

Preparation and Performances of Ethylene–Propylene–Diene Terpolymer/Acrylic Rubber Reinforced with a Dough-Modeling Compound

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ABSTRACT: A novel composite was prepared by the addition of a dough-modeling compound (DMC) reinforcement and an ethylene–propylene–diene terpolymer (EPDM)/acrylic rubber (ACM) matrix. We studied the DMC/EPDM/ACM mass ratio and vulcanizing process by testing the tensile strength, Shore A hardness, elongation at break, and wear and thermal properties. The results show that the mechanical properties, thermal properties, and wear resistance of the composites were good when

the DMC/EPDM/ACM mass ratio was 70/25/75 and the cure conditions were 180°C under 10 MPa for 25 min. The crosslinking structure of the composites was studied by IR, and this further proved the interaction between DMC, ACM, and EPDM. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1803–1808, 2008

Key words: composites; mechanical properties; reinforcement; rubber; thermal properties

INTRODUCTION

With the great speed in the development of science and technology, more and more excellent performances for materials are required.¹ There is a growing interest in the development of special high-strength and high-toughness polymeric materials to replace traditional metals, glasses, and ceramics in many advanced applications. Ma et al.² at South China University of Technology studied the vulcanization behavior of a silicone rubber/acrylic rubber (ACM) blend. Chen et al.³ at Wuhan University of Technology investigated an ACM elastomer that was prepared by *in situ* polymerization in an acetone solution of fluorine rubber and the properties of the obtained ACM/fluorine rubber blend. In these investigations, it was shown that the modified blended rubbers had enhanced toughness behaviors but failed to show enhanced strength properties,⁴ and the problem of shrinkage existed when rubber and plastics were blended,^{5,6} but plastics reinforced by fibers were lower in toughness;⁷ this restricts their material applications.

ACM is a saturated polar rubber; its chemical structure is shown in Figure 1(a). Its composites feature resistance to ozone, oil, heat, and ultraviolet

ray, and so on, but their processability,⁸ tensile strength, and wear resistance are weaker. However, ethylene–propylene–diene terpolymer (EPDM) is a nonpolar and backbone saturated rubber; its chemical structure is shown in Figure 1(b). It exhibits many desirable properties, such as a high impact strength, heat aging, excellent chemical resistance, and good mechanical and dielectric properties; its disadvantages are a slow curing speed, low oil resistance, difficult blending, and lower viscosity. Blends of EPDM and ACM generally improve their properties and have an important meaning theoretically. Nevertheless, their polarities are more different, so it is key that they are cured at the same time for two rubbers. In this study, a great number of experiments were performed to improve the cure process and ensure optimal mass ratios and processing conditions. However, the strength of blends was lower. Hence, to enhance both the toughness and mechanical properties, dough-modeling compound (DMC) was chosen as a suitable modifier for the ACM/EPDM blends.

DMC is a high-performance, lightweight, fiber-reinforced composite, in which unsaturated polyester (UP) is used as the matrix with a shrinking agent, a few crosslinking agents, and filler and in which chopped glass fiber reinforcement is mixed homogeneously.⁹ DMC possess superior mechanical properties, thermal properties, processability, and low shrinkage; it has been widely used in electric appliances, aviation, traffic, architecture, marine crafts, automotive parts,^{10,11} and so on, but its hardness and elasticity are lower.¹²

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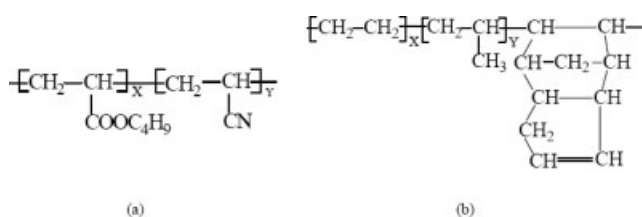


Figure 1 Chemical structures of (a) ACM and (b) EPDM.

The objective of this study was to obtain a new composite of EPDM/ACM reinforced with commercially available DMC, and we studied the preparation technology and the performance.

EXPERIMENTAL

Materials

ACM (grade AR-100) was produced by Chinese Suining Qinglong Acrylic Rubber Factory (Sichuan, China). EPDM (grade 23080P) was produced by Chinese Jilin Chemical Industrial, Inc. (Jilin, China). DMC, as a commercially available product, was purchased from Harbin Insulated Material Factory (Heilongjiang, China); it was a uniform mixture made up of 21 phr UP (Fig. 2) as the matrix, 8 phr shrinkable agent (benzoyl peroxide), 1 phr crosslinking agent (styrene), 50 phr filler, and 20 phr staple glass fiber as reinforcement. Dicumyl peroxide (DCP; chemically pure) was supplied by Shanghai Chemical Reagents Co. of the Chinese Medicine Group (Shanghai, China). The other ingredients, including stearic acid, mercapto benzothiazole [accelerator M; Fig. 3(a)], *N*-cyclohexyl-2-benzothiazyl sulfonamide [accelerator CZ; Fig. 3(b)], and *N*-phenyl- β -naphthylamine (antioxidant D), were all common, commercially available materials and were used as purchased.

Sample preparation

EPDM and ACM, which were cut short and dried previously, were masticated on an XK-160 two-roll mill (Tianjin, China) for 10 min at 45°C, and the nip gap was about 1.0 mm. Next, the mixed rubber was prepared by the addition of various ingredients; the order of process was as follows: EPDM, ACM (raw rubbers masticated) \rightarrow zinc oxide (ZnO), stearic acid (SA), accelerator M, accelerator CZ, antioxidant D \rightarrow carbon black (CB) \rightarrow DCP, sulfur. The details of the formulation of the mixes are given in Table I. The



Figure 2 Chemical structures of UP.

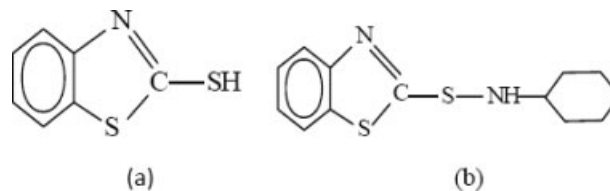


Figure 3 Chemical structures of (a) accelerator M and (b) accelerator CZ.

compounds were mixed in a laboratory-size (XK-160, Tianjin, China) mixing mill at a friction ratio of 1 : 1.1 at a carefully controlled temperature in the range 50–60°C; the nip gap was 2 mm for 20–30 min, and it was a uniform cutting operation. Then, the mixture was mixed with DMC and refined homogeneously on the two-roll mill for 10–20 min at 50°C, and the nip gap was about 1.0 mm. The mixture of compounds with different compositions was molded in an electrically heated hydraulic press (XLB-D350 \times 350) (Shanghai, China) at 180°C for 30 min [or cure time (t_{90}) + 15 min] under 10 MPa (optimum cure conditions).

Characterization

First, the vulcanizate sample was fractured in liquid nitrogen, then the fracture surface was sputtered with gold, and the fracture morphologies of the blending samples were observed by scanning electron microscopy (SEM; model JSM-5200, Jeol Co., Japan). The IR spectra of the blends were recorded at a resolution of 4000 cm^{-1} on an IR-7685 Fourier transform infrared (FTIR) spectrometer (Shanghai Analyzer Plant, Shanghai, China). Tensile tests were performed on dumbbell-shaped specimens according to ISO 37-1994. Shore A hardness was measured at a thickness of 6 mm according to ISO 48-1994. Wear attrition was determined according to BS903A9 with an Akron machine (MN-74, Jingsu, China). The samples were tested, and the average of the values was taken. Heat aging of the samples was performed for 24 h at 200°C by a 401-B air aging oven (Jiangsu Test Mechanical, Ltd., Jingsu, China) according to ISO 188-1998.

RESULTS AND DISCUSSION

Effect of the EPDM/ACM mass ratio on the performance of its vulcanizate

It is widely known that the performances for pure rubber are worse than for rubber blends. According to the construction and performances of the rubbers, EPDM and ACM, with dissimilar polarities, were chosen, and both functions were improved. The effects of the EPDM/ACM mass ratio on the proper-

TABLE I
Fundamental Formulation of the Mixes (phr)

Rubber ^a	CB	DCP	ZnO	SA	Accelerator ^b	Antioxidant D	Sulfur	DMC
100	60	2.5	5.0	2.0	1.0	1.5	1.5	Various

^a Rubber was ACM + EPDM.

^b When EPDM was 100 phr, accelerator M (1.0 phr) was used. When ACM was 100 phr, accelerator CZ (1.0 phr) was used.

TABLE II
Effect of the ACM/EPDM Mass Ratio on the Vulcanizate Performance

EPDM/ACM	100/0	65/35	50/50	35/65	25/75	20/80	0/100
t_{10} (min : s)	1 : 30	1 : 50	1 : 40	2 : 10	2 : 30	3 : 30	4 : 30
t_{90} (min : s)	11 : 30	13 : 50	9 : 20	10 : 30	9 : 50	9 : 30	11 : 20
Tensile strength (MPa)	7.3	4.7	6.6	7.7	8.9	8.0	5.4
Shore A hardness	53	52	66	67	65	65	63
Elongation at break (%)	430	503	439	583	647	612	220
Wear (cm ³ /1.61 km)	4.3	3.3	2.3	1.3	1.2	1.8	3.6
Change before and after aging (200°C × 24 h)							
Tensile strength (%)	3.9	3.2	2.8	1.8	0.9	1.6	5.4
Shore A hardness	15	13	13	9	7	13	17
Elongation at break (%)	-28	-24	-24	-15	-12	-17	-24
Wear (%)	2.2	2.0	1.7	1.6	1.3	1.9	2.0
Change before and after oil immersion (150°C × 200 h)							
Tensile strength (%)	-2.3	-1.8	-1.7	-1.6	-1.0	-1.2	-1.8
Shore A hardness	-12	-11	-9	-9	-4	-5	-11
Elongation at break (%)	-11	-10	-5	-3	4	3	-14
Wear (%)	3.6	3.2	2.8	2.7	2.0	2.2	2.8

ties of the vulcanizates are reported in Table II. As the amount of EPDM decreased or the amount of ACM increased in the recipe, the scorch time (t_{10}) of the vulcanizate gradually increased accordingly as the accelerator CZ delayed t_{90} of ACM; that is, the inductive time (t_{10}) of ACM was elongated.¹³ Thus, t_{10} of pure ACM was the longest, and its t_{90} (11 min 20 s) was as long as that of pure EPDM (11 min 30 s) and ensured curing synchronicity.¹⁴ This could be explained on the basis of cyclohexyl taking up a large space and hindering crosslinking with sulfur; otherwise, accelerator CZ had no connection with EPDM because accelerator CZ was neutral. How-

ever, accelerator M played an important part in the EPDM cure process because accelerator M was acidic. t_{10} and t_{90} for a mass ratio of 50/50 were smaller, which could be explained on the basis of blending size. This ratio makes their separate phase lowest. For certain qualities, the smaller the size is, the shorter that t_{90} is needed; that is, the cure reaction was sped up so that t_{10} and t_{90} of EPDM/ACM 50/50 were shortened.

As the amount of EPDM decreased or the amount of ACM increased, the tensile strength, Shore A hardness, and elongation at break of the vulcanizate gradually increased, but wear decreased. This suggests

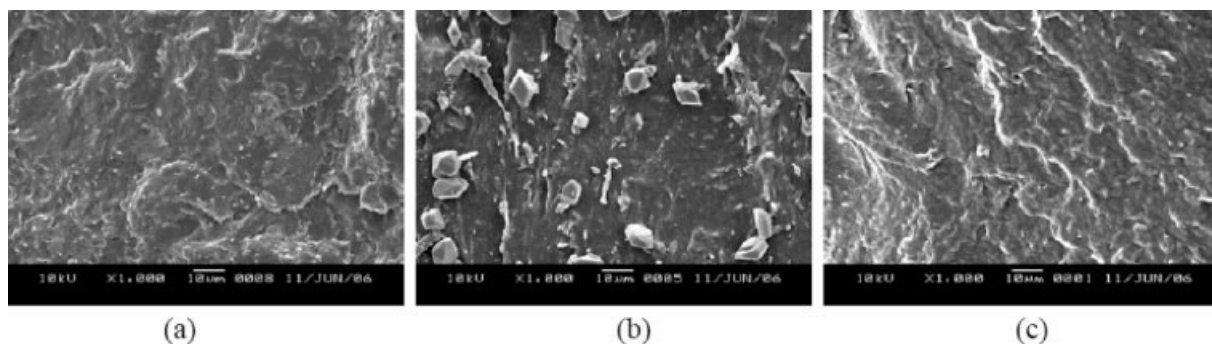


Figure 4 SEM micrographs for the EPDM/ACM blends. The EPDM/ACM mass ratios were (a) 100/0, (b) 65/35, and (c) 25/75.

TABLE III
Effect of the DMC Content on the Blend Properties

DMC (phr)	0	30	50	60	70	80
Tensile strength (MPa)	8.9	10.2	12.7	13.2	14.1	12.9
Shore A hardness	65	67	72	79	81	85
Elongation at break (%)	647	574	445	401	433	308
Wear (cm ³ /1.61 km)	1.2	1.4	1.4	1.3	1.1	1.2

EPDM/ACM = 25/75.

that the wear resistance increased. That is, various performances of the vulcanizate were higher than those of pure rubber except one or two properties, as listed in Table II, such as EPDM/ACM 65/35 and 50/50. This suggests that the blending of two rubbers was beneficial for improving the performances of EPDM and ACM. The mass ratio 65/35 was lowest for the tensile strength and layers in the macroscopic, and the blend's surface was rough. The adherent force of EPDM was worse, EPDM was the continuous phase of the composite, and ACM was in the disperse phase, which made the two rubbers incompatible and layered.^{15,16} On the contrary, when the ACM content was higher and was in the continuous phase (matrix), the performances of EPDM/ACM was improved because the ACM adherent force was better. As an example, SEM photographs of the tensile fracture of EPDM/ACM blends are shown in Figure 4.

Figure 4(a) shows SEM photographs of the tensile fracture for pure EPDM; the fractured surface was tidy and smooth. Figure 4(b) for EPDM/ACM 65/35, obviously, shows a rough surface and incompatible phases. The SEM micrograph for EPDM/ACM 25/75 is illustrated in Figure 4(c); the interface between ACM and EPDM was less obvious than that in Figure 4(b), which could be explained by the fact that the compatibility of EPDM/ACM 25/75 was better, and this further proved the results shown in Table II.

The resistances to oil and heat for the EPDM/ACM blend were much better than those of pure EPDM or ACM; that is, the rubber blended was also beneficial for improving the resistances to oil and heat. As the amount of ACM increased, the performances of the vulcanizates were all improved, except for the elongation at break after heat aging; this could be explained on the basis of further curing in the heat aging process. Crosslinking density increased and made the vulcanizate harden and strengthen.¹⁷ Because the exorbitant density would unbalance force distribution and concentrate some stress, small stresses could break weak bonds in the crosslinking network of the vulcanizates and result in decreased elongation at break.^{18,19}

Effect of DMC on the properties of the ACM/EPDM blends

Because the ACM and EPDM chains were flexible and the interaction between the chains was weak,²⁰ their blends were not available until they were reinforced. However, the reinforcing fillers for the rubber were used to CB.²¹ As shown in Table II, the mechanical properties were low until 60 phr CB was added. On the basis of the previous discussion, a good reinforcing agent, DMC, was chosen as the disperse phase to strengthen the composite. The effects of DMC content on the properties of the ACM/EPDM blends are shown in Table III and Figure 5.

When the DMC content increased, the Shore A hardness and tensile strength of the blends gradually increased, but elongation at break, wear, and change after heat aging decreased. This suggests that the mechanical and thermal resistances were enhanced until DMC reached 70 phr. The properties at 70 phr for DMC appeared to be at a turning point.

The reason is that the rubber and UP were cross-linked by double bonds (C=O) and hydrogen bonds

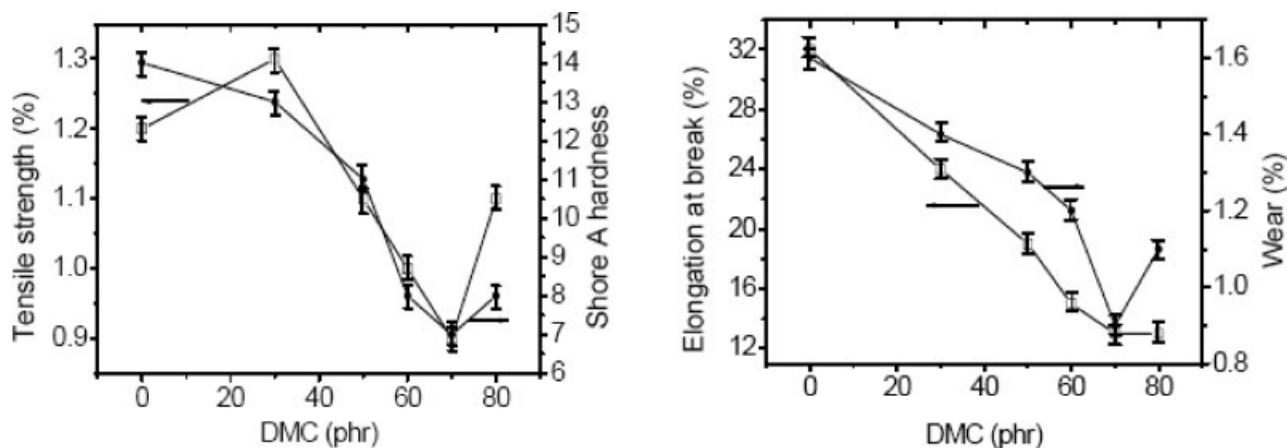


Figure 5 Relation between the DMC contents and changes in the thermal properties at 200°C for 24 h.

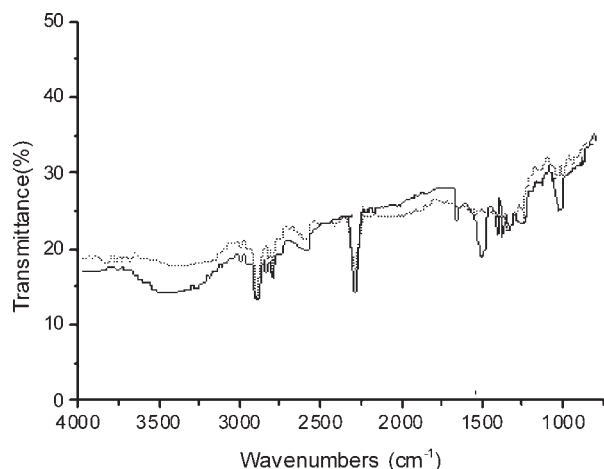


Figure 6 FTIR spectra of (—) DMC/EPDM/ACM and (···) EPDM/ACM.

(C—H) to form hydrogen and ether bonds (C—O—C) on their interface when the DMC content was less than 70 phr, which improved the compatibility between the fiber and matrix and reduced the contact of the fibers; this decreased the stress concentration, the heat expansibility, and the breakdown of the molecule chain. In addition, the short fiber bore the framework function; that is, DMC and the EPDM/ACM blend formed physical entanglements in the fiber and chemical bonding of UP, so that both mechanical and thermal properties of the composites were improved. However, when the DMC content was higher than 70 phr, there was too much DMC in the blend system, and the rubber matrix content was too small to envelop all of scrap DMC to form an effective interface layer. With increasing free spaces of the fiber, the interaction between the fibers increased; the weak interaction and bonding between the fiber and rubber matrix resulted in interface deterioration and the decrease of the mechanical and thermal properties. The results suggest

that the composites with 70 phr DMC were the best; therefore, the DMC/EPDM/ACM mass ratio should be 70/25/75.

The FTIR spectra of the DMC/EPDM/ACM and EPDM/ACM blends are shown in Figure 6. The spectrum of the DMC/EPDM/ACM composite not only retained the characteristic peak at 2920 cm^{-1} for CH_2 , 2240 cm^{-1} for $\text{C}\equiv\text{N}$ stretching, and 1360 and 1570 cm^{-1} for COO symmetrical and asymmetrical stretching but also showed new peaks of $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ at 1730 and 1020 cm^{-1} , which demonstrated the crosslinking bonds, of which UP in DMC bonded EPDM and ACM on the surfaces.

Influence of the cure conditions on the performance of the DMC/EPDM/ACM composites

As mentioned previously, because the cure points of the rubbers were different, both the mass ratio and cure condition had to be considered in the preparation of the samples. The cure conditions were primarily temperature, pressure, and time (i.e., three parameters). The cure temperature mainly depended on the category of raw rubber and cure formulation. Higher temperature easily caused the vulcanizate pyrolysis and performance to decline, even though it could shorten t_{90} and enhance productive effects. Therefore, when the cure temperature was chosen, the rubber category, vulcanizing system, method, and blend construction were all considered. Because some volatile component released under the heat temperature for this cure process, a higher pressure of 10 MPa was needed to eject volatile gas and air from its vulcanizate and prevent blend separation.

t_{90} depended on the formulation, temperature, and pressure. When the time was beyond the limit, the vulcanizate was overcured or lacking; both resulted in a decline in the performance of the vulcanizate. In addition, the added accelerator, a higher temperature, and pressure could all shorten t_{90} .

TABLE IV
Effect of the Cure Conditions on the DMC/EPDM/ACM Composite Properties^a

	Temperature ($^{\circ}\text{C}$) ^b								Time (min) ^c			
	150	155	160	165	170	175	180	185	15	20	25	35
Tensile strength (MPa)	7.3	8.2	10.4	11.0	12.6	13.5	14.1	13.9	9.7	12.1	14.3	13.4
Shore A hardness	51	56	60	68	74	80	81	84	57	69	82	83
Elongation at break (%)	530	521	513	498	490	451	433	449	512	479	467	433
Wear ($\text{cm}^3/1.61\text{ km}$)	2.4	2.1	1.9	1.5	1.4	1.3	1.1	1.2	2.0	1.4	1.1	1.3
Change before and after aging ($200^{\circ}\text{C} \times 24\text{ h}$)												
Tensile strength (%)	5.2	4.3	2.4	1.8	1.0	1.2	0.9	10	4.6	2.8	0.9	1.2
Shore A hardness	18	15	12	8	8	7	6	8	20	13	6	12
Elongation at break (%)	-48	-46	-39	-21	-20	-13	-12	-15	-46	-20	-11	-16
Wear (%)	2.0	1.7	1.2	1.0	1.0	0.9	0.9	1.0	1.9	1.1	0.8	1.0

^a DMC/EPDM/ACM = 70/25/75.

^b t_{90} = 30 min; cure pressure = 10 MPa.

^c Cure temperature = 180°C ; cure pressure = 10 MPa.

As shown in Table IV, when the cure temperature was below 180°C, the cure agents could not decompose into active center to crosslink the rubber fully; the vulcanizate performances were all lower because of a lack of vulcanization. When the temperature was over 180°C, a few crosslinked networks were broken down, and some carbon chains were charred, which resulted in a decline in the performances of the vulcanizates and a little macula on the surface of the vulcanizate at 185°C. Moreover, the activator and accelerator decomposed easily to bring about the cracking of the vulcanizate under the high temperature. However, the performances of the vulcanizate were better at 180°C before and after heat aging. Similarly, the performances of the vulcanizate were best when t_{90} was 25 min. Their performances at less than 25 min were similar to those below 180°C; the crosslinked networks were incomplete or some construction was imperfect because of a lack of vulcanization. Contrarily, when the cure stage was longer than 25 min, the results were similar to those with high temperature. On the basis of the above datum, we concluded that the best cure conditions were 180°C under 10 MPa for 25 min.

CONCLUSIONS

In summary, EPDM and ACM were blended by the adjustment of the EPDM/ACM formulation and the control of the cure conditions. SEM analyses further proved that the compatibility of EPDM/ACM 25/75 was best. For the EPDM/ACM blend reinforced with DMC, the mechanical and thermal properties and the wear resistance of the composites were all improved because the short fiber and UP in DMC bore, respectively, the framework and crosslinking function. The UP could crosslink with EPDM and ACM sufficiently to improve the compatibility, and the crosslinking

bond (C—O) between DMC and EPDM/ACM was formed, as shown by IR analysis. When the DMC/EPDM/ACM mass ratio was 70/25/75 and the curing conditions were 180°C under 10 MPa for 25 min, the performances of the composites were much better than those of EPDM/ACM, EPDM, or ACM.

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