

# Deformation and Fracture of Mg(OH)<sub>2</sub>-Filled Polyolefin Composites under Tensile Stress

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**ABSTRACT:** The tensile behavior of high-density polyethylene (HDPE), polypropylene (PP), and linear low-density polyethylene composites containing a titanate coupling agent and silicone-oil-treated magnesium hydroxide [Mg(OH)<sub>2</sub>] was studied. The increase in the extent of the ultimate elongation of the composites was affected by the yield stress and the strain-hardening tendency of the polymer matrix in the composites. Ethylene-propylene-diene rubber and octane-ethylene copolymer were introduced to adjust the yield stress of PP and HDPE. Although the ultimate

elongation of PP/elastomer and HDPE/elastomer blends was higher than that of virgin PP or HDPE, the ultimate elongation of the filled composites dropped at a high content of Mg(OH)<sub>2</sub>. Scanning electron microscopy showed that the difference in the uniformity of the interface exfoliation decreased with the yield stress of the matrix. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3248–3255, 2003

**Key words:** polyolefins; fillers; fracture

## INTRODUCTION

Semicrystalline polyolefins such as polypropylene (PP), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE) are widely used because of their advantageous properties, including easy processing, corrosion resistance, low density, and low cost, and most polyolefins have high ultimate elongation before tensile fracture. Magnesium hydroxide [Mg(OH)<sub>2</sub>] is one of the inorganic fillers that can be used to achieve flame-retardancy and smoke-suppressing effects and to replace halogen-containing flame retardants, which produce large amounts of corrosive and toxic gases and smoke when exposed to fire. Unfortunately, for the desired flame retardancy to be achieved, a high loading of Mg(OH)<sub>2</sub> is necessary, and this deteriorates the toughness of the polyolefin matrices, as well as the high ultimate elongation.

Our early publications<sup>1–4</sup> on the tensile properties of highly filled polyolefin composites showed that when the silicone-oil-treated filler Al(OH)<sub>3</sub> or Mg(OH)<sub>2</sub> was used with a suitable titanate coupling agent, the ultimate elongation of the composites could be retained at some high level, even at a high loading

of the filler, because of the full development of the debonding of filler particles. A model was proposed by Dubnikova et al.<sup>5</sup> for the tensile behavior of highly filled polyolefin composites with reduced interfacial adhesion, and the effect of the filler particle size was illustrated. In the model, the plastic deformation of the filled polymers was decided by the correlation between the yield stress of the crazelike zone, which was related to the volume fraction of the filler and the yield stress of the matrix, and the debonding stress, which was related to the interfacial adhesion and filler particle size. In this study, three kinds of polyolefins were used as polyolefin matrices with different yield stresses. The yield stress of the matrices was also adjusted by the addition of a small amount of ethylene-propylene-diene rubber (EPDM) or octane-ethylene copolymer (POE). The investigations described in this article were designed to provide further insight into the mechanism of the correlation between the ultimate elongation of the filled composites and the yield stress of the matrices.

## EXPERIMENTAL

The commercial product LLDPE 218w from Saudi Basic Industries Corporation (Riyadh, Saudi Arabia), with melt-flow index of 1.2 g/10 min (190°C, 2.16 kg), and the PP copolymers K8303 and HDPE 5000S, from Yanshan Petrochemical Co., Ltd. (Beijing, China), were used as the matrix polymers. EPDM 4045, from

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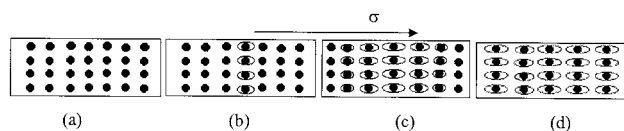
**TABLE I**  
Compounding and Molding Temperatures

Polyolefin	Mixing temperature (°C)	Molding temperature (°C)
HDPE	160	170
LLDPE	170	175
PP copolymer	185	185

Mitsui Petrochemical Industries, Ltd. (Osaka, Japan), and Engage 8210 POE, a copolymer of ethylene and 1-octene from Dow Chemical Co. (Wilmington, DE), were also used. Mg(OH)<sub>2</sub> (Apymag AOH 820, Nabaltec GmbH, Schwandorf, Germany), with a median grain size of 2 μm and a specific surface area of 10 m<sup>2</sup>/g, was used as the filler. The additives used for surface modification were the titanate coupling agent NDZ-130 (Nanjing Shuguang Chemical General Co., Nanjing, China), and 201-50 silicone oil (Shanghai Special Resin Research Institute, Shanghai, China).

The Mg(OH)<sub>2</sub> filler was treated with an organotitanate (2 wt % based on the filler loading). Before the compounding, the filler was mixed with silicone oil (3.3 wt % based on the filler loading) in a minimixer. The components were melt-mixed in the mixing chamber of a Haake RC90 rheometer (Thermo Haake Co., Karlsruhe, Germany) at a given temperature and at a rotor speed of 64 rpm for 12 min. The test specimens for morphology observations and mechanical property testing were prepared via compression molding in the sample form of sheets 1.0 mm and 3.0 mm thick at a given temperature and at a pressure of 15 MPa. The temperatures of mixing and compression molding are listed Table I.

Tensile dumbbell specimens were cut from the 1-mm-thick sheets and tested with an Instron 4465 tensile tester (Instron Corp., Canton, MA) according to ASTM D 638 at a crosshead speed of 50 mm/min. Notched specimens 3 mm thick were tested in a Ray-Ran impact tester (Ray-Ran Test Equipment Ltd., Nuneaton, UK) according to ASTM D 790 with a hammer speed of 3.5 m/s and a pendulum weight of 0.818 kg. The tensile specimens were extended to an elongation of 50% at a crosshead speed of 50 mm/min with the tensile tester; the elongation was maintained, and the load-time curves were recorded automatically with the tensile tester.



**Figure 1** Deformation sketch of the highly filled composites: (a) the nontensile stage, (b) the initiation of the deformed region, and (c,d) the development of the deformed region.

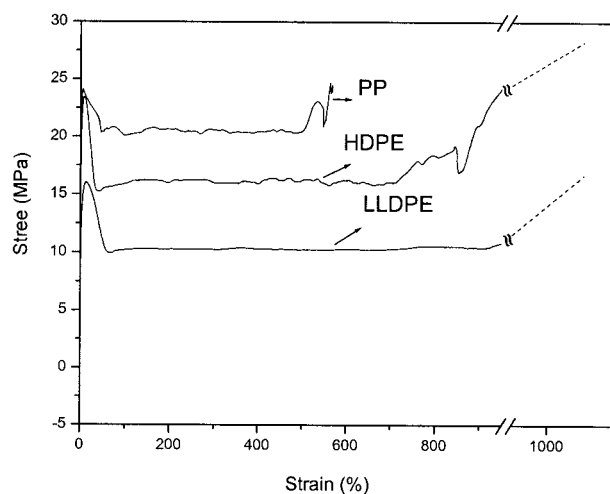
**TABLE II**  
Tensile Properties of Mg(OH)<sub>2</sub>-Filled Polyolefins

Matrix	Filler (vol %)	Ultimate elongation (%)	Yield stress (MPa)	Break stress (MPa)
PP	0	574	24.9	25.6
	15	262	15.4	16.3
	27	233	13.4	14.6
	36	195	10.6	10.7
HDPE	0	>1000	23.4	28.3
	15	650	14.0	10.5
	27	595	12.7	11.6
	36	61	10.1	8.3
LLDPE	0	>1000	16.0	19.5
	15	408	10.6	10.4
	27	30	9.3	6.2
	36	15	7.9	6.4

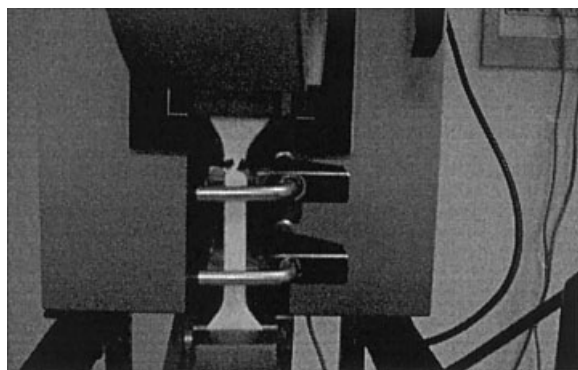
For morphology observations, the surfaces of extended specimens were gold-coated and observed with a Hitachi S-2150 scanning electron microscope (Hitachi Ltd., Co., Tokyo, Japan). For filler dispersion observations, the impact specimens were immersed in liquid nitrogen and then fractured with the Ray-Ran impact tester. The fractured surfaces were coated with a thin layer of gold and observed with the scanning electron microscope.

## RESULTS AND DISCUSSION

Zhuk et al.<sup>6</sup> showed that there is a range of debonding stresses of filler particles for all filled composites. The tensile process of filled polymer composites is shown in Figure 1. The debonding occurs under a certain stress  $\sigma$ , and under such a stress, the matrix may be at the stage of initial (elastic) or strain-hardening states. If it is at the elastic state, more and more particles debond from the matrix as the stress increases until

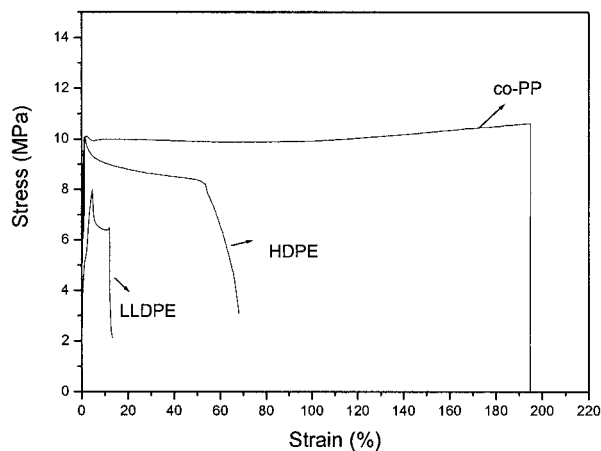


**Figure 2** Stress-strain curves of virgin PP, HDPE, and LLDPE.



**Figure 3** Fracture of the LLDPE/Mg(OH)<sub>2</sub> composite [73 vol % LLDPE and 27 vol % Mg(OH)<sub>2</sub>].

the matrix yields. If the matrix is strong enough, that is, its yield stress is sufficiently high, the debonding occurs in a homogeneous manner so that almost all of the particles are debonded before the matrix yields and easily reach stage d of Figure 1. That often leads to a high ultimate elongation. However, if it is at the strain-hardening state, the strain-hardening tendency of the matrix could play an important role. It determines if the crazelike zones caused by the localized debonding can sustain further development. Unfortunately, the morphology of filled composites is not always perfect; stress concentrations resulting from the imperfections make tensile specimens break at stage d of Figure 1, and the ultimate elongation is perhaps medium. At that point, homogeneous debonding reduces the effects of the stress concentration and is helpful in increasing the ultimate elongation. In an extreme case, if the matrix has low yield stress and the strain hardening is not strong enough, few particles can be debonded, and the crazelike zones are sharply localized. Then, the composites show a quasibrittle fracture at stage b of Figure 1.



**Figure 4** Stress-strain curves of the Mg(OH)<sub>2</sub>-filled polyolefins [64 vol % polyolefin and 36 vol % Mg(OH)<sub>2</sub>].

**TABLE III**  
Effect of EPDM on the Tensile Properties of Mg(OH)<sub>2</sub>-Filled Polyolefin Composites

Matrix	Filler (vol %)	Ultimate elongation (%)	Yield stress (MPa)	Break stress (MPa)
5% EPDM				
PP	0	619	18.5	25.7
	27	38	10.1	9.0
	36	15	9.5	7.9
HDPE	0	>1000 <sup>a</sup>	18.9	24.5
	27	143	9.4	10.1
	36	45	8.6	8.6
LLDPE	0	>1000 <sup>a</sup>	13.7	17.4
	27	23	8.5	6.4
	36	19	7.1	6.0
10% EPDM				
PP	0	627	15.8	22.3
	27	22	9.5	8.5
	36	13	9.4	7.5
HDPE	0	>1000 <sup>a</sup>	14.7	17.8
	27	96	8.6	8.2
	36	43	7.8	6.8
LLDPE	0	>1000 <sup>a</sup>	11.3	13.4
	27	26	7.6	5.5
	36	12	5.3	4.7

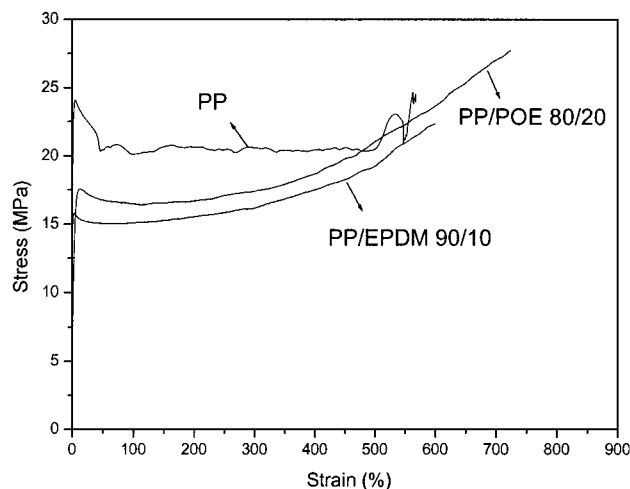
<sup>a</sup> A little higher than HDPE or LLDPE.

The cross section of the matrix decreases as the volume fraction of the filler increases, and so the yield strength of filled composites follows the Nicolais-Narkis equation:<sup>7,8</sup>

**TABLE IV**  
Effect of POE on the Tensile Properties of Mg(OH)<sub>2</sub>-Filled Polyolefins

Matrix	Filler (vol %)	Ultimate elongation (%)	Yield stress (MPa)	Break stress (MPa)
10% POE				
HDPE	0	>1000 <sup>a</sup>	20.6	21.4
	27	545	10.4	11.7
	36	78	9.7	8.0
PP	0	602	20.6	25.8
	27	230	10.8	11.4
	36	154	8.6	8.2
LLDPE	0	>1000 <sup>a</sup>	14.1	17.5
	27	85	8.2	7.9
	36	16	6.9	5.6
20% POE				
HDPE	0	>1000 <sup>a</sup>	18.0	29.4
	27	170	8.5	10.5
	36	76	7.2	6.4
PP	0	691	17.3	27.7
	27	478	9.1	7.9
	36	79	8.2	7.0
LLDPE	0	>1000 <sup>a</sup>	11.9	15.1
	27	112	7.7	7.0
	36	50	5.9	5.1

<sup>a</sup> A little higher than HDPE or LLDPE.



**Figure 5** Stress-strain curves of virgin PP, PP/EPDM, and PP/POE.

$$\sigma_c = \sigma_m(1 - a\phi^{2/3})$$

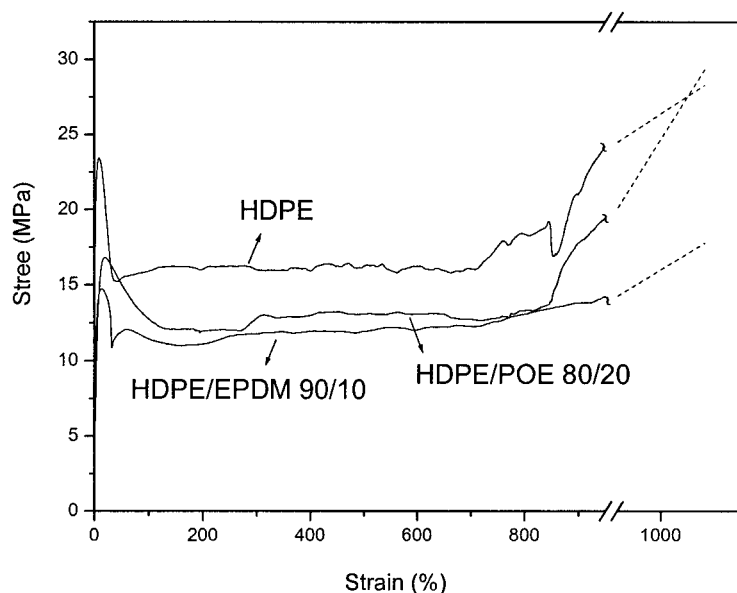
where the subscripts *c* and *m* represent the composite and the polymer matrix and  $\phi$  is the volume fraction of the filler. The value of *a* is related to the adhesion between the matrix and filler. For a spherical filler uniformly distributed in the polymer matrix and with no adhesion to the polymer matrix, *a* is 1.21. Therefore, as the filler fraction increases, the interface between the filler and the matrix increases, whereas the matrix yields at a relatively low load and results in the localization of particle debonding and a drop in the ultimate elongation of the composite.

Three kinds of polyolefins—PP, HDPE, and LLDPE—were used as polymer matrices, and the

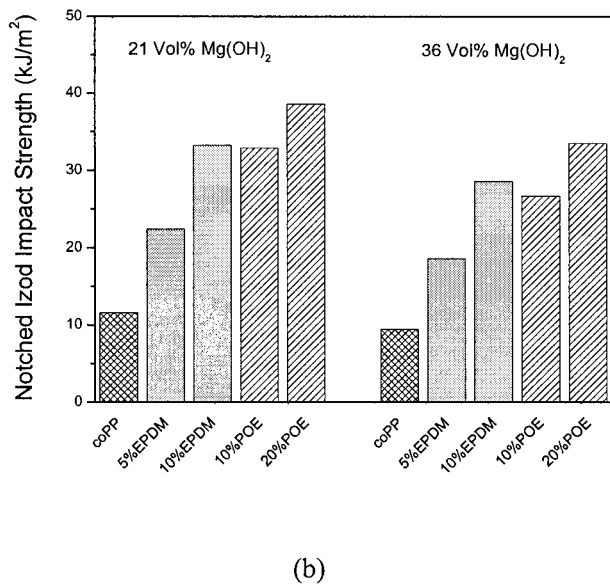
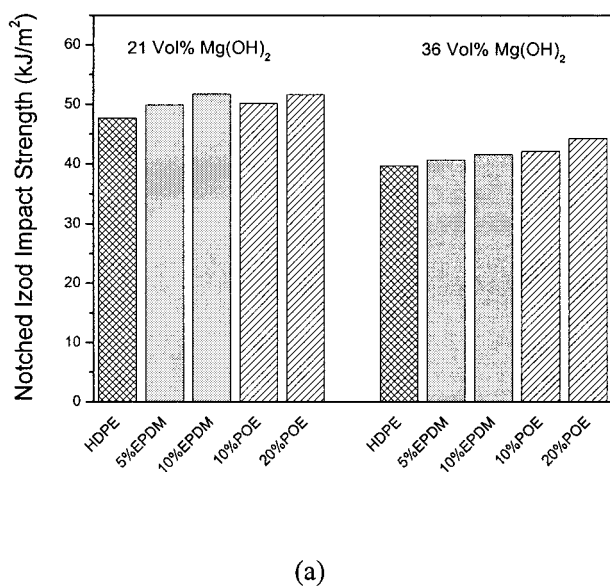
yield stress decreases in that sequence, as shown in Table II and Figure 2. The tensile properties of the virgin polyolefins and filled composites are also listed in Table II. Figure 2 shows that of the three matrices, PP has the highest yield stress. The yield stress of HDPE is a little lower than that of PP, whereas the stress drops remarkably in comparison with that of PP after the yield point. The yield stress of LLDPE is lower than that of PP and HDPE and also drops remarkably after the yield point.

As shown in Table II, a drop in the yield stress and ultimate elongation can be observed as the volume fraction of the filler increases. When LLDPE is filled with a 27% volume fraction of Mg(OH)<sub>2</sub>, the ultimate elongation decreases most dramatically because the crazelike zone cannot expand rapidly, as shown in Figure 3, because the yield stress and the stress after the yield point are very low. Although the matrix is PP, because of the high yield stress and the stress after the yield point, the ultimate elongation remains at a high level even when the volume fraction of Mg(OH)<sub>2</sub> is up to 36%. The break stress of the composites is also listed in Table II; although all the matrices have a strain-hardening tendency, only the filled PP composites have a break stress higher than the yield stress.

The strain-stress curves of polyolefins filled with 36 vol % Mg(OH)<sub>2</sub> are shown in Figure 4. The tensile behaviors of the three composites are quite different. Because PP has the highest yield stress and stress after the yield point, the debonding should develop in the most homogeneous manner of the three composites, and the drop in the tensile stress after the yield point is not distinct. Because of the low yield stress of



**Figure 6** Stress-strain curves of virgin HDPE, HDPE/EPDM, and HDPE/POE.



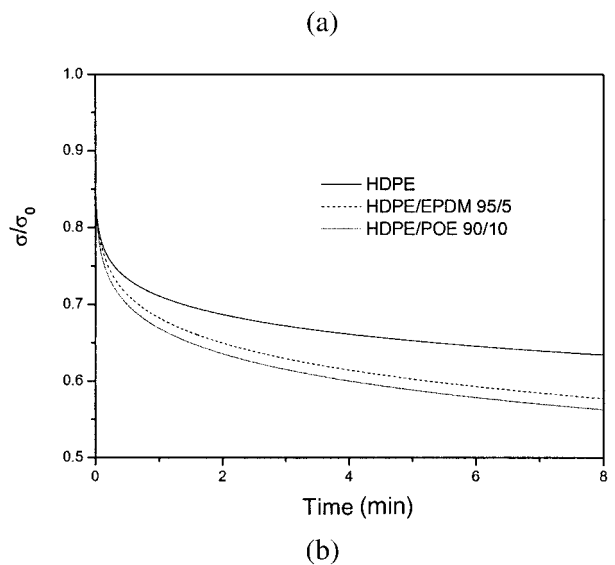
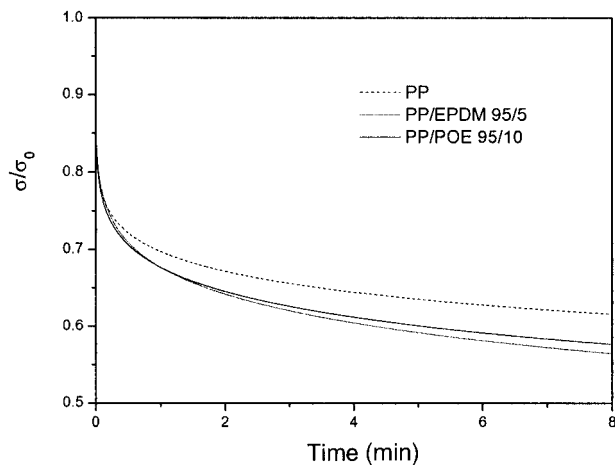
**Figure 7** Impact strength of the  $\text{Mg}(\text{OH})_2$ -filled polyolefin composites [64–73 vol % polyolefin + EPDM or POE and 27–36 vol %  $\text{Mg}(\text{OH})_2$ ]: (a) HDPE, (b) PP.

LLDPE and the apparent drop in stress after the yield point, sharply localized debonding should occur, because of which the crazelike zone is not likely to develop further, and stress concentration causes the specimen to break.

Because the extensometer cannot determine the elongation above 1000%, the values of the ultimate elongation of HDPE and HDPE/EPDM and HDPE/POE blends are compared by the final position of the crosshead. The introduction of these elastomers increases the ultimate elongation of the polymer matrices but does not increase the ultimate elongation of the corresponding filled composites, as shown in Tables III and IV.

The effects of the elastomers EPDM and POE on the tensile behavior of PP and HDPE are shown in Figures 5 and 6. The elastomers change the behavior of PP much more than that of HDPE. The tensile stress increases continuously after the yield point until the break; this kind of strain-hardening effect is more useful for a filled composite designed for high elongation. As for the matrices based on HDPE, they experience a similar drop in the tensile stress after the yield point. At the same time, the introduction of the elastomers inevitably reduces the yield stress of the matrices.

Tables III and IV show that EPDM and POE have some different effects on the tensile properties of polyolefin/ $\text{Mg}(\text{OH})_2$  composites. The microcrystalline crosslinking network of POE enables the PP/POE and HDPE/POE blends to keep a relatively high yield stress in comparison with the blends containing EPDM. The ultimate elongation of the composites con-



**Figure 8** Stress relaxation of the polyolefin matrices: (a) PP and (b) HDPE.

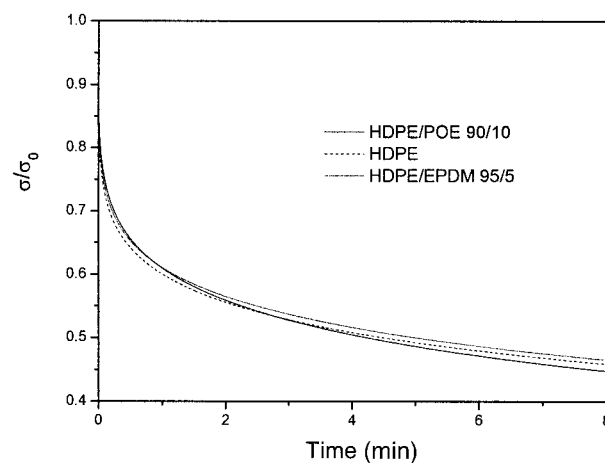
taining POE remains at a higher level than that of the composites containing EPDM. At high contents of POE, the ultimate elongation of the composites also drops obviously at high loadings of Mg(OH)<sub>2</sub>. The filled LLDPE composites cannot reach high ultimate elongations, but as the crystallinity of LLDPE is not as high as that of PP and HDPE, when POE changes the nature of the deformation, the filled composites can obtain a relatively high level of ultimate elongation. Although the elastomer can bring a strain-hardening effect to PP matrices, a high yield strength may play a more important role because the ultimate elongation of highly filled PP/POE and PP/EPDM composites is not higher than that of PP/Mg(OH)<sub>2</sub> composites.

The notched Izod impact strength of the composites is shown in Figure 7. The toughness represented by the impact strength does not agree with the results of the tensile tests, in which the introduction of the elastomers increases the notched impact strength, especially for the filled PP composite. As for the LLDPE composites, they are so flexible that they cannot be broken by the pendulum. This is also interesting because the LLDPE composites have the poorest tensile properties of the studied composites. Because the impact tests are carried out in a very short time interval, the crystalline structure of the polyolefin does not have time to be arranged and orientated completely, whereas in tensile tests, it does reach a further step. However, only local deformation corresponds to the value of the impact strength, whereas the tensile toughness is related to the deformation of the specimen as a whole.

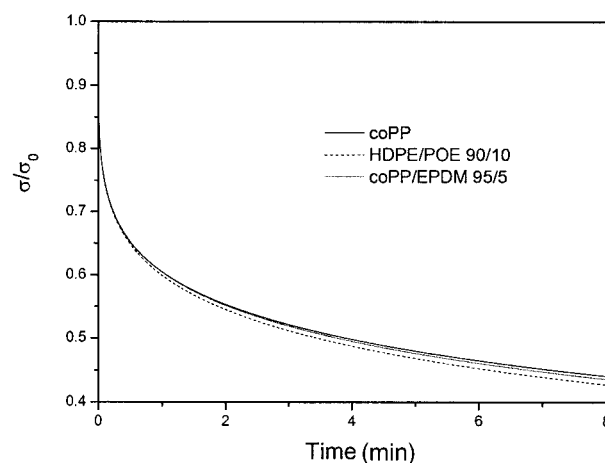
Figures 8 and 9 show the stress relaxations of the polyolefins and their filled composites. The elastomers EPDM and POE increase the speed and degree of the stress relaxation of the polyolefin matrices but affect the stress relaxations of the filled composites less. The degree of relaxation of the filled composites is higher than that of the polyolefin matrices; some of the relaxation of the filled composites is explained by the debonding of the filler particles. The difference in the effects of the elastomers on the stress relaxations of the polyolefin matrices and polyolefin/Mg(OH)<sub>2</sub> composites indicates that the extent of debonding decreases when the elastomers are introduced.

Microscopy observations of the deformed specimens also reveal a correlation between the yield stress of the matrix and the debonding of filler particles. The effect of the POE content in PP/POE/Mg(OH)<sub>2</sub> composites on the debonding of the filler particles is shown in Figure 10. As the POE content increases, the yield stress decreases, and the tendency of a localized debonding area is more obvious.

The filler particle dispersion plays an important role in the finite deformation of highly filled polymer composites. The fracture surfaces of the composites filled



(a)



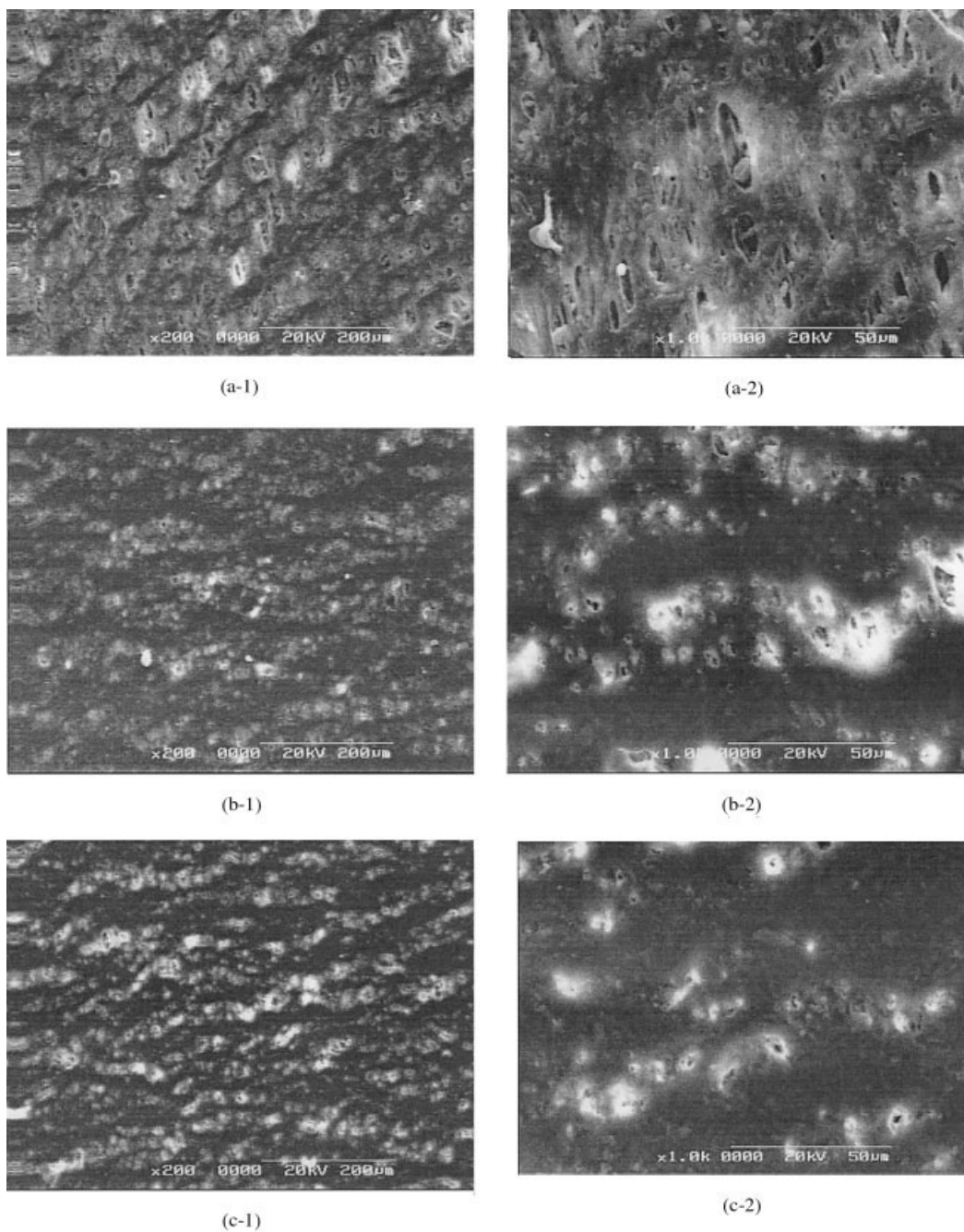
(b)

**Figure 9** Stress relaxation of the Mg(OH)<sub>2</sub>-filled polyolefins [73 vol % polyolefin + EPDM or POE and 27 vol % Mg(OH)<sub>2</sub>]: (a) PP and (b) HDPE.

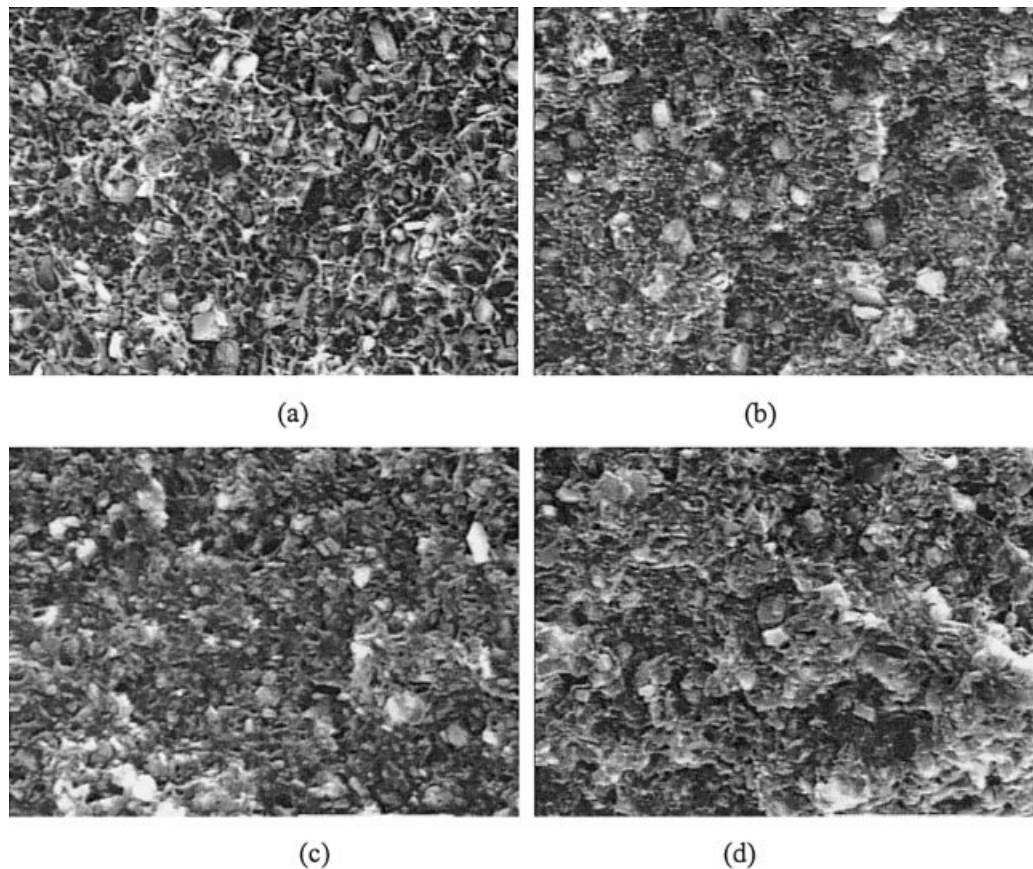
with 27 vol % Mg(OH)<sub>2</sub> are shown in Figure 11. There are only slight differences in the dispersion of the filler particle that can be observed.

## CONCLUSIONS

The yield stress of the polyolefin matrices plays an important role in the development of the debonding of filler particles and, therefore, affects the ultimate elongation of the composites. The strain-hardening tendency of the matrices also affects the ultimate elongation but plays a minor role in comparison with the yield stress. Although the introduction of EPDM and POE increases the ultimate elongation of the matrices to a small extent, it causes a drop in the ultimate elongation of highly filled composites. Scanning elec-



**Figure 10** Microdeformation of the tensile PP/Mg(OH)<sub>2</sub> composite [73 vol % PP and 27 vol % Mg(OH)<sub>2</sub>]: (a) PP, (b) PP/POE 90/10, (c) PP/POE 80/20.



**Figure 11** Filler dispersion in the Mg(OH)<sub>2</sub>-filled polyolefin composites [73 vol % polyolefin or polyolefin + EPDM and 27 vol % Mg(OH)<sub>2</sub>]: (a) HDPE, (b) 95/5 HDPE/EPDM, (c) PP, and (d) 95/5 PP/EPDM.

tron microscopy observations show that the localized tendency of crazelike zones increases together with the POE content in PP/POE/Mg(OH)<sub>2</sub> composites. The introduction of POE or EPDM increases the degree of stress relaxation of the polyolefins but has less of an effect on the stress relaxation of the polyolefin/Mg(OH)<sub>2</sub> composites.

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