

Fracture Morphology of Mg(OH)₂/Polypropylene Composites Modified by Functionalized Polypropylene

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ABSTRACT: The morphologies of the fracture surface under impact and flexural testing of Mg(OH)₂/Polypropylene (PP) composites and their modified composites were investigated by scanning electron microscopy. Experimental results indicated that addition of functionalized polypropylene (FPP) and acrylic acid (AA) and the formation of *in situ* FPP changed the fracture morphologies of Mg(OH)₂/PP composites. We believe that addition of these modifiers improved the interfacial interaction and enhanced the interface adhesion between the particle and the matrix in Mg(OH)₂/PP composites. The degree of improvement was

more significant in Mg(OH)₂/PP composites modified by the formation of *in situ* FPP. At low Mg(OH)₂ content, 2 phr AA exhibited a marked effect, but at high Mg(OH)₂ content, 4 phr AA afforded good effect. Due to the improved interface adhesion by interface interactions the fracture mechanism transformed from interface debonded fracture into a matrix fracture. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2148–2159, 2003

Key words: poly(propylene) (PP); fractures; morphology

INTRODUCTION

The physical and mechanical properties of polypropylene (PP) filled with Mg(OH)₂ depend on the content,^{1–4} morphology,^{5,6} particle size,^{1,7} surface treatment,^{7,8} dispersion¹ of filler, and so on. The addition of Mg(OH)₂ and an increase in the filler content generally decrease the mechanical properties of PP, in particular impact strength. Although the surface treatment of Mg(OH)₂ by organic coupling agents caused an increase in the impact strength of Mg(OH)₂ composites, a decrease in flexural properties was observed.^{1,8} However, PP grafted with AA produced an improvement in the flexural strength of composites. Irregular spherical microporous and needle Mg(OH)₂ benefitted the improved flexural properties.^{5,6} PP filled with smaller sized particles had a higher flexural modulus.⁹ The improved dispersion of Mg(OH)₂ in-

creased the tensile, flexural, and impact strengths of composites.¹ The flame retardancy of composites increased with increased Mg(OH)₂ content,³ in particular above 50 wt % Mg(OH)₂.⁴ The flame retardancy of composites also depends on the dispersion of Mg(OH)₂ and the surface treatment of Mg(OH)₂. The better the dispersion of Mg(OH)₂, is the higher the flame-retardant efficiency.¹ Surface treatment of Mg(OH)₂ cause a decline in the flame retardancy of composites.⁷ The flame retardancy is much better for PP filled by Mg(OH)₂ with smaller size particles and a larger surface area.

However, few studies on the fracture morphology of Mg(OH)₂/PP composites have been reported. In our laboratory, Al(OH)₃/PP composites modified by the addition of functionalized polypropylene (FPP); and grafting monomer and by the formation of *in situ* FPP were prepared. The physical and mechanical properties of modified Al(OH)₃/PP composites were investigated systematically.^{10–14} Recently, modified Mg(OH)₂/PP composites were prepared in our laboratory. Our experimental results found that the Mg(OH)₂ exhibited a heterogeneous nucleation effect on the crystallization of PP, leading to increased crystallization temperatures of PP. The addition of FPP into Mg(OH)₂/PP composites facilitated the nucleation of PP, resulting in accelerated crystallization and the increased crystallization temperature of PP in its composites. The addition of acrylic acid (AA) also caused a crystallization temperatures to be further enhanced of PP in Mg(OH)₂/PP composites, but the

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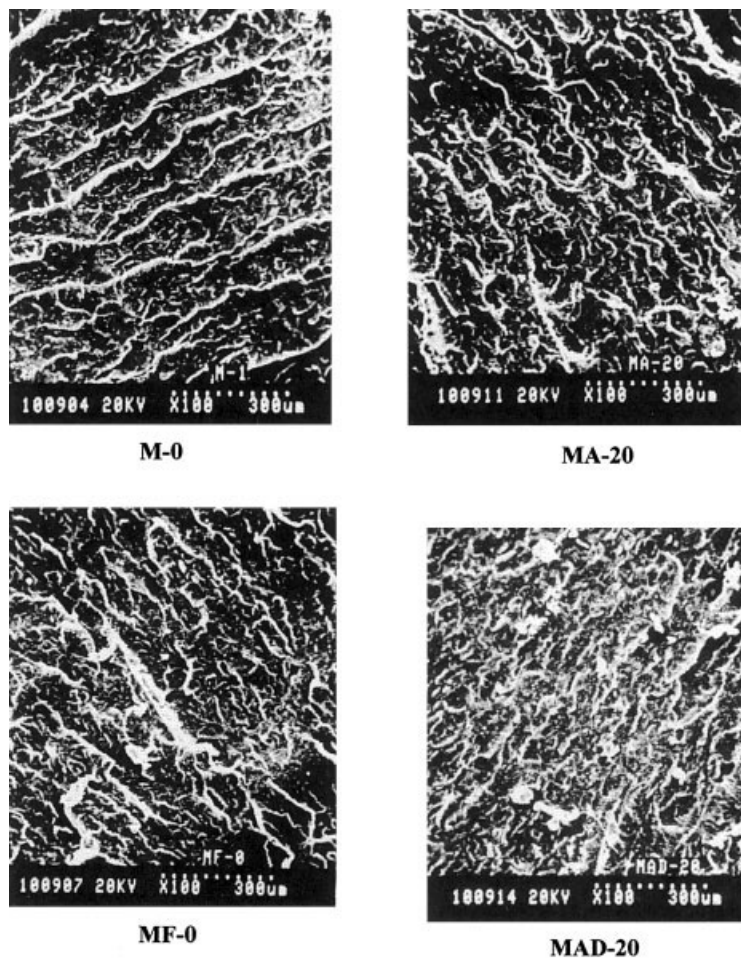


Figure 1 SEM of impact fracture specimens for PP and modified PP (100 \times).

content of AA did not affect the crystallization behavior of PP in its composites. We suggest that the FPP and AA exhibited an activated heterogeneous nucleation of the surface of $\text{Mg}(\text{OH})_2$. A synergistic effect of the $\text{Mg}(\text{OH})_2$ with the FPP and AA produced more significant heterogeneous nucleation on crystallization of PP in $\text{Mg}(\text{OH})_2/\text{PP}$ composites. The spherulite sizes of PP were reduced. The addition of FPP and the formation of *in situ* FPP did not change the crystal form of PP. The addition of AA facilitated the formation of the β crystals of PP, but for the PP modified with AA in the presence of dicumyl peroxide (DCP), the crystal form of PP was not influenced. Because FPP altered the crystallization behavior, crystal form, surface interaction, and so on, the mechanical properties of $\text{Mg}(\text{OH})_2/\text{PP}$ composites were improved.^{15,16} Because of the location of modifiers at the $\text{Mg}(\text{OH})_2$ and PP interface, modifiers interacted with the surface of $\text{Mg}(\text{OH})_2$ and improved the interfacial adhesion between $\text{Mg}(\text{OH})_2$ and PP, accordingly causing a variation in the fracture morphology of $\text{Mg}(\text{OH})_2/\text{PP}$ composites. Therefore, the fracture morphology of modified $\text{Mg}(\text{OH})_2/\text{PP}$ composites under impact and flex-

ural conditions were examined in this study to investigate the interfacial interactions and fracture mechanisms of the modified $\text{Mg}(\text{OH})_2/\text{PP}$ composites.

EXPERIMENTAL

Materials

Powered PP, F401, and pelletized PP, CTS-700, were commercial products of Guangzhou Yin Zhu PP Ltd. (Guangzhou, China). Chemical-grade AA was purchased from Shanghai Feida Industrial Trade Ltd. (Shanghai, China) and was used without further purification. Chemical-grade DCP, used as an initiator for the AA grafting reaction, was obtained from Shanghai Chemical Reagent Stocking and Providing Station Pool Enterprise Central Factory (Shanghai, China). $\text{Mg}(\text{OH})_2$ was a commercial product of Zhejiang Chemical Plant (Zhejiang, China). The solvent, acetone, was obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China).

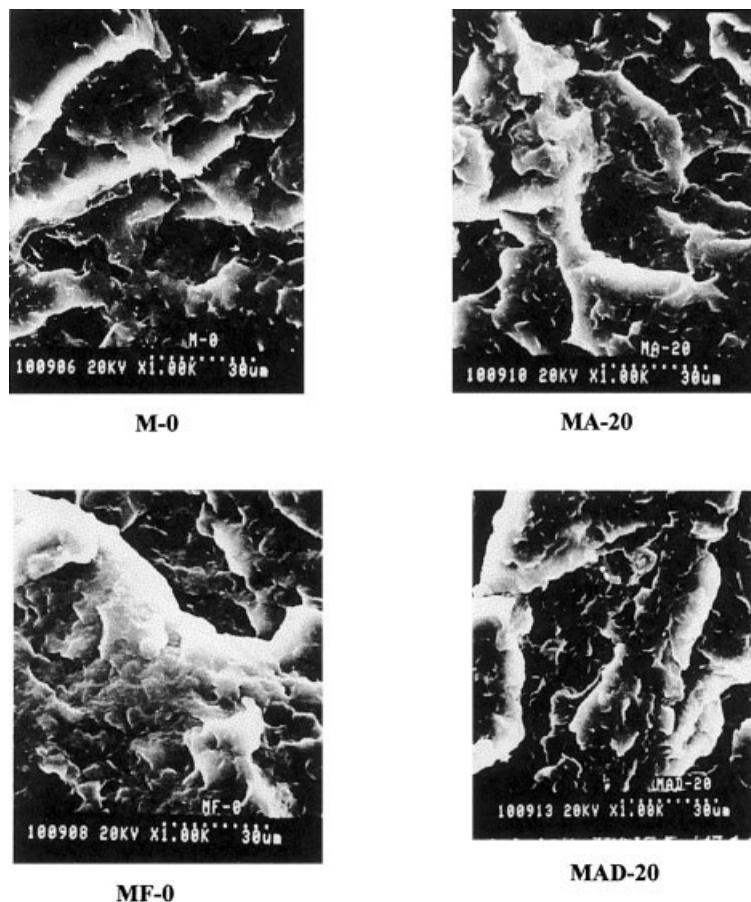


Figure 2 SEM of impact fracture specimens for PP and modified PP (1000 \times).

Preparation of composites

Preparation of FPP

DCP and AA were dissolved in acetone and totally blended with powdered PP in a GH-10 high-speed mixing machine (Beijing Plastic Machine Factory, Beijing, China). After the acetone had completely evaporated, the mixture of AA and DCP was coated on the surface of the powdered PP, and the pretreated PP was prepared. The pretreated PP was then extruded with a SHJ-53

twin-screw extruder (Nanjing Aviation Institute Xinli Plastic Machine Factory, Wanjing, China) at temperatures of 185–190 °C with the screw speed set at 60 rpm. The extruded products, the PP grafted by AA (FPP), were frozen inline in a water bath, dried, and granulated.

Preparation of $\text{Mg}(\text{OH})_2$ /PP composites modified by the formation of *in situ* FPP

$\text{Mg}(\text{OH})_2$, DCP, AA, and pelletized PP were totally blended with a high-speed mixing machine, and the

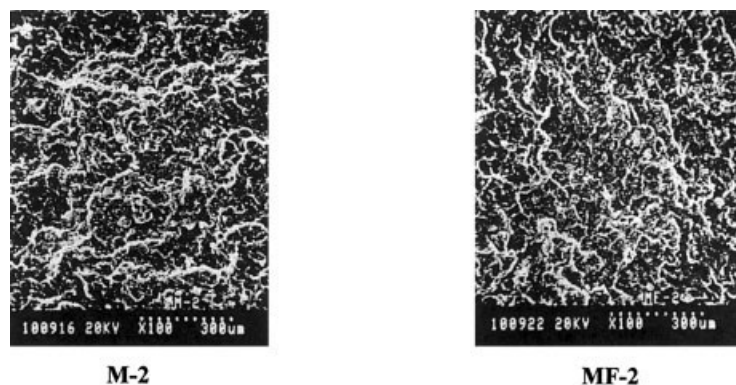


Figure 3 SEM of impact fracture specimens for $\text{Mg}(\text{OH})_2$ (20 wt %)/PP composites modified by the addition of FPP (100 \times).

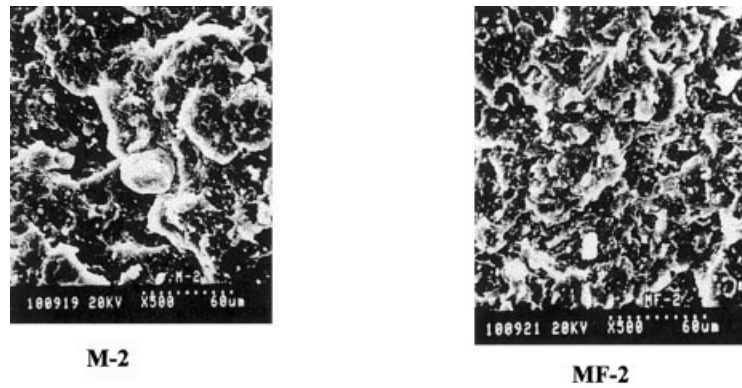


Figure 4 SEM of impact fracture specimens for $Mg(OH)_2$ (20 wt %)/PP composites modified by the addition of FPP (500 \times).

mixtures were then extruded by a twin-screw extruder at temperatures of 185–190 °C with the screw speed set at 60 rpm. The extruded products were granulated and named as $Mg(OH)_2/PP$ composites modified by *in situ* FPP.

granulated and named as $Mg(OH)_2/PP$ composites modified by additive FPP.

Preparation of $Mg(OH)_2/PP$ composites modified by the addition of FPP

Preparation of the test specimens of $Mg(OH)_2/PP$ composites

$Mg(OH)_2$, premade FPP, and pelletized PP were totally blended with a high-speed mixing machine, and the mixtures were then extruded by a twin-screw extruder at temperatures of 185–190 °C with the screw speed set at 60 rpm. The extruded products were

The pelletized $Mg(OH)_2/PP$ composites modified by different methods were injection molded into GB (National Standard of China) test specimens with a CJ150 ME-NC injection molding machine (Zhengde Plastic Mechanical Ltd. Co., China), set with a barrel temperature profile ranging from 190 to 210°C.

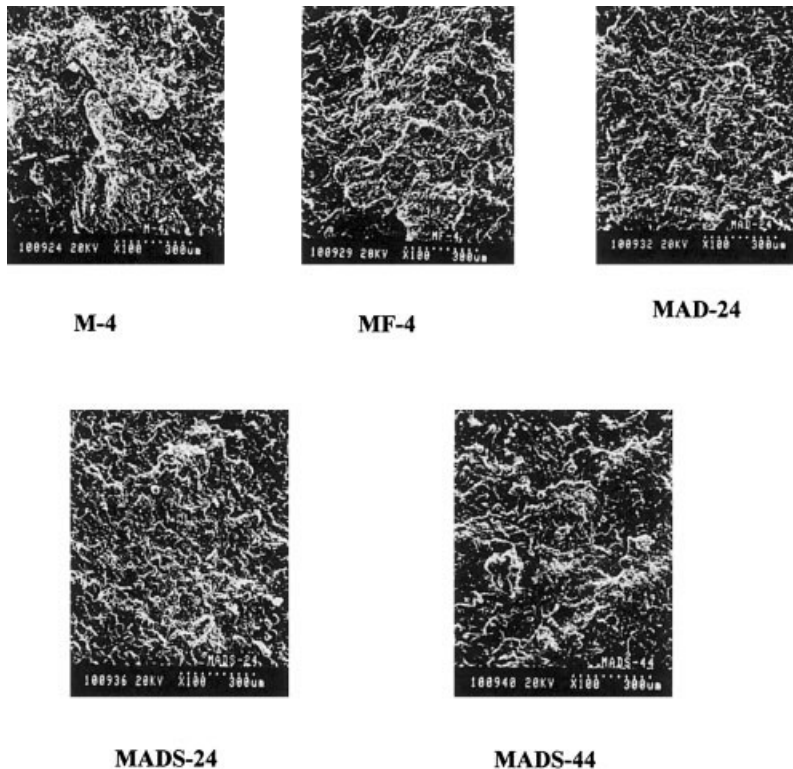


Figure 5 SEM of impact fracture specimens for $Mg(OH)_2$ (40 wt %)/PP composites modified by the addition of FPP or *in situ* FPP (100 \times).

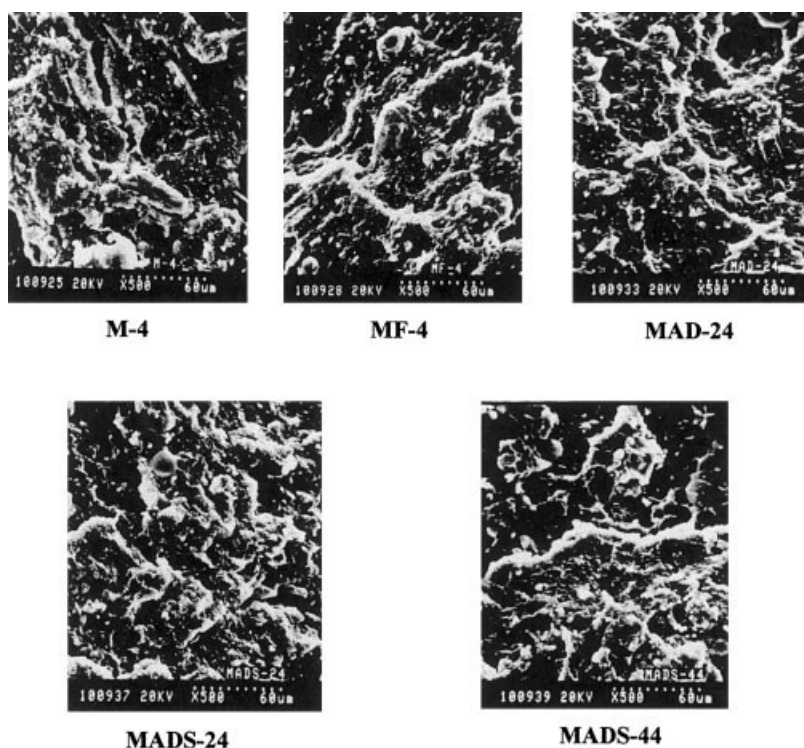


Figure 6 SEM of impact fracture specimens for $\text{Mg}(\text{OH})_2$ (40 wt %)/PP composites modified by *in situ* FPP (500 \times).

Determination of impact and flexural test

A notched impact test was performed on a XJJ-5 impact testing machine (Chengde Test Machine Factory, Hebei Province, China) with procedures given in GB/T1043-93. Flexural testing was carried out on a LWK-5 electronic universal tension testing machine (Guangzhou Test Machine Factory, Guangzhou, China after GB1040-92 with a crosshead speed of 10 mm/min.

Observation by scanning electron microscopy (SEM)

Test specimens were fractured under impact and flexion, and then the fracture surfaces were gold coated and observed with a HS-520 scanning electron microscopy (Hitachi, Japan).

RESULTS AND DISCUSSION

Fracture morphology of impact specimens

Fracture morphologies of pure PP (M-0), PP containing 5 phr FPP (MF-0), PP modified with 2 phr AA (MA-20), and PP modified by AA in the presence of DCP (MAD-20) are shown in Figures 1 and 2. The fracture surfaces of PP and modified PP exhibited a typical radiate morphology under impact. However, difference in the morphologies of the fracture surfaces between pure PP and modified PP were clearly visible.

The typical radiate morphology of M-0 was much clear than those of modified PP. The fracture surface of M-0 was smoother, whereas those of modified PP become irregular, especially the more complicated fracture surface of MAD-20.

The morphologies of the fracture surfaces of $\text{Mg}(\text{OH})_2$ /PP composites filled with 20 wt % $\text{Mg}(\text{OH})_2$ and by the addition of FPP are presented in Figures 3 and 4. Differences in the morphologies of fracture surfaces between $\text{Mg}(\text{OH})_2$ /PP composites (M-2) and $\text{Mg}(\text{OH})_2$ /PP composites modified by FPP (MF-2) were observed. Compared with pure and modified PP (Figs. 1 and 2), the addition of $\text{Mg}(\text{OH})_2$ resulted in the disappearance of the radiate morphology of the fracture surface of PP and much finer fracture surface. We suggest that addition of FPP improved the dispersion of $\text{Mg}(\text{OH})_2$ in the matrix and increased the interfacial adhesion between the $\text{Mg}(\text{OH})_2$ and matrix.

Figures 5 and 6 show the morphologies of the fracture surface of $\text{Mg}(\text{OH})_2$ /PP composites and the modified composites filled with 40 wt % $\text{Mg}(\text{OH})_2$. The impact fracture surface of unmodified M-4 was irregular, and the particle dispersion was poor with some particle aggregation. Crack propagation and fracture occurred at the particle-matrix interface. For $\text{Mg}(\text{OH})_2$ /PP modified by FPP (MF-4), the addition of FPP improved the dispersion of $\text{Mg}(\text{OH})_2$ particles in the matrix and decreased the particle aggregation due to the improved interfacial interaction. The fracture surfaces showed a more regular and finer structure. In

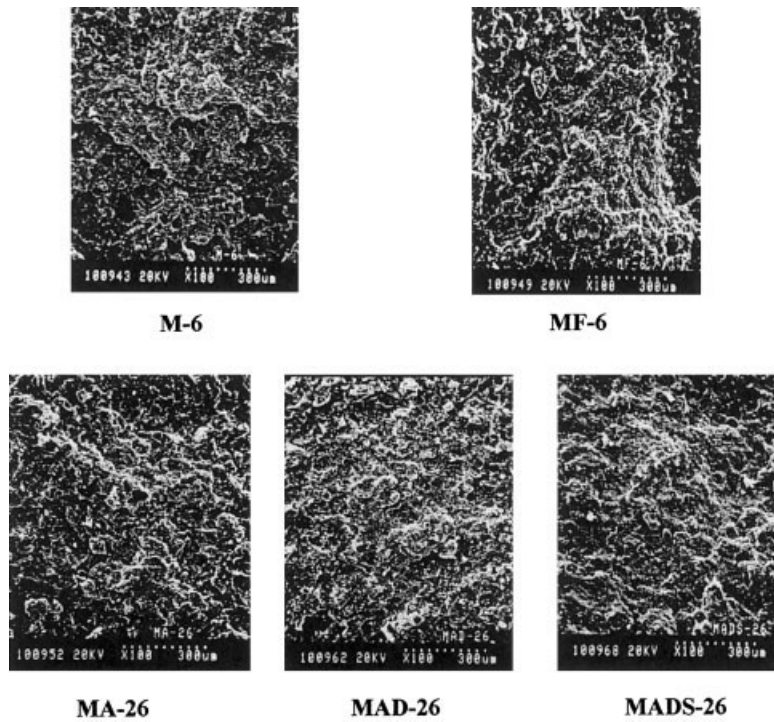


Figure 7 SEM of impact fracture specimens for $Mg(OH)_2$ (60 wt %)/PP-modified composites (100 \times).

the $Mg(OH)_2/PP$ modified by the formation of *in situ* FPP (MAD-24), the smoothness of the fracture surface increased more. The addition of an oxidation resistant (MADS specimens) afforded no marked effect on the

morphology of the fracture surface of $Mg(OH)_2/PP$ composites modified by the formation of *in situ* FPP. As shown in Figure 6, differences in the morphologies of the fracture surfaces between $Mg(OH)_2/PP$ com-

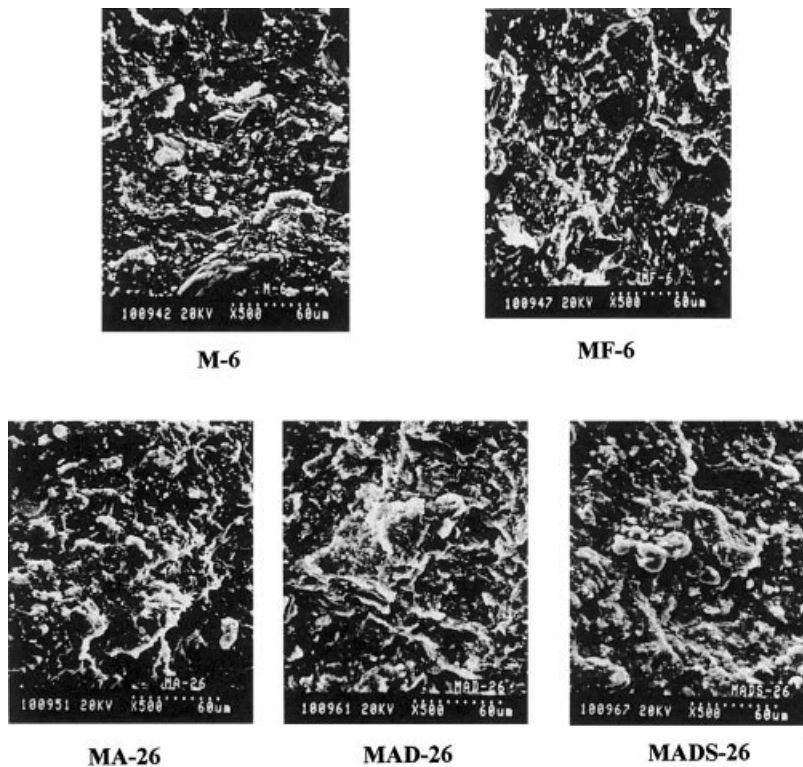


Figure 8 SEM of impact fracture specimens for $Mg(OH)_2$ (60 wt %)/PP-modified composites (500 \times).

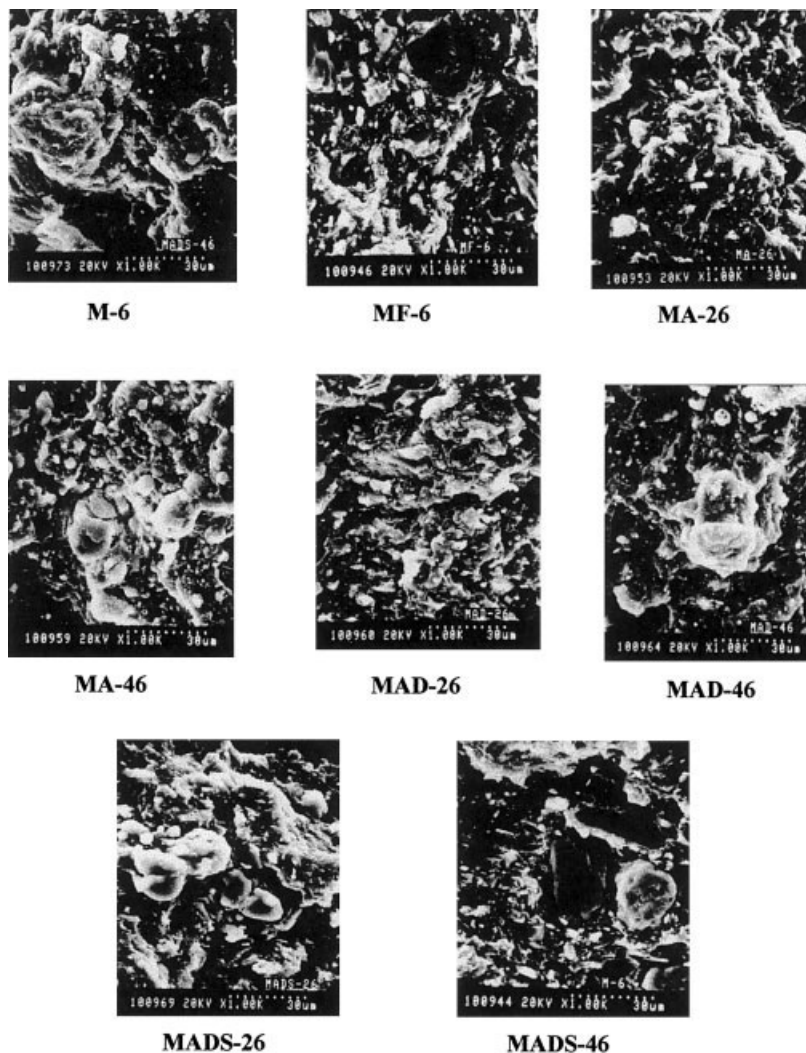


Figure 9 SEM of impact fracture specimens for $\text{Mg}(\text{OH})_2$ (60 wt %)/PP-modified composites (1000 \times).

posites modified by *in situ* FPP and $\text{Mg}(\text{OH})_2$ /PP composites modified by additive FPP were observed. There was a crack on the fracture surface of unmodified M-4 due to poor interfacial adhesion. The addition of FPP resulted in improved compactness and a decreased complication of the fracture surface. For MAD-24, no filler particles were observed on the frac-

ture surface. We believe that the improved interfacial interaction by the formation of *in situ* FPP was greater than that by addition of FPP.

Figure 7 and 8 illustrate the morphologies of the fracture surfaces of $\text{Mg}(\text{OH})_2$ /PP composites and the modified composites filled with 60 wt % $\text{Mg}(\text{OH})_2$. Because the effect of high $\text{Mg}(\text{OH})_2$ content on the

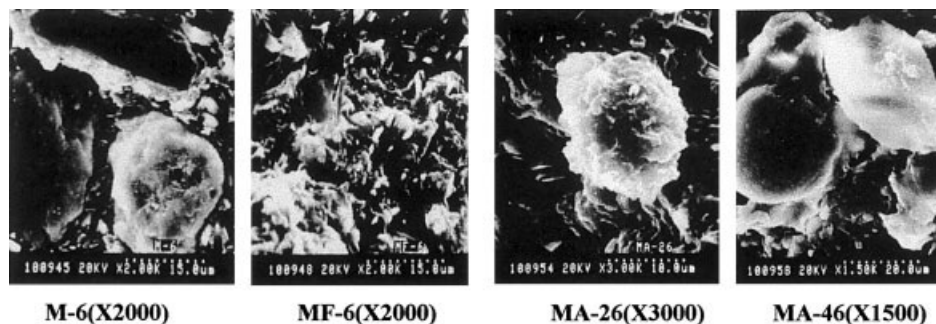


Figure 10 SEM of impact fracture specimens for $\text{Mg}(\text{OH})_2$ (60 wt %)/PP-modified composites.

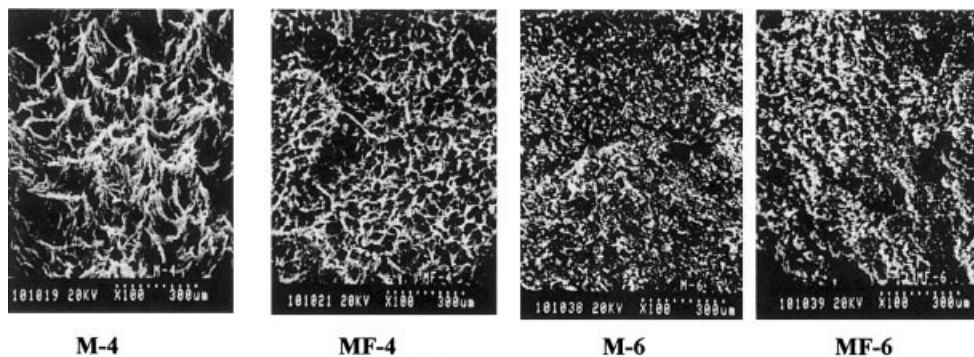


Figure 11 SEM of flexural fractured specimens for $Mg(OH)_2$ (60 wt %)/PP-modified composites (100 \times).

morphologies of the fracture surfaces was much greater than that of the modifiers, the differences of morphologies could hardly be distinguished. Lots of particle were observed on the fracture surfaces of unmodified and modified composites. However, the difference in morphologies could be observed at 1000 \times magnification (Fig 9). Although the morphologies of the fracture surfaces of $Mg(OH)_2/PP$ composites were not greatly influenced by the addition of FPP, less particle aggregation was observed. For the $Mg(OH)_2/PP$ composites modified by the addition of AA (MA-26), the morphologies of the fracture surfaces were slightly improved but not significantly. As the AA content was up to 4 phr, no particles existed on the fracture surface. Similar results were obtained for the

modified $Mg(OH)_2/PP$ composites by the addition of an oxidation resistant (MADS-26 and MADS-46). At higher magnification (Fig. 10), the changes in the morphologies at the particle surface were clearly visible. Unmodified M-6 had a smooth particle surface, and no adhesion between the particle and the matrix was observed. For MF-6 modified by the addition of FPP, the interfacial adhesion between the particle and the matrix was slightly enhanced. In MA-26 modified by the addition of AA, the particle surface was encapsulated by a lot of the matrix. As the AA content was increased, more significant encapsulation was obtained for MA-46. We suggest that the addition of AA more significantly improved the interfacial interaction and adhesion between the particle and the matrix.

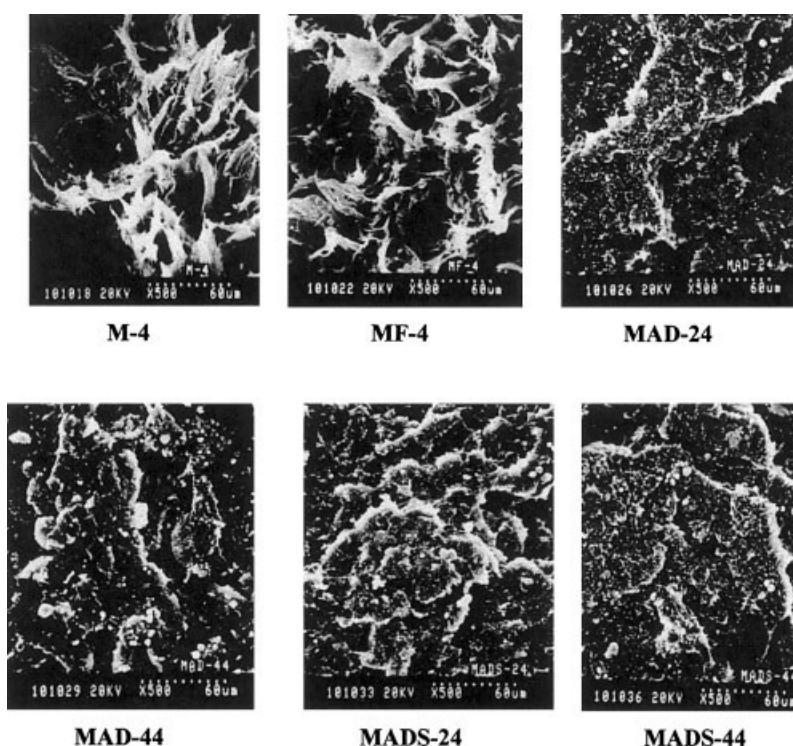


Figure 12 SEM of flexural fracture specimens for $Mg(OH)_2$ (40 wt %)/PP composites modified by the addition of FPP or *in situ* FPP (500 \times).

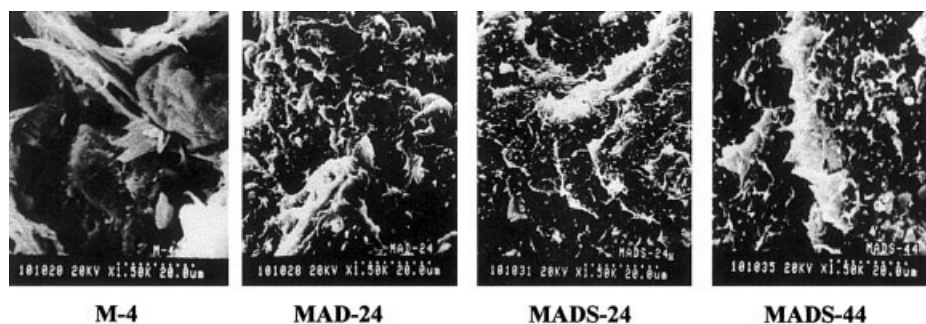


Figure 13 SEM of flexural fracture specimens for $\text{Mg}(\text{OH})_2$ (40 wt %)/PP composites modified by *in situ* FPP (1500 \times).

Therefore, the addition of FPP or AA could lead to an improvement in the mechanical properties of $\text{Mg}(\text{OH})_2$ /PP composites.

Fracture morphology of flexural specimens

Generally, impact testing is carried out in very short time to fracture the specimen. The rate of fracture of the specimen is too fast for the molecule chain to move, so it is hard to distinguish the finer change from the morphologies of the fracture surface of the impact specimen. Flexural testing is performed to impart a load to the sample to produce a slow fracture at a given speed. It benefits the deformation of matrix in the interface between the filler and the matrix and more clearly distinguishes the differences in the morphologies of the fracture surfaces of different specimens. Therefore, the morphology of the flexural fracture surface was further investigated.

Figure 11 shows the morphologies of the fracture surfaces of $\text{Mg}(\text{OH})_2$ /PP composites and the composites modified by the addition of FPP. Due to the poor interfacial adhesion of unmodified M-4 filled with 40 wt % $\text{Mg}(\text{OH})_2$, lots of thick fibrils were formed between particles. For the modified MF-4, the addition of FPP resulted in the formation of thin fibrils between particles, accompanied by more uniform particle dispersion on the fracture surface. The addition of FPP was favorable to the dispersion of $\text{Mg}(\text{OH})_2$ particles in the matrix. For the composites filled with 60 wt %

$\text{Mg}(\text{OH})_2$, the differences in the morphology of the fracture surface were less significant than that with 40 wt % $\text{Mg}(\text{OH})_2$ content, regardless of the addition of FPP, due to the great influence of high filler loading.

Figure 12 presents the morphologies of the fracture surfaces of $\text{Mg}(\text{OH})_2$ /PP composites and the modified composites filled with 40 wt % $\text{Mg}(\text{OH})_2$. Although the addition of FPP produced a finer fibril on the fracture surface, the interfacial adhesion between particle and matrix was hardly improved. No adhesion was observed between the particle and the matrix, which was the same as for unmodified composites. For the composites modified by AA in the presence of DCP, fibrils no longer existed on the fracture surface. No particles were observed on the fracture surface. We believe that the fracture did not occur at the interface between the particle and the matrix. However, the increase in AA content and the addition of the oxidation resistant did not much affect the morphologies of the flexural fracture surfaces. At a magnification of 1500 \times (Fig. 13), the difference could be seen more clearly. In the unmodified composites, the particles at the fracture surface departed from the matrix, and the matrix was markedly torn into thick fibrils. For the modified composites, MAD-24, MADS-24, and MADS-44, no fibril morphologies were observed. We believe that the formation of *in situ* FPP in the preparation process of composites improved the interfacial interaction and increased the interface adhesion between the particle and the matrix. The fracture no

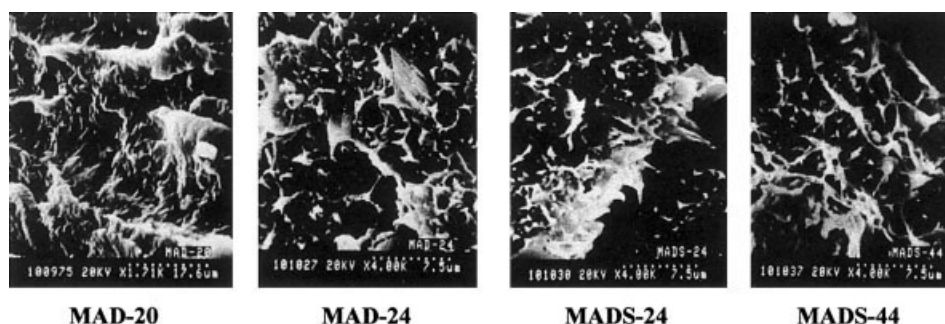


Figure 14 SEM of flexural fracture specimens for $\text{Mg}(\text{OH})_2$ (40 wt %)/PP composites modified by *in situ* FPP (4000 \times).

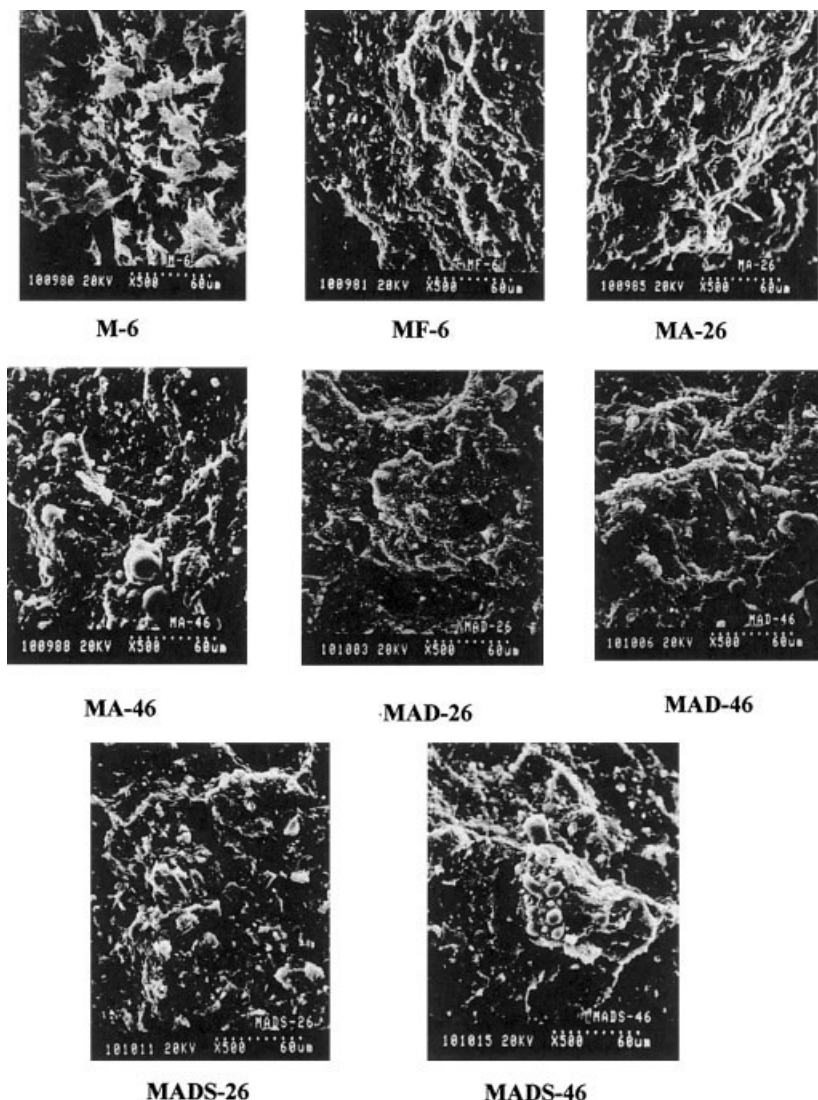


Figure 15 SEM of flexural fracture specimens for $\text{Mg}(\text{OH})_2$ (60 wt %)/PP-modified composites (500 \times).

longer occurred at the interface between the particle and the matrix. At a magnification of 4000 \times (Fig. 14), very fine fibril morphologies were also observed on the fracture surface of composites modified by the formation of *in situ* FPP.

In the unmodified $\text{Mg}(\text{OH})_2/\text{PP}$ composites filled by 60 wt % $\text{Mg}(\text{OH})_2$, apparently larger fibril morphologies and debonded fracture in the interface between the particle and the matrix were observed due to poor interfacial adhesion (Figs. 15–17). In modified composites, no larger fibril morphologies on the fracture surface were observed. The morphologies of the fracture surfaces of composites modified by the addition of AA (MA-26) were similar to those of composites modified by the addition of FPP (MF-6). As the AA content was increased or DCP was added, the morphologies of the fracture surface of modified composites turned more compact. $\text{Mg}(\text{OH})_2/\text{PP}$ compos-

ites modified by the addition of AA in the presence of DCP did not exhibit the fibril morphologies. We believe that no adhesion occurred at the interface between the particle and the matrix in the unmodified composites. Fracture under impact and flexural testing took place at the interface between the particle and the matrix. The observed fibril morphologies at the fracture surface were the result of the extended matrix bound particles. In MA-26 and MA-46, modified by the addition of AA, the interface adhesion was improved, and the fracture occurred in the matrix. The particles were encapsulated with the matrix on the fracture surface. For the composites modified by the addition of AA in the presence of DCP and the oxidation resistant, it was hard to see any particle of filler in the fracture surface of MAD-46, MADS-26, and MADS-46. The particles of $\text{Mg}(\text{OH})_2$ were all encapsulated. A lot of very fine filaments on the fracture surface and in the

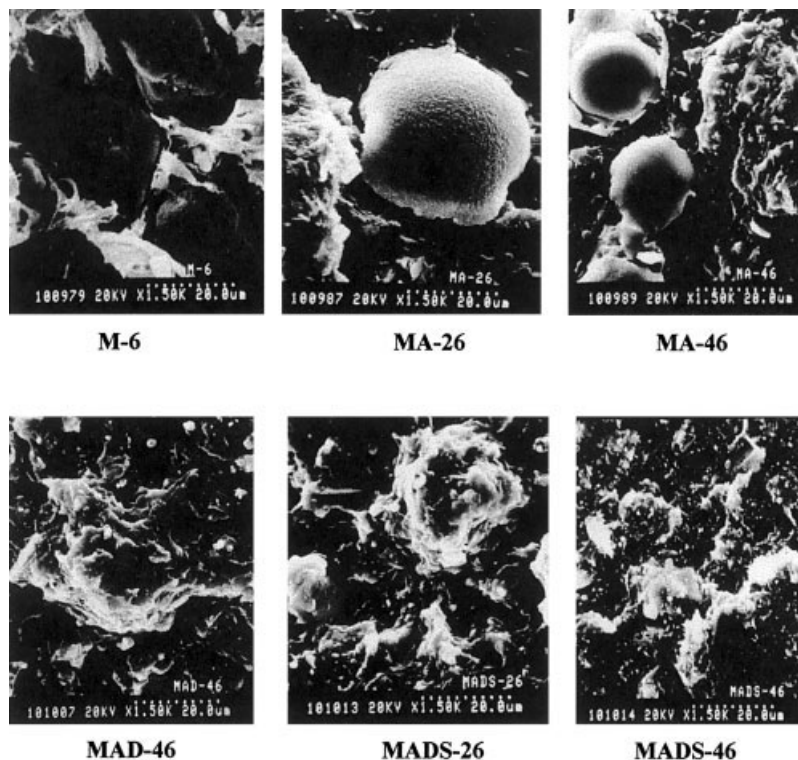


Figure 16 SEM of flexural fracture specimens for $\text{Mg}(\text{OH})_2$ (60 wt %)/PP-modified composites (1500 \times).

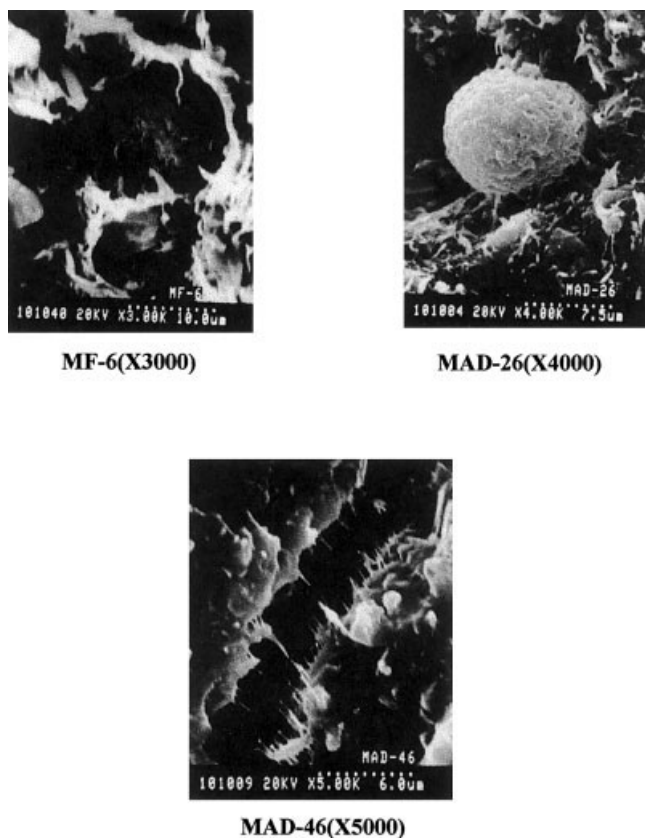


Figure 17 SEM of flexural fracture specimens for $\text{Mg}(\text{OH})_2$ (60 wt %)/PP-modified composites.

crack were observed. This was different from the longer and larger fibril morphology observed in unmodified $\text{Mg}(\text{OH})_2$ /PP composites.

CONCLUSIONS

The investigation of the morphologies of fracture surfaces under impact and flexural testing indicated that the addition of FPP and AA and the formation of *in situ* FPP changed the fracture morphologies of $\text{Mg}(\text{OH})_2$ /PP composites. We believe that the addition of FPP and AA and the formation of *in situ* FPP improved the interfacial interaction and enhanced interface adhesion between the particle and the matrix in $\text{Mg}(\text{OH})_2$ /PP composites. The degree of improvement was more significant in $\text{Mg}(\text{OH})_2$ /PP composites modified by the formation of *in situ* FPP. At low $\text{Mg}(\text{OH})_2$ content, 2 phr AA exhibited a marked effect, but at high $\text{Mg}(\text{OH})_2$ content, 4 phr AA afforded good effect. Due to the improved interface adhesion by interface interaction, the fracture mechanism transformed from interface debonded fracture into the matrix fracture.

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