

# Surface Modification of Calcium Carbonate Used for Polypropylene Blending with Dimeric Aluminates

KAIRONG LIAO,<sup>1\*</sup> XUOXIN CHEN,<sup>1</sup> and CHENMOU ZHENG<sup>2</sup>

<sup>1</sup>Institute of Polymer Science, Zhongshan University, Guangzhou, China, 510275, and <sup>2</sup>Department of Chemistry, Zhongshan University, Guangzhou, China, 510275

## SYNOPSIS

Three kinds of dimeric aluminates (2DH-306, 2DH-324, and 2DH-335) have been used for surface modification of calcium carbonate ( $\text{CaCO}_3$ ) particles. The dimeric aluminates were shown to have an appreciable coupling effect at the interfaces between the light calcium carbonate (L- $\text{CaCO}_3$ ) and polypropylene (PP) in the blends by mechanical property study and SEM observation. In the 2DH-306 modified L- $\text{CaCO}_3$ /PP (25/75) system, the impact strength exceeded that of the nonmodified system by more than 30 kJ/m<sup>2</sup>. X-ray study showed that the dimeric aluminates had a synergistic effect with L- $\text{CaCO}_3$  on the formation of PP  $\beta$ -crystal, which would exert an important influence on the elongation ratio at break for the L- $\text{CaCO}_3$ /PP blends. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Calcium carbonate ( $\text{CaCO}_3$ ) has been widely used as a filler in polymer processing. It is essential that the  $\text{CaCO}_3$  surface be modified before it is used as the filler for polymer blending; this ensures a good bounding performance at the interfaces between polymer matrix and the filler particles. Aluminates<sup>1,2</sup> have recently received much attention in as coupling agents for  $\text{CaCO}_3$  surface modification, but dimeric aluminates in this aspect have seldom been reported. Therefore, attempts using monoisopropoxytriolatealoxane (2DH-306), monoisopropoxytri(diisooctylphosphato)aloxane (2DH-324), and monoisopropoxytri(isooctoxyl, isooctylphosphonato)aloxane (2DH-335) as coupling agents for  $\text{CaCO}_3$  surface modification in polypropylene (PP) blending, respectively, were made in our lab, and their coupling effects at the interfaces between  $\text{CaCO}_3$  particles and PP were studied through mechanical property testing, X-ray diffraction, and SEM observation.

## EXPERIMENTAL

### Materials

Dimeric aluminates were prepared according to the method described elsewhere.<sup>3</sup> Light calcium carbonate and ultrafine  $\text{CaCO}_3$  powder (UF- $\text{CaCO}_3$ ) were supplied by Jiabang Chemical Factory and Guangping Factory, respectively. Liquid paraffin came from Japan, with  $\eta = 100$  cp at 30°C. Polypropylene was available from Beijing Yanshan General Petrochemical Plant with  $MV = 22.0 \times 10^4$ .

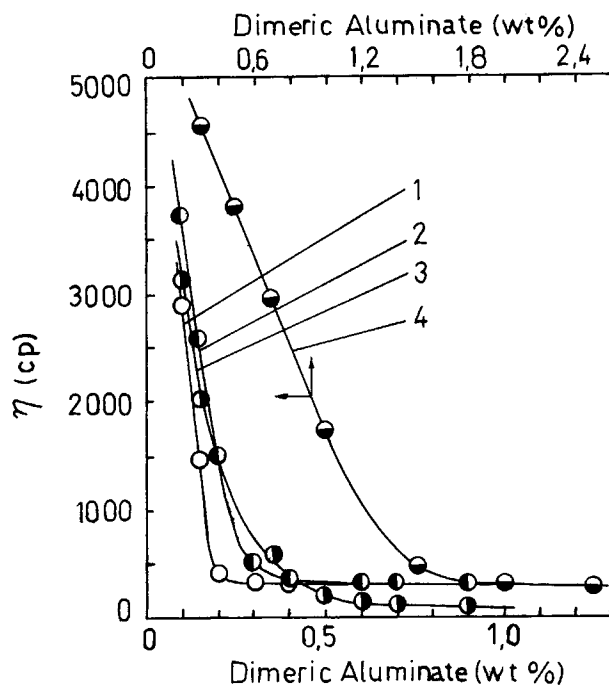
### $\text{CaCO}_3$ Surface Modification

$\text{CaCO}_3$  was put in a three-necked flask equipped with a mechanical stirrer, into which a 0.5 to 2.0 wt % dimeric aluminate in petroleum 120 solution was added dropwise through a syringe while stirring. Then vigorous stirring was provided for another 10 min, and finally the dimeric aluminate coated  $\text{CaCO}_3$  was dried at 120°C for 1.5 to 2 h.

### Viscosity Measurement

Viscosity of modified and unmodified  $\text{CaCO}_3$ /liquid paraffin suspension systems was measured at 30°C  $\pm 0.2^\circ\text{C}$  by an NDJ-79 rotatory viscometer made by Shanghai Fudan University. In general, the viscosity

\* To whom correspondence should be addressed.



**Figure 1** Effect of content of dimeric aluminates on the viscosities ( $\eta$ ) of  $\text{CaCO}_3$ /liquid paraffin systems with  $\text{CaCO}_3$ /liquid paraffin = 0.6. (1) 2DH-335/L- $\text{CaCO}_3$ ; (2) 2DH-324/L- $\text{CaCO}_3$ ; (3) 2DH-306/L- $\text{CaCO}_3$  (the  $\eta$  of liquid paraffin used is 20 cp at  $30^\circ\text{C}$ ); (4) 2DH-324/UF- $\text{CaCO}_3$ .

of the suspension systems was stable; however, three measurements were conducted for each suspension system and the average of them was used for plotting.

#### Preparation of L- $\text{CaCO}_3$ /PP Blends

A mixture of the dimeric aluminate coated L- $\text{CaCO}_3$  and PP pellets was put into the mixing chamber of an XSS-300 torque rheometer for molten mixing for 10 min at  $190^\circ\text{C}$  and 32 rpm under 5 kg.

#### Mechanical Property Testing

Samples for testing were prepared by mold pressing at  $200^\circ\text{C}$  under 5 MPa for 5 min and then cooled down by about  $15^\circ\text{C}/\text{min}$ . A sample size of  $50 \times 8 \times 5 \text{ mm}^3$  was taken for Charpy impact strength testing on a pendulum impact tester with a gap span of 40 mm. A sample size of  $15 \times 10 \times 5 \text{ mm}^3$  was taken for static bending testing on a dynamic and static tester. Dumbbell shape samples with a size of  $40 \times 8 \times 0.8 \text{ mm}^3$  were taken for tensile strength and elongation testing on an XL-100A tester manufactured by Guangzhou Material Testing Factory.

#### SEM Observation

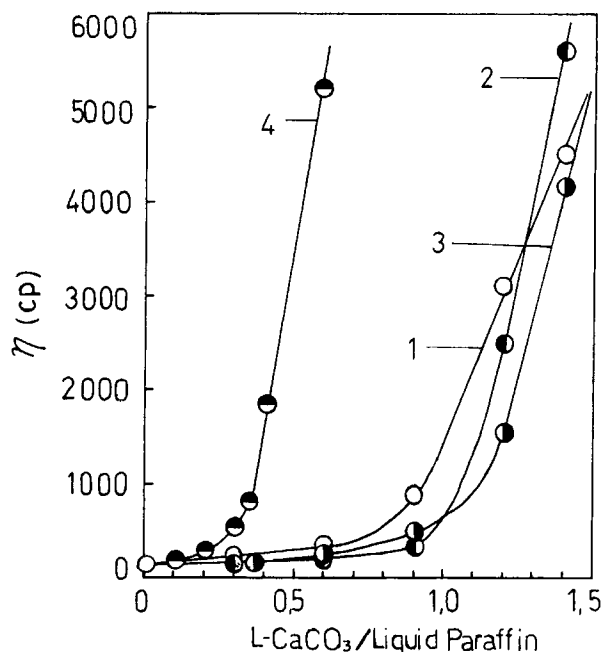
Morphological observation was performed on a Hitachi S-520 SEM. The samples used were shaped with a scalpel to provide a plain facet for observation, and the facet was etched with 2 mol/L HCl for 4 h and then washed clean with distilled water before being observed.

#### X-Ray Diffraction

X-ray diffraction was carried out on a Shimadzu XD-3A diffractometer with a scanning rate of  $4^\circ/\text{min}$ . The relative content  $K$  of PP  $\beta$ -form crystal in a total amount of PP crystals for L- $\text{CaCO}_3$ /PP blends was calculated according to Turner's method<sup>4</sup>:

$$K = \frac{H_{\beta_1}}{H_{\beta_1} + (H_{\alpha_1} + H_{\alpha_2} + H_{\alpha_3})}$$

where  $H_{\alpha_1}$ ,  $H_{\alpha_2}$ , and  $H_{\alpha_3}$  are the heights of the three strong equatorial  $\alpha$ -form peaks (110), (040), and (130) and  $H_{\beta_1}$  is the height of the strong single  $\beta$  peak at  $2\theta = 15.6^\circ$ .



**Figure 2** Effect of L- $\text{CaCO}_3$  content on the viscosities ( $\eta$ ) of L- $\text{CaCO}_3$ /liquid paraffin systems. (1) 2DH-335 (0.3 wt %); (2) 2DH-324 (0.5 wt %); (3) 2DH-306 (0.9 wt %); (4) without coupling agent.

Table I Mechanical Properties of L-CaCO<sub>3</sub>/PP Blends\*

L-CaCO <sub>3</sub> /PP	σ <sub>i</sub> (kJ·m <sup>-2</sup> )			σ <sub>b</sub> (MPa)			σ <sub>t</sub> (MPa)			ε (%)				
	2DH-324	2DH-335	2DH-306	2DH-324	2DH-335	2DH-306	2DH-324	2DH-335	2DH-306	2DH-324	2DH-335	2DH-306		
10/90	54.8	58.1	69.3	40.7	51.4	50.6	55.8	28.9	28.4	31.8	140.1	53.8	24.4	24.8
20/80	45.3	48.4	60.6	36.4	49.1	49.0	49.6	26.9	27.5	26.3	102.4	68.8	117.6	66.6
25/75	38.8	53.3	66.0	34.6	47.7	46.6	47.6	25.1	24.5	25.5	—	100.0	113.8	22.5
30/70	34.3	31.3	40.2	25.5	54.1	48.6	56.8	23.1*	23.2*	22.6*	45.5*	30.9*	42.2*	19.7*
35/65	34.7	25.5	23.2	11.1	44.3	43.7	45.4	25.6	22.7	23.9	34.4	26.3	22.9	31.3
40/60	19.0	21.9	36.4	13.1	42.1	44.3	45.8	22.3	23.6	22.5	16.3	31.9	24.8	5.8
50/50	14.8	15.1	24.5	7.5	35.7	37.2	42.5	21.1	22.9	20.0	14.1	7.3	21.3	5.4

\* Data in Table I are the average of five measurements.  
 σ<sub>i</sub>—impact strength (30°C); the average standard derivation = ±7.6 kJ m<sup>-2</sup>; PP: 57.0 kJ m<sup>-2</sup>.  
 σ<sub>b</sub>—bending strength (30°C); the average standard derivation = ±2.0 MPa; PP: 66.3 MPa.  
 σ<sub>t</sub>—tensile strength (32°C); the average standard derivation = ±0.6 MPa; PP: 34.1 MPa; \*T = 21°C.  
 ε %—elongation ratio at break (32°C); the average standard derivation = ±13%; PP: 16.7%; \*T = 21°C.

RESULTS AND DISCUSSION

Effects of Dimeric Aluminates on CaCO<sub>3</sub> Modification

Curves of viscosity of a CaCO<sub>3</sub>/liquid paraffin suspension system versus dimeric aluminate content (wt %, relative to the amount of CaCO<sub>3</sub>) used for CaCO<sub>3</sub> modification are shown in Figure 1. The results indicate that the viscosities of the CaCO<sub>3</sub>/liquid suspension systems decrease rapidly with the increase of dimeric aluminate content used for CaCO<sub>3</sub> modification at a fixed CaCO<sub>3</sub>/liquid paraffin ratio and then level off after a certain critical point, implying that the dimeric aluminates exert a certain modification effect on the surfaces of CaCO<sub>3</sub> particles. It is easy to visualize that when CaCO<sub>3</sub> filler is subjected to dimeric aluminate, it will be coated with dimeric aluminate and the CaCO<sub>3</sub> particles become less polar, thus preventing them from coagulating and making them disperse more easily in nonpolar liquid media. From the inflexion points of the vis-

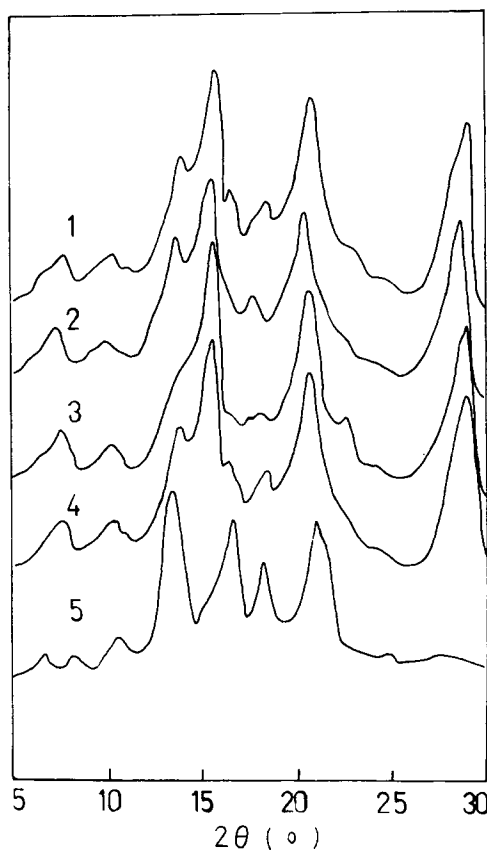
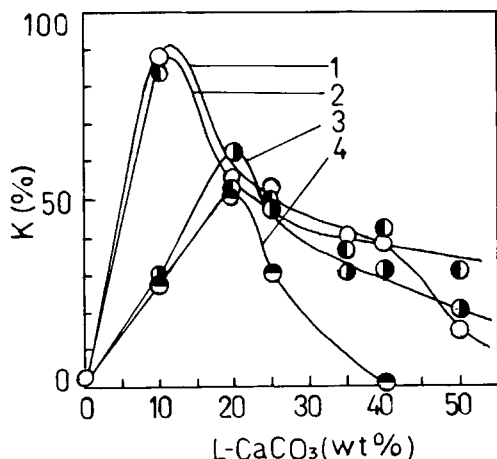


Figure 3 WAXD spectra of L-CaCO<sub>3</sub>/PP blends. (1) L-CaCO<sub>3</sub> (0.8 wt % 2DH-335)/PP = 20/80; (2) L-CaCO<sub>3</sub> (1.0 wt % 2DH-324)/PP = 20/80; (3) L-CaCO<sub>3</sub> (0.9 wt % 2DH-306)/PP = 20/80; (4) L-CaCO<sub>3</sub>/PP = 20/80; (5) PP.



**Figure 4** Relationship between blend composition and  $\beta$ -crystal content ( $K$ ) in total amount of PP crystals. (1) 2DH-335 (0.8 wt %); (2) 2DH-324 (1.0 wt %); (3) 2DH-306 (0.9 wt %); (4) without coupling agent.

cosity curves, the appropriate contents for L- $\text{CaCO}_3$  modification—2DH-335  $\approx$  0.20 wt %, 2DH-324  $\approx$  0.35 wt %, and 2DH-306  $\approx$  0.50 wt %—were found, respectively. The molecular weights of the three types of dimeric aluminates are nearly the same; however, the appropriate content of dimeric aluminates for  $\text{CaCO}_3$  modification varied greatly with the types of dimeric aluminates (i.e., 2DH-306 > 2H-324 > 2DH-335). This may be related to the difference of molecular architectures and can be explained by the fact that the amount needed to form a monomolecular layer of 2DH-306 on the  $\text{CaCO}_3$  particle surface is the greatest one of the three types of dimeric aluminates due to the closest proximity of the molecules with linear oleoyl groups. As for 2DH-335, the appropriate content is the smallest one of the three due to the least proximity of the dimeric aluminate molecules with three isoocetyl isooctyl phosphonato bulky groups, which results in severe steric hindrance.

UF- $\text{CaCO}_3$  is in the form of ultrafine powder and thus has a larger specific area; therefore, the appropriate content of dimeric aluminate (2DH-324) for its modification is much greater than that for L- $\text{CaCO}_3$ , as shown in Figure 1.

Viscosity of the L- $\text{CaCO}_3$ /liquid paraffin system versus L- $\text{CaCO}_3$  content is shown in Figure 2. It can be found that the incipient points of viscosity enhancement for the dimeric aluminate modified suspension systems appear much later than for the nondimeric aluminate modified system, further indicating that the dimeric aluminates have an improving effect on the surfaces of  $\text{CaCO}_3$  particles.

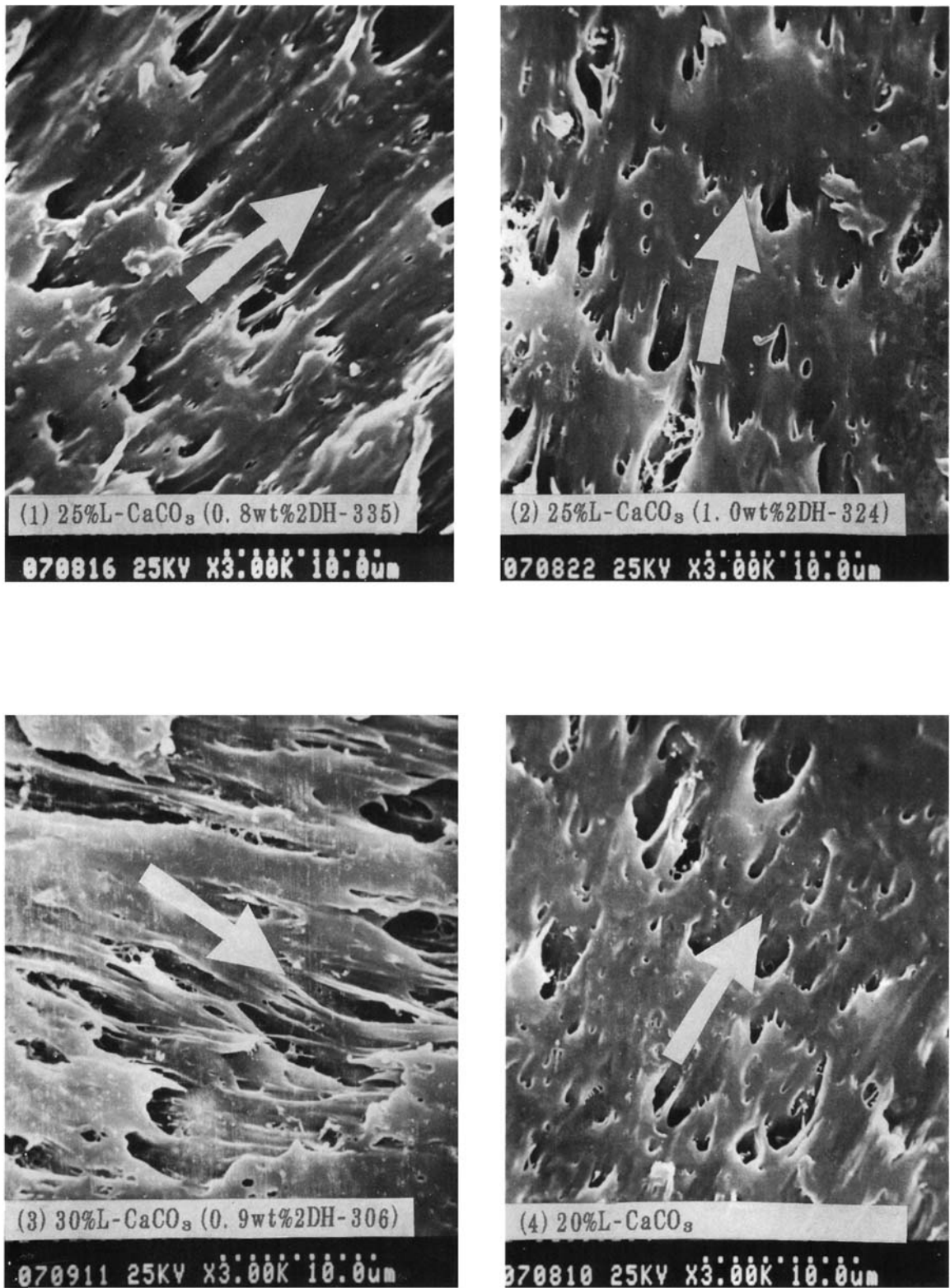
### Effect of Dimeric Aluminates on the Properties of $\text{CaCO}_3$ /PP Blends

It is desired that the  $\text{CaCO}_3$ -filled PP would increase its impact strength while maintaining its bending and tensile strengths and its elongation ratio at break. 2DH-324 (1.0 wt %), 2DH-335 (0.8 wt %), and 2DH-306 (0.9 wt %) treated L- $\text{CaCO}_3$  was used for PP blending, and the mechanical properties are listed in Table I in comparison with those of the nondimeric aluminate treated system. It can be seen from Table I that the bending and tensile strengths of the dimeric aluminate treated L- $\text{CaCO}_3$ /PP blends are slightly lower than that of the nondimeric aluminate treated corresponding system, but the impact strengths and elongation ratios at the break of the dimeric aluminate treated L- $\text{CaCO}_3$ /PP blends are higher than that of the nondimeric aluminate treated corresponding system. It has been shown that the corresponding monomeric aluminates [i.e., isopropyl dioleoyl aluminate (DH-306), isopropyl di(di-isooctylphosphato) aluminate (DH-324), and isopropyl di(isooctyl, isooctylphosphato) aluminate (DH-335), respectively] do exhibit similar modification effects on the surfaces of L- $\text{CaCO}_3$  particles according to the results of viscosity measurements<sup>5</sup>; however, they hardly provide improvement in mechanical properties for blends with L- $\text{CaCO}_3$ /PP = 25/75, which is the ratio that is more practical in application, even though the L- $\text{CaCO}_3$  and PP used are the same as those used in this work. Therefore, the results in Table I show that the dimeric aluminates used here are more promising for practical application in PP modification than the corresponding monomeric aluminates. Of the three dimeric aluminate treated L- $\text{CaCO}_3$ /PP systems, the 2DH-306-treated L-

**Table II** The Relative Content ( $K\%$ ) of PP  $\beta$ -Crystal in Total Amount of PP Crystals

L- $\text{CaCO}_3$ /PP	Dimeric Aluminates (wt %)*			
	1.0 2DH-324	0.8 2DH-335	0.9 2DH-306	None
PP	0.7	0.8	0.5	0.9
5/95	63.9	66.0	45.1	—
10/90	83.7	87.6	30.2	29.2
20/80	52.4	55.0	62.4	52.0
25/75	50.9	53.0	47.3	30.3
35/65	37.1	40.0	30.0	—
40/60	42.3	39.1	31.3	$\sim$ 0
50/50	30.8	14.5	20.2	$\sim$ 0

\* Relative to the amount of L- $\text{CaCO}_3$  in the blends.



**Figure 5** SEM micrographs of L-CaCO<sub>3</sub>/PP blends (arrows in pictures refer to the directions of the applied force from the scalpel). (1) L-CaCO<sub>3</sub> (0.8 wt % 2DH-335)/PP = 25/75; (2) L-CaCO<sub>3</sub> (1.0 wt % 2DH-324)/PP = 25/75; (3) L-CaCO<sub>3</sub> (0.9 wt % 2DH-306)/PP = 30/70; (4) L-CaCO<sub>3</sub>/PP = 20/80.

CaCO<sub>3</sub>/PP system provides the best mechanical properties, and its impact strength is even higher than that of pure PP roughly by 10 kJ/m<sup>2</sup> and that of the nondimeric aluminate treated system by about 30 kJ/m<sup>2</sup> when L-CaCO<sub>3</sub>/PP ≤ 25/75.

The fact that the bending and tensile strengths of all the dimeric aluminate treated systems are somewhat lower while the impact strengths and elongation ratios at break are higher than those of the nondimeric aluminate treated corresponding system may be due to the coupling effect of the dimeric aluminates and particularly the formation of PP β-crystal in the blends.

It can be seen from X-ray diffraction patterns (Fig. 3) of L-CaCO<sub>3</sub>/PP blends that a peak appearing at  $2\theta = 15.6^\circ$ , which is the characteristic of PP β-crystal, is enhanced when L-CaCO<sub>3</sub> is modified with dimeric aluminates. But the peak of PP without L-CaCO<sub>3</sub>, which only contains dimeric aluminates and is equivalent to that in the aforementioned corresponding CaCO<sub>3</sub>/PP system, is the same as that of pure PP. This suggests that the dimeric aluminates alone have no promotion effect on the nucleation of PP β-crystal, while L-CaCO<sub>3</sub> and dimeric aluminates together have a synergistic effect on the nucleation and crystallization of PP β-crystal. As shown in Table II, the relative content *K* of β-form crystal in the total amount of PP crystals is relevant to the content of L-CaCO<sub>3</sub> in the blends. Further study shows that it is also related to the PP materials used, and a detailed discussion of this subject is found in ref. 6.

It is known that PP β-crystal is more easily deformed than the α-form, and this would impart toughness to its mechanical property. The variation of *K*-values versus L-CaCO<sub>3</sub>/PP is shown in Figure 4, which indicates that the *K*-values are basically in conformity with the elongation ratios at break, except for some variation for the system with 2DH-335. The

variation of β-crystal content of each dimeric aluminate treated system is also consistent with that of the impact strength as shown in Table I.

### The Coupling of Aluminates in L-CaCO<sub>3</sub>/PP Blends

The SEM micrographs (Fig. 5) show that there are cavities in various shapes with clear-cut edges for the HCl etched sample without dimeric aluminate, whereas there are cavities with frill or fringe along the applied force from the scalpel in samples containing dimeric aluminates. It can be deduced from the cavity structure that the dimeric aluminates in L-CaCO<sub>3</sub>/PP act as coupling agents to hold the filler and PP resin tightly. In agreement with the mechanical results, the morphologies also show that 2DH-306 has the best coupling effect, and this can be explained by the fact that the long oleoyl branches in 2DH-306 molecules would anchor deeply into the PP matrix, resulting in more strong bonding between L-CaCO<sub>3</sub> particles and PP resin and serving as a shock absorber.

### REFERENCES

1. W. Zhang, T. Chen, and W. Chen, *China Plastics* (in Chinese), **2**, 23 (1988).
2. U.S. Patent, 3,905,936.
3. C. Zheng, S. Liao, K. Huang, and K. Liao, *Acta Sci. Nat. Univ. Sunyatseni* (in Chinese), **31**, 67 (1992).
4. J. A. Turner, J. M. Aizlewood, and D. R. Beckett, *Makromol. Chem.*, **75**, 134 (1964).
5. K. Liao, C. Zheng, and Y. Ou, *Polym. Mat. Sci. and Eng.*, (in Chinese), in press.
6. K. Liao, X. Chen, and C. Zheng, *Chem. J. Chinese Univ.* (in Chinese), **16**, 143 (1995).

Received April 19, 1994

Accepted December 13, 1994