

# Preparation and Properties of Polytetrafluorethylene Filled Ethylene–Propylene–Diene Monomer Composites

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**ABSTRACT:** Ethylene–propylene–diene monomer/polytetrafluorethylene (EPDM/PTFE) composites based on EPDM and electron beam irradiated PTFE powders (MS-II, MS-III, and MS-V, with mean diameter 5  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 0.1  $\mu\text{m}$ , respectively) were prepared by a mechanical compounding technique. The curing characteristics, morphologies, mechanical properties, and abrasion behaviors of these composites were investigated. The curing measurements indicated that the addition of lower loading of MS-III or MS-V enhanced the lubrication of EPDM compounds and delayed the curing process. The morphological structure of the composites demonstrated that the MS-III and

MS-V were uniformly dispersed in EPDM matrix and the efficient polymer–filler interfacial interactions were constructed. In comparison with EPDM/MS-II and EPDM/MS-III, EPDM/MS-V exhibited outstanding tensile strength, tear strength, elongation at break, and abrasion resistance due to the nanometer particle dimension and good dispersion of MS-V as well as the stronger interfacial interactions between MS-V and the EPDM matrix. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3734–3740, 2012

**Key words:** composites; rubber; polytetrafluorethylene; strength

## INTRODUCTION

Polymer research is widely focusing on the development of polymer composites with various nanometer size particles during the last decades, which have engrossed considerable attention and interest of the scientists worldwide.<sup>1–4</sup> Among various synthetic rubbers available, ethylene–propylene–diene monomer (EPDM), combines a saturated polymer backbone with residual unsaturated as side groups, appears to be a better choice, because of its easy processibility and higher resistance to heat, to weathering, to oxygen, to ozone and to salinity. As a result, EPDM is extensively used in many different molded and extruded applications for various industry segments such as automotive sealing systems, building profiles, electrical powder cables, white side walls of tires, roofing sheet, belting, and sport-

ing goods as well as insulator compounds used in solid propellant rocket motors.<sup>5–8</sup> However, the strength of EPDM gum is too lower for industrial applications. It must be reinforced by fillers to obtain adequate strength. An elastomer is mixed with another one for three reasons: to improve properties of the original material, to improve processibility, or to lower costs.<sup>9</sup> The modified polytetrafluorethylene (PTFE) micropowder which is produced by exposing commercial PTFE to electron beam radiation is commonly used as additive to a wide variety of applications.<sup>10</sup> Electron beam irradiated PTFE micropowder filled styrene-butadiene-styrene (SBS), chloroprene rubber (CR), acrylonitrile-butadiene-rubber (NBR), and EPDM were produced which was potentially used as abrasion-resistance materials and seal materials.<sup>11–13</sup>

Rubber based composites can be prepared by various methods. The mechanical compounding technique is the most promising one in industrialization due to its simplicity of preparations. Rubber based nanocomposites exhibit mechanical and chemical properties very different from their bulk counterpart and micro-composites, because of the nanoscale dispersion of reinforcement fillers and their higher surface-to-volume ratio.<sup>14</sup> In this work, three species of PTFE powders, i.e., MS-II, MS-III, and MS-V, with mean diameter of 5  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 0.1  $\mu\text{m}$ , respectively, were used as reinforcing fillers to prepared EPDM/PTFE composites. The curing

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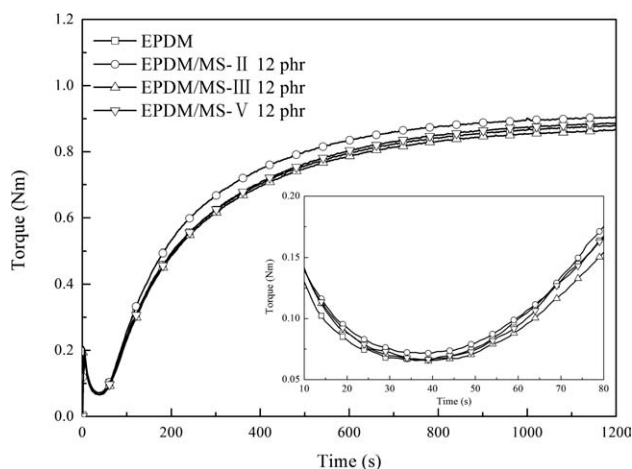


Figure 1 Curing curves of EPDM/PTFE 12 phr.

characteristics, morphologies, mechanical properties, and abrasion behaviors of those composites were investigated.

## EXPERIMENTAL

### Materials

Experiments were carried out with EPDM vistalon 2504N (ExxonMobil Chemical), in which the diene species is ethylidene norbornene (ENB). The EPDM was composed of 55.5 wt % ethylene, 40.7 wt % propylene and 3.8 wt % ENB having mooney viscosity of ML(1 + 4) 25 at 125°C. Electron beam irradiated PTFE powders, i.e., MS-II, MS-III, and MS-V (with mean diameter 5  $\mu\text{m}$ , 1  $\mu\text{m}$ , and 0.1  $\mu\text{m}$ , respectively, Shanghai ADD Nano-ST Co., China) were used as received. And the irradiation doses of MS-II, MS-III, and MS-V were 150 kGy, 200 kGy, and 300 kGy, respectively. The irradiation process was carried out in the presence of air and at room temperature. The vulcanization curatives: zinc oxide (ZnO), stearic acid (SA), triallyl isocyanurate (TAIC), 2-mercaptobenzimidazole (MB), poly(1,2-dihydro-2,2,4-trimethyl-quinoline) (RD), bis(1-methyl-1-phenylethyl) peroxide (DCP), and sulfur (S) were commercial products, and the formed mixing was, EPDM: 100 phr, ZnO: 5 phr, SA: 0.5 phr, RD 0.5 phr, MB: 0.5 phr, TAIC: 1.5 phr, S: 0.4 phr, DCP: 3 phr, PTFE: various.

### Sample preparation

Compounding was performed in an XK160 open two-roll mill (Shanghai Yayue Rubber and Plastics Machinery Co., China) at room temperature. The compounds were left overnight before vulcanization. Then the compounds were subjected for compression molding in an electrically heated hydraulic

press at 170°C for the optimum curing time ( $T_{90}$ ) to get square sheets of  $13 \times 12 \times 0.2 \text{ cm}^3$  size.

## Characterization

Curing characteristics were derived from an MDR 2000 rheometer (Shanghai D and G Machinery Equipment Co., China) at 170°C according to ISO 3417: 1991.

The tensile and tear tests were measured on a Reger 3010 universal testing machine (Shenzhen Reger Instrument Co., China) at a crosshead speed of 500 mm/min. Measurements of tensile and tear properties of all specimens were conducted at 25°C according to relevant ISO standards, ISO 37: 2005 and ISO 34-1: 2004.

Abrasion resistance was determined on an Akron machine (Wuxi Liyuan Electronic and Chemical Equipments Co., China) according to GB/T 1689-1998.

Morphologies of fracture and abrasion surfaces of samples were examined with a SU-1510 SEM (Hitachi, Japan) at an activation voltage of 15.0 kV after coated with thin layers of gold.

## RESULTS AND DISCUSSION

### Curing characteristics

The compound torque increased dramatically during curing, and so it can be used as a monitor to investigate the curing process.<sup>15</sup> Figures 1 and 2 show the curing curves of EPDM and its compounds containing 12 phr and 24 phr PTFE powders, respectively. The results indicated that the minimum torque ( $M_L$ ) and maximum torque ( $M_H$ ) were significantly influenced by the dimension and loading of PTFE powders.

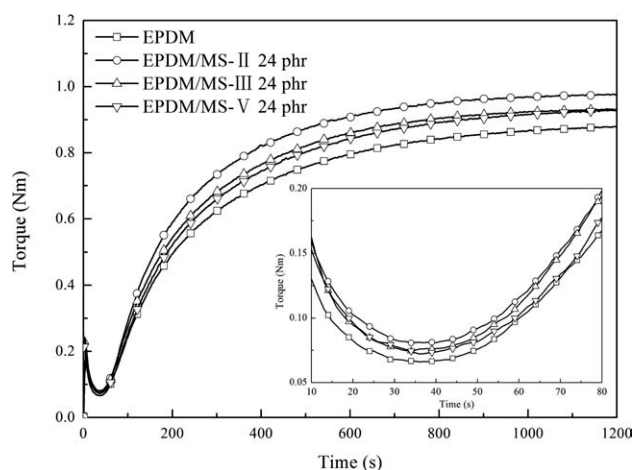
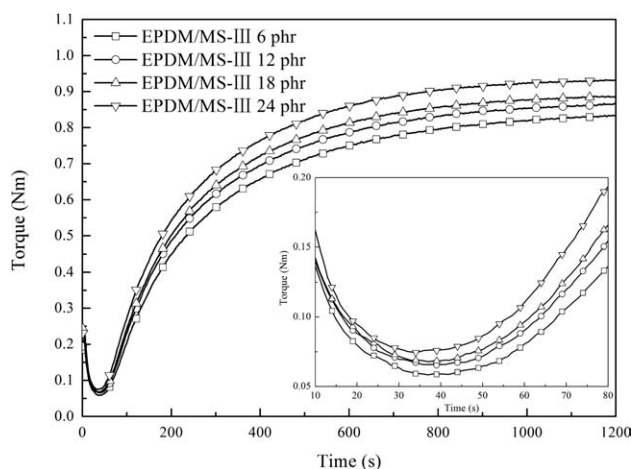


Figure 2 Curing curves of EPDM/PTFE 24 phr.

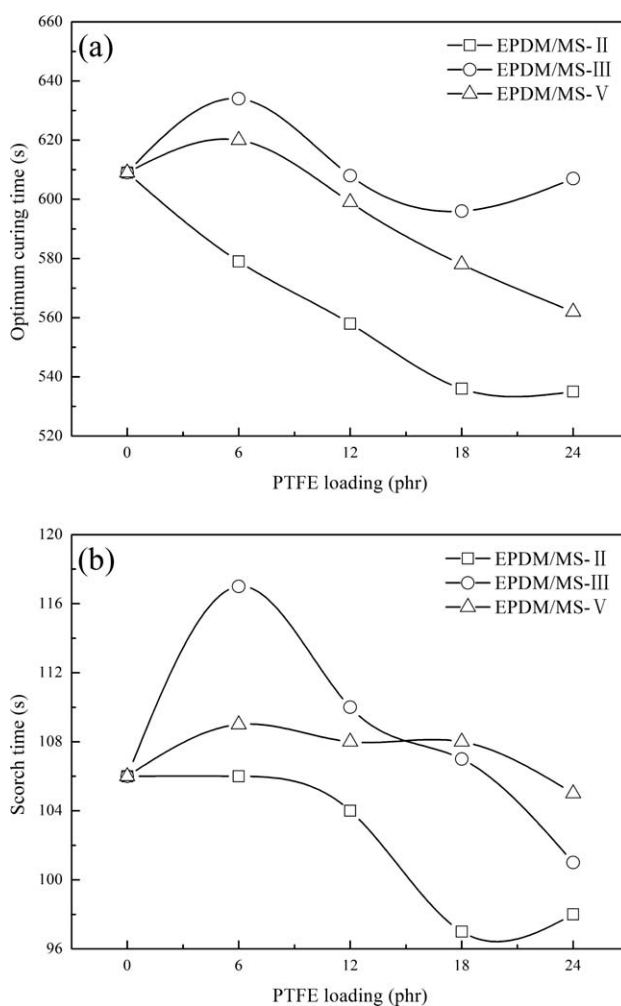


**Figure 3** Curing curves of EPDM/MS-III with various MS-III loadings.

It is well known that  $M_L$  gives an idea upon the viscosity or plasticity of the rubber compounds. The lower the  $M_L$  value, the lower the viscosity. Normally, the addition of fillers increases the  $M_L$  value because the rubber–filler interactions constrain the motion of rubber chains and increase the viscosity of the rubber compounds. However, EPDM, EPDM/MS-III, and EPDM/MS-V exhibited approach  $M_L$  values in Figure 1. The viscosity of EPDM compounds was almost not influenced by the addition of lower loading of MS-III and MS-V. This might be attributed to an evident lubrication effect resulted from the low friction coefficient of PTFE powders that were dispersed and embedded in the EPDM matrix. The lubrication effect effectively offset a proper increase of  $M_L$  value. However, EPDM/MS-III and EPDM/MS-V exhibited higher  $M_L$  values than EPDM in Figure 2, which indicates that the increase of viscosity could not be completely offset by the lubrication effect when the PTFE loading was higher. The increase of PTFE loading obviously increased the viscosity of the compounds, and hence increased the  $M_L$  value. The conclusion is further confirmed by Figure 3, where the  $M_L$  value increased with increasing the loading of MS-III. Furthermore, Figure 2 demonstrates that the  $M_L$  value was also influenced by the PTFE particle size. The larger the PTFE particle size, the higher the  $M_L$  value. In comparison with EPDM, EPDM/MS-III and EPDM/MS-V, EPDM/MS-II showed higher  $M_L$  value, due to the serious absence of nanoeffect of MS-II.

In comparison with  $M_L$ ,  $M_H$ , which depends on the cross-link density of the vulcanized compounds, as shown in Figures 1–3, exhibited almost the same trend.  $M_H$  increased with PTFE loading, and the  $M_H$  values of EPDM/MS-III and EPDM/MS-V were lower than that of EPDM/MS-II. When the filler

loading was below 12 phr,  $M_H$  values of EPDM/MS-III and EPDM/MS-V were lower than that of EPDM. According to Khan et al., electron beam irradiation induces  $-\text{COOH}$  groups on the powder surface, and the concentration of  $-\text{COOH}$  groups increases with increasing the irradiation dose.<sup>10–13</sup> It clearly that the finer the PTFE powders, the more the  $-\text{COOH}$  groups are induced under the same electron beam irradiation conditions. Therefore MS-II and MS-V should possess the lowest and highest concentration of COOH groups respectively. At the same time, higher structure and specific surface area should also be obtained for the finer PTFE powders. The factors mentioned above increased the absorption of curing agents to the finer PTFE powders, and hence delayed the curing process. As can be seen in Figure 4, EPDM/MS-III and EPDM/MS-V showed longer optimum curing time ( $T_{90}$ ) and scorch time ( $T_{s2}$ ) than EPDM/MS-II due to their lower particle size. It was notable that for EPDM/MS-III and EPDM/MS-V,  $T_{90}$  and  $T_{s2}$  increased with increasing filler



**Figure 4** Optimum curing time ( $T_{90}$ ) and scorch time ( $T_{s2}$ ) of EPDM/PTFE: (a)  $T_{90}$ , (b)  $T_{s2}$ .

loading up to 6 phr. Further increase of filler loading decreased  $T_{90}$  and  $T_{s2}$ , indicating that the curing process of EPDM/MS-III and EPDM/MS-V was accelerated. However, less than 12 phr or 18 phr,  $T_{90}$  and  $T_{s2}$  of EPDM/MS-III and EPDM/MS-V were still longer than that of EPDM. The above results illustrated that there was a balanceable state of saturation for the PTFE powders function on the vulcanization of EPDM/MS-III and EPDM/MS-V. Before the balanceable state, the higher the filler loading, the higher the values of  $T_{90}$  and  $T_{s2}$ ; but after the balanceable state, the higher the filler loading, the lower the values of  $T_{90}$  and  $T_{s2}$ . While for EPDM/MS-II compounds, however,  $T_{90}$  and  $T_{s2}$  decreased gradually as the loading of MS-II increased.

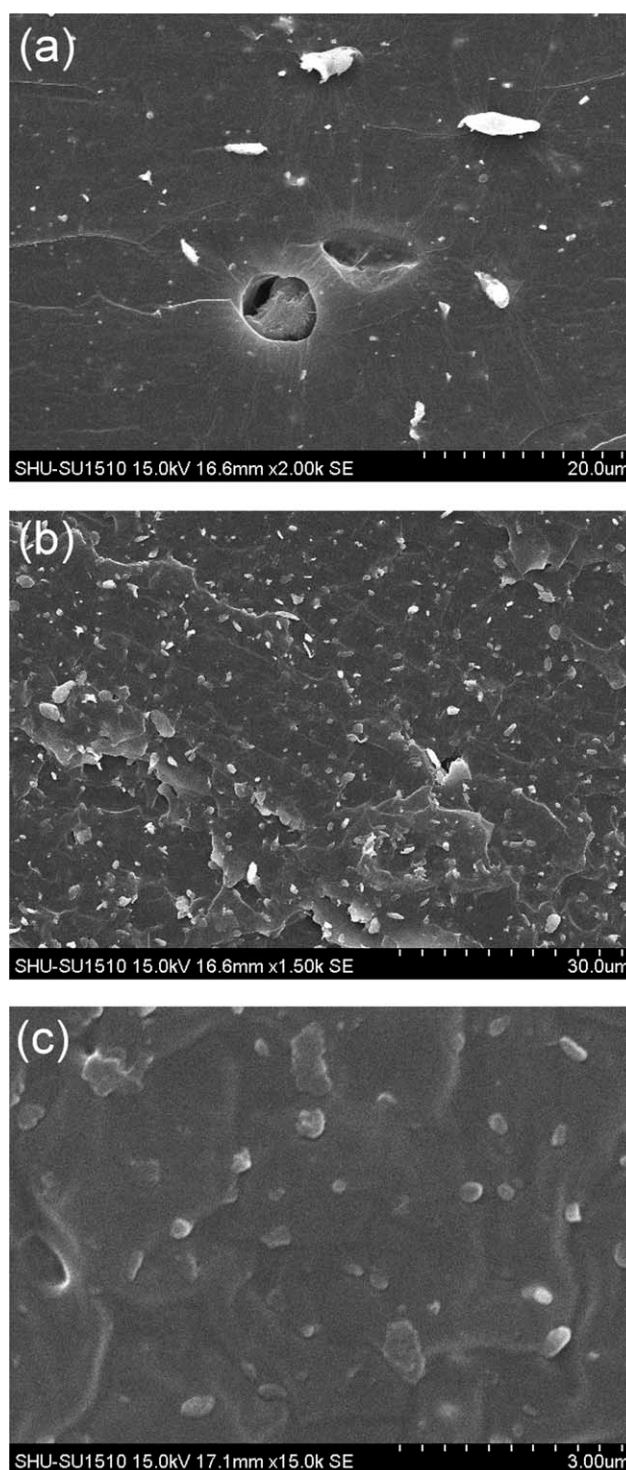
### Morphology

The morphology is often considered to be of crucial importance for the mechanical properties of composites.<sup>16</sup> An efficient dispersion of fillers in the polymer matrix and an adequate polymer–filler interfacial adhesion are two essential factors control the performance of polymer based composites.<sup>17–20</sup> The  $-\text{COOH}$  groups on the surface of PTFE could react with ZnO during the mixing process of the rubber compounds.<sup>12</sup> The generated zinc complex should facilitate the cross-link on the surfaces of PTFE particles and chemical bonds between EPDM matrix and PTFE particles should be formed. Given the higher concentration of  $-\text{COOH}$  groups of lower size PTFE powders, however, more chemical bonds should be formed, and hence the better interfacial interactions should be obtained. The fracture surfaces of EPDM/PTFE 18 phr composites, observed by SEM, are shown in Figure 5. Voids and sharp interfacial boundaries can be observed clearly on the fracture surface of EPDM/MS-II 18 phr in Figure 5(a), which were possibly resulted from the poor compatibility between MS-II and EPDM matrix, and hence might deteriorate the mechanical properties. Whereas, Figure 5(b,c) demonstrate that MS-III and MS-V were uniformly dispersed in EPDM matrix, particularly MS-V appearing blurred interfacial boundaries, which indicated expected reinforcing effect might be achieved.

### Mechanical properties

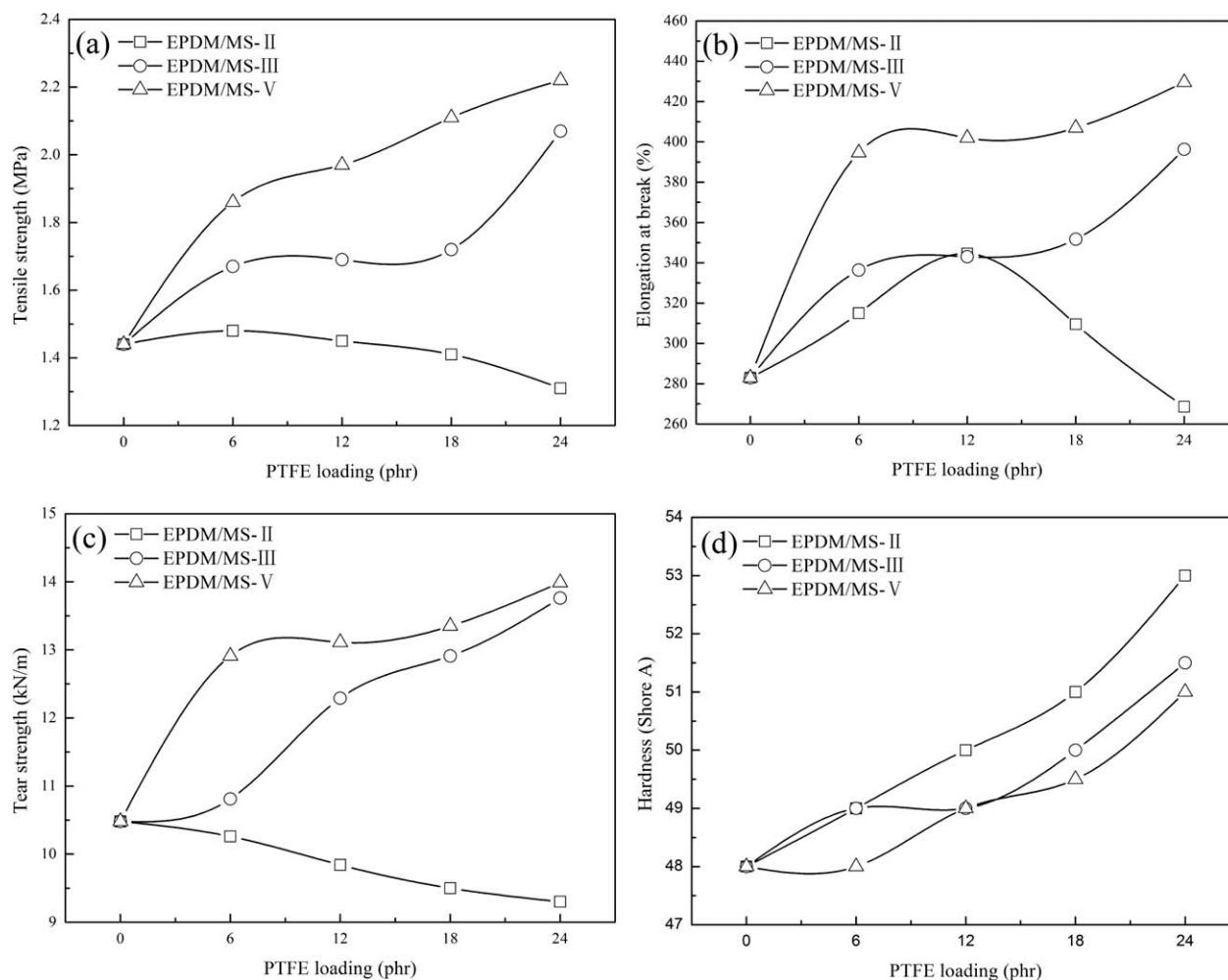
The mechanical properties of EPDM/PTFE composites are summarized in Figure 6. In comparison with EPDM and EPDM/MS-II, a marked increase of mechanical properties could be observed for EPDM/MS-III and EPDM/MS-V.

As shown in Figure 6(a), the tensile strength increased with the decrease of the PTFE powder dimension. For EPDM/MS-III and EPDM/MS-V, the tensile strength increased with increasing the filler



**Figure 5** SEM images of EPDM/PTFE 18 phr: (a) EPDM/MS-II, (b) EPDM/MS-III, (c) EPDM/MS-V.

loading, while for EPDM/MS-II, the tensile strength increased when the loading was below 6 phr and then decreased. At 24 phr loading of MS-III and MS-V, the tensile strengths at break of composites were 2.07 MPa and 2.22 MPa, respectively. Whereas for EPDM/MS-II, with the loading of 6 phr and 24 phr, the tensile strength of composites was 1.48 MPa and

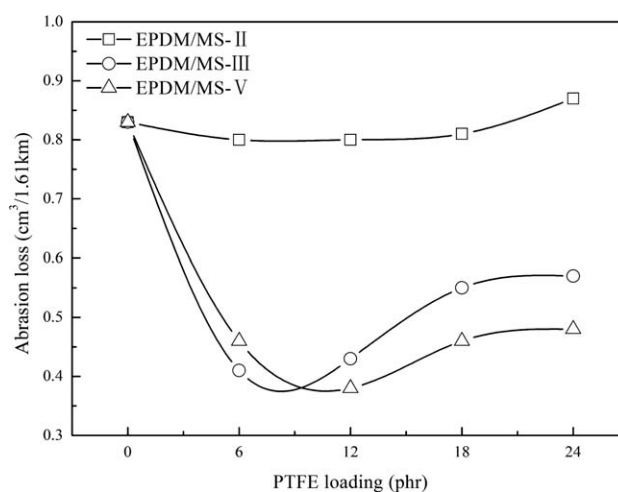


**Figure 6** Mechanical properties of EPDM/PTFE: (a) tensile strength, (b) elongation at break, (c) tear strength, (d) hardness.

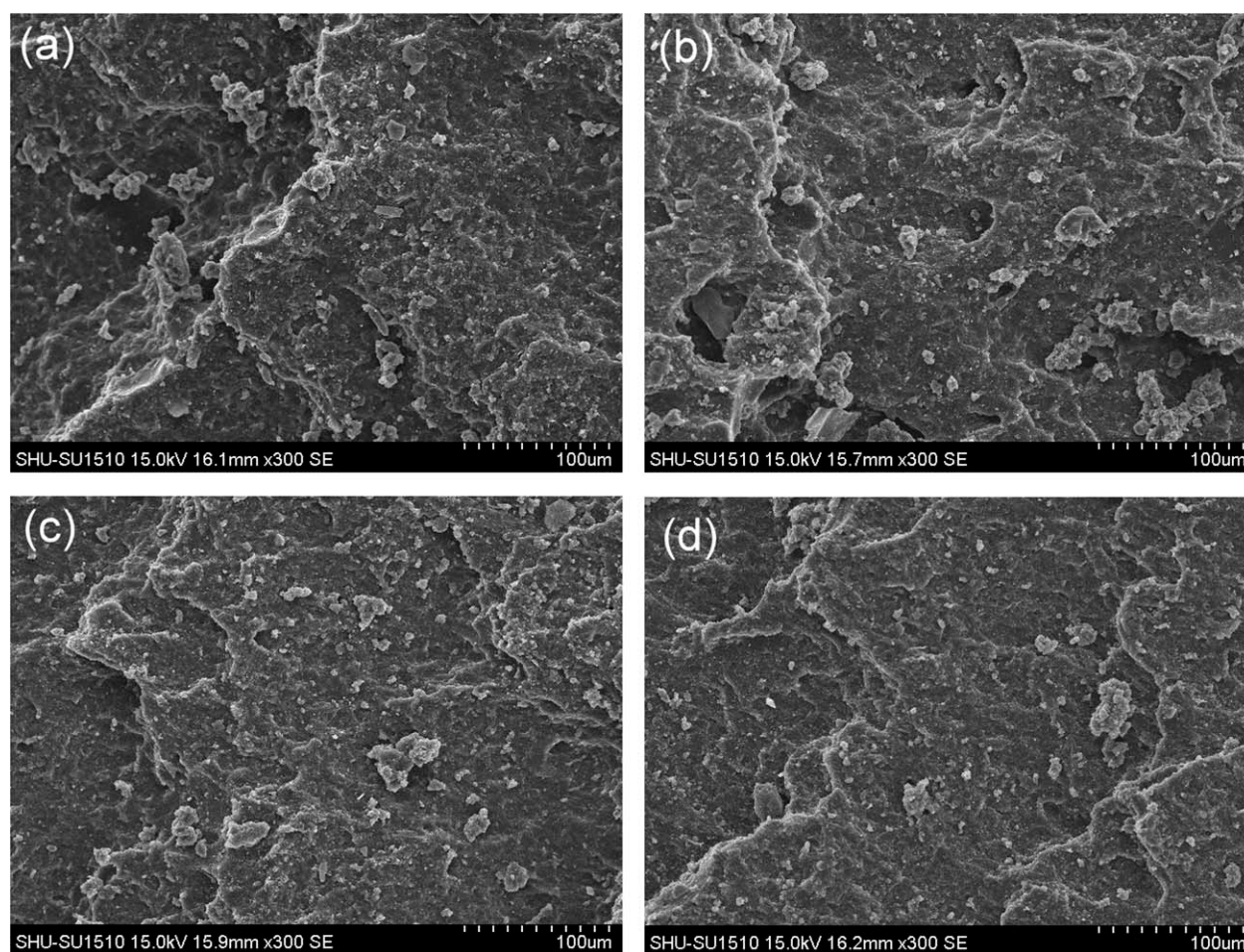
1.31 MPa, respectively. The similar trend for elongation at break and tear strength can also be found in Figures 6(b,c), respectively. Generally, mechanical properties of a filled rubber based composite are influenced by the filler dimension, the filler dispersion, and the rubber–filler interactions. Finer filler dimension corresponds to larger specific surface area, increasing the opportunities of chemical bonds occurrence between fillers and rubber molecules. When the rubber samples are stretched, the breakage depends on the amount of stress concentration points or filler inhomogeneities within rubber. For EPDM/MS-III and EPDM/MS-V, finer dimension and homogenous dispersion of fillers within EPDM matrix resulted in better mechanical performances than EPDM, while for EPDM/MS-II, the larger dimension of MS-II induced weak spots and voids, with which the composite could not endure larger deformation and finally the rupture happened. However, as can be seen from Figure 6(d), EPDM/MS-II exhibited a higher hardness compared with EPDM/MS-III and EPDM/MS-V.

### Abrasion resistance

Figure 7 shows the abrasion loss of EPDM/PTFE composites. Abrasion behavior of rubber based



**Figure 7** Abrasion loss of EPDM/PTFE.



**Figure 8** SEM images of abraded surfaces of EPDM/PTFE: (a) EPDM, (b) EPDM/MS-II 12 phr, (c) EPDM/MS- III 12 phr, (d) EPDM/MS-V 12 phr.

composites was decided by periodic tear and tensile action on the sample surface. On the one hand, the introduction of PTFE powders increased the lubrication of the composites, the powders were transmitted to the abrasion surface and formed a lubricant film during the abrasion process, and therefore it decreased the friction coefficient and increased the abrasion resistance. On the other hand, the introduction of PTFE powders increased the number of stress concentration points within the whole matrix, particularly when the filler possessed a larger dimension. This increased the opportunities of bulk breakage, and hence decreased the abrasion resistance. In this work, a filler loading of 6–12 phr was found to enhance the abrasion resistance of EPDM/MS-III and EPDM/MS-V greatly. In particular, EPDM/MS-V exhibited the highest abrasion resistance, because its nanostructure improved the mechanical and lubrication properties of the nanocomposites.

Figure 8 shows the abraded surfaces of EPDM/PTFE composites when the filler loading was 12 phr. From Figure 8(a), severe coarse surface, loose frag-

ments, and grains worn away from the matrix were observed, which displayed a classic fracture wear behavior of EPDM. Figure 8(b) also shows some cracks or separations on the abrasion surface which might due to some MS-II particles were pulled out from the EPDM matrix during abrasion test. Figures 8(c,d) show both relatively smooth and less bulk fractures, which indicate that the good adhesion between fillers and EPDM matrix was achieved. Obvious reinforcing effect of MS-III and MS-V in EPDM matrix decreased the degree of bulk fracture.

## CONCLUSIONS

EPDM based composites filled with three different electron beam irradiated PTFE powders were prepared by mechanical compounding. Curing measurements showed that MS-III or MS-V, in comparison with MS-II, enhanced the lubrication of EPDM compounds, decreased the  $M_L$  value and delayed the curing process. The morphology of composites illustrated that MS-III and MS-V were uniformly dispersed in EPDM matrix and adequate polymer-filler

interfacial adhesion were formed, while for EPDM/MS-II, holes and sharp interfacial boundaries could be observed clearly on fractured surfaces. As a result, EPDM/MS-III and EPDM/MS-V exhibited higher mechanical properties than EPDM/MS-II. MS-III and MS-V within compounds showed excellent lubrication effect due to its homogeneous dispersion in EPDM matrix and strong interfacial interactions with EPDM molecules, therefore they decreased the abrasion loss of composites. As a comparison, MS-II particles were pulled out from EPDM matrix and the abrasion resistance of EPDM/MS-II was almost not improved.

## References

1. Roj, S.; Das, A.; Thakur, V.; Mahaling, R. N.; Bhowmick A. K.; Heinrich, G. *Mater Des* 2010, 31, 2151.
2. Liu, Y.; Li, L.; Wang, Q. *J Appl Polym Sci* 2010, 118, 1111.
3. Kim, I. J.; Kim, W. S.; Lee, D. H.; Kim, W.; Bae, J. W. *J Appl Polym Sci* 2010, 117, 1535.
4. Zheng, Y.; Zheng, Y.; Ning, R. *Mater Lett* 2003, 57, 2940.
5. Martin, G.; Barrès, C.; Cassagnau, P.; Sonntag, P.; Garois N. *Polymer* 2008, 49, 1892.
6. Zhao, Q.; Li, X.; Gao, J. *Polym Degrad Stab* 2007, 92, 1841.
7. Ismail, H.; Pasbakhsh, P.; Ahmad Fauzi, M. N.; Abu Bakar, A. *Polym Test* 2008, 27, 841.
8. Zhao, Q.; Li, X.; Gao, J.; Jia, Z. *Mater Lett* 2009, 63, 116.
9. Gu, Z.; Song, G.; Liu, W.; Li, P.; Gao, L.; Li, H.; Hu, X. *Appl Clay Sci* 2009, 46, 241.
10. Schierholz, K.; Lappan, U.; Lunkwitz, K.; *Nucl Instrum Methods Phys Sect B* 1999, 151, 232.
11. Khan, M. S.; Lehmann, D.; Heinrich, G.; Franke, R. *Wear* 2009, 266, 200.
12. Khan, M. S.; Lehmann, D.; Heinrich, G. *Acta Mater* 2009, 57, 4882.
13. Khan, M. S.; Franke, R.; Lehmann, D.; Heinrich, G. *Tribol Inter* 2009, 42, 890.
14. Arroyo, M.; López-Manchado, M. A.; Herrero, B. *Polymer* 2003, 44, 2447.
15. Qi, Q.; Wu, Y.; Tian, M.; Liang, G.; Zhang, L.; Ma, J. *Polym* 2006, 47, 3896.
16. Kaneko, M. L. Q. A.; Yoshida I. V. P. *Appl Polym Sci* 2008, 108, 2587.
17. Du, M.; Guo, B.; Lei, Y.; Liu, M.; Jia, D. *Polymer* 2008, 49, 4871.
18. Wang, Y.; Hu, Y.; Chen, L.; Gong, X.; Jiang, W.; Zhang, P.; Chen, Z. *Polym Test* 2006, 25, 262.
19. Pasbakhsh, P.; Ismail, H.; Ahmad Fauzi, M. N.; Abu Bakar, A. *Appl Clay Sci* 2010, 48, 405.
20. Carretero-González, J.; Retsos, H.; Verdejo, R.; Toki, S.; Hsiao, B. S.; Giannelis, E. P.; López-Manchado, M. A. *Macromolecules* 2008, 41, 6763.