A Study on HDPE/Sulfonated EPDM-Treated $CaCO_3$ Blends

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ABSTRACT: In this article, sulfonated ethylene-propylene-diene monomer terpolymer (H–SEPDM) was used to treat $CaCO_3$ particles. $CaCO_3$ particles are encapsulated by H–SEPDM through the reaction of sulfonic acid group (—SO_3H) in H–SEPDM with $CaCO_3$ to improve the interface adhesion of $CaCO_3$ with HDPE. In case the treated $CaCO_3$ is blended with HDPE, a brittle–ductile transition occurs. The impact strength of the blend rises sharply at 25–30 wt % $CaCO_3$, and amounts to more than 700 J/m, four times as high as that of HDPE at 30 wt % $CaCO_3$, without much loss of its yield strength and modulus. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2140–2144, 2001

Key words: high density polyethylene; sulfonated EPDM; calcium carbonate; polyblend

INTRODUCTION

The stiffness and toughness are two key parameters for constructional polymer materials. Polymers modified with rubber or elastomer can get rather high impact strength; however, the yield strength and modulus will decrease a lot. Some researchers[1,2] have revealed that the increasing of impact strength can be mainly attributed to the outer layer of rubber particles; inner materials play only a little part on impact strength, but because the rubber particles as a whole are soft and easy to deform, modulus and yield strength will suffer from serious damage. The problem has been solved to a certain extent by toughening polyolefin with ionomer or some specialized rigid fillers.[3–5] To get blends with both good rigidity and good toughness, sulfonated EPDM was used in this article to wrap rigid $CaCO_3$ particles before they are blended with HDPE in hopes that the $CaCO_3$ could keep the dispersed phase rather more rigid to prevent the modulus and yield strength from heavy loss; at the same time the rubber in the particles outlayer would toughen the HDPE as well.

EXPERIMENTAL

Materials and Sample Preparation

Materials

EPDM: EP24 (Japan), propylene content 43%, iodine value 15 g/100 g rubber light $CaCO_3$: (China), 300 mesh, HDPE: 6098 (China), MI 0.47 g/10 min.

Preparation of H–SEPDM

To a 5% EPDM solution of cyclohexane, acetyl sulfonate was added at room temperature. The reaction was terminated after 30 min by ethyl alcohol, then added in the aging-resistant agent. Sulfonation level: 1.1075 mol/kg, about 80% diene units of EPDM are sulfonated. The acetyl sulfonate was synthesized by reaction of equal mol of

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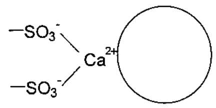

Figure 1 Scheme of the reaction of H–SEPDM with $CaCO_3$.

acete anhydride and concentrated sulfonic acid in ethylene dichloride solutions below 5°C for 10 min.

Preparation of HDPE/H–SEPDM-Treated $CaCO_3$ Blends

$CaCO_3$ was treated by H–SEPDM cyclohexane solution and dried. Then HDPE, with a certain amount of treated $CaCO_3$, was blended in a twin roller at 150°C for a period of 15 min. The blends were molded into 1 mm and 4 mm sheets for mechanical property tests.

Measurement and Characterization

Tensile strength: measured with an INSTRON 4302 universal testing instrument (U.K.) according to GB1040-79, tension speed: 100 mm/min.

Impact strength: measured according to GB1843-80 with XJ-40 (China) impact strength testing machine.

SEM observation: the specimens was plated with carbon, then observed through scanning electron microscope (X-650, Japan).

Contact angles: $CaCO_3$ and treated $CaCO_3$ were pressed into tablets, then measured the contact angles with water or liquid wax through a contact angle testing instrument.

RESULTS AND DISCUSSION

The Reaction between H–SEPDM and $CaCO_3$

The sulfonic acid groups (—SO_3H) in sulfonated EPDM(H–SEPDM) will decompose at high temperature and become dark black. In that case, it is used to treat $CaCO_3$; however, H–SEPDM does not decompose,[6] indicating —SO_3H group in H–SEPDM reacts with $CaCO_3$ during treatment according to the scheme shown in Figure 1. The surface energy of filler is lowered (Table I), showing the interphase adhesion of $CaCO_3$ with plastics is improved also.

Table I Contact Angles of $CaCO_3$ and Treated $CaCO_3$ with Water or Liquid Wax

	$CaCO_3$	Treated $CaCO_3$
Water	0°	83°
Liquid wax	0°	0°

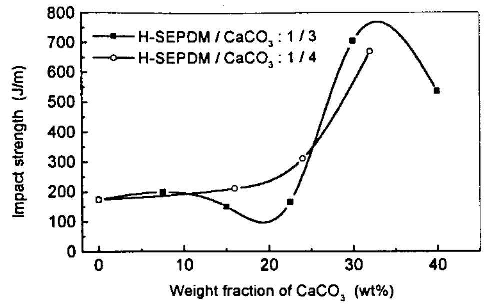

Figure 2 Impact strength of HDPE/treated $CaCO_3$ vs. weight fraction of $CaCO_3$.

Mechanical Properties

As shown in Figure 2, a brittle–ductile transition can be observed. The impact strength of the

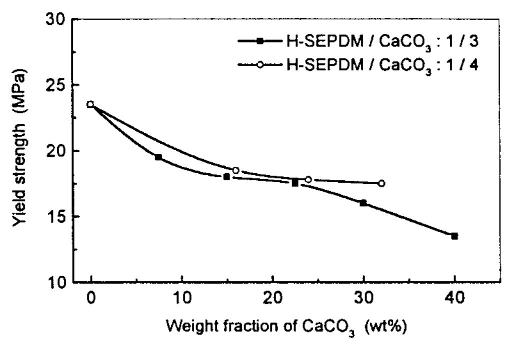

Figure 3 Yield strength of HDPE/treated $CaCO_3$ vs. weight fraction of $CaCO_3$.

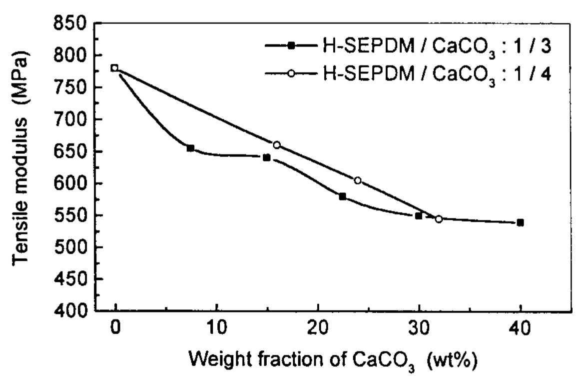

Figure 4 Tensile modulus of HDPE/treated $CaCO_3$ vs. weight fraction of $CaCO_3$.

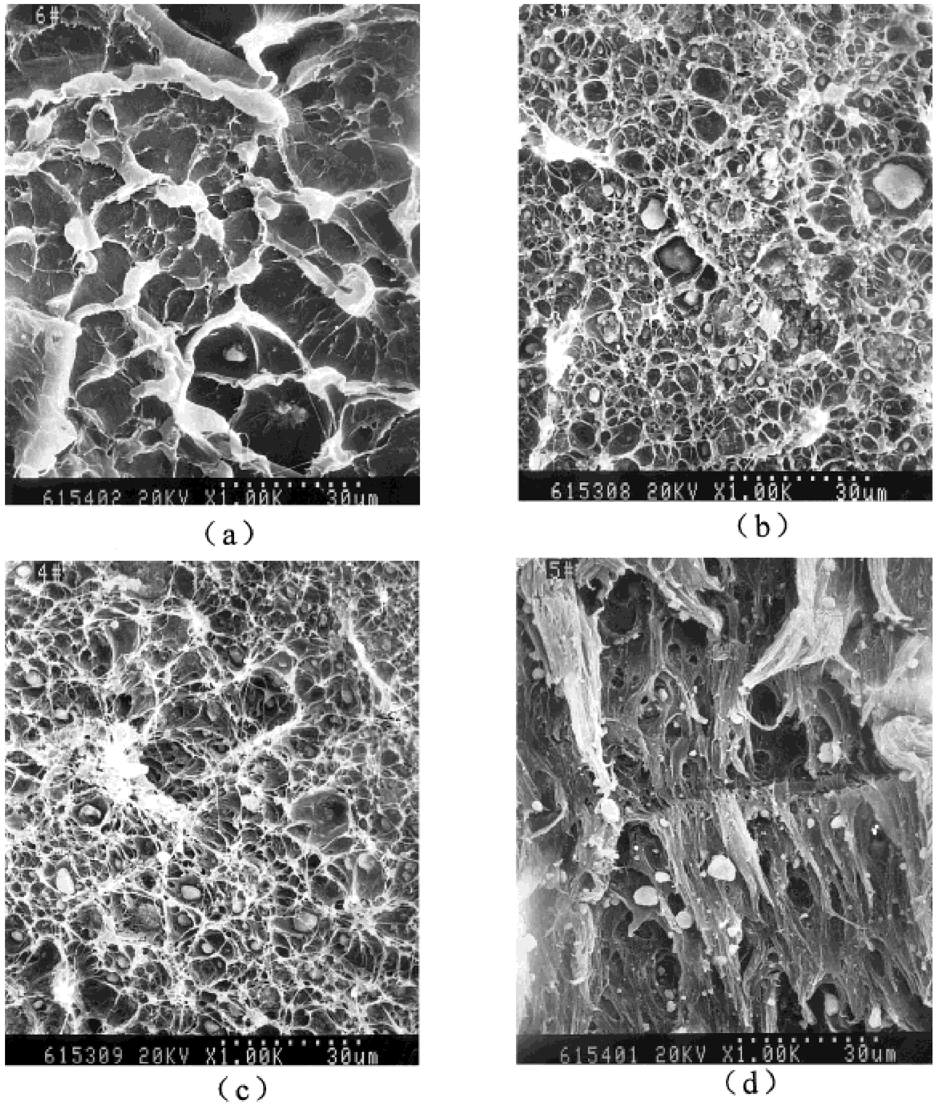

Figure 5 SEM of impact-fractured surfaces of HDPE/H–SEPDM/$CaCO_3$ blends (a) HDPE, (b) HDPE/H–SEPDM/$CaCO_3$: 80/5/15, (c) HDPE/H–SEPDM/$CaCO_3$: 70/7.5/22.5, and (d) HDPE/H–SEPDM/$CaCO_3$: 60/10/30.

HDPE/treated $CaCO_3$ blends goes up sharply with treated $CaCO_3$ content at its range from 25 to 30 wt %. The impact strength of HDPE/treated $CaCO_3$ (70/30) amounts to more than 700 J/m, four times as high as that of HDPE.

As shown in Figures 3 and 4, the yield strength and tensile modulus decrease slowly with the amount of $CaCO_3$ added in. The materials finally get good rigidity and a rather high toughness as well as a lower price because of much $CaCO_3$ added in.

Mechanism

The brittle–ductile transition phenomenon present in HDPE/treated $CaCO_3$ blends accords with that discovered by S. Wu.[7] Stress field will be induced around filler particles scattered in the matrix as a force being imposed on. To those blends containing a small amount of fillers, the stress field is only slightly affected by each other because of the large interparticle distance, and

Table II Mechanical Properties of HDPE/EPDM/$CaCO_3$ Blends HDPE/(EPDM/$CaCO_3$) : 60/40

EPDM/$CaCO_3$	$\frac{1}{3}$	$\frac{1}{5}$
Impact strength (J/m)	479.0	153.0
Yield strength (MPa)	13.9	15.2

Table III Mechanical Properties of HDPE/H–SEPDM/$CaCO_3$ Blends

H–SEPDM/$CaCO_3$	$\frac{1}{3}$	$\frac{1}{5}$
Impact strength (J/m)	>700	250.4
Yield strength (MPa)	16.6	16.7

HDPE/(H–SEPDM treated $CaCO_3$): 60/40.

fracture takes place mainly through craze propagation and cavitation. Only when the interparticle distance is decreased to a critical matrix ligament thickness, the influence of stress field of particles on each other is pretty strong, and will lead to plastic deformation of the matrix and make a contribution to the toughness. On the other hand, excess filler will make the structure of blend loose and the impact strength lower than

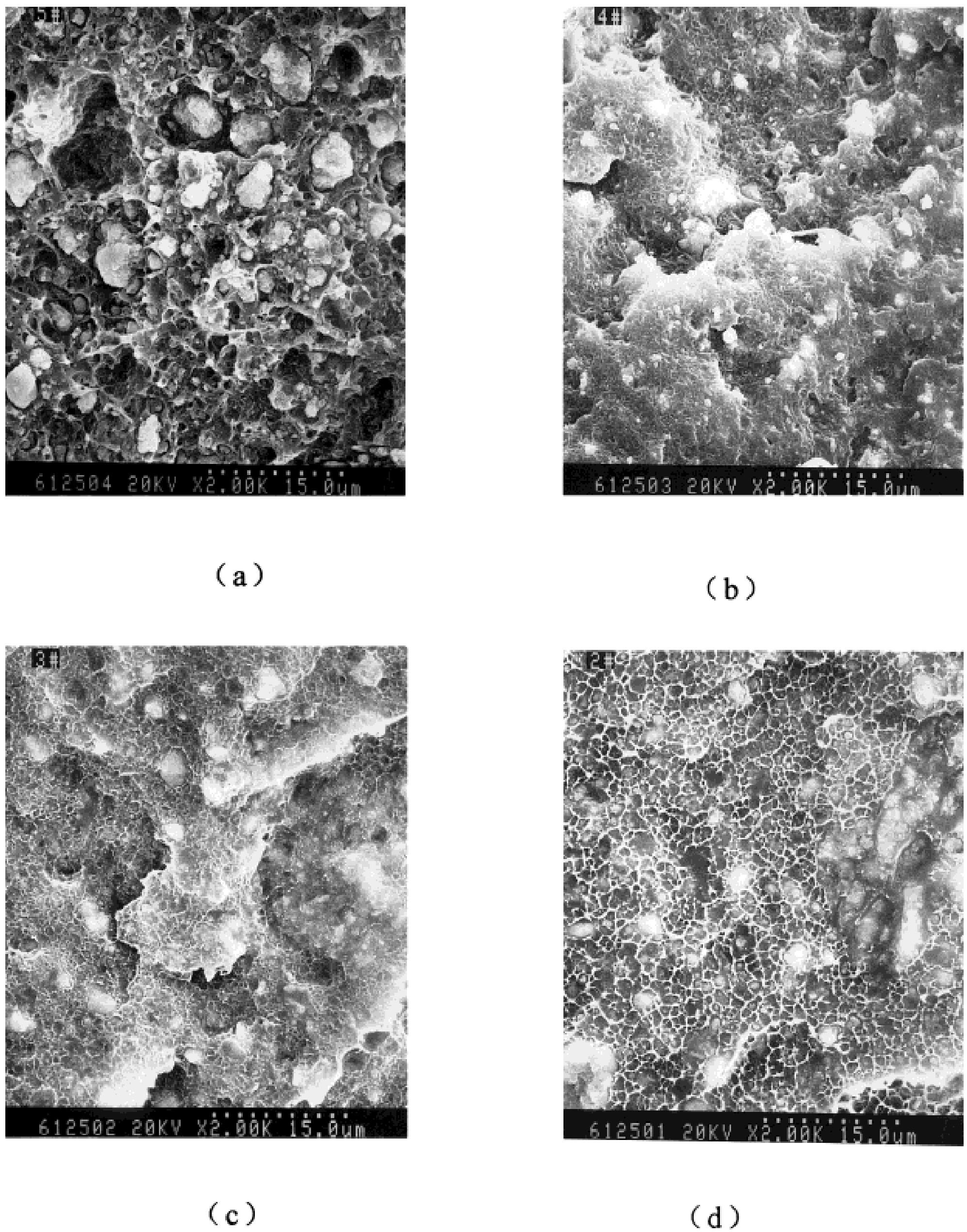

Figure 6 SEM of surface fractured in liquid nitrogen (a) HDPE/EPDM/$CaCO_3$: 60/6.7/33.3, (b) HDPE/EPDM/$CaCO_3$: 60/10/30, (c) HDPE/H–SEPDM/$CaCO_3$: 60/6.7/33.3, and (d) HDPE/H–SEPDM/$CaCO_3$: 60/10/30.

the maximum. Figure 5 shows the impact-fractured surfaces of HDPE/treated $CaCO_3$. When $CaCO_3$ amounts to 30 wt %, cold flow of the HDPE matrix could be clearly observed [Fig. 5(d)], which it is quite different to the other three containing no or a less amount of $CaCO_3$ [Fig. 5(a)–(c)].

Data listed in Table II are the mechanical properties of materials prepared through blending HDPE with EPDM and $CaCO_3$. Compared with the HDPE filled with H–SEPDM-treated $CaCO_3$ (Table III), the latter is much better either in rigidity or toughness. As shown in Figure 6, the interphase adhesion is much poorer in HDPE/EPDM/$CaCO_3$ [Fig. 6(a) and (b)] than in HDPE/treated $CaCO_3$ [Fig. 6(c) and (d)].

CONCLUSION

The reaction between —SO_3H of H–SEPDM and $CaCO_3$ results in encapsulation and lower surface energy, $CaCO_3$ was powerful after encapsulation, making it very easy to be blended with HDPE. The rubber in the particle outlayer would toughen the HDPE. This is the reason why the toughness of the blend is enhanced up to four times that of HDPE without much loss of its yield strength and modulus. The brittle–ductile transition of the blends occurs at weight fraction of $CaCO_3$ ranging from 25 to 30%.

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