Effects of Silicone Oil and Polymeric Modifiers on the Mechanical Properties of Highly Filled LLDPE

SONG ZHU, YONG ZHANG, YINXI ZHANG

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

ABSTRACT: The effects of coupling agents, silicone oil, and three types of polymeric modifiers on the mechanical properties of linear low density polyethylene (LLDPE) composites highly filled with aluminium hydroxide [$Al(OH)_3$] were studied. Polymeric modifiers that contain polar groups, such as silane-grafted polyethylene (Si-g-PE) and acrylic-acid-grafted ethylene-vinyl acetate copolymer (AA-g-EVA), improve the mechanical properties dramatically, while nonpolar modifiers improve them to some extent. When $Al(OH)_3$ was treated using a titanate coupling agent, the silicone oil increased the impact strength and elongation at break of the LLDPE/$Al(OH)_3$ composites. Introduction of a polymeric modifier containing polar groups destroys the beneficial effects of silicone oil on film mechanical properties, while the introduction of a nonpolar elastomeric polymeric modifier retains the high impact strength and elongation at break. SEM analyses provide the indirect evidence of the encapsulation of silicone oil around the filler. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 121–128, 2002

Key words: linear low density polyethylene; aluminium hydroxide; silicone oil; encapsulation

INTRODUCTION

Polyethylene (PE) has been widely used in various fields because it has good physical and mechanical properties. However, PE is a combustible material, and its oxygen index is about 18, which hinders its practical applications. For many years halogen-containing flame-retardant agents have been used in order to make flame-retardant PE materials. However, these give off smoke and hazardous gases during the composite burning. Recently, nonhalogen flame-retardant agents have become the major trend for the development of fire-retardant polymer materials. Aluminium hydroxide has been widely used in polyolefin composites for this purpose.[1] However, the use of large amounts of inorganic filler, which is necessary to achieve the required flame resistance, drastically decreases the mechanical properties of the filled polymers.[2]

To achieve improvement of mechanical properties, many techniques are used, including surface treatment of fillers with fatty acid, fatty-acid derivatives and coupling agents, such as silanes and titanates, introduction of elastomeric or functionalized polymers into the matrix, etc. Interfacial adhesion between the polymer matrix and the filler plays an important role in determining the mechanical properties of the blend. Extensive work has been done in such fields.[3–16] Weak or strong adhesion can be reached by virtue of different modifications of fillers or matrices, which

result in different mechanical properties of the resulting composites. Jancar et al.[3,4] and Dubnikova et al.[5] studied filled polypropylene (PP) composites having strong or weak adhesion and concluded that strong adhesion leads to increased modulus and tensile strength, whereas zero adhesion causes decreased tensile strength and increased elongation at break. Fang et al.[6] studied the tensile behavior of filled PP and very low density polyethylene (VLDPE) and reached the same conclusion. Liu et al.[7] and Fu et al.[8] suggested that weak adhesion is sufficient for high toughness in the case of the existence of a soft interlayer between filler particles and polymer matrix. In the studies of Wang et al.[9] and Jancar et al.,[10] when the filled composites contain elastomeric impact modifiers, the morphology of the composites is determined by the polarity of matrices and elastomers.

Our previous work[11,12] showed that silicone oil and special surface modification have a large effect on the elongation at break and notched-Izod impact strength of the high density polyethylene (HDPE) composites containing high loadings of $Mg(OH)_2$ or $Al(OH)_3$. In this article, the mechanical properties of linear low density polyethylene (LLDPE) composites highly filled with $Al(OH)_3$ were studied, in which coupling agents, polymeric modifiers and silicone oil were used to achieve different interfacial adhesions. The mechanism of fracture in tension was also discussed.

EXPERIMENTAL

Materials

Commercial LLDPE 218 w, from Saudi Basic Industrial Company (Riyadh, Saudi Arabia), melt flow index (MI) of 1.2 g/10 min (190°C, 2.16 kg), was used as the matrix polymer. $Al(OH)_3$, APYRAL 60, from Nabaltec GmbH, Schwandorf, Germany, with average particle size of 0.7~1.5 μm and specific surface area of 5~8 m^2/g, was used as the filler.

The additives used were: (1) Silane coupling agent KH-550 (Nanjing Shuguang Chemical General Company, Nanjing, China), (2) Titanate coupling agent NDZ-130 (Nanjing Shuguang Chemical General Company), (3) Silicone oil 201-50 (Shanghai Special Resin Research Institute, Shanghai, China), (4) Silane-grafted HDPE Polidan T/A (Si-g-PE), a commercial product of Padanaplast SpA, Roccabiana, Italy, with a MI of

0.33 g/10min (190°C, 5 kg), (5) Acrylic-acid-graft EVA copolymer (AA-g-EVA), containing 3% acrylic acid, VA content of 15% and a MI 2 g/10 min (190°C, 2.16 kg) (6) ethylene–propylene-diene terpolymer (EPDM) 4045, from Mitsui Petrochemical Industries Ltd., Tokyo, Japan, and (7) Engage 8210, a copolymer of ethylene and 1-octene from Dow Chemical Company, Wilmington, DE, with a MI of 8.0 g/min (190°C, 2.16 kg).

Compounding

$Al(OH)_3$ filler was untreated or treated with the silane oftitanate at 2 wt% based on the filler content. LLDPE, $Al(OH)_3$ and other additives were mixed in the mixing chamber of a HAAKE rheometer RC90 at 165°C at a rotor speed of 64 rpm for 12 min.

Specimen Preparation

Test specimens for morphology observation and mechanical properties testing were prepared by compression molding samples in the form of sheets of 1.0 mm or 3.0 mm in thickness at 175°C and a pressure of 15 MPa for 5 min and at room temperature for 10 min.

Mechanical Properties

Tensile dumbbell specimens were cut from the 1 mm-thick sheets and were tested using an Instron 4465 tensile tester according to Chinese Standard GB-1040-79 at a cross-head speed of 50 mm/min. Notched specimens of 3 mm in thickness were tested in a RAY-RAN impact tester according to Chinese Standard GB-1043-79 using a hammer speed of 3.5 m/s and a pendulum weight of 0.818 kg.

Morphology Observation

For morphology observation, the tensile specimen surfaces were gold-coated and observed using a HITACHI-S-2150 scanning electron microscope (SEM).

RESULTS

Mechanical Properties

As shown in Table I, the modification of $Al(OH)_3$ filler using the two coupling agents leads to improved impact strength of the LLDPE/$Al(OH)_3$ composites. The silane coupling agent increases

Table I   Effects of Coupling Agents and Silicone Oil on the Mechanical Properties of Al(OH)$_3$ Filled LLDPE^a

Coupling Agent	Silicone Oil (phr)	Notched Impact Strength (kJ/m^2)	Tensile Yield Strength (MPa)	Elongation-at-Break (%)
Untreated	0	3.7	12.6	1
Silane	0	46.0	15.2	43
	5	44.5	12.9	50
	10	32.1	8.2	4
Titanate	0	18.2	11.5	3
	5	36.9	7.9	151
	10	25.9	5.0	360

^{a} Basic Formulation: LLDPE 100 phr, Al(OH)$_3$ 140 phr.

the yield strength and elongation at break of the composites, while the titanate has little effect on such properties.

In our previous work[11,12] it had been reported that silicone oil could improve the impact strength and elongation at break of highly filled HDPE composites if the fillers were modified using a suitable coupling agent. In this study, when Al(OH)$_3$ was treated using either of two kinds of coupling agents, silicone oil addition yields different mechanical property results. As shown in Table I, when the Al(OH)$_3$ is treated using the silane coupling agent and the loading of silicone oil is 10 phr, the mechanical properties are poorer compared with the silane-treated Al(OH)$_3$. When the loading of silicone oil is 10 phr and the Al(OH)$_3$ is treated by the titanate, the elongation at break of the composite increases to 360% and the yield strength decreases 60%.

In our study, three types of polymeric modifiers were used to investigate the effects of polymeric modifiers on mechanical properties of highly filled LLDPE. Si-g-PE is a rigid copolymer containing polar groups and AA-g-EVA is an elastomeric copolymer containing polar groups. EPDM and Engage are nonpolar elastomeric copolymers.

Si-g-PE and AA-g-EVA, which contain polar groups, both improve the mechanical properties of filled LLDPE. The effects of the Si-g-PE and AA-g-EVA contents on the mechanical properties of untreated Al(OH)$_3$ filled LLDPE are shown in Figure 1, in which the Al(OH)$_3$ filler is untreated. Notched-Izod impact strength increases dramatically when the polymeric modifiers are introduced (Fig.1), the yield strength increases slightly, and the elongation at break increases, but is still beneath the level of 100%.

The modifications of the composites using polymeric modifiers also depend on the surface mod-

ification of the filler. When the Al(OH)$_3$ is treated using the silane coupling agent, (Table II) a small amount of Si-g-PE and AA-g-EVA can also increase the mechanical properties evident at the content of 5%, based on the matrix content; the notched-Izod impact strength is still the most significantly improved; the elongation at break is close to 100%; and yield strength is up to 18.6 MPa when 5% Si-g-PE is added. When the coupling agent is titanate, the effect is not so significant.

Nonpolar elastomeric polymer modifiers can also enhance the impact properties of LLDPE filled with untreated Al(OH)$_3$, but the effects are not as dramatic as for the polymeric modifier containing polar groups (Table II). The yield strength drops slightly as the content of EPDM or Engage increases, and the elongation is still rather low. When Al(OH)$_3$ is modified using the silane coupling agent, the effect of polymeric modifier type becomes less evident except for a slight decrease in yield strength.

Table II and Figure 2 show that blending of silicone oil with AA-g-EVA or Si-g-PE does not result in further improvements in mechanical properties. When the filler is silane-coupling-agent-treated Al(OH)$_3$, the yield strength, notched-Izod impact strength, and elongation at break change slightly with increasing loading of silicone oil and show a considerable decrease when the loading of silicone oil is 10 phr. Table II also shows that when the polymeric modifier is EPDM or Engage, which are nonpolar elastomer, the yield strength is retained, and the elongation at break and notched-Izod impact strength decrease. On the other hand, the treatment of filler using titanate coupling agent together with silicone oil provides high elongation at break and some improvement in impact strength, at the

price of decreased yield strength. When the Si-g-PE or AA-g-EVA is added, all the mechanical properties deteriorate, especially the elongation at break. When the polymeric modifier is EPDM
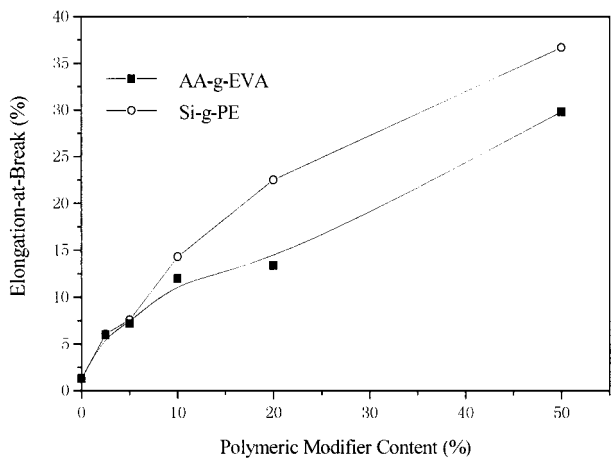

(a)

(b)

(c)

or Engage, the elongation at break is retained at the level of 150% and the notched-Izod impact strength increases, while the yield strength is still very low.
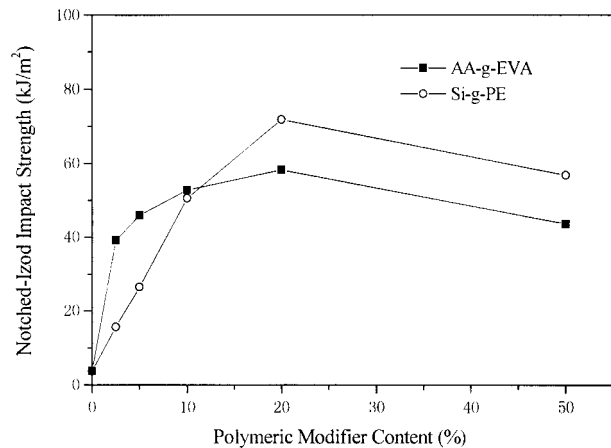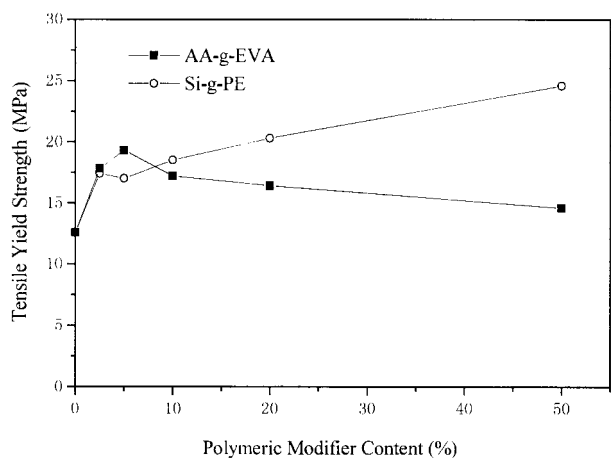
Morphology

SEM of surface of tensile specimens can be used to study the tensile behavior of filled polymers.[6] Surfaces of tensile specimens were observed using SEM and the results are shown in Figure 3. These photos show indirect evidence of the encapsulation of silicone oil. In Figure 3(a), when $Al(OH)_3$ is treated using the titanate coupling agent alone, the interaction between the filler and the matrix is weak. The region of debonding can be observed adjacent to the undebonding region with a distinct dividing line. When the silicone oil is added, as shown in Figure 3(b), the two kinds of regions can also be observed, but the division between the regions is much more slur, which shows the well developed debonding region that leads to a rather high elongation at break.

As shown in Figure 3(c and d), less debonding can be observed in the matrix when the filler is treated using silane coupling agent, whether it contains silicone oil or not. This is because of the enhanced adhesion between the fillers and the matrix polymers.

DISCUSSION

The expression proposed by Turczanyi et al.[13,14] describes the yield stress of filled polymer:

$$\sigma_{yc} = \frac{1 - v_f}{1 + 2.5v_f} \, \sigma_{ym} \exp(Bv_f) \qquad (1)$$

where σ_y is yield stress, the subscripts c and m represent the composite and matrix, respectively, and v_f is the volume fraction of the filler. The factor B accounts for interfacial interactions, filler-specific-surface area, and properties of both matrix-filler interlayer and unfilled matrix:

Figure 1   Effect of polymeric modifier content on the mechanical properties of LLDPE/Al(OH)$_3$ composites. (a) Notched-Izod impact strength, (b) tensile yield stress, (c) elongation at break. LLDPE + polymeric modifier 100 phr, Al(OH)$_3$ 140 phr. The content of copolymers is based on matrix wt %.

Table II   Effect of Polymeric Modifiers[a] and Silicone Oil on the Mechanical Properties of LLDPE/Al(OH)$_3$ Composites[b]

Coupling Agent	Polymeric Modifier	Content (%)	Notched Impact Strength (kJ/m^2)	Tensile Yield Strength (MPa)	Elongation-at-Break (%)
Without silicone oil					
Untreated	Control	0	4.4	13.8	2
	AA-g-EVA	5	46.0	19.3	7
	AA-g-EVA	10	52.8	17.2	12
	Si-g-PE	5	26.5	17.0	8
	Si-g-PE	10	50.7	18.5	14
	Engage	5	25.5	11.9	5
	EPDM	5	22.7	12.6	5
	EPDM	10	25.8	11.5	6
Silane	Control	0	46.0	15.2	43
	AA-g-EVA	5	60.9	16.7	59
	Si-g-PE	5	74.2	18.6	92
	Engage	5	51.5	11.8	40
	EPDM	5	44.9	12.9	39
	EPDM	10	40.0	12.1	42
Titanate	Control	0	18.2	11.5	3
	AA-g-EVA	5	33.1	14.0	4
	Si-g-PE	5	14.0	16.0	4
	Engage	5	15.2	9.0	8
	EPDM	5	14.5	10.5	11
With 5 phr silicone oil					
Silane	Control	0	44.5	12.9	50
	AA-g-EVA	5	65.4	13.9	65
	Si-g-PE	5	65.3	15.6	51
	Engage	5	35.4	12.1	4
	EPDM	5	38.8	12.9	7
Titanate	Control	0	36.9	7.9	151
	Si-g-PE	5	10.9	11.7	2
	AA-g-EVA	5	15.0	10.2	13
	Engage	5	36.7	5.4	136
	EPDM	5	46.7	7.9	175

[a] The content of Polymeric modifier is based on the matrix wt %.
[b] Base Formulation: LLDPE + Polymeric modifier 100 phr, Al(OH)$_3$ 140 phr.

$$B = (1 + \kappa \cdot \gamma \cdot \rho_f \cdot A_f)\ln(\sigma_{yi}/\sigma_{ym}) \qquad (2)$$

In Equation 2, κ is a semi-empirical constant, γ is the filler surface free energy, ρ_f and A_f are the density and specific surface-area of the filler, respectively, and σ_{yi} is the strength of the interlayer.

Silane coupling agent or polymeric modifiers containing polar groups, such as Si-g-PE and AA-g-EVA, result in high adhesion and the σ_{yi}. The value of B and σ_{yc} increases. The titanate coupling agent induces the encapsulation of silicone oil on the surfaces of the filler particles. The adhesion between the filler and the matrix become zero, the yield stress of the interlayer decreases, which reduces the value of B and σ_{yc}.

Bazhenov[15] has suggested that filler may suppress necking and initiate yielding in crazelike zones if the particles are treated by an antiadhesive agent and the adhesion with the polymer matrix is weakened. Nicolais and Nicodema[16] and Lavengood et al.[17] explained that if the propagating crack encounters a filler particle to which the matrix is not strongly adherent, the interfacial debonding can effectively blunt the tip of the crack and prevent or slow down the further propagation of the crack. The encapsulation of silicone oil can act as the antiadhesive, as mentioned above, to maintain the elongation at a rather high level.

Dubnikova et al.[5] described the crazelike process in much more detail. The Nicolais–Narkis
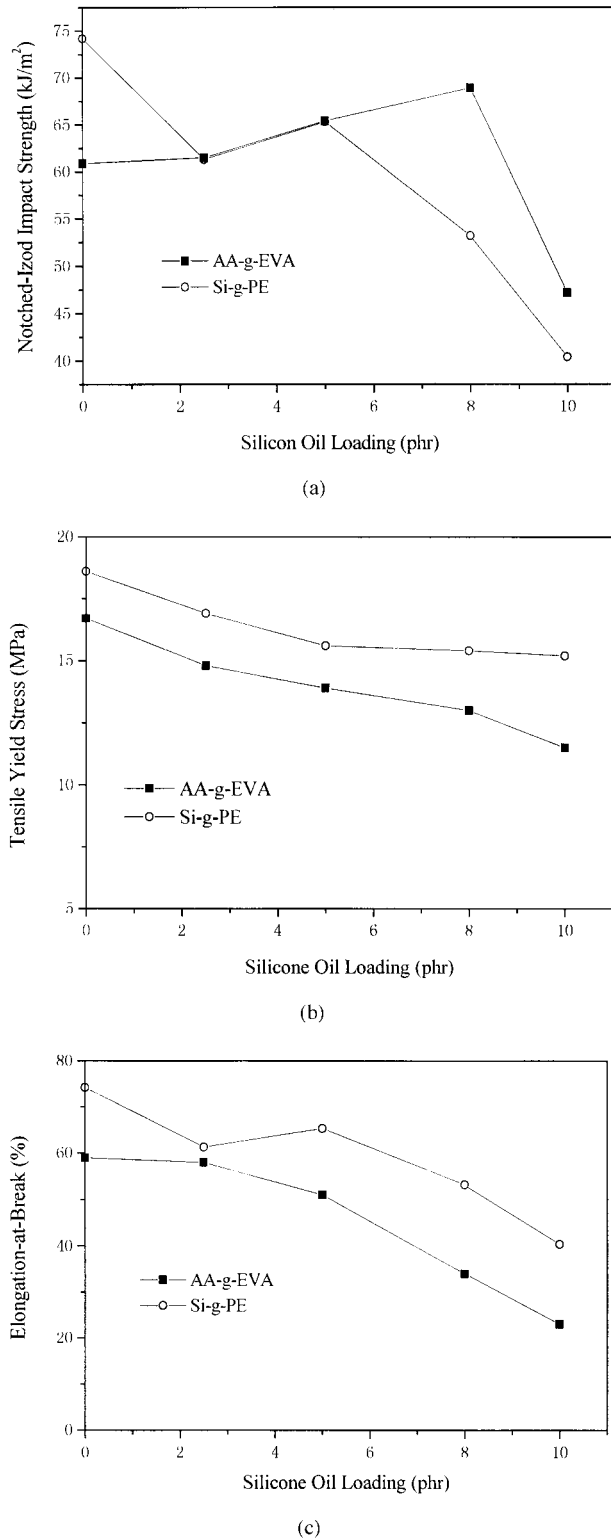
Figure 2   Effect of silicone oil loading on the mechanical properties of LLDPE/grafted copolymer/Al(OH)$_3$ composites. (a) Notched-Izod impact strength, (b) tensile yield stress, (c) elongation at break. LLDPE 95 phr, polymeric modifier 5 phr, silane modified Al(OH)$_3$ 140 phr.

equation[18,19] was used to determine the further debonding of the particles in the vicinities of the craze banks:

$$\sigma_{cz} = \sigma_{bh}(1 - a\phi^{2/3}) \tag{3}$$

where the subscripts cz and bh represent crazelike zones and bulkhead, the polymer enclosed the filler particles, inside the crack. The pore fraction inside the crazelike zones is equal to the filler volume content, ϕ. The value of a is related to the adhesion between the matrix and filler. In spherical fillers uniformly distributed with no adhesion, a becomes 1.21. Another parameter, σ_d, should be introduced to describe the effect of the silicone oil in highly filled LLDPE. σ_d is the stress value sufficient for the exfoliation from the surface of the given particle. When σ_d is less than σ_{cz}, further debonding of the particles in the vicinities of the craze banks will occur. If the craze flow mechanism is not realized, the value of σ_{bh} should be the same as that of polymer matrix until the fracture. According to Equation 3, even in the case of weak adhesive strength, new debonding formation in the process of further stretching will be prohibited at sufficiently high filler loading. If the bulkheads are in the stage of plastic flow, which is the effect of silicone oil in Al(OH)$_3$ filled LLDPE, the value of σ_{bh} can be increased during further elongation and the value of σ_{cz} can raised in the process of further drawing. The debonding occurring at the developed or even final drawing stages can be achieved.

Liu[7] and Fu[8] suggest that the formation of a soft interlayer between filler particles and polymer matrix can improve the impact strength of highly filled polymer composites. Their stress calculations inside the soft inclusion revealed that even weak adhesion can be sufficient to relieve the high localized stresses in the matrix. In our study, when Al(OH)$_3$ is treated using titanate, the perfect encapsulation of silicone oil on the surface of Al(OH)$_3$ acts as a soft interlayer to achieve improved impact strength. On the other hand, enhanced adhesion between LLDPE and Al(OH)$_3$, which is the effect of the silane coupling agent or the polymeric modifiers, contain polar groups can also increase the impact strength due to the flexible nature of LLDPE.

When the silicone oil is blended with the AA-g-EVA or Si-g-PE in LLDPE/Al(OH)$_3$ composites, there should be a competition between the encapsulation of the two different modifiers. The encap-
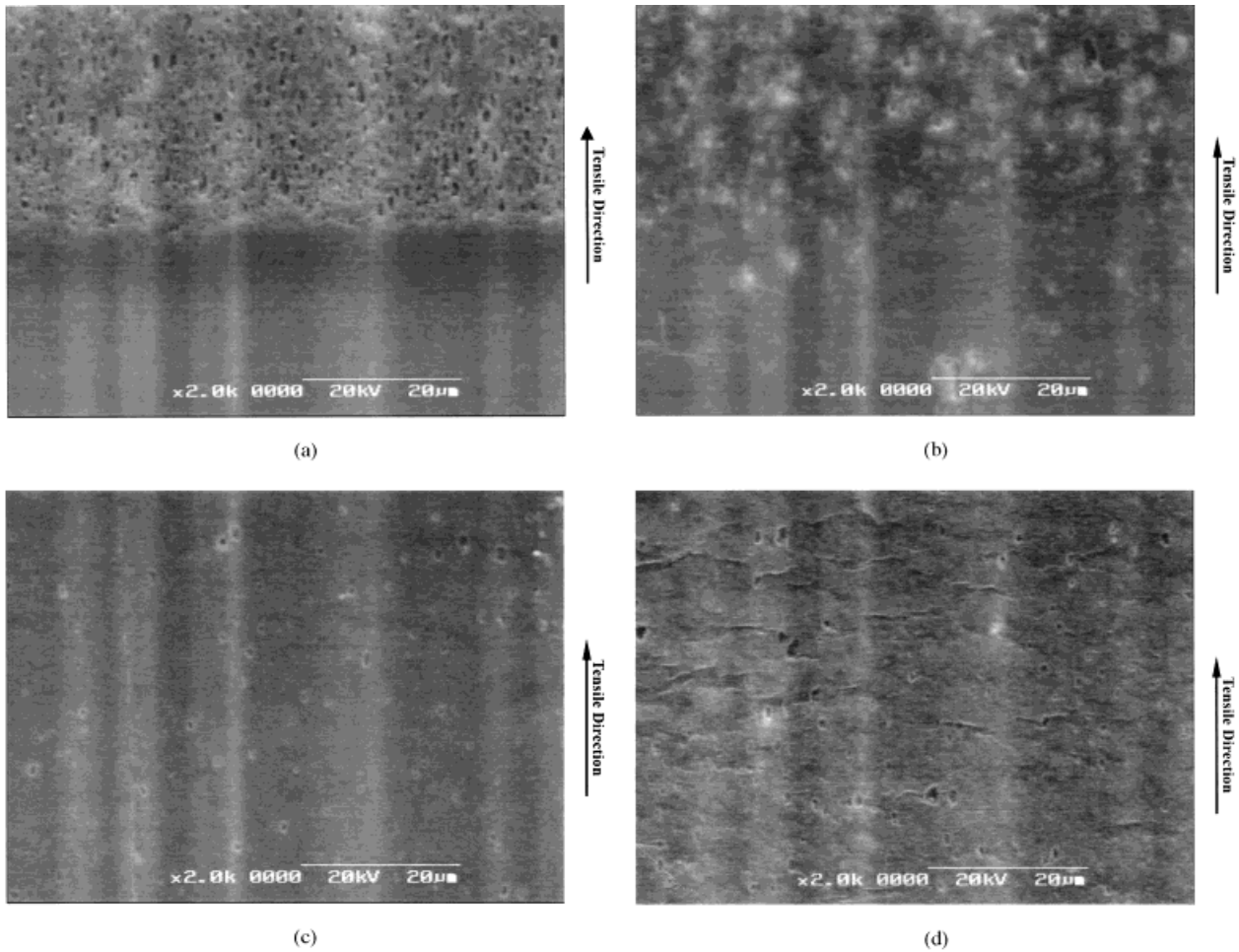
Figure 3 Morphology of side surface of tensile specimens. (a) LLDPE/ Al(OH)$_3$ (titanate modified), (b) LLDPE/ Al(OH)$_3$ (titanate modified)/silicone oil, (c) LLDPE/ Al(OH)$_3$ (silane modified), (d) (c) LLDPE/ Al(OH)$_3$ (silane modified)/silicone oil.

sulation of both is probably inhabited or imperfect, which results in stress concentration and deteriorates the overall mechanical properties. Nonpolared EPDM and Engage have little effect on the encapsulation of silicone oil, so the impact strength of the composites increases when the two kinds of elastomers are added.

CONCLUSIONS

The mechanical properties of the of LLDPE/ Al(OH)$_3$ composites apparently depend on polarity of the modifiers. The silane coupling agent or the polymeric modifiers containing polar groups improve the mechanical properties of the composites, particularly the impact strength. Silicone oil, together with the titanate coupling agent, increases the elongation at break and impact strength of the composites and decreases the yield strength. When the silicone oil is used together with AA-g-EVA or Si-g-PE, the mechanical properties of the composites are deteriorated. When the silicone oil is used together with EPDM or Engage, the elongation at break and impact strength of the composites increase, and the yield strength decreases.

The interfacial adhesion between the LLDPE matrix and Al(OH)$_3$ filler affects the mechanical properties of the composites. The polarity of the polymeric modifiers has large effect on the adhesion. The silane coupling agent and the polymeric modifiers containing polar groups enhance the adhesion. Silicone oil and the titanate coupling agent weaken the adhesion.

The morphology study clearly demonstrates that apparent debonding between polymer matrix and filler particles occurs in highly filled LLDPE when the adhesion between LLDPE and Al(OH)$_3$ is weakened using the titanate coupling agent. When the silicone oil is used together with titanate coupling agent, the debonding can develop well during the whole extension stage.

REFERENCES

1. Shaw, R. J. Flame Retardants '83; Plastics & Rubber Institute and British Plastic Federation: London, UK, 1983, 4-1.
2. Miyata, S.; Imahashi, T.; Anabuki, H. J Appl Polym Sci, 1980, 25, 415.
3. Jancar, J.; Kucera, J. J Polym Eng, 1990, 30, 707.
4. Jancar, J.; Kucera, J. J Polym Eng, 1990, 30, 714.
5. Dubnikova, I. L.; Muravin, D. K.; Oshmyan, V. G. Polym Eng Sci, 1997, 37, 1301.
6. Fang, Z. P.; Hu, Q. L. Angew Makromol Chem, 1999, 265, 1.
7. Liu, S. H.; Nauman, E. B. J Mater Sci, 1990, 25, 2071.
8. Fu, Q. Polymer, 1995, 36, 2397.
9. Wang, J.; Tung, J. F.; Ahmad Fuad, M. Y.; Hornsby, P. R. J Appl Polym Sci, 1996, 60, 1425.
10. Jancar, J.; Dibenedetto, T. J Mater Sci, 1995, 30, 2438.
11. Zhang, Y.; Yang, J. H.; Zhu, S.; Wang, Y. L.; Zhang, Y. X. Presented at the 16th Annual Meeting of the Polymer Processing Society, Shanghai, China, June 18–23, 2000.
12. Zhang, Y.; Yang, J.; Peng, Z.; Wang, Y.; Zhu, S.; Zhang, Y. Polym Polym Compos, 2000, 8, 471.
13. Turczanyi, B.; Pukanszky, B.; Kelen, F. J Mater Sci Lett, 1988, 7, 160.
14. Pukanszky, B.; Turczanyi, B.; Tudos, F. In Proceedings of the 2nd Conference on Interface in Polymer Composition, Cleveland, Ohio, Elsevier: New York, 1988.
15. Bazhenov, S. Plastics Additives, Pritchard, G., Ed.; Chapman & Hall: London, 1998; 252.
16. Nicolais, L.; Nicodemo, L. Int J Polym Mater 1974, 4, 229. 17 Lavengood, R.; Nicolais L.; Narkis, M. J Appl Polym Sci 1973, 17, 1177. 18 Nicolai, L.; Narkis, M. Polym Eng Sci 1971, 11, 194.
19. Jancar, J.; Dibenedetto, A. T. J Mater Sci, 1995, 30, 1601.