Preparation and Properties of Dough-Modeling Compound/Fly Ash/Reclaim Powder Composites

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ABSTRACT: A novel composite was prepared with reclaim powder (RP) matrix, dough-modeling compound (DMC) reinforcement and fly ash (FA) filler in this article. The compatibility and crosslinking construction of the FA/RP composites were respectively, studied by the polarizing microscope and IR, the optimal formulation and experimental process were determined by measuring the mechanical properties such as shore A hardness, tensile strength, elongation at break, wear resistance and the thermal stability. The results showed that DMC/FA/RP composites exhibited extremely high mechanical and thermal properties when the mass ratio of the DMC/FA/RP composites was 45/25/100, and the cure condition is at 145°C for 30 min under 9 MPa.
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Key words: rubber; reinforcement; filler; composites

INTRODUCTION

With the great speed development of the car industry, more rubbers are needed home, but the store of the raw rubbers cannot meet require, and they are mostly imported from the abroad.[1] In addition, the rubber price has been increasing in recent years, such as natural rubber (NR) is from several thousands to thirty thousands Yuan/ton.[2] Less and less crude oil can be exploited, results in synthetic rubber production descending, and upward price trend, therefore, the attention is focused on the utilization of waste rubber at present.[3–5]

On the side, various damaged tires are widely world, and turn into a new topical on the environment contamination.[6–8] However, there are two approaches to utilize waste rubber: firstly product reclaimed rubber, secondly process reclaim powder (RP).[9] Because the waste rubber is classified thermoset polymer, it can not be degraded, much expensive cost of the reclamation and utilization, and technically difficult.[10,11] Developed countries had discarded reclaimed rubber in 1970s, and mainly produced the RP. It has been producing increasingly in our country.

It is similar to utilization of RP, more countries have realized that exploding ''industry waste residue'' is important,[12,13] and effectively relief the shortage of natural and energy resource, prevent from environmental pollution.[14,15] China is one of producing coal countries in world, coal will be mostly energy in the future,[16,17] consequently, the making use of fly ash (FA) is of significant interest in the present times because of the focus on recycling of materials, and decreasing environmental contamination. This research is based on using two industrial waste materials to make composite materials, that is, FA and RP were blended to prepare composites by using r-Aminopropyltriethoxysilane silane coupling agent (KH-550). However, the mechanical properties of FA/RP composites were imperfect. Through studied the configuration and performances of the composites, dough-modeling compound (DMC) was used as the reinforcement,[18] which is an unsaturated polyester used as the matrix with a low shrinking agent, crosslinking agent, filler, and chopped glass fiber mixed homogeneously. Owing to good mechanical properties, thermal properties, processability and low contractibility, DMC has been widely utilized in the electric appliances, autocar manufacture, aviation, traffic, and architecture fields.[19–21] The objective of this study is to obtain a new composite modified with DMC reinforcement, FA filler, and RP matrix, and study the preparing technology and performances.

EXPERIMENTAL

Materials

RP and FA as industry products were produced by Chongqing Maolin industry trade and Qiqihar

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power plant, respectively. Silane coupling agent as grade KH-550 (r-Aminopropyltriethoxysilane $H_2NCH_2CH_2CH_2Si—(OC_2H_5)_3$) was supplied by Nanjing Shuguang Chemical Factory. Aluminate coupling agent as grade DL-441 was supplied by Polymer Experimental Factory of Fujian Normal University. DMC as industry product was purchased from Harbin insulated material factory, which is a uniform mixture made up of 21 phr unsaturated polyester used as matrix, 8 phr shrinking agent, 1 phr crosslinking agent, 50 phr filler, and 20 phr staple fiber used as reinforcement. Dicumyl peroxide (DCP) as chemical pure was supplied by Shanghai chemical reagents company of Chinese medicine group. The other ingredients such as sulfur, stearic acid (SA), and so on, were all common commercially avail materials and were used as purchased.

Sample preparation

RP and FA were dried previously at 100°C for 30 min, placed, and then previously mixed with the ingredients in the high speed mixer at 45–50°C for 20 min. After that, the mixed rubber was prepared by adding sulfur and DCP, coupling agent and DMC on XK-160 two-roll mill for 15 min at 55–60°C, while the nip gap was about 4.0 mm, details of the formulation of the mixes are given in Table I. The mixture of compounds with different compositions was molded in an electrically heated hydraulic press (XLB-D350 × 350) at 150°C for 25 min under 8 MPa.

Characterization

Tensile tests were performed on dumbbell-shape specimens according to ISO 37-1994. Shore A hardness was measured on the thickness 6 mm according to ISO 48-1994. Wear attrition was determined according to BS903A9 using an Akron machine (MN-74). 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) according to ISO 188-1998.

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.).

The IR spectrum of the blends recorded at a resolution of 4000 cm^{-1} on an IR-7685 Fourier transforms infrared (FTIR) spectrometer (Shanghai analyzer plant).

The vulcanizate samples cut into hyaloids slices were observed by a polarizing microscope (Nanjing Shiye).

RESULTS AND DISCUSSION

Influence of fly ash content on the composites properties

FA was used as filler in the composites, a large number of experiments were done to find the optimal blend ratio shown as Figure 1.

The tensile strength, Shore A hardness and wear of the composites increase gradually with adding FA, but elongation at break presents downturn. When the FA is more than 35 phr, there are no results, because FA and RP blended on two-roll mill is too difficult to prepare the sample. The polarizing micrographs of FA/RP composites are shown as Figure 2.

By the help of the polarizing characteristics, the polarizing microscope studies the birefringence of the crystalloid, mineral, fiber, and so on,[22] and its principle is similar to biological microscope. More holes in Figure 2(a) illuminate worse filling effect, that is, FA do not fill completely in the rubbers to lead to them worse bonding, and compatibility. When used 25 phr FA such as Figure 2(c), the interface of the composites is not clear, has few holes and shows better compatibility. It suggests that the FA fills fully in the rubbers to lead to them bonding, and improve mechanical properties of FA/RP composites. When used 30 phr FA such as Figure 2(d), both present phases respectively, and worse compatibility, so the mechanical properties are bad. It further validates results in Figure 1. RP with over FA results in blends fluidity rapidly descending, and bubbles in the composites lead to process difficulty. It can be seen that its viscidity is low because of plentiful lower molecule weight in RP, and FA and RP can not blend completely.[23] Taking into account thermal properties, 25 phr FA is best suitable.

Effect of coupling agent on composites properties

FA and RP, first is inorganic material, and last organic material, are difficult to blend. As shown in

TABLE I
Fundamental Formulation of the Mixes (phr)

RP	Fly ash	DMC	DCP	SA	Accelerator M	Antioxidant D	Sulfur	Coupling agent
100	Variant	Variant	2.0	4.0	1.5	2.0	1.5	1.5

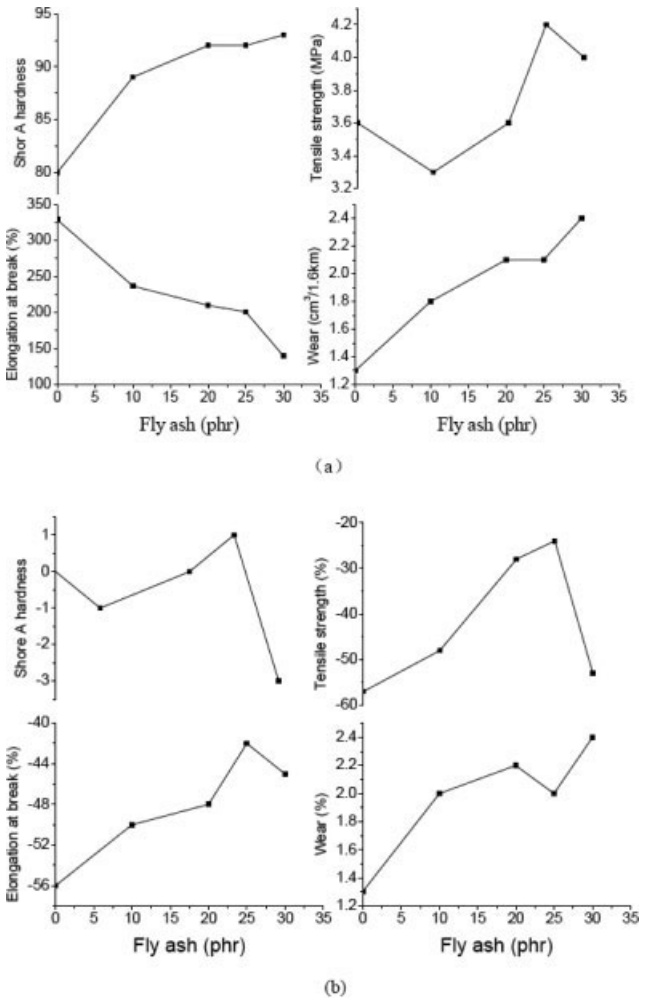

Figure 1 Effect of fly ash contents on composites properties (a) Before heat ageing (b) Change after heat ageing (200 °C × 24 h).

Figure 1, the tensile strength and elongation at break of the samples are lower, so this composite is useless. The coupling agent was introduced to improve both crosslinking. The coupling agents suitable for rubbers have two categories: aluminate and silane coupling agent, the effects of coupling agents on the composites properties are shown in Table II.

The molding process of the composites is slowly with adding aluminate coupling agent, but the vulcanizates more hold together, and do not break. However, the samples with silane coupling KH-550 (that is $H_2NCH_2CH_2CH_2Si—(OC_2H_5)_3$) mold fast, and not hold together to form products, but the properties of the vulcanizates are better than the front. It can be seen that the groups $(OC_2H_5)_3$ in the silane coupling KH-550 easily bond SiO_2 in FA to form steady chemical construction, so that FA/RP composites use silane coupling KH-550 as the coupling agent. As seen in Table II, the properties of the samples with the coupling agent are better than those without and pure rubber powder. It suggests that the coupling agent with two groups can crosslink FA and RP to from chemical bonding and physical entanglement, and mechanical and thermal properties of FA/RP composites using KH-550 coupling agent is improved obviously.

Shore A hardness of the samples increase gradually with adding KH-550, but the tensile strength, elongation at break, wear and thermal properties appear the best turning point when KH-550 is 2 phr. It can be seen that silane coupling KH-550 will decomposes redundant ethoxy group with adding the coupling at high temperature, it makes the group bond with RP, and results in the macromolecule chain of the rubber to break down.[24] So overfull coupling agent do not place coupling role, it makes Shore A hardness of the samples increase gradually, and other properties firstly increase, and then decrease.

Effect of adding orders of the ingredients on composites properties

The adding order of the ingredients effects composites properties like the coupling agent. As shown in Table III, the mechanical properties were the worst when all ingredients mixed together in the previous mixing such as Sample A, Sample C was worse, and Sample B was best. It can be seen that all ingredients mixed together in the previous mixing especially coupling agent, the ethoxy group $((OC_2H_5)_3)$ could react with curing accelerant to make the surface of the vulcanizates present many bubbles. It makes cure agent abate function, and the mechanical properties decrease. Moreover, the free radical of sulfur self-cured when the sulfur and accelerant M were added together. No other than the curing agent and accelerant M were mixed with the rubber respec-

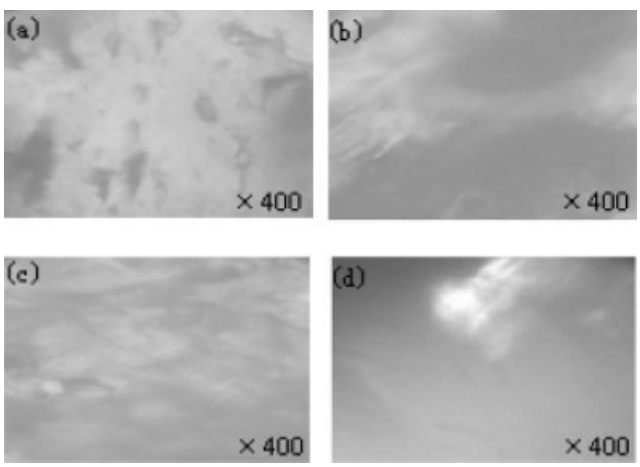

Figure 2 Polarizing micrographs of fly ash/RP composites with fly ash. (a) 10 phr, (b) 20 phr, (c) 25 phr, (d) 30 phr.

TABLE II
Effect of Coupling Agent on Composites Properties

Sample	Aluminate coupling agent (phr)			Silane coupling agent KH-550 (phr)				
	1.0	2.0	3.0	1.0	1.5	2.0	2.5	3.0
Shore A hardness	88	89	90	90	92	92	94	95
Tensile strength (MPa)	8.1	8.6	8.4	8.6	8.9	9.5	9.1	9.0
Elongation at break (%)	266	301	289	340	360	389	337	320
Wear (cm^3/1.6km)	1.4	1.4	1.3	1.1	1.0	0.8	0.8	1.0
Change before and after ageing (200°C × 24 h)								
Shore A hardness	2	2	1	1	−1	0	0	−2
Tensile strength (%)	−36	−28	−35	−32	−28	−26	−23	−35
Elongation at break (%)	−47	−33	−40	−34	−32	−28	−30	−32
Wear (%)	2.2	1.9	1.8	1.8	1.6	1.3	1.3	1.5

Fly ash : RP =25 : 100.

tively, such as Sample B, the curing action would be notable, and curing agent decomposes to across-link with rubber. In sum, the best order of adding ingredients was that the accelerant M and SA firstly are added in the previous mixing, secondly mixed sulfur and DCP, and KH-550 finally.

Influence of cure condition on composite properties

The cure is an absolutely necessary and important process for the rubber. The cure conditions are primarily temperature, pressure, and time (namely three parameters).

As shown in Table IV, when the cure temperature is 130°C, the mechanical properties is lower. As the cure temperature increases, Shore A hardness, tensile strength and elongation at break, wear resistance and thermal properties increase, and the properties are the best at 145°C. Because the lower cure temperature 130°C results in a lack of vulcanization, and RP and FA do not combine fully, but the higher cure temperature 160°C leads to over cure, crosslinked networks are broken down, and so the properties decrease.

The composites properties appear turning point under the cure pressure 9 MPa, and are the worst under 7 MPa because the samples do not press fully lead to delaminate, and so the properties become worse. But the over pressure accelerates sample breaking down under 10 MPa, and effects mechanical properties.

In addition, when the cure time increases, Shore A hardness of the vulcanizate enhances, but the other mechanical and thermal properties appear turning point for the cure time 40 min. However, the properties are bad when the cure time is 15 min or 50 min, it is reason that the blend canot crosslink for the lack time 15 min, but the crosslinked blend are broken down and appear over cure phenomena for over 40 min, therefore make sure that the best cure condition is at 145°C for 40 min under 9 MPa.

FTIR analysis of fly ash/RP composites

Fourier transforms infrared spectrum (FTIR) spectra of RP with (b) and without FA (a) were shown in Figure 3. When the wavenumbers were more than 1300 cm^{-1}, their FTIR spectra were wondrously similar, but shown different in less than 1300 cm^{-1}, The spectrum of FA/RP composite emerge not only Si—O new stretching peak at 1079.41 and 1030.41 cm^{-1}, but also three stretching peaks of C—H at 900–600 cm^{-1}, it suggests that the RP and the organic group of silane coupling form the crosslinking bonds C—H. Two curves mainly differ from crosslinking bonds with FA. In addition, both present the stretching peaks of hydroxyl O—H at 3400 cm^{-1}, and the peak without FA was more than that with because of water in the silane coupling. Minim water appears the characteristic peak at 3400 cm^{-1} for the

TABLE III
Effect of Ingredients Adding Orders on Composites Properties

Sample	A	B	C
Shore A hardness	88	94	91
Tensile strength (MPa)	8.5	9.4	9.1
Elongation at break (%)	199	289	225
Wear (cm^3/1.6 km)	1.0	0.8	0.9
Change before and after ageing (200°C × 24 h)			
Shore A hardness	1	0	0
Tensile strength (%)	−35	−26	−34
Elongation at break (%)	−29	−28	−30
Wear (%)	2.1	1.3	1.5

Fly ash : RP : KH-550 = 25 : 100 : 2.
A: All ingredients mix directly in the previous mixing.
B: Accelerant M and SA firstly are added in the previous mixing, secondly mixed sulfur and DCP, and KH-550 finally.
C: Accelerant M and SA firstly are added in the previous mixing, and mixed sulfur, DCP and KH-550.

TABLE IV
Effect of Cure Condition on composites Properties

Sample[a]	Cure temperature (°C)[b]					Cure pressure (MPa)[c]				Cure time (min)[d]					
	130	140	145	150	160	7	8	9	10	15	20	30	40	45	50
Shore A hardness	84	90	94	94	92	85	90	94	93	80	89	92	94	93	94
Tensile strength (MPa)	8.3	8.8	9.5	9.4	9.0	9.4	8.9	9.5	9.1	8.1	8.9	9.1	9.5	9.4	8.7
Elongation at break (%)	158	204	294	289	199	163	244	294	232	192	239	279	301	289	199
Wear (cm^3/1.6 km)	1.3	1.0	0.8	0.8	0.9	1.1	0.8	0.7	0.8	2.3	1.5	1.0	0.7	0.9	0.9
Change before and after ageing (200°C × 24 h)															
Shore A hardness	1	−1	0	−2	−2	1	2	1	−3	2	−1	−1	0	1	1
Tensile strength (%)	−38	−28	−26	−27	−29	−31	−22	−19	−20	−21	−16	−17	−11	−18	−20
Elongation at break (%)	−40	−37	−28	−32	−35	−56	−35	−22	−21	−47	−36	−34	−25	−25	−33
Wear (%)	1.9	1.7	1.3	1.5	1.8	1.1	1.8	1.3	1.7	2.1	3.0	1.7	1.4	1.5	1.8

[a] Fly ash : RP : KH-550 = 25 : 100 : 2.
[b] Cure pressure 8.0 MPa, cure time 25 min.
[c] Cure temperature 145°C, cure time 25 min.
[d] Cure temperature 145°C, Cure pressure 9.0 MPa.

O—H, it explain that the RP without FA contain remainder coupling agent, contrarily, there is a small quantity of coupling agent in FA/RP composites, which demonstrate that coupling agent places the crosslinking role between FA and RP.

Influence of DMC on composite properties

Though the coupling agent acted, the interaction between the FA and RP chains was weaker, that is, the tensile strength and elongation at break in Table IV were lower. On the basis of aforesaid, a good reinforcing agent, DMC, was chosen as disperse phase of composite to strengthen, the effects of DMC content on the properties of FA/RP composites were shown in Figure 4.

Shore A hardness, tensile strength, elongation at break and wear of the composites change with adding DMC. The tensile strength and elongation at break reach a maximal value at 45 phr DMC, and wear is minimal, it suggests that the wear resistance is best. Nevertheless, the hardness increases gradu-

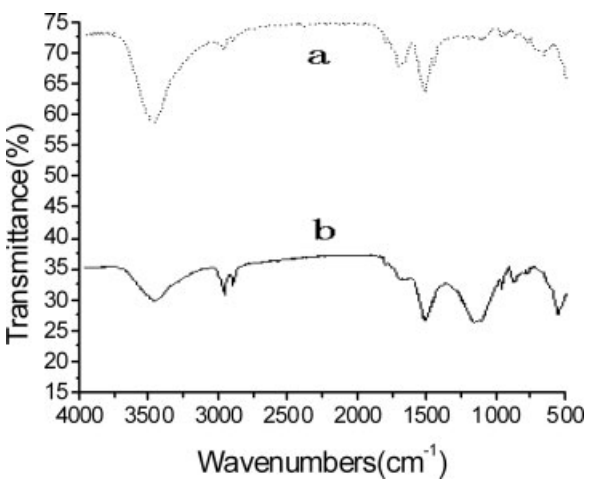

Figure 3 FTIR spectra of RP without (a) and with (b) fly ash.

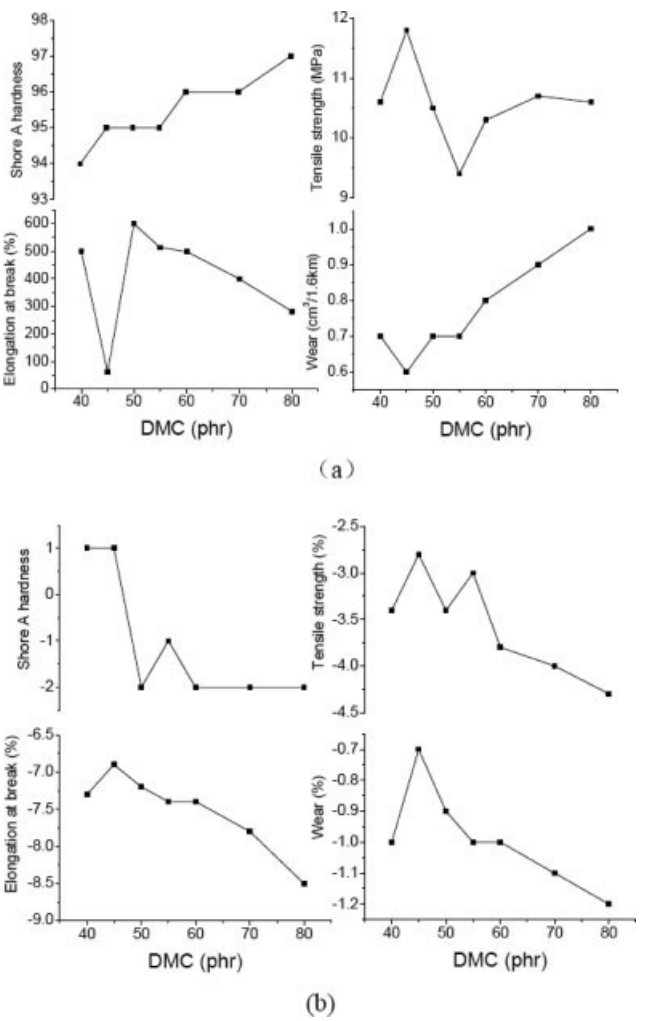

Figure 4 Effect of DMC content on properties of fly ash/rubber powder (a) Before heat ageing (b) Change after heat ageing (200 °C ×24 h).

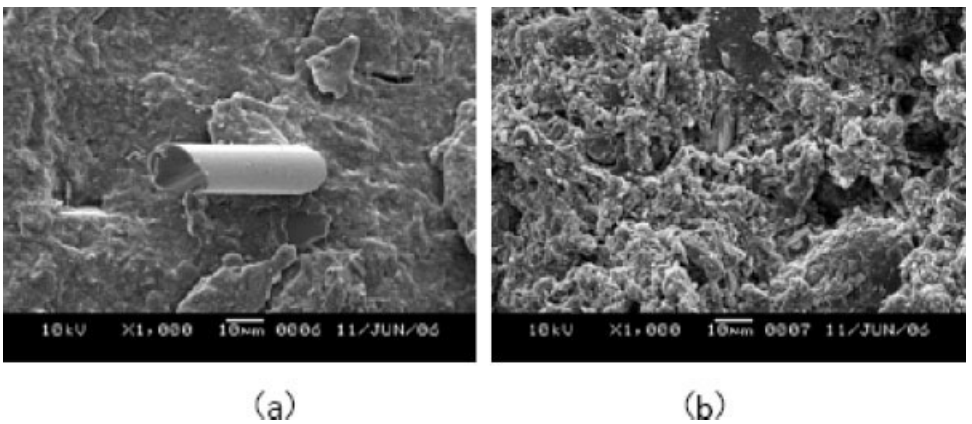

Figure 5 SEM graphs of tensile fracture of fly ash/RP composites with (a) and (b) without DMC.

ally with the loading of DMC, and reaches 97 at 80 phr, but the composites lose the precious flexibility at the same time, that is, easily bring on the fracture and breakdown (elongation at break is 282), and go faraway to expected purpose. The mechanical properties slightly decline after heat aging, which it suggests that DMC/ash fly/RP composites possess better thermal stability. As contrasted with Tables II–IV and Figure 4, the properties of DMC/ash fly/RP composites are much better than that of ash fly/RP without adding DMC.

The reason is that the rubber and unsaturated polyester (UP) are crosslinked compactly by double and hydrogen bonds to form hydrogen and ether bond (C—O—C), when DMC content is less than 45 phr. Which it improves the compatibility of fiber and matrix,[25] and reduces the contact of the fibers, so decreases the stress concentrate as well as heat expansibility and the molecule chain breaking down. In addition, the short fiber bears framework function, that is to say, DMC and ash fly/RP composites form physical entanglement and chemical bonding, so that the mechanical and thermal properties of the composites are improved. However, when DMC content is more than 45 phr, overmuch DMC in blend system, the rubber matrix content is too little to envelop all scrap to form effective interface layer. With increasing free spaces of the fiber, the interaction between the fibers increases, the weak interaction and bonding between the fiber and rubber matrix result in the interface deterioration, and mechanical, and thermal properties decrease. For example, SEM photographs of tensile fracture of FA/RP composites (a) with DMC and (b) without are shown in Figure 5. The results suggest that the integrated properties of ash fly/RP composites with 45 phr DMC is better than those without, therefore make sure DMC/ash fly/RP mass ratio is 45/25/100.

CONCLUSIONS

In summary, the waste FA may be used as filler in FA/RP composites, but canot been added overdose, and blend too difficult to form sample. Moreover, KH-550 was used as coupling agent. The coupling agent crosslinking with FA and RP was proved by IR spectrogram to from Si—O and C—H bonds, and improve the compatibility and processing environment of the FA/RP composites. The adding order of the ingredients also effect composites properties, the best one is that the accelerant M and SA firstly are added in the previous mixing, secondly mixed sulfur, and DCP, and KH-550 finally. On the side, DMC plays a reinforcing role in the FA/RP composites, and the mechanical and thermal properties as well as wear resistance are all improved, because the short fiber and UP in DMC bear respectively, the framework and crosslinking function between FA and RP to improve the compatibility. The best formula and curing condition of the DMC/FA/RP composites are 45/25/100, and at 145°C for 40 min under 9 MPa. The mechanical and thermal properties of FA/RP composites using DMC reinforcement are improved obviously.

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