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Properties of CB/SBR Rubber Composites Filled by Carbon Blacks Used as Catalysts for Hydrogen Production through Hydrocarbon Decomposition

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Key words: Carbon blacks, Composite, Rubber reinforcement, Mechanical properties

Abstract: In this work, the reinforcing action of carbon blacks in rubber was investigated by SEM and UTM measurements which allow a testing of the surface and mechanical properties. In order to gain an insight into the different properties between carbon blacks before and after methane/propane decomposition, various composites were prepared with SBR synthetic rubber and different carbon blacks with four loading ratios. The results were analyzed with the aim of finding suitable conditions for decomposition reaction to cut down the net cost for hydrogen production through hydrocarbon decomposition.

1. Introduction

Despite the fact that carbon black is not only the most widely used but also the oldest active filler in rubber compounds and that a huge amount of research work has been carried out to characterize, describe and understand this kind of filler, the reinforcement effect in filler-loaded rubber is not satisfactorily explained [1].

In term of rubber reinforcement, the most important carbon black properties are fineness (particle size distribution), structure (aggregate size and shape distribution) and surface activity and composite properties also depend greatly on carbon black loading [2].

In this work, the properties of filled composites and carbon blacks were tested. The test results will be further discussed to find suitable conditions for decomposition reaction to cut down the net cost for hydrogen production via hydrocarbon decomposition.

2. Experimental

Carbon black N330 fluffy (N330-f) was obtained from DC Chemical. Co., Ltd.. SBR-1502 was provided by Kumho Petrochemical Co., South Korea. The properties were shown in table 1. Methane/propane decomposition was carried out in a fluidized bed reactor. The samples denoted by N330-f-m and N330-f-p were respectively raw N330-f black used as catalysts in methane and propane decomposition.

The compounding formulations are reported in Table 2. Mixing experiments were carried out in a Haake Rheomix 600 mixing head [3]. Before measuring mechanical properties of the composites, filled SBR rubbers were cured at 1MPa and 145℃ for 35 min [4].

Table 1. Properties of SBR-1502 synthetic rubber

properties	Values
Volatile matter (wt%)	0.17
Total ash (wt%)	0.26
Organic acid (wt%)	5.56
Free soap (wt%)	0.03
Bound styrene (wt%)	23.2
Raw MV (ML 1+4,100℃)	51.7
Comp. MV (ML 1+4,100℃))	79.5
Tensile strength 35' (Kgf/cm^2)	294.0
Elongation 35' %	430
300% modulus 35' (Kgf/cm^2)	200

Table 2. Compounding formulations

Ingredients	Loading (phr [a])
SBR-1502	100
Carbon blacks	0~20~30~40~60
Zinc oxide	5
Stearic acid	2
Dispersive agent [b]	3
Accelerator [c]	1
Sulfur	2

[a] parts per hundred of rubber by weight.

[b] EF44.

[c] N-Oxydiethylene-2-benzothiazolesulfenamide.

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BET surface area and pore size distribution were determined by N_2 adsorption at 77K with a surface analyzer (Automatic Volumetric Sorption Analyzer, Autosorb-1, Quantachrome). The resistivity of carbon blacks was tested by a digital multi-meter. The tensile strength of composites was determined by a UTM machine at room temperature with a crosshead speed of 500mm/min according to ASTM testing method.

3. Results and discussion

Table 3 shows the properties of N330-f black before and after reaction. N330-f-m showed larger pore volume and higher BET surface area than raw N3330-f black, but in case of N330-f-p both the pore volume and BET surface area decreased.

Fig.1 shows the TEM image of N330-f black after used as catalyst, the part of jet black was supposed to be primary black and that with grey color was supposed to be carbon deposit. Fig. 2 shows the SEM images of N330-f before and after reaction. After methane decomposition, carbon deposited on the surface of raw carbon blacks uniformly, so after reaction the surface of carbon black was in state of floccule. This also means a kind of more irregular surface morphology and more surface defect in the micro structure of N330-f-m black. It can be the reason for the increase of surface area and total pore volume. But for N330-f-p, the aggregate size is larger than raw N330-f black, so surface area and total pore volume decreased.

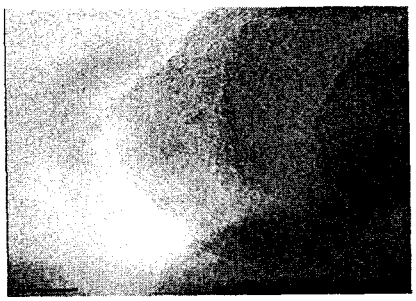
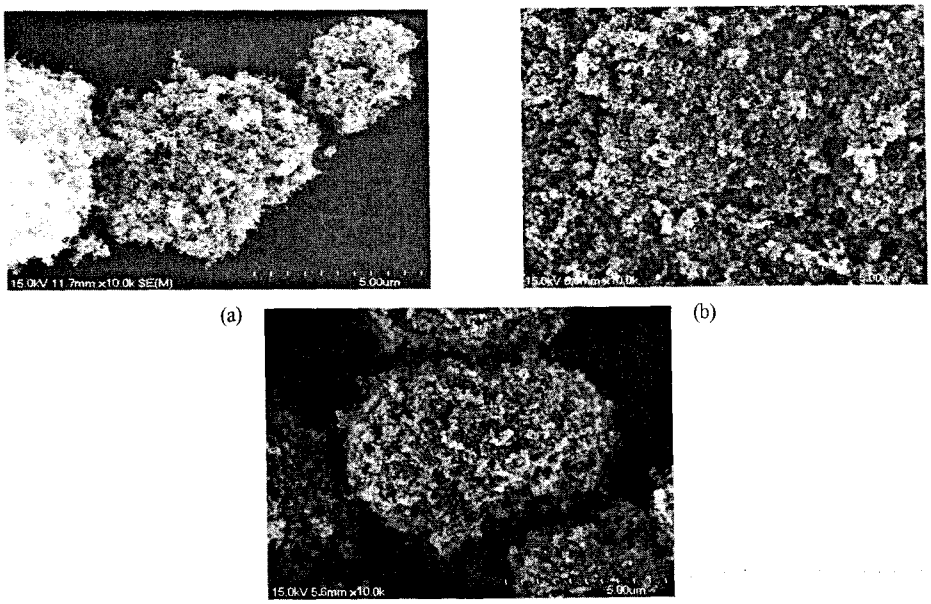


Fig. 1. HR-TEM image of N330-f after reaction.

Table 3. Properties of N330-f carbon blacks before and after reaction

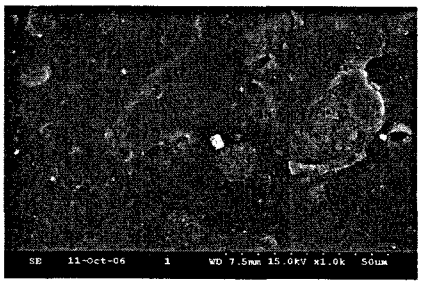
Sample	Weight gain/ %	Resitivity/ Ω•cm	Meso pore volume/ $cc \cdot g^{-1}$	Micro pore volume/ $cc \cdot g^{-1}$	Total pore volume/ $cc \cdot g^{-1}$	BET/ $m^2 \cdot g^{-1}$
Raw N330-f	0	0.0744	0.10406	0.03667	0.14073	74
N330-f-m (900℃ 1Umf)	9	0.0775	0.1157	0.03964	0.15534	83
N330-f-p (750℃ 1Umf 8hr)	28.3	0.0985	0.09385	0.02976	0.12361	61



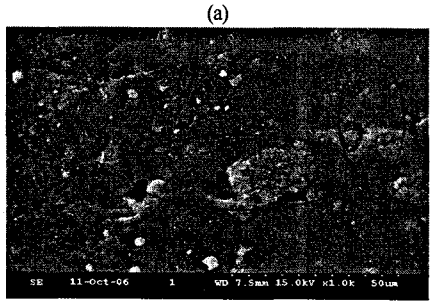
(a) (b)

(c)

Fig. 2. SEM images of (a) raw N330-f, (b) N330-f-m and (c) N330-f-p (×10,000).



(a)



(b)

Fig. 3. SEM images of CB/SBR composites with loading ratio (a) 20 phr and (b) 60 phr (N330-f-p) (×1000).

SEM images of CB/SBR composites with loading ratio of 20phr and 60phr are shown in Fig. 3. It can be clearly seen that with increasing loading ratio, carbon blacks could not uniformly distribute in SBR rubber. It is supposed that with high loading ratio the aggregates of N330-f-p may flocculate with each other because of low viscosity of the polymer matrix during the vulcanization process, so high loading ratio may cause flaws in rubber.

Table 4 shows the mechanical properties of CB/SBR composites. As the carbon black loading ratio increasing in rubber, tensile strength increased to a maximum value then decreased. It is supposed that with low loading ratio the polymer can not be occluded very well by carbon blacks, the increase in carbon black loading, or the number of carbon black aggregates contribute to an increase in the length of the rupture path, but further increase in carbon black loading simply create flaws which cause the decrease of tensile strength. The composites made by SBR mixed with N330-f-m showed higher tensile strength and elongation than those made by SBR mixed with raw N330-f. But in case of N330-f-p, the tensile strength decreased compare with composites mixed with raw black. It is supposed that the surface area and the micro structure defects of N330-f-m increased caused by the carbon deposit on the surface of carbon black aggregates. This led to a high probability of physical entrapment of the polymeric chains in the carbon black micro structural defects, and a better networking in composite. But for N330-f-p, the aggregate size is larger than raw black, which means a higher structure and lower surface area after reaction, so with the same loading ratio the distance between fillers decreased and it is hard to form a good network in composites. The modulus of all composites increased with loading ratio as shown in Fig. 4. It is supposed that carbon blacks stiffen the rubber by replacing the polymer with rigid, non deformable particles, so higher loading ratio of carbon black caused bigger modulus value.

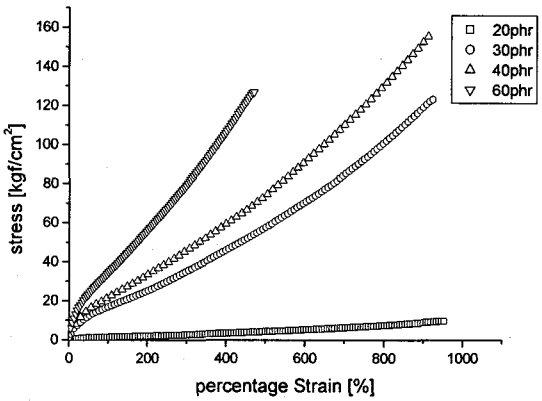


Fig. 4. Stress versus percentage strain of CB/SBR composites (raw N330-f).

Table 4. The mechanical properties of CB/SBR composites

Black ratio/ Phr	Tensile strength/ MPa			Percentage of 300 modulus/ MPa			Percentage of elongation at break/ %		
	Raw N330-f	N330-f-m	N330-f-p	Raw N330-f	N330-f-m	N330-f-p	Raw N330-f	N330-f-m	N330-f-p
0	1.414	~	~	0.7683	~	~	862.6	~	~
10	2.320	~	~	0.9628	~	~	977.8	~	~
20	6.65	7.917	5.287	1.743	1.465	1.630	1004.83	1669	1133
30	11.075	13.56	9.557	1.922	1.774	2.105	1482	1901	1387
40	12.094	13.61	12.73	2.8204	2.537	2.858	1290	1423	1312
60	11.80	13.29	11.02	4.121	4.663	4.921	784.4	805.6	687.7

4. Conclusion

In this work, properties of CB/SBR composites filled by carbon blacks used as catalysts in hydrocarbon decomposition were studied. The surface area and structure of carbon blacks after reaction were found to cause significant changes in the mechanical properties of rubber. With increasing of carbon black loading in the composites, the tensile strength increased to a maximum value then decreased with the higher loading. The composites made by SBR mixed with N330-f-m showed higher tensile strength and elongation than that mixed with raw carbon black but those with N330-f-p showed reverse trend. The modulus of the composites always increased with increasing carbon black loading.

References

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