

Fractal Analysis of Worn Surfaces of ZnO Whisker/Natural Rubber-Styrene Butadiene Rubber-Butyl Rubber Composites

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ABSTRACT: The wear resistance of zinc oxide whisker (ZnOw)/natural rubber-styrene butadiene rubber-butyl rubber (NR-SBR-BR) composites showed that a tetra-needle like ZnOw, which is treated by a coupling agent, improved the wear resistance of the rubber composites. The topography of the worn surfaces of the ZnOw/NR-SBR-BR composites was fractal, and the fractal dimension and abrasion loss

decreased synchronously as the ZnOw content increased in the composites. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 667–670, 2003

Key words: rubber; zinc oxide whisker; composites; worn surface; fractal

INTRODUCTION

Polymer composites have been widely applied as wear resistance materials, and rubber composites have been the subject of investigation for a long time. Although the wear loss of rubber composites is far less than other matrix materials under the same conditions, statistical data show that the wear loss of rubber materials is more than 4.3×10^8 kg every year in the United States.¹ Therefore, investigations on improving the wear resistance and the related mechanisms appear more and more important.² Zinc oxide whisker (ZnOw) is a new kind of whisker with a tetra-needle shape in microimaging and single crystalline structure, and it possesses versatile comprehensive properties and multifunctions.³ The tensile strength and modulus of this whisker are about 10^4 and 2.5×10^5 MPa, respectively. Our earlier report indicates that ZnOw has good effects on improving the properties of wear resistance and enhancement.⁴ In the present article, ZnOw/natural rubber-styrene butadiene rubber-butyl rubber (NR-SBR-BR) composites were prepared and the wear resistance was tested. The fractal behavior of the worn surfaces of ZnOw/NR-SBR-BR composites was preliminarily observed and analyzed.

EXPERIMENTAL

Materials

The ZnOw, which is a white fluffy powder with a tetra-needle shape in microimaging (see Fig. 1), was prepared as in our earlier reports.^{5–7} The average length of the needles of the whiskers is 15 μm , and the average basal diameter of the needles is 0.6 μm . The NR, SBR, BR, other materials, and compounding of composites are listed in Table I.

Procedure for composite preparation

The NR, SBR, and BR were processed using a traditional two-step procedure, which was mastication followed by milling on an XK-230 opening mixer. The traditional types of ingredients and quantity of additives were used in the composites, and the pretreated ZnOw was added when all the other materials and auxiliary agents had been well mixed. The curing condition of the mill-mixed stock was tested on a C2000E rotorless cure meter, and the vulcanizing procedure was followed on an XLB-D platen vulcanizing press to obtain the composite specimens for testing.

Wear resistance test of composites

The wear resistance tests of the specimens were conducted on an MH-74 Akelon abrasion-testing machine. The rotating velocities of the sample wheel and the emery wheel were 76 rpm (1.27 s^{-1}) and 33 rpm (0.55 s^{-1}), respectively, and the angle between the

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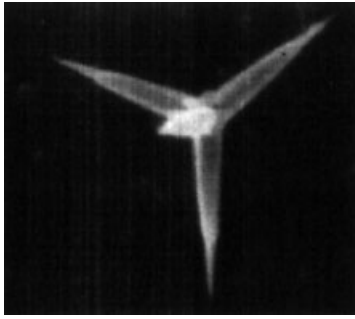


Figure 1 An scanning electron microscope image of ZnOw (original magnification $\times 1200$).

shafts of the two related wheels was 15° . A pressure of 26.7 N was loaded on the sample during the wearing. The experiments were carried out at a temperature of 25°C and humidity of 65%, and 3000 rings of wearing were designed for the sample wheel.

Studies on abraded surfaces of composites

The morphology of the abraded surface was observed on an Amary 1845 field emission scanning electron microscope. The fractal profiles of the worn surfaces were determined on a Tosh-450 profilometer and treated by a MST-343 surface analyzer.

RESULTS AND DISCUSSION

Wear resistance effect of ZnOw on rubber composite

From the relationship between the values of the wear loss and the ZnOw contents in the composites, which are shown in Figure 2, the same result as the ZnOw/NR composites⁴ was obtained. This indicated that the wear loss decreased as the ZnOw content increased.

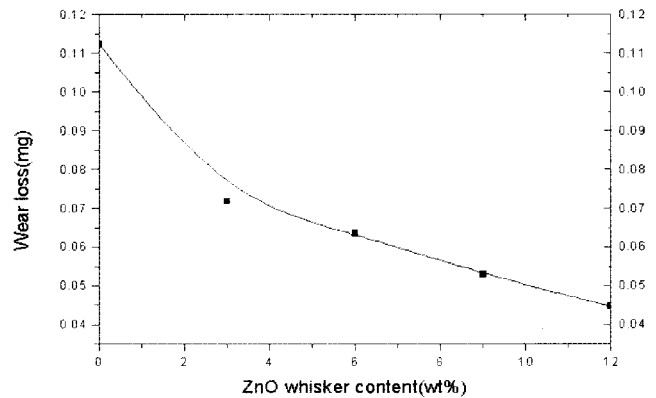


Figure 2 The variation of the wear loss due to the ZnOw content in the ZnOw/NR-SBR-BR composites.

Morphology of worn surfaces

Figure 3 shows the scanning electron microscope images of the morphology of the abraded surfaces of the rubber composites without ZnO whiskers or containing 3, 6, 9, and 12 wt % ZnOw.

This group of images showed that the worn surfaces had similar terraced field structures that became increasingly slender as the ZnO whisker contents increased in the composites. These images are very similar to the fractal phenomena found by Stupark et al.⁸⁻¹⁰ in the investigation of the affect of friction work input on the abrasion of rubber composites. This implies that the structure of the worn surfaces of ZnOw/NR-SBR-BR composites appears to be fractal in character with the variation of the ZnOw contents.

Analysis of fractal behavior of worn surface

The fractal concept, which was created and promulgated by Mandelbrot,¹¹ is a mathematical tool that produces a quantitative description of an otherwise

TABLE I
Compound Formulations

Materials	Dosage (parts clay wt)	Note
NR	70	
SBR	20	S1000
BR	10	
ZnO powder	5	
Stearic acid	2.5	
Carbon black	40	N330
Antioxidant D	1.0	
Sulfur	0.5	
Accelerant		
N-Oxydiethylene-2-benzothiazole sulfenamide (NOBS)	3.0	
Tetramethyl thiuram disulfide (TMTD)	0.7	
ZnO whisker	0, 3, 6, 9, 12 wt %	Pretreated by coupling agent ⁴
Condition for curing (min/ $^\circ\text{C}$)	20/145	10-MPa pressure

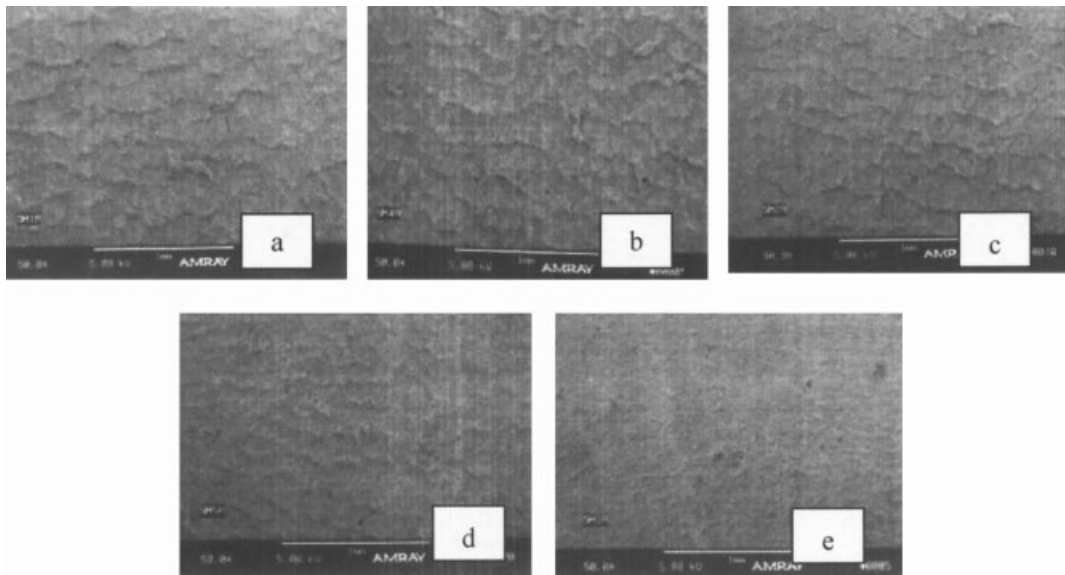


Figure 3 Images of the worn surfaces of ZnO/NR-SBR-BR composites (a) without ZnOw or containing (b) 3, (c) 6, (d) 9, and (e) 12 wt % ZnOw.

indescribably rugged line or surface. The essential principle of fractal analysis is that the measured value of an irregular line or surface depends on the length or area of the measuring device. The smaller the line or surface of the measuring device is, the greater length or area will be obtained for the fine details of the smaller size of a measuring device. The relationship of the size of a mathematical fractal surface (L) and the value of the measuring device (R) can be expressed as¹²

$$L \propto R^{1-D} \tag{1}$$

where D is the fractal dimension. For a smooth line or surface, the values of the lengths or areas measured by any size measuring device give the equal Euclidian dimension of 1 for a line or 2 for a surface. For an irregular surface, the D value will be fractal.

The fractal behavior of rubber composites at different levels of frictional work was observed and analyzed by Stupark et al.⁸⁻¹⁰ Until now, there no distinct

progress has been made on the relationship between the fractal dimension and the abrasion mechanism.²

From Figures 3 and 4, which give the SEM images of the abraded surfaces, it can obviously be found that the worn surfaces of ZnOw/NR-SBR-BR composites have the distinct behavior of a fractal.

The following equation can be deduced from formula (1):

$$\lg L_N = (1 - D)\lg R_m \tag{2}$$

where L_N is the normalized length of the fractal object and R_m is the diameter of the measuring disk. Formula (2) indicates that the plots of $\lg R_m$ versus $\lg L_N$ will be a straight line. The fractal dimension D can be obtained from its slope. From the experimental data according to eq. (2), which are shown in Figure 5, it can be seen that the experimental results coincide with the above prediction of the fractal principle. The values of the fractal dimension were calculated and are summarized in Table II, and the relationships are

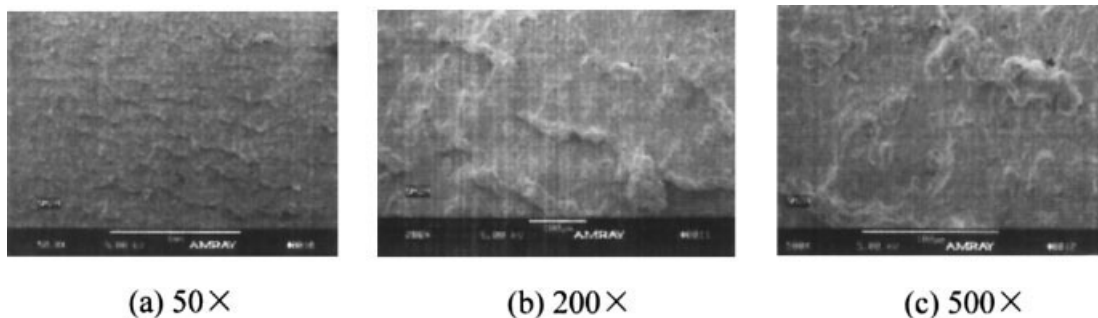


Figure 4 Images of the worn surface of ZnOw/NR-SBR-BR composites under different original magnifications (6 wt % ZnOw).

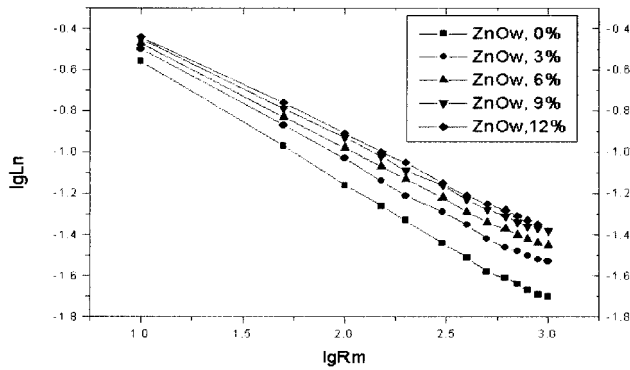


Figure 5 The fractal plots of the profilometry data.

drawn in Figure 6. A graph of the wear losses versus the fractal dimensions is plotted in Figure 7.

Note from Figures 6 and 7 that the abrasion loss and fractal dimension decreased linearly as the ZnOw content was increased in the composites. Because the value of the fractal dimension corresponds to the roughness of the surface,¹² and the surface roughness relates to the abrasion loss,⁴ it can be deduced that the

TABLE II
Fractal Dimensions of Worn Surfaces

Sample	ZnO Content (wt %)	Fractal Dimension
a	0	1.58
b	3	1.52
c	6	1.49
d	9	1.47
e	12	1.46

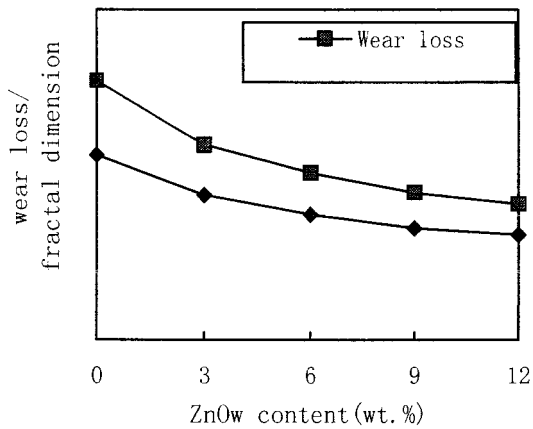


Figure 6 Plots of the wear loss and fractal dimension versus ZnOw.

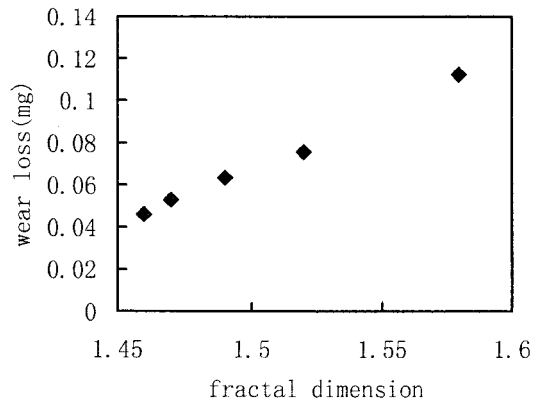


Figure 7 Plots of the wear loss versus the fractal dimensions.

extent of the wearing of rubber composites can be judged by the value of the fractal dimension of the abraded surface if it is under the same conditions and by the same mechanism of abrasion.

CONCLUSIONS

1. The worn surfaces of NR-SBR-BR and ZnOw/NR-SBR-BR composites appear to be fractal.
2. The fractal dimension decreases with increasing ZnOw content in the composites, which characterizes the decrease in roughness of the worn surface with increasing ZnOw content.
3. The abrasion loss and the fractal dimension decrease linearly if it is under the same wear conditions. The fractal dimension can be used as a characteristic for the degree of abrasion.

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