

# Tensile Properties and Stress Whitening of Polypropylene/Polyolefin Elastomer/Magnesium Hydroxide Flame Retardant Composites for Cable Insulating Application

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**ABSTRACT:** Flame retardant polypropylene (PP) composites were prepared by combining random polypropylene with uncoated and surface-treated forms of magnesium hydroxide filler and elastomeric modifiers, with and without maleic anhydride functionalization. Four types of magnesium hydroxide (MDH) with different surface treatments were compounded at amounts up to 60% by weight to PP/polyolefin elastomer (POE) matrix resin to obtain a series of composites. The tensile strength and elongation at break were measured. MDH coated with polymeric material was found to give a high elongation at break value com-

pared with the values obtained with uncoated and vinyl silane and amino silane coated MDH. Two types of POE, i.e., neat and maleic anhydride grafted POE (POEgMA), were used to investigate the stress whitening of composites in bending deformation. POEgMA used composites showed no stress whitening while neat POE used composites showed whitening when bended. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2311–2318, 2005

**Key words:** polypropylene; mechanical properties; flame retardance; polyolefins; voids

## INTRODUCTION

Polypropylene (PP) is made nonflammable generally by the use of organohalogen type fire retardants. This method, however, poses such problems as toxicity of fire retardants, corrosion during melt processing, and emission of smoke and toxic fumes in processing and fires. Therefore, much attention has been paid to such fire retardants as aluminum hydroxide (ATH) and magnesium hydroxide (MDH), which are nontoxic and avoid the above-mentioned difficulties. These flame retardants are perhaps the most environmentally friendly flame retardants since both release just water vapor during fire. However, ATH begins to dehydrate at about 180°C and is hence unusable for such thermoplastics resins as PP whose processing temperature is at least about 200°C. MDH, on the other hand, has the advantage that its decomposition into MgO and H<sub>2</sub>O starts at a relatively high temperature (300–320°C), thus allowing it to be processed in plastics for which ATH is not thermally stable enough.

Both ATH and MDH have some drawbacks. To be effective in flame retardancy, high filler loading (60 wt %) is necessary, resulting in a significant loss in mechanical properties, especially in elongation at break and stress whitening in bending deformation.<sup>1–6</sup>

Recently there has been a great demand to develop PP-based resin as cable insulating material in the cable industry. This is particularly true for automotive cable insulation applications where plasticized PVC and PE/EVA are the main polymers currently used. PVC, although a better fire retardant polymer than polyolefins, is a source of health and environmental problems due to potentials for release of chlorine-containing chemicals. PE/EVA, on the other hand, has a certain limitation in its low application temperature. Therefore, it is expected that PP-based resin is the most promising material that can replace PVC or PE/EVA. For the application of PP type resin for cable insulating materials, not only flame retardancy but also flexibility and tensile properties, e.g., tensile strength and elongation at break, must be satisfied. Generally, the flexibility of PP can be improved by blending with elastomers such as ethylene propylene copolymer (EPR) and ethylene-propylene-diene monomer (EPDM). Polyolefin elastomer (POE) is a poly(ethylene-octene) copolymer developed using a metallocene

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TABLE I  
Compounding Formulations of PP/POE/MDH Composites

Code	PP (wt %)	POE (wt %)	POEgMA (wt %)	PPgMA (wt %)	MDH (H5) (wt %)	MDH (H5A) (wt %)	MDH (H5IV) (wt %)	MDH (H5HV) (wt %)
1	100	—	—	—	—	—	—	—
2	—	100	—	—	—	—	—	—
3	—	—	100	—	—	—	—	—
4	40	—	—	—	60	—	—	—
5	40	—	—	—	—	60	—	—
6	40	—	—	—	—	—	60	—
7	40	—	—	—	—	—	—	60
8	50	—	50	—	—	—	—	—
9	60	—	40	—	—	—	—	—
10	70	—	30	—	—	—	—	—
11	80	—	20	—	—	—	—	—
12	90	—	10	—	—	—	—	—
13	20	20	—	—	60	—	—	—
14	20	—	20	—	60	—	—	—
15	20	—	20	—	—	60	—	—
16	20	—	20	—	—	—	60	—
17	20	—	20	—	—	—	—	60
18	19.75	—	19.75	0.5	—	—	—	60
19	19.5	—	19.5	1	—	—	—	60
20	18.5	—	18.5	3	—	—	—	60
21	17.5	—	17.5	5	—	—	—	60
22	23.7	—	15.8	0.5	—	—	—	60
23	27.65	—	11.85	0.5	—	—	—	60
24	31.6	—	7.9	0.5	—	—	—	60
25	35.55	—	3.95	0.5	—	—	—	60

catalyst by Dow Chemical Co. POE is characterized by a narrow molecular weight distribution and homogeneous comonomer distribution. Compared with conventional EPR or EPDM elastomers, POE exhibits the advantage of mechanical properties when blended with PP.<sup>7–13</sup>

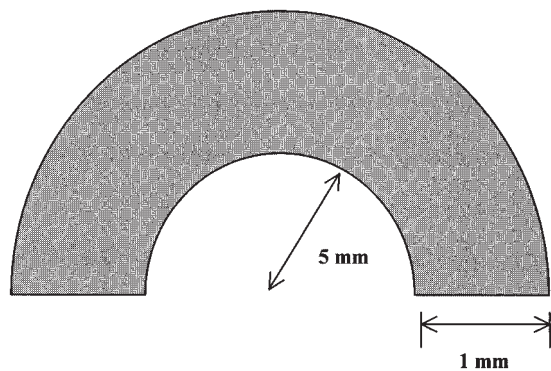
PP composites filled by MDH particles have been studied. The morphology, size, dispersion, and applied surface coating on particles influence the mechanical properties of MDH filled PP composites.<sup>14–18</sup> Miyata et al. found that the tensile yield strength decreased in proportion to the increase in the incorporated amount of MDH because there was no adhesion between the filler and the polymer matrix. However, surface coating with sodium stearate was shown to enhance the compatibility with the resin but did not afford a chemical bonding between the filler and matrix.<sup>14</sup> Jancar and Kucera found that PPgMA molecules were chemically bonded on the filler surface due to the acid–base interaction between carboxyl groups grafted on PPgMA and hydroxyl groups from the filler surface. On the other hand, surface coating with stearic acid led to the reduction in tensile yield strength compared to composites containing pure MDH due to the lower thermodynamic work of adhesion.<sup>15</sup> However, systematic investigations on the effect of filler surface treatment and the effect of functionalized POE incorporation into PP matrix have not been reported.

In this study, we prepared PP/POE/MDH composites with four different types of MDH and with two different types of POE and investigated their tensile properties as well as stress whitening in bending deformation. Finally, we tried to find the best compounding formulation of PP/elastomer/MDH composite for cable insulating applications.

## EXPERIMENTAL

### Materials

Random PP used in this study was R724J supplied by LG-Caltex Co., Korea (density = 0.90 g/cm<sup>3</sup>, melt flow rate = 1.9 g/10 min at 230°C, 2.16 kg load) Two types of POE were incorporated into this matrix, Engage 8150 (comonomer content = 39 wt %, density = 0.868 g/cm<sup>3</sup>, melt flow rate = 0.5 g/10 min at 190°C, 2.16 kg load) obtained from DuPont Dow Elastomer and Fusabond MN 493D obtained from DuPont. The latter grade is maleic anhydride grafted POE (POEgMA) containing 0.3 wt % maleic anhydride. Maleic anhydride grafted polypropylene (PPgMA) containing 2.6 wt % maleic anhydride was supplied by Honam Petrochemical Co., Korea ( $M_w = 49,600$ ,  $M_w/M_n = 2.2$ ) Four types of MDH, employed as flame retardant, were used. The grade names are Magnifin H5, H5A, H5IV, and H5HV, supplied by Martinswerk GmbH. The average particle size was 1.0  $\mu\text{m}$  and the specific



**Figure 1** Schematic illustration of stress whitening observation in bending deformation.

surface area was 5.0 m<sup>2</sup>/g. H5 is a pure MDH. H5A, H5IV, and H5HV are surface coated MDH with vinyl silane, amino silane, and polymeric material, respectively. Pure MDH fillers have a highly polar surface that is hydrophilic rather than oleophilic in characters and is not readily wetted by organic fluids, such as hydrocarbon solvents, oil, and molten polyolefins. The surface properties can be changed by chemisorption of surface active reagents, such as fatty acids, which have both alkyl chains and polar functional groups within their structure. H5A is vinyl silane coated and H5IV is amino silane coated. H5HV is known as special material coated and the nature of this coating material is not open. Nuclear magnetic resonance and Fourier transform infrared spectroscopy analysis in our lab revealed that the coating material of H5HV was based on poly(dimethylsiloxane).

### Compounding

For the composite formation, PP, POE, PPgMA, and MDH were dry mixed and melt compounded in a mixing head (Haake Rheomix 600, Haake Rheocord 9000 system). Their compounding formulations are listed in Table I. The weight ratio of MDH in total composite was 60 wt %. It is possible to obtain UL94-V0 flammability classifications (at 3 mm thickness) with this filler in PP using 60 wt %. Because the primary aim of this study was not to optimize flammability, all MDH levels were maintained at this value to consider the effect of the modified POE and the effect of MDH surface coating on tensile properties and stress whitening. Each sample was prepared at 180°C and a rotor speed of 100 rpm for 10 min. Upon completion of compounding, the molten polymer was removed and then compression molded at 190°C and 15 metric ton of pressure to prepare a test specimen.

### Characterization

The tensile strength and elongation at break were determined using a universal testing machine at 25°C

according to ASTM D638 and the head speed was 50 mm/min. Samples were prepared from 1.0-mm-thick compression molding sheet, from which test specimens were cut using a die. All measurements were done in five replicates and the value was averaged. A JEOL JSM-35 scanning electron microscope (SEM) was used to observe phase morphology and filler dispersion. Samples were prepared by brittle fracturing under liquid nitrogen and the surfaces of specimens were gold coated. Stress whitening in bending deformation was observed by the naked eye. Sheets prepared by compression molding with thickness 1 mm were bent in a 5-mm radius of curvature. The schematic illustration of stress whitening observation in bending deformation is shown in Figure 1. Specimens that did not show stress whitening when bent are termed nonwhitened specimens in Table II.

## RESULTS AND DISCUSSION

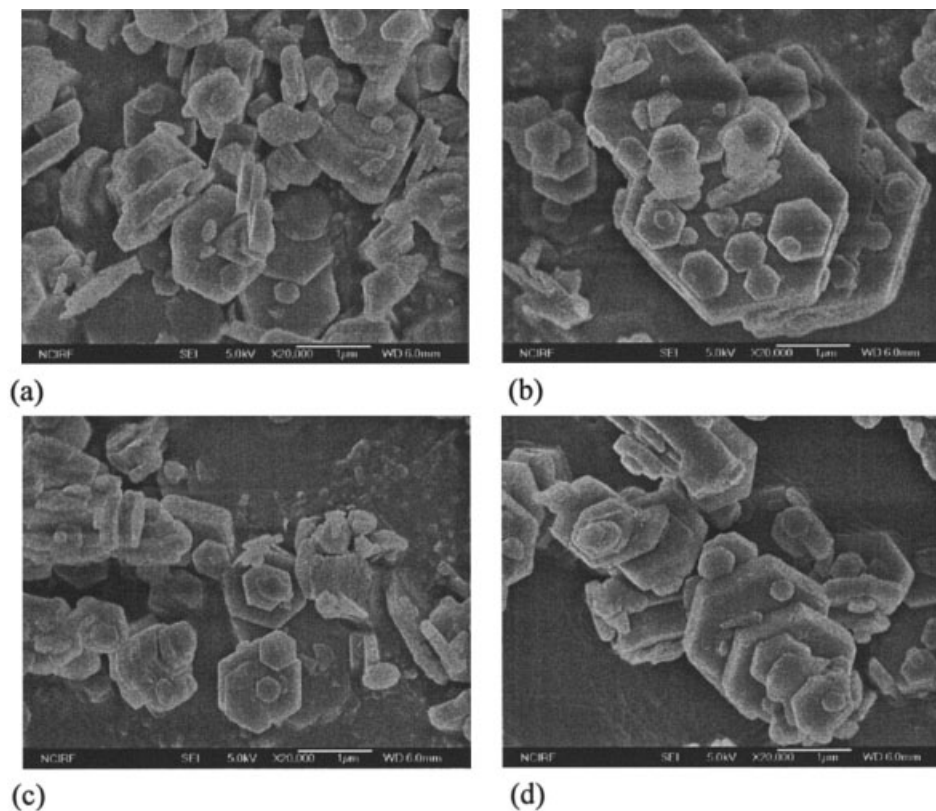
### Tensile properties of PP/MDH composites

SEM images of the uncoated and coated MDHs at a magnification of 20,000 revealed same particle struc-

**TABLE II**  
Tensile Properties and Stress Whitening of  
PP/POE/MDH Composites

Code	Tensile strength at yield (MPa)	Tensile strength at break (MPa)	Elongation at break (%)	Stress whitening under bending <sup>a</sup>
1	28	43	1190	Non
2	2.3	42.6	1953	Non
3	2.2	12.6	1564	Non
4	—	16	12	High
5	—	17.3	12	High
6	—	17.7	13	High
7	13.3	14.1	318	High
8	9.6	23.6	1222	Non
9	12.8	33.1	1325	Non
10	15.3	35.6	1333	Non
11	18.6	36.6	1166	Non
12	23.1	41.5	1210	Non
13	11.3	12.1	333	High
14	10.1	17.1	196	Non
15	10.6	16.1	156	Non
16	10.4	17.1	140	Non
17	8.2	10.0	322	Non
18	8.4	10.5	320	Non
19	9.8	11.8	251	Non
20	11.8	12.9	101	Non
21	11.9	12.1	28	High
22	10.1	16.4	586	Non
23	11.2	16.1	475	Non
24	11.7	15.1	450	Medium
25	12.9	15.1	365	High

<sup>a</sup> Non, no stress whitening occurred; high, stress whitening occurred highly; medium, stress whitening occurred intermediately.



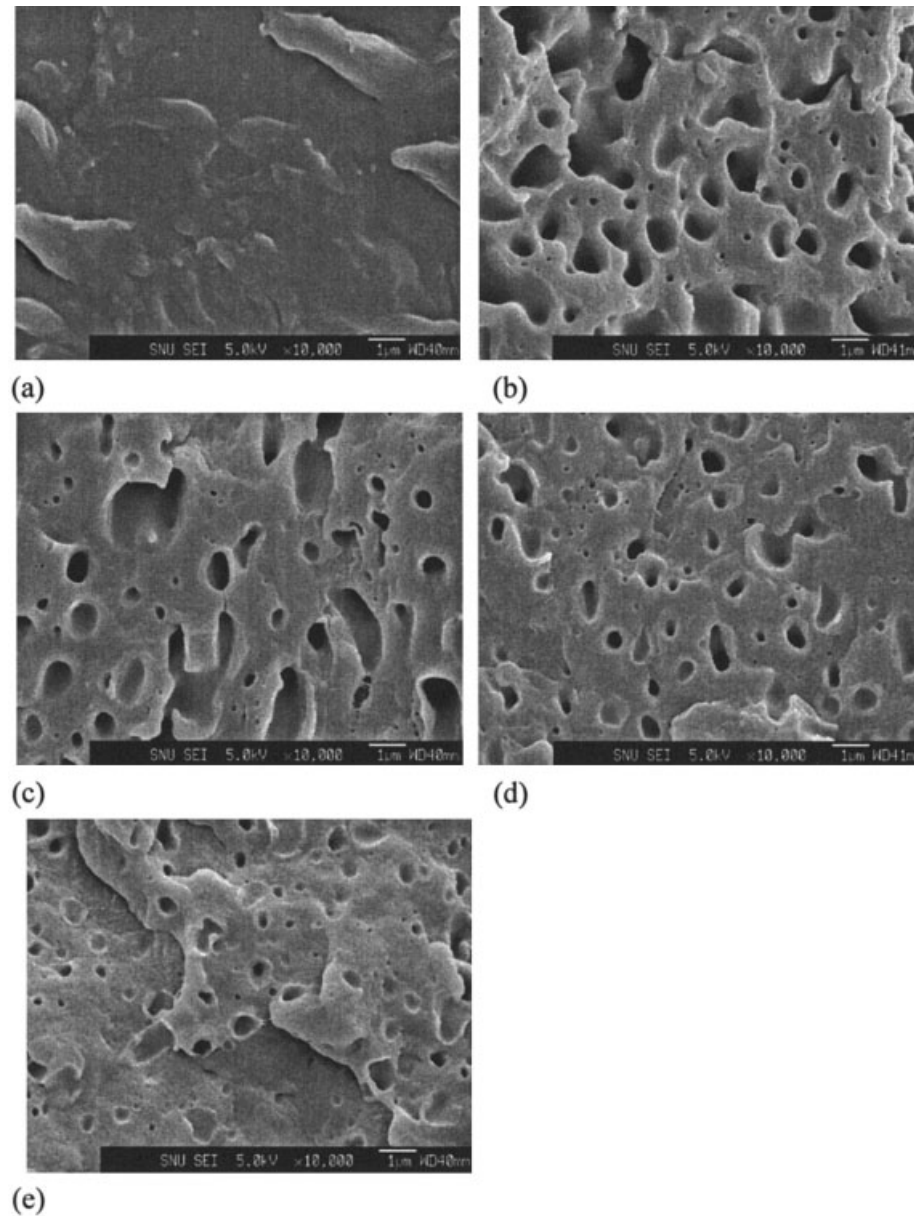
**Figure 2** Morphology of the fillers observed by SEM: (a)  $\text{Mg}(\text{OH})_2$  particles H5 (pure), (b)  $\text{Mg}(\text{OH})_2$  particles H5A (vinyl silane coated), (c)  $\text{Mg}(\text{OH})_2$  particles H5IV (amino silane coated), (d)  $\text{Mg}(\text{OH})_2$  particles H5HV (polymeric material coated).

tures in Figure 2. MDH consisted of regular hexagonal plates 1.0  $\mu\text{m}$  in diameter with small groups of plates agglomerated into secondary particles. These agglomerates had an average particle size of 0.5  $\mu\text{m}$ . Tensile results of PP/MDH composites are presented in Table II. In general, MDH flame retardant causes a decrease in the tensile properties of composites. Comparing tensile properties of neat PP (sample 1) and MDH composites containing 60 wt % (samples 4, 5, 6, and 7) confirms the marked fall in tensile strength and, in particular, elongation at break, due to the presence of the filler, except for sample 7. With a filler loading of 60 wt % of MDH H5, H5A, and H5IV, elongation at break was reduced from an original level of 1190% to 12–13%. This must be associated with a weak filler/matrix interface in the composites. The dispersed particles of MDH act limiting the plastic flow of the PP matrix and promoting an early failure of the specimen, which results in low value of elongation at break. In the case of PP/MDH(H5HV) composite, elongation at break amounted to over 300%. This high value of elongation at break was noticeable. It might be caused by better dispersion of filler and good compatibility between filler and PP. All samples showed stress whitening in bending deformation so severely that simple PP/MDH composites were not suitable for cable insulating applications. So it would be necessary to in-

corporate an elastomeric part in the matrix resin to tailor the required properties of the composite and to improve the stress whitening resistance in bending deformation.

#### Dispersion morphology of elastomer in PP matrix

A set of PP/POEgMA blends containing 50, 40, 30, 20, and 10 wt % POEgMA, respectively, was prepared. Their tensile properties are shown in Table II. SEM was used to investigate the relative phase morphologies in binary phase composites. To distinguish between the spatial location of elastomer and PP phase, samples were etched with *n*-heptane to remove the elastomeric component. The phase morphology after etching of the PP<sub>50</sub>POEgMA<sub>50</sub>, PP<sub>60</sub>POEgMA<sub>40</sub>, PP<sub>70</sub>POEgMA<sub>30</sub>, PP<sub>80</sub>POEgMA<sub>20</sub>, and PP<sub>90</sub>POEgMA<sub>10</sub> blends are displayed in Figure 3(a–e), respectively, and reveals small spherical domains dispersed in the PP matrix. The number of domains somewhat increased and their average diameter increased as the concentration of elastomer was increased to 40 wt %. As the concentration of elastomer was increased further to 50 wt %, it seemed that the phase morphology had transformed to a cocontinuous phase. The tensile test results show that increasing elastomer content reduced the yield strength. The reason of yield strength



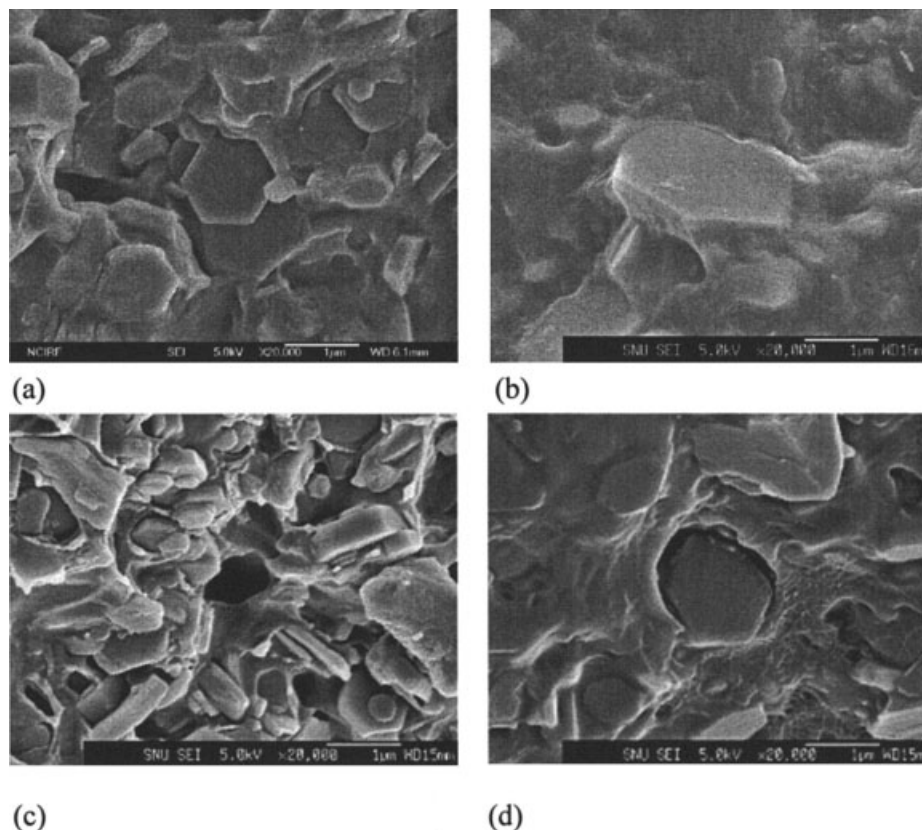
**Figure 3** SEM images of PP/POEgMA blends prepared by removing POEgMA phase with *n*-heptane etching: (a) PP<sub>50</sub>POEgMA<sub>50</sub>, (b) PP<sub>60</sub>POEgMA<sub>40</sub>, (c) PP<sub>70</sub>POEgMA<sub>30</sub>, (d) PP<sub>80</sub>POEgMA<sub>20</sub>, (e) PP<sub>90</sub>POEgMA<sub>10</sub>.

decrease with increasing elastomer content can be attributed to the fact that, since elastomer particles have very low modulus compared to PP, there is little or no stress transfer from matrix to elastomer particles. Therefore, elastomer particles had almost the same effects as microvoids on these mechanical properties. The results of tensile strength revealed that the blends containing 30, 40, and 50 wt % POEgMA showed tensile yield strength around 10–15 MPa and high elongation at break. For automotive cable insulating composites, particularly in the engine bay, where exposure to high temperature for considerable periods of time (e.g., the widely recognized “class 3” in requirement to survive 3000 h at 125°C), together with

exposure to engine oil, windscreen washer fluid, and other aggressive fluids is commonplace, it is necessary to have high elongation at break and sufficient thermal stability properties for long-term service. To the author’s knowledge, the composite materials that are applicable industrially must have 10–13 MPa tensile strength and minimum 250% elongation at break.

#### Stress whitening and tensile properties of PP/elastomer/mdh composites

A set of PP/POE/MDH composites was prepared using POE, POEgMA, and four types of MDH (samples 13, 14, 15, 16, and 17). Figure 4 shows the SEM

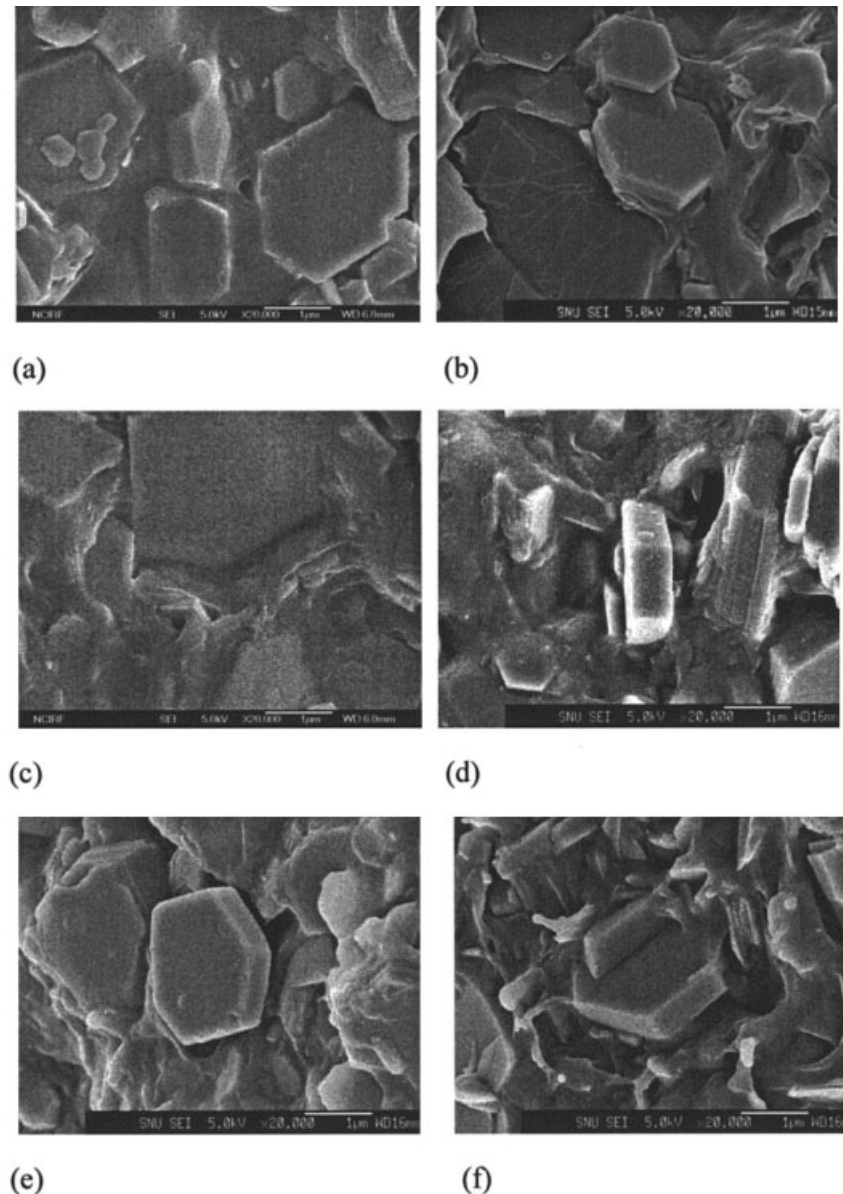


**Figure 4** SEM images of fractured and etched surfaces: (a) PP/POE/MDH(H5) (fractured), (b) PP/POEgMA/MDH(H5) (fractured), (c) PP/POE/MDH(H5) (fractured and etched with *n*-heptane), (d) PP/POEgMA/MDH(H5) (fractured and etched with *n*-heptane).

images of two composites fractured and etched with with *n*-heptane surfaces prepared using POE and POEgMA, respectively. Figure 4(a) and 4(c) shows that PP and POE have little affinity for uncoated MDH filler due to large surface energy differences. Interaction between the components is very limited, resulting in extensive particle dewetting from the fracture surface. In the SEM image of POEgMA used composite instead of pure POE [Fig. 4(b) and 4(d)], POEgMA adhered strongly to the surface of the filler, forming a low modulus layer around a rigid core. This surface covering prevents particles from being easily dewetted in bending deformation and consequently reduces stress whitening. Stress whitening is the phenomenon that voids created in deforming polymer scatter light and manifest themselves as white marks on the plastic. Stress whitening tests revealed that PP/POE/MDH composite showed white marks when bent, but PP/POEgMA/MDH showed no stress whitening. From this result, it seems that the best ways to reduce stress whitening in bending deformation is to make a soft filler–polymer interface and to form a covering layer using functionalized elastomer. However, when PP/POEgMA was combined with polymeric material treated MDH (sample 17), a distinctly different morphology was revealed [Fig. 5(a) and 5(b)]. The frac-

tured surface was much smoother than seen with sample 14, and the filler particles remained well wetted by matrix, indicating a high degree of compatibility between matrix and filler. There is no indication that extensive filler encapsulation by elastomer has occurred. However, sample 17 showed no stress whitening and the highest elongation at break.

A set of PP/POEgMA/MDH(H5HV) composites containing 60 wt % MDH was prepared with PPgMA. (samples 18, 19, 20, and 21). Figure 5(c–f) shows the SEM images of these four composites' fractured surfaces. The increasing concentration of maleic anhydride in the PP phase resulted in a gradual increase of tensile yield strength and a gradual decrease of elongation at break. Figure 5(c–f) shows that the increase of the amount of maleic anhydride in the PP phase caused the separation between filler and elastomer, leading to the stiffening of the ternary composite. Changes in the interfacial tension of each component pair can be achieved with compatibilizer. In this case, PPgMA might improve the interface between PP matrix and filler and consequently filler might be dispersed more in the PP phase. When the elastomer and rigid filler are separated in the PP matrix, the filler tends to produce microcracks when bending deformation is applied. Our stress whitening test showed this phenomenon (sample 21).



**Figure 5** SEM images of fractured and etched surfaces of PP/POEgMA/MDH(H5HV) with PPgMA: (a) 0 wt % (fractured) (b) 0 wt % (fractured and etched with *n*-heptane), (c) 0.5 wt % (fractured), (d) 1 wt % (fractured), (e) 3 wt % (fractured), (f) 5 wt % (fractured).

To find the best formulation for cable insulating applications, a set of PP/POEgMA/MDH(H5HV) composites, changing PP/POEgMA weight ratio from 60/40 to 90/10 with constant PPgMA 0.5 wt % content, was prepared (samples 22, 23, 24, and 25). The results of tensile tests show that the increase of PP phase in the matrix resulted in the increase of tensile yield strength and stress whitening. This might be caused by the reduction of elastomer phase in the matrix. Among the test samples, sample 22 showed the highest elongation at break. The elastomer content of this sample is 15.8 wt % to the total composite and the corresponding matrix which has same blend ratio as sample 9, containing 40 wt % elastomer. The tensile

result of sample 9 showed the highest elongation at break. This may be caused by the strain-hardening effect promoted by the addition of elastomer. This kind of strain hardening effect is thought to be more useful for a filled composite designed for high elongation at break. Sample 23 showed the best suitable tensile strength properties with good elongation at break without stress whitening.

## CONCLUSIONS

The tensile results and microstructures reported in this work promise a breakthrough in the development of PP/elastomer/MDH ternary composites for PP-based

cable insulating material. By the correct control of microstructure it was possible to obtain a variety of MDH composite materials with targeted and optimal performance for the specific requirements of cable insulating applications. It was apparent that the addition of POEgMA instead of neat POE resulted in improved stress whitening resistance in bending deformation. By combining uncoated MDH with neat POE, it was shown that MDH particles and elastomeric modifier existed as separately dispersed phases. On the other hand, POEgMA was found to give an elastomeric interlayer between MDH particles and the PP matrix. Evidence of this encapsulation was provided from the analysis by SEM. PP composites, compounded using surface-treated MDH by polymeric material and POEgMA containing 0.3 wt % MA, gave the highest elongation at break value and no stress whitening, in which there might be good interfacial compatibility between filler and matrix and also well-dispersed filler particles.

## References

1. Sain, M.; Park, S.; Suhara, F.; Law, S. *Polym Degrad Stabil* 2004, 83, 363.
2. Titelman, G.; Gonen, Y.; Keidar, Y.; Bron, S. *Polym Degrad Stabil* 2002, 77, 345.
3. Velasco, J.; Morhain, C.; Arencon, D.; Santana, O.; MasPOCH, M. *Polym Bull* 1998, 41, 615.
4. Yu, L.; Wang, W.; Xiao, W. *Polym Degrad Stabil* 2002, 77, 69.
5. Chiu, S.; Wang, W. *Polymer* 1951 1998, 39.
6. Rotheron, R.; Hornsby, P. *Polym Degrad Stabil* 1996, 54, 383.
7. Lopez, M.; Valle, M.; Sapunar, R.; Quijada, R. *J Appl Polym Sci* 2004, 92, 3008.
8. Silva, A.; Rocha, M.; Countinho, F.; Bretas, R.; Scuracchio, C. *J Appl Polym Sci* 2001, 79, 1634.
9. Silva, A.; Tavares, M.; Politano, D.; Countinho, F.; Rocha, M. *J Appl Polym Sci* 2005, 1997, 66.
10. Silva, A.; Rocha, M.; Countinho, F.; Rocha, M.; Countinho, F.; Bretas, R.; Scuracchio, C. *J Appl Polym Sci* 2000, 75, 692.
11. Kontopoulou, M.; Wang, W.; Gopakumar, T.; Cheung, C. *Polymer* 2003, 44, 7495.
12. Carriere, C.; Silvis, H. *J Appl Polym Sci* 1997, 66, 1175.
13. Godail, L.; Packham, D. *J Adhesion Sci Technol* 2001, 15, 1285.
14. Miyata, S.; Imahashi, T.; Anabuki, H. *J Appl Polym Sci* 1980, 25, 415.
15. Jancar, J.; Kucera, J. *Polym Eng Sci* 1990, 30, 714.
16. Cook, M.; Harper, J. F. *Adv Polym Tech* 1998, 17, 53.
17. Liauw, C.; Khunova, V.; Lees, G.; Rotheron, R. *Macromol Symp* 2003, 194, 191.
18. Chiang, W.; Yang, W.; Pukanszky, B. *Polym Eng Sci* 1992, 32, 641.