sup>1–8</sup> Ultrafine particles with large surface area and high surface activity were extensively studied as the rubber enhancer giving the promise of drastic improvements in mechanical properties with a small dose of filler particles.<sup>9–11</sup> However, with highly active surfaces, they tend to aggregate tightly, which could easily ease the great reinforcements mentioned above. Some measures, such as intercalation method,<sup>12–15</sup> sol-gel processing,<sup>5,16,17</sup> modifying the surface of particles,<sup>18,19</sup> were carried out to solve

this problem. But they are not representative in the universality of dispersing filler particles. The intercalation method mainly limits to the layered particles, and the sol-gel method limits to the ceramic ones (such as SiO<sub>2</sub> and TiO<sub>2</sub>). In addition, the sol-gel method has its limits by the strict experimental conditions that are hard to control. The surface modification one seems to be facile and universal.

In this article, a new method was put forward to disperse ultrafine particles uniformly in rubber matrix. Composites of EPDM/TiO<sub>2</sub> in which TiO<sub>2</sub> particles were surface modified with MPS and preultrasonically dispersed, and EPDM was grafted with MA were successfully prepared. Remarkable improvements in mechanical and thermal properties of EPDM were studied. This work provides a potential way for crosslinking EPDM matrix with inorganic filler in a convenient method.

## EXPERIMENTAL

### Materials

EPDM was supplied by Yangtse Petrol-Chemical (Nanjing, China) with an ethylene content of 70%, ENB type and ML<sub>1+4</sub> 100°C = 70. TiO<sub>2</sub> with the size of about 300 nm was supplied by Nanjing Titanium Dioxide Chemical Co., Ltd. (Nanjing, China). The maleic anhydride (MA) and benzoyl peroxide (BPO), xylene, and acetone were purchased from Shanghai Chemical Agent (Shanghai, China),  $\gamma$ -methacryloxypropyl trimethoxysilane (MPS) was

Correspondence to: H. Baixing (cwmndf@nju.edu.cn).

supplied by Nanjing Coupling Agent (Nanjing, China). All the agents above are analytical purified. BPO was purified by recrystallization, and other agents were used as received without further purification.

### Surface treatment of TiO<sub>2</sub>

TiO<sub>2</sub> (2 g) was added into the solution in which 0.8 g MPS was dissolved in 200 mL butanone, followed by an ultrasonic dispersing treatment for 5 min. The mixture remained refluxed at 80°C for 2 h. After cooling to room temperature, TiO<sub>2</sub> treated by MPS (denoted as TMPS) was detached from the mixture by centrifugation and was dried at 80°C.

### Preparation of the composites

EPDM (8.0 g) and 1.4 g MA were dissolved in 200 mL xylene at 100°C. With nitrogen protected, the solution that BPO was dissolved in 40 mL xylene was dropped into the mixture within 3 h, and then the temperature was maintained for another 1 h. After cooling to 60°C, 120 mL acetone was dropped into the mixture. Then the deposit was completely dissolved in 200 mL xylene again at 100°C. The solution that TMPS was preultrasonically dispersed in 40 mL xylene was poured into the mixture. BPO (0.1 g) dissolved in 40 mL xylene was dropped into the flask with nitrogen protected simultaneously. The reaction was continued for 4 h, and then the temperature was maintained for 1 h. After the system temperature cooled to 60°C, 150 mL acetone was added into the flask with a vigorous stirring for 4 h. The deposit was isolated and dried at room temperature. To get the compared data, EPDM-g-MA/TiO<sub>2</sub> composites were also prepared similarly.

### SEM measurement

The fracture surfaces of different samples were obtained at liquid nitrogen temperature and then observed by a LEO 1530VP SEM (Germany). The operation voltage was 10 kV.

### ATR-FTIR measurement

The attenuated transmission reflectance (ATR) technique was used to determine the chemical modification before and after special treatment was carried out. A Nexus 870 FTIR spectrophotometer was used to record the ATR-FTIR spectra of the samples.

### Tensile measurement

The sample plates (~1 mm thick) were modeled into 15 mm span tensile test specimens. Tensile test were

performed with a crosshead speed of 200 mm/min on an Instron 4200 (Instron, UK).

### Measurement of swelling and solution

The results of swelling and solution were used to confirm the degree of crosslinking. EPDM-g-MA, EPDM-g-MA/TiO<sub>2</sub>, and three EPDM-g-MA/TMPS composites samples were picked out and divided into six portions. Each portion was weighed accurately ( $w_0$ ). These samples were put into xylene and the reaction was continued for 1, 3, 6, 12, 24, 48 h at 30°C. Then the samples were quickly wiped and weighed accurately ( $w_1$ ). Finally, the samples were dried in vacuum at room temperature and weighed again ( $w_2$ ). The ratio of swell and solution were determined using the following equations:

$$\text{Swelling}(\%) = \frac{w_1 - w_2}{w_2} \times 100$$

$$\text{Solution}(\%) = \frac{w_0 - w_2}{w_0} \times 100$$

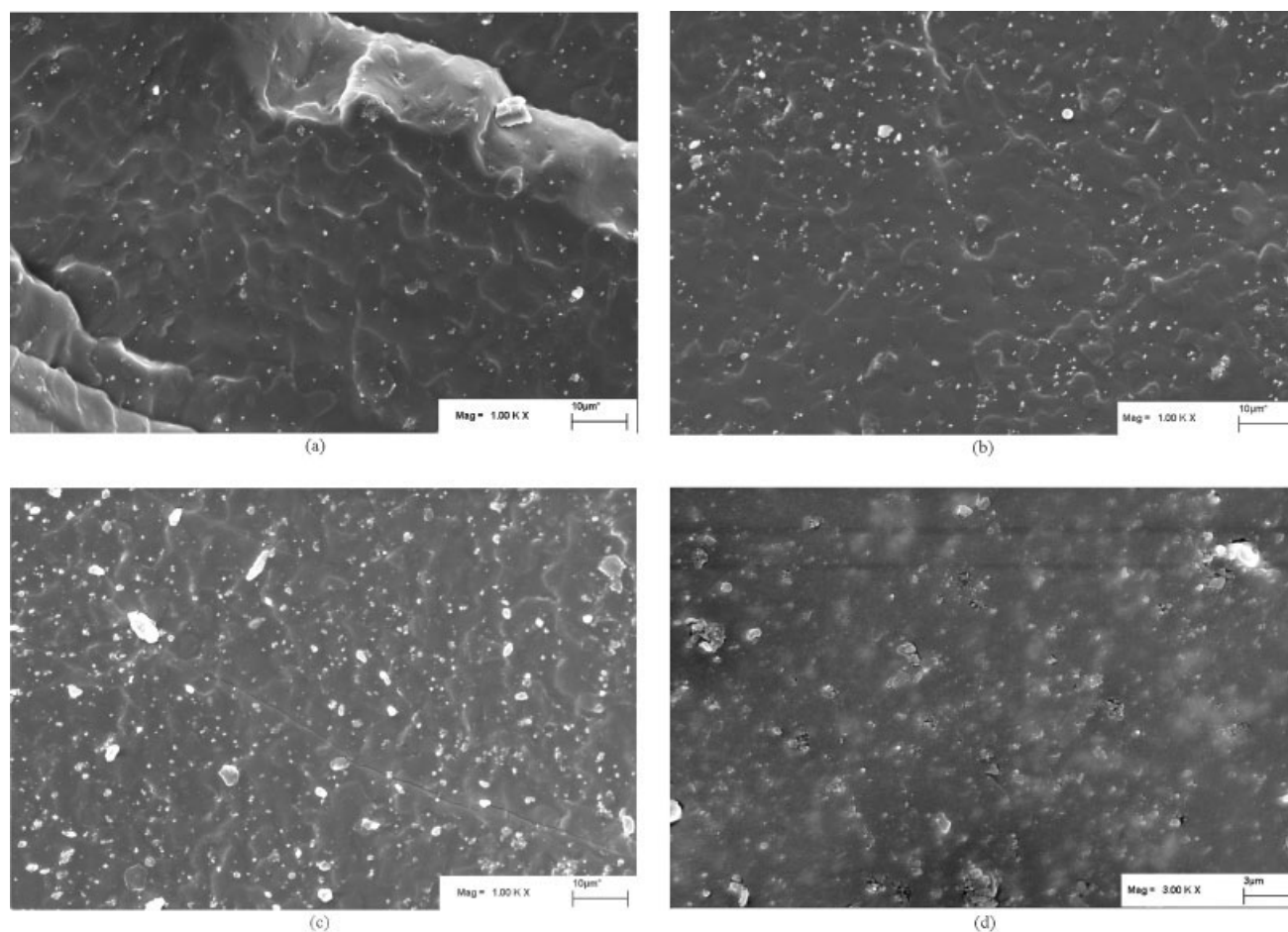
### TGA measurement

TGA measurement was carried out on a Perkin-Elmer TGA under the following condition: sample weight 1.5–3 mg, calefactive speed: 20°C/min, calefactive range from room temperature to 800°C under nitrogen atmosphere.

## RESULTS AND DISCUSSION

### Dispersion of filler particles

An initial investigate into the microcosmic morphologies of filler particles in EPDM matrix was showed by SEM in Figure 1. Selected images were chosen from a larger body of images of fracture surface to be representative of the state of the dispersion seen throughout the sample. The dispersion of TiO<sub>2</sub> particles treated with MPS in EPDM matrix was compared with different loadings [Fig. 1(a–c)] as well as with no MPS treated one [Fig. 1(d)]. It can be seen that the particles were dispersed uniformly in EPDM matrix in lower TMPS filler loadings of 2.5% wt and 7.5% wt [Fig. 1(a–b)]. Compared Figure 1(d) of no MPS treated ones with Figure 1(b) of TMPS 7.5% wt, we can observe that EPDM filled with pristine TiO<sub>2</sub> shows serious aggregates than with TMPS filled ones. It's possible that the agglomerations of TiO<sub>2</sub> were broken down into smaller particulates during the ultrasonic processing, and the synchronous surface modification by MPS on these particulates lowered down the surface energy of particles by the introduction of hydrophobic groups. On the other



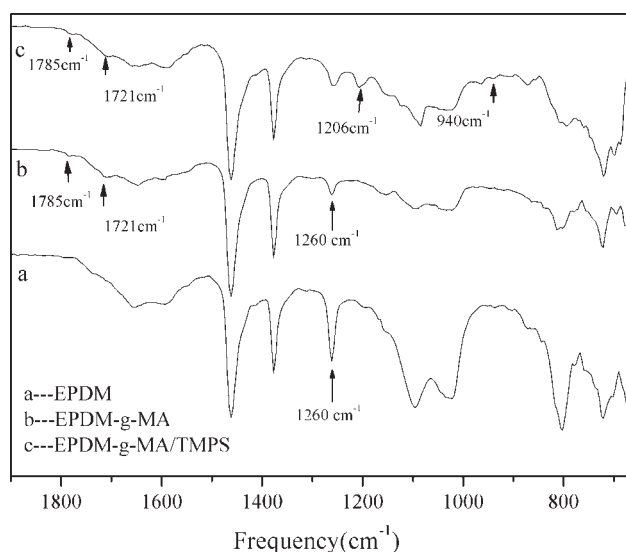
**Figure 1** SEM image of samples of different filler loadings (a) 2.5% TMPS, (b) 7.5% TMPS, (c) 12.5% TMPS, (d) 7.5% TiO<sub>2</sub>.

hand, MPS afforded steric hindrance of interparticles, which prevented these particulates from further aggregation. However, more agglomerations were observed at higher filler loadings, and the size of some agglomerations could achieve about 10 µm [Fig. 1(c)]. It's considered that with the increase of filler content, the interparticle distance was small. Although the pristine TiO<sub>2</sub> agglomerations could be broken down in the ultrasonic processing, they could rejoin together easily and form new agglomerates before the surface of the so-called particulates were modified.

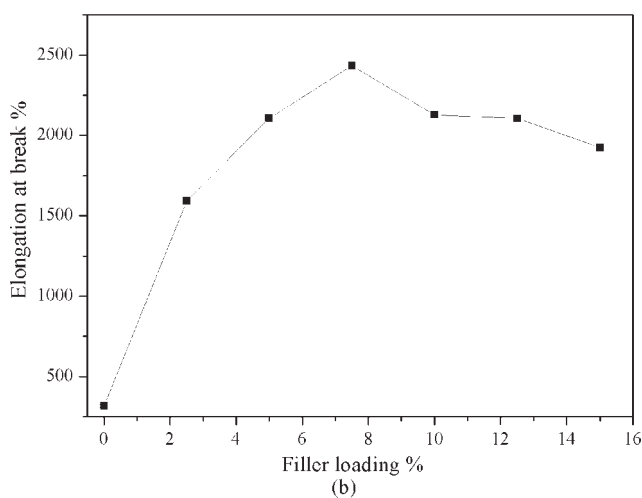
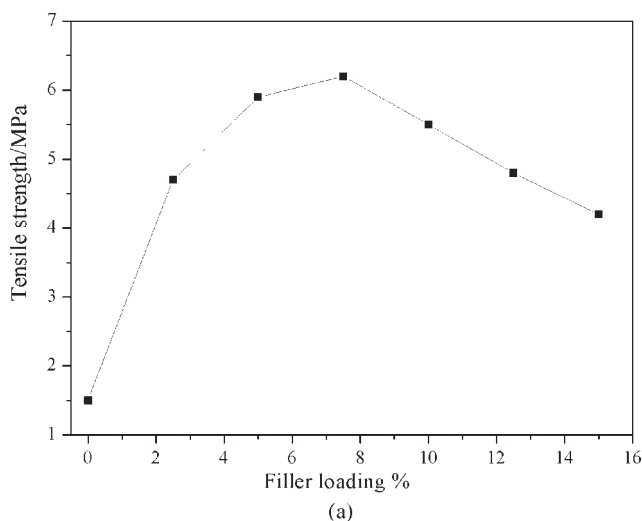
### Interfacial compatibility

In addition to uniform dispersion, the interfacial compatibility is also an important role for the improvement of EPDM within organic fillers. Seen from Figure 1(a–c), EPDM matrix had a well-knit combination with TiO<sub>2</sub> in EPDM-*g*-MA/TMPS composites, which suggested good interfacial compatibility. It can be inferred from these images that the surface modification of TiO<sub>2</sub> and grafting EPDM with MA, which were verified by the ATR-FTIR spectra

in Figure 2, resulted in the improvement of interfacial compatibility. Compared with the spectrum of EPDM [Fig. 2(a)], EPDM-*g*-MA showed two additional peaks appeared at 1785 cm<sup>-1</sup>, 1721 cm<sup>-1</sup> [Fig. 2(b)],



**Figure 2** ATR-FTIR spectra of different samples.



**Figure 3** Mechanical tests of EPDM-g-MA/TMPS and EPDM-g-MA/TiO<sub>2</sub> with different filler loading (a) tensile strength (b) elongation at break.

which were corresponding to the vibration of carbonyl group of MA. The peak at 1260 cm<sup>-1</sup>, however, showed a decreased absorption, which was mainly due to the replacement of hydrogen atom by carbon atom in MA to form a quaternary carbonic structure. All the above observation suggested that MA had been grafted onto EPDM. Compared with EPDM-g-MA, EPDM-g-MA/TMPS [Fig. 2(c)], additional peaks at 940 cm<sup>-1</sup> could be attributed to Si—O—Ti stretching vibration,<sup>20</sup> 1206 cm<sup>-1</sup> could be ascribed to antisymmetric vibration of C—O—C introduced by MPS, which suggested that MPS had been modified onto TiO<sub>2</sub> particles. Therefore, grafted EPDM was more polar and treated filler particles were less polar. In this way, the interfacial compatibility would be improved by increasing the interaction between EPDM and TiO<sub>2</sub>. On the other hand, EPDM-g-MA here also acted as the compatibilizer between EPDM and TiO<sub>2</sub>, which contributed to the

**TABLE I**  
Swell Percentage Test of Different Samples

	1 h	3 h	6 h	12 h	24 h	48 h
EPDM-g-MA	223	433	513	616	668	690
EPDM-g-MA/2.5% TMPS	173	179	181	182	185	187
EPDM-g-MA/7.5% TMPS	167	174	178	179	172	184
EPDM-g-MA/12.5% TMPS	120	159	160	163	164	166
EPDM-g-MA/7.5% TiO <sub>2</sub>	170	178	188	192	198	204

improvement of interfacial compatibility. However, some dark area surrounding filler particles was observed in Figure 1(d), which suggests poor interfacial compatibility of EPDM-g-MA/TiO<sub>2</sub>. Since the graft efficiency of EPDM was very low (about 3%), the polarity of most EPDM molecules were still unchanged, which caused poor interfacial compatibility while blended with polar pristine TiO<sub>2</sub> particles.

**Mechanical analysis**

Figure 3 showed the tensile strength and the elongation at break of the composites with different filler loadings. It can be seen that with the increase of TMPS content, the tensile strength and the elongation at break all increased more sharply. While the TMPS content was no more than 7.5% wt, tensile strength and the elongation at break increased as the filler content did. The tensile strength increased from 1.5 MPa for EPDM-g-MA to 6.2 MPa for EPDM-g-MA/7.5%TMPS and the elongation at break from 317 to 2435% correspondingly. Liu et al.<sup>21</sup> has previously prepared EPDM/montmorillonite composites by melt blending method. Although the particle size of TiO<sub>2</sub> is much larger than the layer of montmorillonite, the improvement in mechanical performances is similar to EPDM/montmorillonite composite. When the content of TMPS exceeded 7.5% wt, the tensile strength and the elongation at break were decreased by reason of the aggregation of TMPS particles that lead to the decrease of interfacial area. The mechanical improvements of EPDM-g-MA/TiO<sub>2</sub> were nearly similar to those of pristine EPDM.

Swelling and solution test were taken out to determine the crosslinking degree of the composites. It can be seen from Tables I and II that the swelling

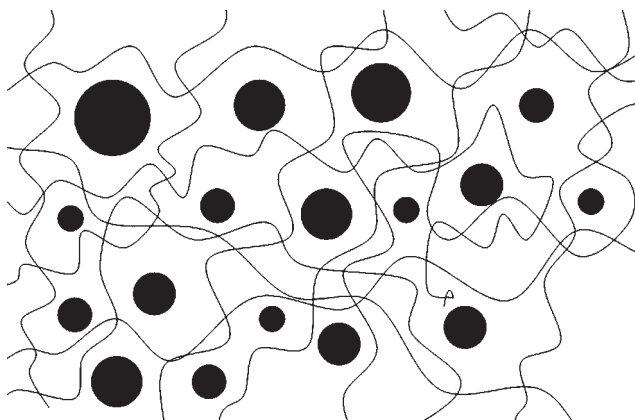
**TABLE II**  
Solution Percentage Test of Different Samples

	1 h	3 h	6 h	12 h	24 h	48 h
EPDM-g-MA	0.9	1.5	2.2	2.7	2.9	3.0
EPDM-g-MA/2.5% TMPS	0.6	1.1	1.4	2.0	2.6	2.8
EPDM-g-MA/7.5% TMPS	0.4	0.6	1.1	1.4	2.1	2.2
EPDM-g-MA/12.5% TMPS	0.2	0.4	0.8	1.2	1.8	2.0
EPDM-g-MA/7.5% TiO <sub>2</sub>	0.7	1.1	1.0	1.9	2.7	3.0

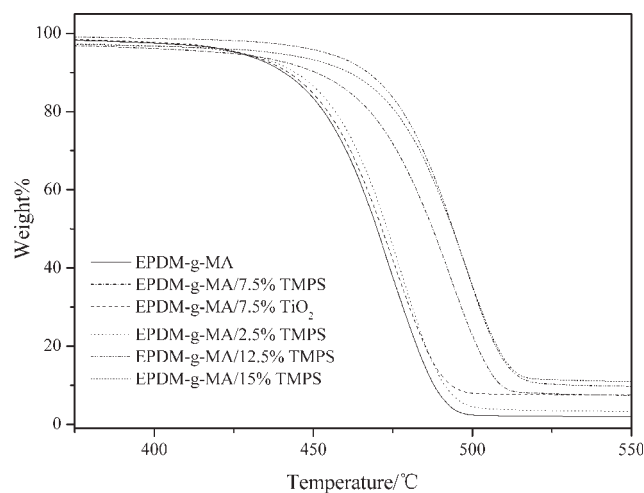
and solution results of composites filled by TMPS were smaller than those of EPDM-g-MA, and the higher TMPS content samples contained the lower swelling and solution displayed. Furthermore, TMPS filled composites showed smaller swelling and solution than TiO<sub>2</sub> filled ones. Consequently, EPDM-g-MA/TMPS had a larger crosslinking degree than EPDM-g-MA/TiO<sub>2</sub>, and the more TMPS filled the larger crosslinking degree EPDM-g-MA/TMPS had. Seen from the above results, it is reasonable that EPDM-g-MA/TMPS performed better in mechanical properties by reason of higher crosslinking degree, better interfacial compatibility, and better dispersion of filler particles as illustrated in Figure 4. However, a decreased trend was showed in both tensile strength and elongation at break when TMPS filler exceeded 7.5% wt though having similar interfacial compatibility and even larger crosslinking degree, which may be caused by the aggregation of ultrafine filler particles at higher filler contents.

### Thermal properties

Figure 5 showed the TGA thermograms of different samples in nitrogen atmosphere. It can be seen that the decomposition temperature of EPDM-g-MA/TMPS was much higher than that of pristine EPDM while that of EPDM-g-MA/TiO<sub>2</sub> was nearly the same as pristine EPDM. With the increment of filler loadings, the decomposition temperature increased and reached the maximum at the filler loading of 12.5% wt (the increment was about 20°C). The increase in resistance to thermal decomposition resulted for the fact that ultrafine TiO<sub>2</sub> particles were able to sustain high temperature and to retard the heat to diffuse into EPDM matrix. With further increment of filler loadings, no further increases in thermal resistance of composites were observed. One possibility is that with higher TMPS content, for example 15% wt, TMPS particles aggregated more



**Figure 4** Sketch of the filler particles with homogeneous dispersion in polymer/inorganic composites.



**Figure 5** TGA thermograms of different samples.

seriously in EPDM matrix, which made the decline in thermal resistance. The results of TGA were consistent with the previous SEM and mechanical analysis.

### CONCLUSIONS

Composites of EPDM/TiO<sub>2</sub> in which TiO<sub>2</sub> particles were surface modified with  $\gamma$ -MPS and preultrasonically dispersed and EPDM was grafted with MA were successfully prepared. Good interfacial compatibility and homogeneous dispersion of filler particles were observed from SEM images. The tensile strength increased from 1.5 MPa for EPDM-g-MA to 6.2 MPa for EPDM-g-MA/TMPS and the elongation at break from 317 to 2435% correspondingly. Swell and solution test confirmed the evident crosslinking structure of the composites. The results of TGA showed that the thermal stability of the composites was greatly improved provided with the increment in decomposition temperature by about 20°C.

### References

1. Mele, P.; Marceau, S.; Brown, D.; Puydt, Y. D.; Alberola, N. D. *Polymer* 2002, 43, 5577.
2. Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
3. Bokobza, L.; Chauvin, J. P. *Polymer* 2005, 46, 4144.
4. Bokobza, L. *J Appl Polym Sci* 2002, 85, 2301.
5. Yoshikai, K.; Ohsaki, T.; Furukawa, M. *J Appl Polym Sci* 2002, 85, 2053.
6. Choi, S. S.; Chung, K. H.; Nah, C. W. *Polymer Adv Technol* 2003, 14, 557.
7. Choi, S. S. *J Appl Polym Sci* 2001, 79, 1127.
8. Nugay, N.; Erman, B. *Macromol Symp* 2001, 169, 269.
9. Cai, H. H.; Li, S. D.; Tian, G. R.; Wang, H. B.; Wang, J. H. *J Appl Polym Sci* 2003, 87, 982.
10. Jordan, J.; Jacob, K. I.; Tannenbaum, R.; Sharaf, M. A.; Jasiuk, I. *Mater Sci Eng A* 2005, 393, 1.
11. Thostenson, E. T.; Li, C. Y.; Chou, T. W. *Compos Sci Technol* 2005, 65, 491.

12. Ma, J.; Yu, Z. Z.; Kuan, H. C.; Dasari, A.; Mai, Y. W. *Macromol Rapid Commun* 2005, 26, 830.
13. Kato, M.; Tsukigase, A.; Tanaka, H.; Usuki, A.; Inai, I. *J Polym Sci* 2006, 44, 1182.
14. Zheng, H.; Zhang, Y.; Peng, Z. L.; Zhang, Y. X. *Polym Test* 2004, 23, 217.
15. Usuki, A.; Tukigase, A.; Kato, M. *Polymer* 2002, 43, 2185.
16. Bandyopadhyay, A.; Bhowmick, A.K.; Sarkar, M. D. *J Appl Polym Sci* 2004, 93, 2579.
17. Dewimille, L.; Bresson, B.; Bokobza, L. *Polymer* 2005, 46, 4135.
18. Zhang, Q.; Tian, M.; Wu, Y. P.; Lin, G.; Zhang, L. Q. *J Appl Polym Sci* 2004, 94, 2341.
19. Yan, H. X.; Tian, G. H.; Sun, K.; Zhang, Y.; Zhang, Y. X.; Fan, Y. Z. *J Polym Sci Part B: Polym Phys* 2005, 43, 573.
20. Bai, B.; Zhao, J. L.; Feng, X. *Mater Lett* 2003, 57, 3914.
21. Liu, B. L.; Ding, Q. J.; He, Q. H.; Cai, J.; Hu, B. X.; Shen, J. *J Appl Polym Sci* 2006, 99, 2578.