Studies on the Strength and Wear Resistance of Tetrapod-Shaped ZnO Whisker–Reinforced Rubber Composites

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ABSTRACT: Zinc oxide whisker with a tetrapod shape was treated with a coupling agent using an orthogonal design and was mixed into the substrate of natural rubber to obtain the composites. The results of the experimental tests show that the tensile strength of the composites progressively increases with an increased amount of the related whisker. The experiments also indicate that the rubber reinforced by the tetrapod-shaped ZnO whisker is distinct isotropy. The wear tests demonstrate that the composites containing ZnO whisker appear to have good wear-resistance behavior. © 20012001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1520–1525, 2001

Key words: Key words: ZnO whisker; surface treatment; rubber composites; tensile strength; wear test

INTRODUCTION

Much progress has been made in recent years with low-dimensional materials such as nanometer powder, whisker, and monomolecular film because they possess several distinct advantages over conventional materials. The ZnO whisker is a kind of single crystal that exhibits a needlelike tetrapod-shape. It has four needlelike arms extending from the same center in four directions in three-dimensional space (Fig. 1).[1,2] The combination of tetrapod-shape morphology, single-crystal structure, and multifunctional character of zinc oxide makes this a material that possesses unique properties such as isotropy, antistatic effect, semiconductivity, wear resistance, vibration insulation, and microwave absorption.[3]

Natural rubber (NR) is a widely used flexible polymer material. It is of practical importance in developing short-fiber-reinforced rubber composites as engineering polymers because of its high strength-to-weight ratio and of its ease of manufacture. Much work has been done on short-fiber-reinforced NR or other rubber composites that show an obvious anisotropy.[4,5] The wear behaviors and mechanisms of polymer materials have attracted more and more attention.[6] Uchiyama et al.[7,8] studied the influence of short fibers and their orientations on the wear property of rubber composites, and their results indicate that fiber orientation has a strong effect on specific wear rates. In the experiments the short fibers were designed to specific orientations, and clearly the composites had anisotropy. The purpose of the present work is to prepare an isotropic and mul-

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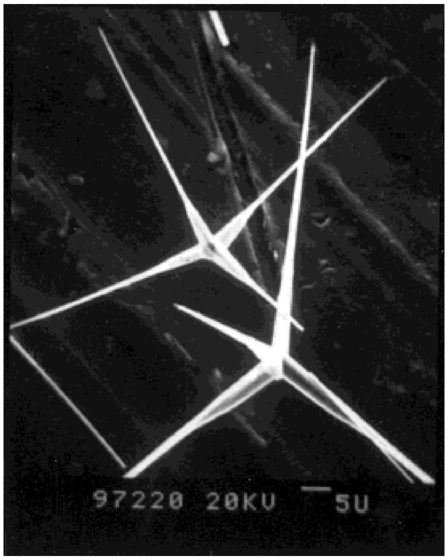


Figure 1 SEM photograph of ZnO whisker.

tifunctional material by taking advantage of the new additive ZnO whisker, which has a tetrapod-shaped morphology.

EXPERIMENTAL

Materials

The tetrapod-shaped ZnO whisker was prepared in our laboratory. The details were reported in our earlier studies,[1,2] and the physical parameters of the whisker in this experiment are shown in Table I. Grade-one bacon natural rubber was used as the substrate. The coupling agents and other specimens or additives were used without further purification and treatment unless otherwise mentioned. The formulae of the coupling agents used in the present experiments are—SI-69: $(OC_2H_5)_3SiCH_2CH_2S_4(CH_2)_3Si(OC2H5)_3$; AK811-5: $CH_2{=}CHSi(OC_{12}H_{24}OCH_3)_3$; A-189: $HSC_3H_6Si(OCH_3)_3$; and S-881: $(CH_3)_2CH\text{-}OTi(OCOC_{17}H_{35})_3$.

Surface Treatment of ZnO Whisker

The surface of the ZnO whisker was treated first with a certain amount of coupling agent solution; then the treatment was done after keeping the mixture in an oven at a designated temperature for a certain duration. An orthogonal design was used to seek the optimum conditions for the treatment; the kind and the amount of the coupling agent, the temperature, and the duration of drying in the oven were designated as the factors; and four levels of each factor were involved in the orthogonal project.

Preparing of the Composites

The natural rubber was processed using the traditional two-step procedure, which is mastication followed by milling on the XK-230 model opening mixer. The traditional types of ingredients and quantity of additives were used in the composites, and the tetrapod-shaped ZnO whiskers were 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 curemeter, and the vulcanizing procedure was followed on an XLB-D platen vulcanizing press in order to obtain the reinforced composite, which was the test specimen.

Property Test of the Composites

The tensile test of the samples was carried out in a computer controlled DXLL—5000 tensile ma-

Table I Physical Parameters of ZnO Whisker

Properties	Descriptions
Content of ZnO (%)	⩾99.99
Length of the needles (m)	3.0×10^{-5}—1.0×10^{-4}
Width of the needles (m)	2.0×10^{-7}—8.0×10^{-6}
Density (g/m^3)	5.96×10^6
Thermal stability	1720°C sublimation
Electrical resistivity (Ω · m)	7.14×10^{-2}
Tensile strength (MPa)	9.86×10^4
Modulus (MPa)	3.47×10^5
Thermal expanding constant (%/°C)	4.21×10^{-6}
Thermal conductivity [J/(s · m · K ·)]	24.5 (95°C)

Table II Factors and Levels of the Modification Condition

Factors/Levels	Coupling Agent	Amount of the Coupling Agent (wt.)[a]	Temperature of Baking (°C)	Time of Baking (h)
1	SI-69	0.5	100	1
2	AK811-5	1.0	120	2
3	A-189	2.0	140	3
4	S-881	4.0	160	4

[a] The weight ratio of the coupling agent to the whisker.

chine, and five specimens of each sample were tested. The morphology and fracture surfaces of samples were examined in an Amary 1845 field emission scanning electron microscope. The wear-resistance tests of the vulcanized rubber composites were conducted on an MH-74 Akelon abrasion-testing machine. The rotate 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 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 conducted at a temperature of 25°C and a humidity of 65%.

RESULTS AND DISCUSSION

Surface Modification of ZnO Whisker

The importance and the necessity of surface modification of particle- or fiber-filled polymer composites have been reviewed.[9,10] Actually, most treatments in commercial use are chosen to bond the organic molecule chemically to the filler surface, and organosilicon compounds are in widespread use as modifiers for inorganic fillers (particle and fiber). In the present work, the coupling agents used and their amounts and the conditions of the treatment are summarized in Table I. The factors and levels of the orthogonal experiments of $L_{16}(4^4)$ are shown in Table II. The results of the analysis indicate that SI-69 is the most proper coupling agent for the ZnO whisker surface modification, and its appropriate amount should be 2% (weight ratio of the agent to the whisker); the optimum temperature and duration are 120°C and 2 h, respectively. Comparing Figure 1 with Figure 2, which is the SEM image of the whisker with the optimum treatment condition, it can be seen that the needles modified are covered by a homogenous layer of the agent.

Figure 3 shows the SEM images of the fracture morphology of the composites, in which (a) relates the modified ZnO whisker with the optimum condition and (b) is the whisker without pretreatment. It can be seen that the needles of the whisker and the substrate of rubber in Figure 3(a) have formed a good adherence, while the fracture surface in Figure 3(b) shows obvious holes, which are formed by the needles of the whisker having been pulled out. This can be explained by the good effect of the surface treatment of the whisker in the composite of Figure 3(a).

Tensile Strength of the Composites

In general, short fibers have characteristics of anisotropy. As reinforcement, fibers in a composite will take an advantage in distribution, and the strength of the composite along the direction of

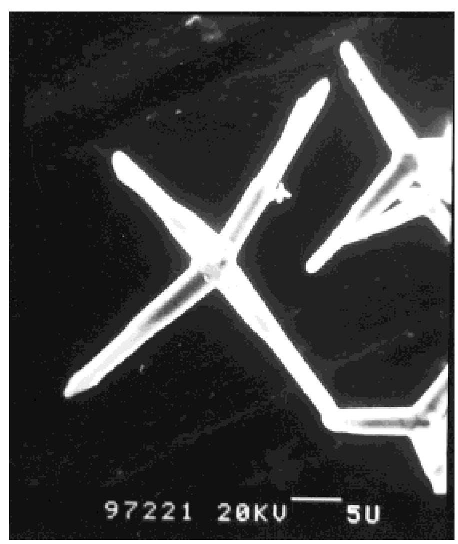
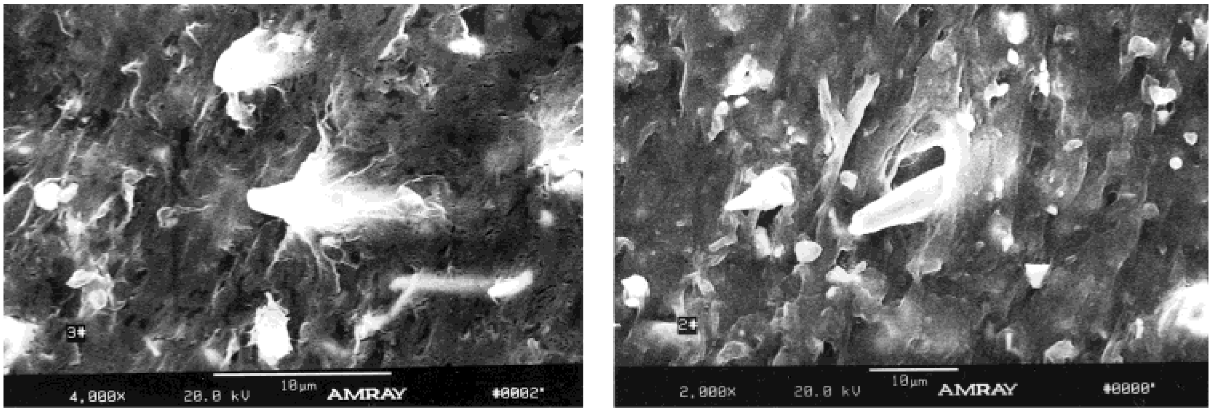


Figure 2 SEM photograph of modified ZnO whisker.



(a) (b)

Figure 3 SEM images of the fracture morphology of the composites comparing: (a) whisker treated under optimum conditions and (b) whisker without surface treatment.

the fiber orientation is much higher than in other directions. The experimental data and the standard deviations of the tensile strengths of ZnO whisker–modified rubber composites were summarized in Table III, for which the Grubbs method[11] was used to determine whether data were accepted or omitted. From Table III, it can be seen that ZnO whisker has a positive effect on reinforcing the natural rubber and decreasing the aging rate of the material, and the composites appear to be isotropic. This result can be explained by the whisker being used as reinforcement for the tetrapod-shaped morphology, and the whiskers disperse uniformly in three dimensions in the matrix, even if some are broken during the process (Fig. 4).

Wear-Resistance Property

Natural rubber is widely applied as a wear-resistance material. As a single crystalline, ZnO whisker has a very high strength and modulus. In theory, it will be effective in improving the wear-resistance property of the composite materials. The results in Figure 5, which shows plots of the wear losses versus the amounts of the ZnO whisker in the natural rubber composite, coincide with this deduction.

Figure 6(a,b) shows the SEM images of the worn surfaces of natural rubber and the composite with 12% whisker, respectively. It can be seen that the worn surface of the natural rubber has accumulated stacks of debris, while the composite

Table III The Tensile Strengths of the Composites of NR/ZnO Whisker

The Cont. of ZnO Whisker (wt.)	Tensile Strengths and Standard Deviations (MPa)						Ratio of Tensile Loss (%)
	Before Aging				After Aged[a]		
	Direction a[b]	S[c]	Direction B[d]	S[b]	Direction A	S[c]	
0	22.02	0.13	21.98	0.09	20.31	0.16	7.8
3	22.65	0.10	22.60	0.13	21.72	0.17	4.1
6	23.02	0.11	22.99	0.16	22.24	0.16	3.4
9	23.60	0.15	23.63	0.12	22.86	0.20	3.1
12	23.95	0.13	23.89	0.16	23.38	0.14	2.4

[a] The aging condition is 100°C × 72 h.
[b] The author defined a direction on the composite.
[c] Standard deviation of each sample: $S = [\Sigma (a-\underline{a})^2/(n-1)]^{1/2}$, $n = 5$.
[d] The direction orthogonalized A.

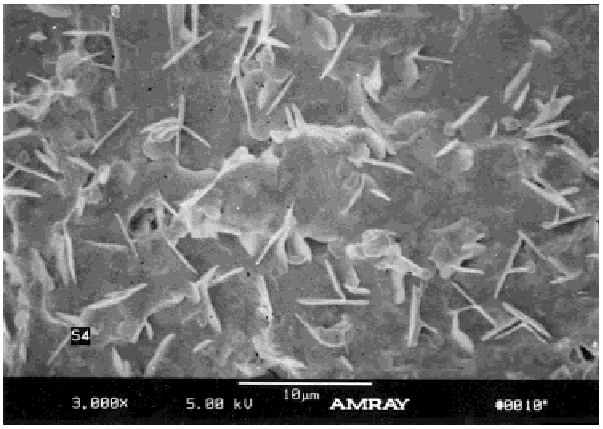


Figure 4 Distribution of ZnO whisker in the rubber composites.

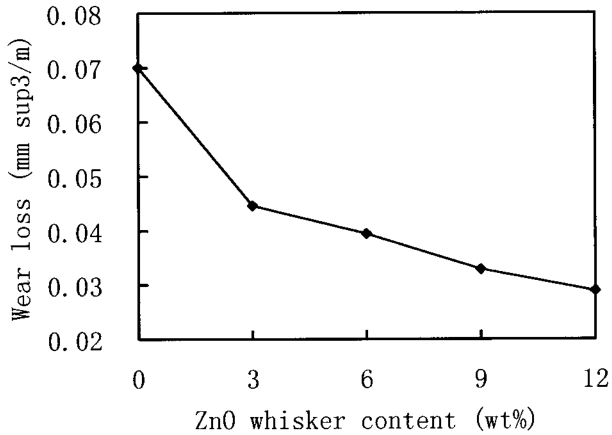
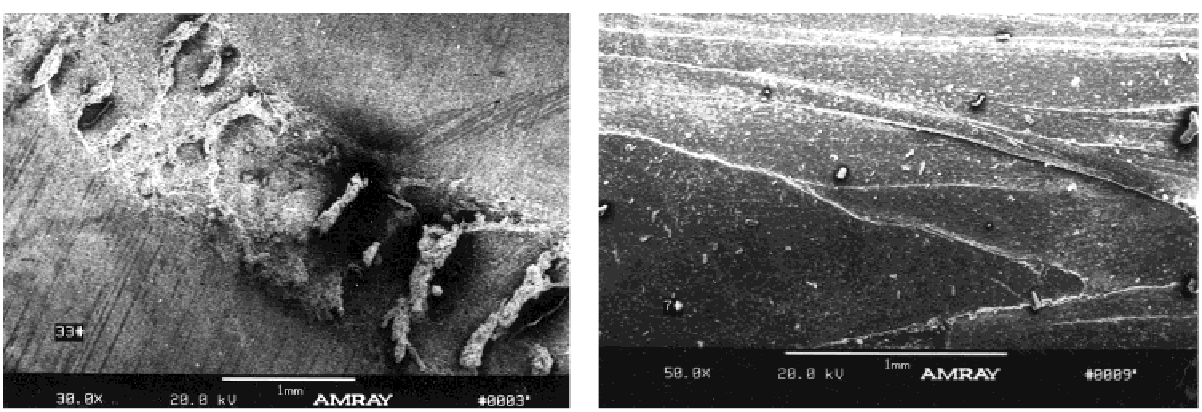


Figure 5 Variation of wear loss due to ZnO whisker content in the natural rubber composites.

containing 12% ZnO whisker appears a relative flat surface.

Chen et al.[12,13] studied the wear behavior of short-fiber-reinforced polymer and found that the self-lubricating thin film that forms on the contact surface during the wearing process played a dominate role in suppressing transverse cracks. Uchiyama et al.[7,8] showed that fiber orientation had an obvious effect on the wear property of a short-fiber-reinforced rubber composite. The effect of decreasing the wear loss of rubber materials containing ZnO whisker can be explained by several aspects. First is very high strength and modulus of the short fiber used in the present work. It plays an important role in preventing both the initiation and propagation of cracks that may occur in unreinforced rubber materials on contact surfaces. Whisker needles with high modulus bear much of the wear action on the surface of the material. Second is the random orientation of the needles of the whisker in the composite. The angle between the orientation of fibers and the direction of sliding has an important effect on the wear property.[7,14] In the ZnO whisker–reinforced composite, the needles of the whisker disperse uniformly in three dimensions, and a lot of them are coincidentally distribute in the most favorable direction, producing the least wear loss. Third is the tetrapod-shaped morphology of the ZnO whisker, which plays a coordinated role with each of the four combined needles of the whisker to transmit both the force added by loading or



(a) (b)

Figure 6 SEM photos of the worn surface of the rubber composites: (a) rubber composite without ZnO whisker and (b) rubber composite containing 12 wt % ZnO whisker.

friction and the heat generated during the wear process.

CONCLUSIONS

The following conclusions were drawn from this study:

1. The surface-modified zinc oxide whisker, which has a peculiar tetrapod-shaped morphology, has a positive effect on reinforcing natural rubber, and the composites containing the related whisker appear distinct in isotropy and aging resistance.
2. The values of wear loss of natural rubber containing the ZnO whisker decrease progressively with the amount increase in whisker.

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