

Toughening and Reinforcement of HDPE/CaCO₃ Blends by Interfacial Modification–Interfacial Interaction

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ABSTRACT: To improve the mechanical properties and structure of HDPE/CaCO₃ composites, a type of modifier, consisting mainly of carboxylated polyethylene (CPE), and a type of CaCO₃ grafted with acrylamide (CaCO₃-A) were used. The carboxyl group content of CPE was from 1 to 10%. The amide group content on the surface of the modified CaCO₃ was from 0.2 to 1.8%. The interfacial structure and interaction of ternary blends of HDPE, CPE, and CaCO₃-A were studied. The results indicate that the higher the amide group content and the carboxyl group content, the higher the tensile and impact strength. This behavior has been attributed to a series of chemical and physico-chemical interactions taking place between the two components during the blending process which were confirmed by FTIR and extraction experiments. The improvement of interfacial adhesion by the CPE and CaCO₃-A was also clearly revealed in the SEM of the fracture surface. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1275–1281, 1997

Key words: HDPE/CaCO₃; interfacial modification; mechanical properties; interaction

INTRODUCTION

The scope of the application of filled plastics can be widened considerably if the fracture toughness can be improved. Traditionally, this can be achieved by a coupling agent treatment of fil-

lers,^{1–3} but the toughness improvement is accompanied by the deterioration of the tensile strength because of the plasticizing effect of the coupling agent. This disadvantage is overcome by polymer grafting^{4,5} and acid–base interaction between the two phases^{6,7} because chemical bonding between the polymer matrix and filler will offer the best bonding of composites.

It is well known that HDPE filled with CaCO₃ particles is very brittle. To obtain good interface adhesion between the HDPE matrix and the

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Table I Structural Properties of Modified CaCO₃

Sample	Amide Group Content (%)	Mean Particle Size (μm)	Density of Accumulation (g/cm^3)
CaCO ₃	0	4.7	0.33
CaCO ₃ -A ₁	0.2	5.0	0.30
CaCO ₃ -A ₂	0.5	5.1	0.30
CaCO ₃ -A ₃	0.7	5.2	0.28
CaCO ₃ -A ₄	1.0	5.2	0.28
CaCO ₃ -A ₅	1.2	5.4	0.27
CaCO ₃ -A ₆	1.4	5.6	0.26

CaCO₃ filler, two options are possible: One is to chemically modify the HDPE, and the other is to provide a surface graft treatment to the filler. By adopting both options, incorporating reactive groups into the composite, we can expect to heighten the synergistic effect. This article reports the properties and interfacial interaction of a composite made up of HDPE, carboxylated polyethylene (CPE), and CaCO₃ filler grafted with acrylamide (CaCO₃-A).

EXPERIMENTAL

Materials

The HDPE used was B6012 made by Tonen sekaiyu k. k. Co.; its melt index (MI) was 0.15 (g/10 min), and its density was 0.951. The CaCO₃ used was of a particle size no less than 1250 mesh. The acrylamide-grafted CaCO₃ (CaCO₃-A) was prepared in our laboratory with an amide group content on its surface of 0.2–1.8%. Its structural properties are listed in Table I. The CPE used was also prepared in our lab, with a carboxyl group content of 1, 5.6, and 10.2 wt %. The thermal properties of CPE are reported in Table II.

Table II Thermal Properties of CPE

Sample	Carboxylation (Wt %)	T_g (°C)	T_m (°C)
CPE-1	1.0	—	129
CPE-2	5.6	-25	125
CPE-3	12	-17	122

Sample Preparation

The CPE was first melt-blended with HDPE in a single-screw extruder (Brabender Plasticoder) at 165°C for 3 min; then, the filler was added, and the composite was homogenized at 220°C for 5 min to give a well-blended composite. The samples for mechanical measurements were prepared by mold pressing at 180°C under a pressure of 80 kg/cm² in the form of sheets 1.0 and 4.0 mm in thickness. These were then punched to dumbbell shape or machined in the form of bars.

Measurement and Characterization

Tensile properties were measured on an XL-100 tensile tester, according to the Chinese standard GB 1040-79. Testing was done at a temperature of 25°C and a speed of 1000 mm/min. Notched Izod impact strength was measured with an Izod UJ-40 impact tester, according to Chinese standard GB 1843-80. Testing was carried out at 25°C, and the mean value of six measurements for each group of samples was taken. Flexural strength was measured with an LJ-500 tensile tester, according to Chinese standard GB 1042-79. Testing was done at 25°C, and the mean value of six measurements was taken.

Xylene Extraction Procedure

About 10–11 g of sample was ground to a powder of 20 mesh. The sample was dried in a vacuum oven for 12 h at 70°C and weighed to ± 1 mg. The material was then left in 200 cc of boiling xylene for 10 h. The insoluble fraction of the extraction was dried in a vacuum oven at 70°C until it

Table III Mechanical Properties of HDPE and Its Composites

	Tensile Strength (MPa)	Impact Strength (J)	Ultimate Elongation (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)
HDPE	24.3	230	800	40.1	1098
HDPE/CaCO ₃ (80/25)	27.2	47	205	42.5	1200
HDPE/CPE/CaCO ₃ (70/10/25)	34.0	178	700	35.8	988
HDPE/CPE/CaCO ₃ -A ₆ (70/10/25)	37.3	500.1	900	44.9	1280

reached a constant weight. The amount of the xylene insoluble fraction was evaluated.

FTIR Analysis

The FTIR spectra were recorded on a Fourier transform infrared spectrometer model NICOLET from 400 to 4000 cm⁻¹ at a resolution of 2 cm⁻¹. Samples for FTIR studies were prepared by compressing blends with KBr.

SEM Observation

The interfacial adhesion between CaCO₃ and the HDPE phase was investigated with the help of scanning electron microscopy (SEM: Hitachi-S520, Japan) by observing the surface of fractured bars. The surfaces of the impact-fractured specimens were coated with gold to avoid charging under an electron beam.

RESULTS AND DISCUSSION

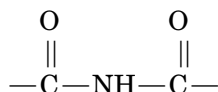
The data listed in Tables III and IV show the mechanical properties of the HDPE composites. With the addition of CPE to the HDPE/CaCO₃ composite, the impact strength of the composites is enhanced substantially, and with the application of CaCO₃-A, at the same time, the toughening and reinforcing effect can be increased still more. Interfacial treatment results in a significant increase in strength properties of the composites. For the HDPE/CPE/CaCO₃-A (70/10/25) composite, the tensile strength, impact strength, and flexural strength were much higher than those of pure HDPE. The impact strength of the composite reaches more than nine times the value of the unmodified HDPE/CaCO₃ (80/25) composite, amounting to 500 J/m, and the tensile strength of the composite is 37.4 MPa, much higher than that of HDPE (24 MPa). Thus, it can

Table IV Effect of Interfacial Modification on Mechanical Properties of Composites

Sample	Tensile Strength (Mpa)	Flexural Strength (Mpa)	Impact Strength (J/m)
HDPE/CPE-2/CaCO ₃ -A ₁	32.5	42.6	197.6
HDPE/CPE-2/CaCO ₃ -A ₂	33.6	43.2	201.6
HDPE/CPE-2/CaCO ₃ -A ₃	33.1	42.8	241.7
HDPE/CPE-2/CaCO ₃ -A ₅	34.8	43.2	243.8
HDPE/CPE-3/CaCO ₃ -A ₁	34.8	43.2	251.6
HDPE/CPE-3/CaCO ₃ -A ₂	36.1	43.0	307.8
HDPE/CPE-3/CaCO ₃ -A ₃	36.4	43.5	335.2
HDPE/CPE-3/CaCO ₃ -A ₅	37.3	44.9	500.1

HDPE/CPE/CaCO₃-A = 70/10/25.

1790 cm⁻¹, which corresponds to the >C=O stretching of the five-membered saturated-ring anhydrides.⁶ The acrylamide-grafted CaCO₃ (CaCO₃-A) is characterized by a strong absorption near 1650 cm⁻¹ [Fig. 1(b)] corresponding to the >C=O stretching vibration of the primary amides in the solid phase.⁶ The spectrum of extracted insoluble products was shown in Figure 1(c). The intensity of the >C=O stretching of the associated carboxyl group is greatly reduced. The >C=O stretching vibration of the associated H-bonded amide (1650 cm⁻¹) disappears and a new peak in this spectrum is observed at 1670 cm⁻¹. This peak may be assigned to the asymmetric >C=O stretching band of a diacyl amine group:



with another broad band at 1775 cm⁻¹ due to the symmetric >C=O stretching of the same group. From the above discussion, the newly formed

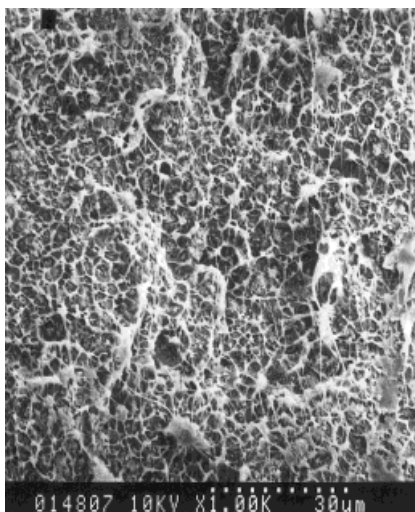


Figure 3 SEM micrograph of impact-fractured surface of HDPE/CaCO₃ (80/25) composite.

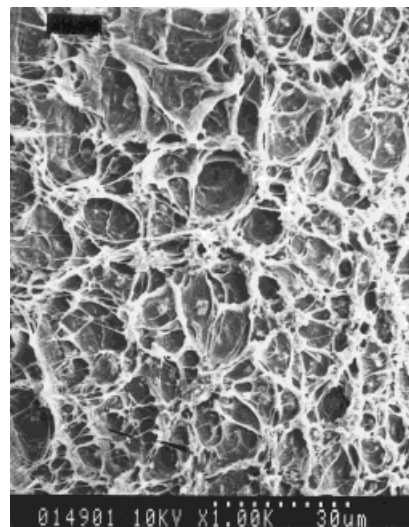


Figure 4 SEM micrograph of impact-fractured surface of HDPE/CPE/CaCO₃ (70/10/25) composite.

structure and interaction may be assumed when the composite is processed (Fig. 2).

The change of the fracture behavior of the composite is clearly revealed by the SEM of the fractured surface (Fig. 3–5). It is obvious that there is substantial debonding of two phases before yielding in the composite of HDPE/CaCO₃ (80/25), and the surfaces of CaCO₃ particles are perfectly clean (Fig. 3). It can be concluded that there is almost no adhesion at the HDPE/CaCO₃ interface. Figure 4 shows the SEM micrograph of the fractured surface for the HDPE/CPE/CaCO₃ ternary composite. Owing to the introduction of CPE, the interfacial adhesion was improved partially. Important morphological changes occurred on addition of CaCO₃-A. The morphology of HDPE/CPE/CaCO₃-A composites shows better interfacial compatibility over the above two composites. As shown in Figure 5, there is an excellent adhesion between matrix and the particles; the two-phase structure disappears and many interpenetrating fibriforms are formed on the fractured surfaces which apparently bond the two phases together. With an increased carboxyl-group and amide-group content, the fibering effect is more obvious, indicating the presence of interactions between the CPE matrix and CaCO₃-A particles. The scheme for interfacial modification of the HDPE/CaCO₃ composite is shown in Figure 6. Owing to the incorporation of reactive groups into the composite, the strong interaction between the

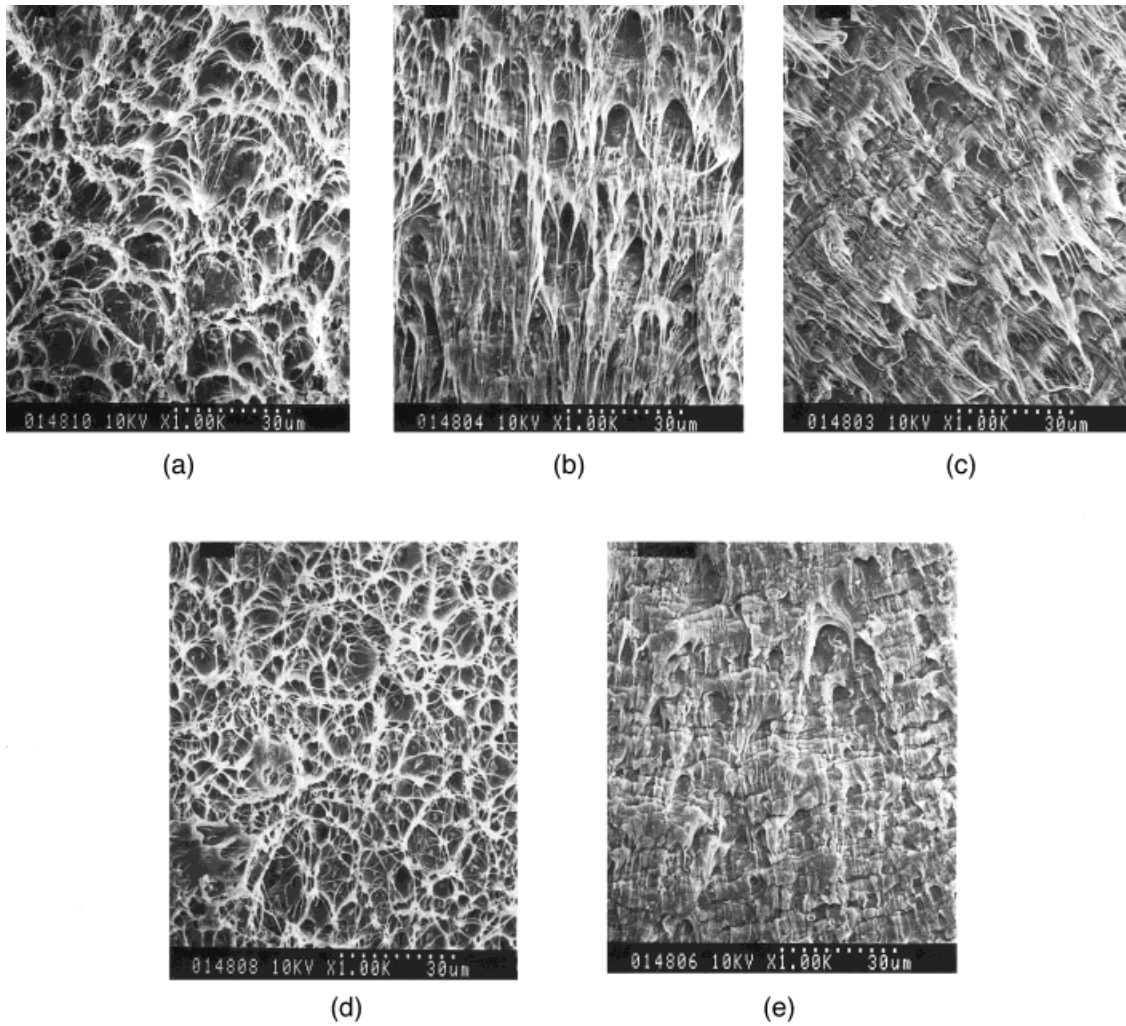


Figure 5 SEM micrographs of impact-fractured surfaces of HDPE/CPE/CaCO₃-A composites: (a) HDPE/CPE-1/CaCO₃-A₂; (b) HDPE/CPE-2/CaCO₃-A₄; (c) HDPE/CPE-3/CaCO₃-A₆; (d) HDPE/CPE-1/CaCO₃-A₂ etched with xylene; (e) HDPE/CPE-3/CaCO₃-A₆ etched with xylene.

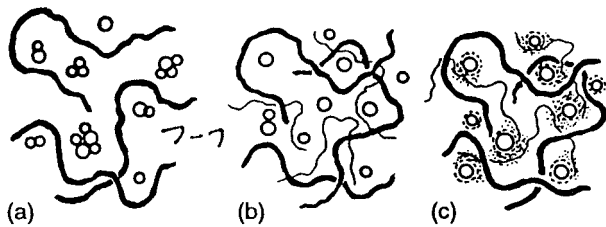


Figure 6 Schematic representation for interfacial modification of HDPE/CaCO₃ composite: (a) HDPE/CaCO₃; (b) HDPE/CPE/CaCO₃; (c) HDPE/CPE/CaCO₃-A.

filler and polymer transformed structurally the composite into an interpenetrating polymer network.

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REFERENCES

1. Q. Fu and G. Wang, *Polym. Eng. Sci.*, **32**, 94 (1992).
2. Q. Fu and G. Wang, *Polym. Int.*, **30**, 3091 (1993).

3. Q. Fu and G. Wang, *J. Appl. Polym. Sci.*, **49**, 1985 (1993).
4. W. Chiang and W. Yang, *J. Appl. Polym. Sci.*, **35**, 807 (1988).
5. R. Li, Y. Wang, and G. Wang, in *Proceeding of 1993 Spring Meeting of MRS*, Pittsburgh, PA, April 12–16, 1993, H2.11.
6. M. F. Fredrick, *Rub. Chem. Technol.*, **57**, 328 (1986).
7. R. Li, Y. Wang, and G. Wang, *Polym. Mater. Sci. Eng.*, **10**, 119 (1994).
8. G. Socrates, in *Infrared Characteristic Group Frequencies*, Wiley-Interscience, New York, 1980, p. 73.