Polymer Journal, Vol. 38, No. 5, pp. 498–502 (2006)

NOTES

Morphology, Antimicrobial and Mechanical Properties of Nano-TiO_2/Rubber Composites Prepared by Direct Blending

Gui LIN,[1,3] Ming TIAN,[2] Yong-Lai LU,[1] Xiu-Juan ZHANG,[2] and Li-Qun ZHANG[1,2,†]

[1]*Key Laboratory for Nanomaterials, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*
[2]*Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*
[3]*Center of Sealing and Damping Technology, Aerospace Research Institute of Materials and Processing Technology, Beijing 100076, People's Republic of China*

(Received October 4, 2005; Accepted January 12, 2006; Published May 15, 2006)

KEY WORDS Antimicrobial Property / Morphology / Titanium Dioxide (TiO_2) / Rubber / [doi:10.1295/polymj.38.498]

Titanium dioxide (TiO_2) has been studied extensively as a photocatalyst and photoactive material for environmental cleanup, such as wastewater treatment, antifouling, deodorizing, antibacterial.[1–4] In comparison with micro-TiO_2 powders, nano-TiO_2 powders have far higher photoactivity due to their nano effect, so that nano-TiO_2 has much wider application field. On the other hand, polymer materials have been widely used in some situations where antimicrobial and antipollution properties are highly demanded, for instance, food package, refrigerator and furniture. Incorporating nano-TiO_2 particles into a polymer is considered as a feasible way to satisfy this requirement. For this reason, there had been many studies on antimicrobial properties, mechanical properties and rheological properties of nano-TiO_2/plastics composites.[1,5,6] Nevertheless, as for rubber composites, micro-TiO_2 is usually used as white pigment or non-reinforcing filler, and to date, there are only a few researches on the antimicrobial property of micro-TiO_2/rubber composites though this property is essential for some rubber products. Very recently, Gao *et al.*[8] and Iketani *et al.*[9] reported that the nano-TiO_2/silicone rubber films, prepared by fluidifying sedimentation and so-gel method, exhibited high photocatalystic activity. However, they did not investigate antimicrobial properties of these films. In this work, it was the first time that nano-TiO_2/rubber composites had been prepared by directly blending nano-TiO_2 with rubber. The antimicrobial and mechanical properties and micro-morphology of nano-TiO_2/rubber composites were studied. The effect of thermal-oxidative aging on both antimicrobial and mechanical properties of these composites was also investigated.

EXPERMENTAL

Materials and Preparation of Specimens

Two kinds of nano-TiO_2 powders were used in this work. One, developed by a researching group in Beijing University, is composed of 99% anatase crystal and has the diameter of 20–40 nm, which is denoted by BT. The other is P25, one of the most efficient photocatalysts produced by Degussa Corp. (Germany) and consisted of 70% anatase crystals and 30% rultile crystals, with an average diameter of 30 nm and a specific area of $500\,m^2\,g^{-1}$. Natural rubber (NR, NR-SCR5) and nitrile-butadiene rubber (NBR, N220s) with the nitrile content of 41.5 wt. % and the Mooney point (ML1+4@ 100 °C) of 56 produced by JSR Corp. (Japan) were used as polymer matrix. The other reagents are commercial products.

The TiO_2/rubber compounds were mixed on a tow-roll miller according to the formulations described in Table I. Subsequently, these compounds were cured at 150 °C for their optimal curing time (*i.e.*, T_{90} determined by a Disc Oscillating Rheometer) to obtain cross-linked TiO_2/rubber composites.

Measurements and Characterization

The thermal oxidative aging experiments were performed at 100 °C for NR or 120 °C for NBR for 72 h according to ISO 188-1988 standard. The hardness (Shore A) of the composite was examined according

†To whom correspondence should be addressed (Tel: +86-10-64421186, Fax: +86-10-64433964, E-mail: zhangliqunghp@yahoo.com).

Table I. The Formulation of Nano-TiO_2/Rubber Composites

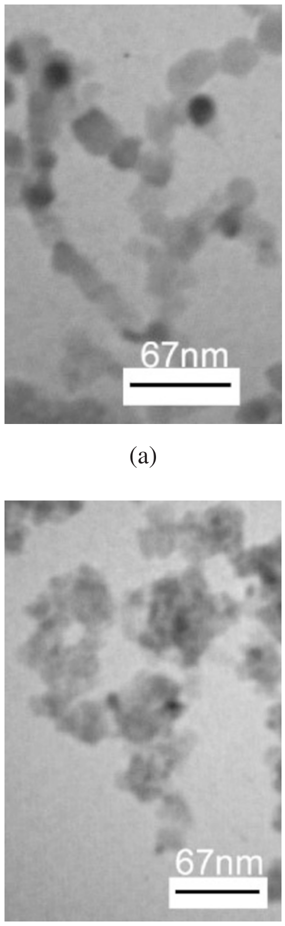
	BT/NR	BT/NBR	P25/NR
Rubber/phr[a]	NR: 100	NBR: 100	NR: 100
Nano-TiO_2/phr	BT: 0, 1, 2, 3, 4, 5	BT: 0, 1, 2, 3, 4, 5	P25: 0, 1, 2, 3, 4, 5
Zinc oxide/phr	5.0	5.0	5.0
Stearic acid/phr	1.0	1.0	1.0
Sulfur/phr	2.0	2.0	2.0
Accelerator M[b]/phr	0.5	—	0.5
Accelerator DM[c]/phr	—	1.5	—

[a]phr is the abbreviation of per one hundred weight-parts rubber; [b]2-mercaptobenzthiazole; [c]dibenzthiazyl disulphide.

to ISO 48-1994 standard. The tensile properties of composites including stress at 100% strain and tensile strength were tested according to ISO 37-1994 standard. Antimicrobial properties of prepared TiO_2/rubber composites were evaluated according to corresponding standards (FZ/T01021-92 and GB1597-1995). The bacterium suspension (10^6 colony forming units per milliliter, CFU/ml) was uniformly coated on the surfaces of nano-TiO_2/rubber and rubber without nano-TiO_2 (blank sample) cured sheets with the dimension of $10 \times 5 \times 2\,mm^3$. These sheets coated with bacterium were stored at 25 °C in ambient air for 24 h. The average numbers of bacterium on nano-TiO2/rubber samples and blank samples were examined. Consequently, the antimicrobial property of the nano-TiO_2/rubber composite can be calculated by using following equation,

$$Antimicrobial\ property = \frac{ABN_B - ABN_C}{ABN_B} \times 100\% \quad (1)$$

where ABN_B and ABN_C represent average bacterium numbers on blank and the composite samples, respectively. The ultra-thin sections of BT/rubber and P25/rubber composites were cut under about −100 °C by using a microtome and collected on the copper grids. In order to avoid the disturbance of ZnO and other agents, these additives were not added to the composites used in TEM experiments. TEM observations on TiO_2 powders, and BT/rubber and P25/rubber composites were performed on an H-800-1 transmission electronic microscope (Hitachi, Japan).



(a)

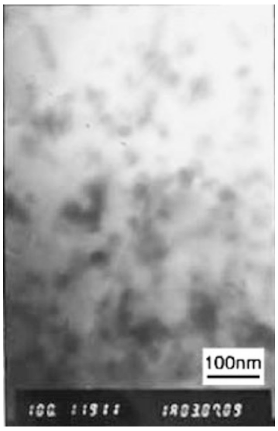
(b)

Figure 1. TEM photographs of nano-TiO_2 powders: (a) BT; (b) P25.

RESULTS AND DISCUSSION

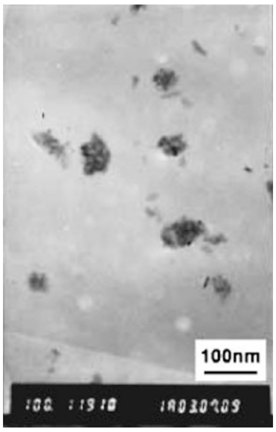
Micro-morphologies of TiO_2 Powders and TiO_2/Rubber Composites

Figure 1 shows transmission electron microscope (TEM) images of BT and P25 powders. It can be clearly seen that the dimensions of both powders are at nanometer level. Figure 2 displays TEM images of BT/NR, BT/NBR and P25/NR composites containing 5 phr TiO_2. It can be seen that both BT and P25 particles are dispersed uniformly in polymer matrixes at nano level. However, the dispersion state of TiO_2 in BT/NR composites is finer than those in BT/NBR and P25/NR composites. The dimension of dispersed TiO_2 particles in BT/NR is about 20–50 nm, which is similar to the size of original BT particles, and no apparent agglomerates of BT particles can be observed in Figure 2a. The diameters of dispersion in BT/NBR and P25/NR are within the range from 60 to 80 nm, and are larger than those of their



(a) BT/NR

(b) BT/NBR



(c) P25/NR

Figure 2. TEM photographs of nano-TiO_2/rubber (5/100) composites.

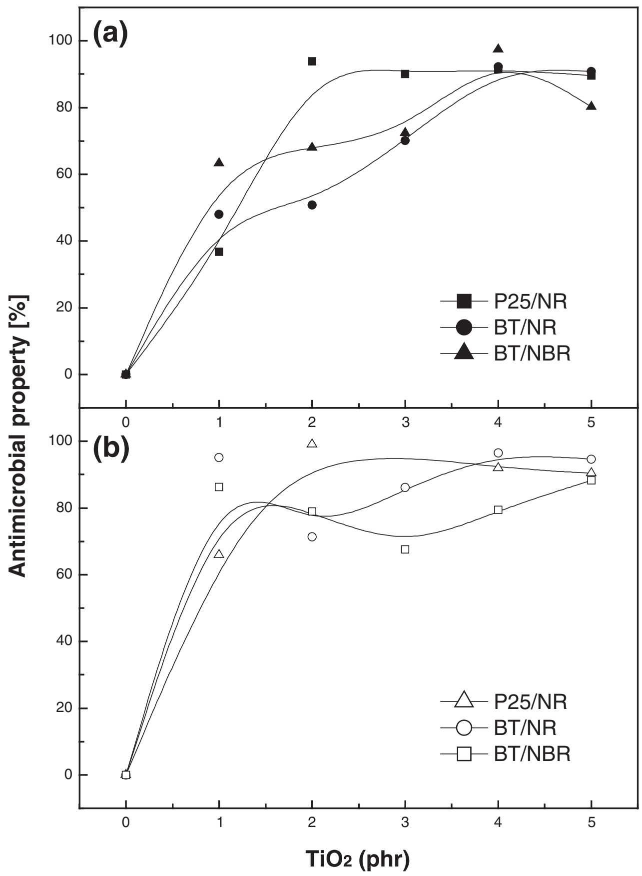


Figure 3. Influence of filling amount of TiO_2 on antimicrobial properties of TiO_2/rubber composites before (a) and after (b) thermal oxidative aging. 0 phr represents the gum rubber vulcanizates.

original TiO_2 particles, indicating the existence of agglomerates. It also can be found from Figures 2b and 2c that the dimension of agglomerates in P25/NR is slightly larger than that of in BT/NBR. Generally, the dispersion level of nano-inorganic particles in a polymer composite is related to the viscosity of matrix, the agglomeration forces among nano-particles, the surface tension difference between polymer and inorganic fillers, as well as the shear force during the blend processing.[10,11] The stress-induced crystallization feature of NR results in high viscosity during mixing, and as a result, the finer dispersion of TiO_2 was observed in NR composite.

Antimicrobial and Mechanical Properties of Nano-TiO2/Rubber Composites

The antimicrobial properties of BT/NR, BT/NBR and P25/NR before and after thermal oxidative aging are shown in Figures 3a and 3b, respectively. In comparison with pure rubber matrixes, addition of only 1 phr nano-TiO_2 can substantially improve the antimicrobial properties of materials. Within the loading range of nano-TiO_2 involved in this work, the antimicrobial properties of BT/NR and BT/NBR increase with TiO_2 content increasing. While that of P25/NR firstly increases with TiO_2 content, and then changes little when the loading of P25 exceeds 2 phr. Figure 3a also illustrates that the antimicrobial properties of BT/NR and BT/NBR composites are somewhat lower than those of P25/NR, especially at low TiO_2 content. As a matter of fact, the mechanism of the heterogeneous photocatalysis begins by the irradiation of semiconductor (*i.e.*, TiO_2) with energy superior or equal to the band gap.[7] There is ejection of electrons (e^-) from the valence band to the conduction band with formation of positive holes (h^+). The electrons might react with O_2 to form ${O_2}^-$, while the positive holes might react with H_2O to form hydroxyl radical (•OH). Both ${O_2}^-$ and •OH have high activity to attack organic bacterium and result in their degradation. In general, the ejection process is mainly determined by two factors: the crystal type of nano-TiO_2 and the dispersion level of nano-TiO_2 in polymer matrix. Anatase TiO_2 is more photosensitive than rutile and brookite TiO_2 to form electron-hole pairs. Smaller dimension of dispersion TiO_2 particles facilitates ejection of electro-hole pairs from the inner of particles. If only these two factors are considered, the antimicrobial properties of BT/rubber composites, especially BT/NR systems, should be superior to those of P25/rubber composites. However, our experimental results reveal that there should be some other factor dominating this antimicrobial process. Besides ejection of electron-hole pairs, the reactions among electrons, holes, O_2 and H_2O are also essential to final antimicrobial properties of composites. In nano-TiO_2/rubber composites, the rubber matrix around TiO_2 dispersion particles impedes diffusion of electrons or holes from inside to the surface of composites, where electrons and holes might react with adsorbed H_2O and O_2 to form $O_2{}^-$ and •OH. The fine dispersion of nano-TiO_2 benefits ejection of electro-hole pairs, but in this case, the interfacial interactions between TiO_2 and rubber matrix are also strong, resulting in strong impeding effect against diffusion of electron-hole pairs and subsequent reactions. While poor dispersion of nano-TiO_2 generally means relatively weak interfacial interactions between TiO_2 and rubber matrix, which facilitates diffusion of electron-hole pairs in the composite. Consequently, P25/rubber composites with relatively poor dispersion morphology possess better antimicrobial properties. Our results also imply that the finer dispersion of TiO_2 in polymer matrix does not always lead to better antimicrobial property. Figure 3b depicts the antimicrobial properties of BT/NR, BT/NBR and P25/NR after thermal oxidative aging. The results demonstrate that nano-TiO_2/rubber composites have long-term effective antimicrobial properties.

Figure 4 displays the mechanical properties of these composites. It can been seen that the hardness (Shore A) used to characterize the compressive characteristics, stress at 100% strain and tensile strength of TiO_2/rubber composites change little with TiO_2 content increasing, which is likely attributed to limited filling amount of nano-TiO_2.[10] As described in the previous section, excellent antimicrobial properties of nano-TiO_2 arise from $O_2{}^-$ and •OH formed by photocatalysis process. Therefore, there is an important question: whether these products also accelerate the aging course of rubber. The mechanical properties of TiO_2/rubber composites after thermal oxidative aging were examined. The results are also shown in Figure 4. For NR and NBR gum vulcanizates, the hardness and stress at 100% of theirs after aging are slight improved. The tensile strength of NR gum vulcanizate was dramatically enhanced by thermal aging; while the tensile strength of NBR gum vulcanizate was decreased a lot. This change in mechanical properties induced by aging is likely attributed to the change of cross-linking density caused by thermal aging.[11,12] Figure 4 also reveals that incorporation of nano-TiO_2 into rubber makes little effect on mechanical properties after thermal aging, indicating that nano-TiO_2 does not accelerate the aging course of matrix rubbers.

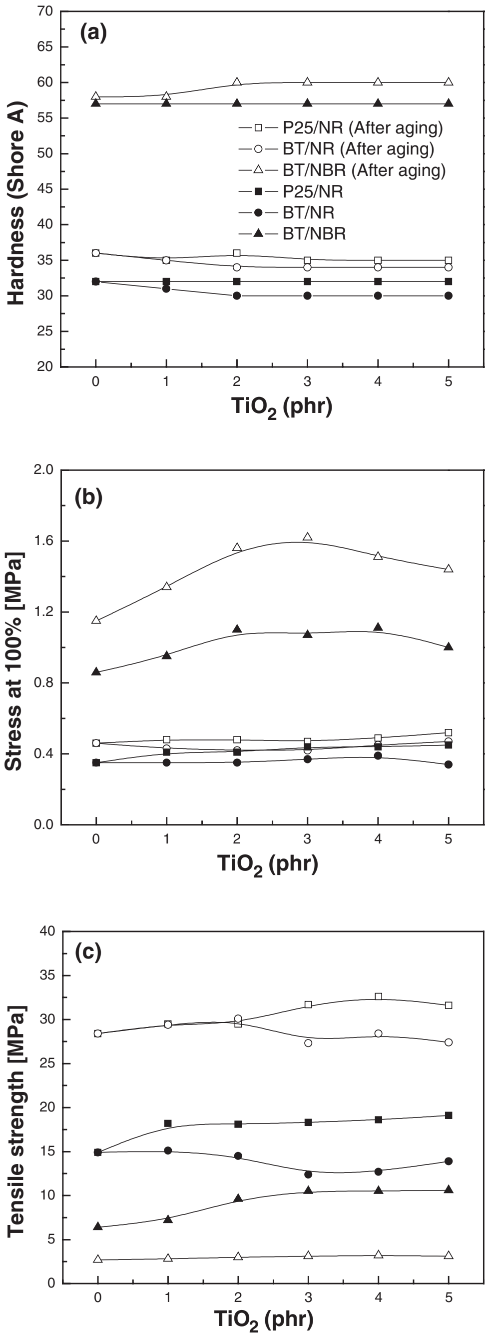


Figure 4. Influence of filling amount of TiO_2 on mechanical properties of TiO_2/rubber composites before (solid symbols) and after (open symbols) thermal oxidative aging: (a) hardness (Shore A); (b) Stress at 100% strain; (c) Tensile strength. 0 phr represents the gum rubber vulcanizate.

CONCLUSIONS

By compounding small amount of nano-TiO_2 with rubber, the resulted composites were endowed with good antimicrobial ability. The antimicrobial property of the nano-TiO_2/rubber composite is somewhat influenced by the dispersion state of nano-TiO_2, and out of authors' expectation, the relatively bad dispersion state would lead to relatively good antimicrobial property. Small amount of nano-TiO_2 have little reinforcing effect on the matrix rubber, and do not accelerate the aging course of matrix rubber.

Acknowledgment. This work was generously supported by Key Project of Nature Science Foundation of Beijing City (B203001).

REFERENCES

1. Y.-Q. Tong, M. Tian, R.-F. Xu, W.-K. Hu, L. Yu, and L.-Q. Zhang, *Acta Mater. Comp. Sinica*, **20**, 88 (2003).
2. A. Sclafani, L. Palmisan, and E. Davi, *J. Photochem. Photobiol.*, A, **56**, 113 (1991).
3. O. Legrini, E. Oliveros, and A. M. Braun, *Chem. Rev.*, **93**, 671 (1993).
4. M. Toshihiro, A. Donald, P. S. Tryk, K. Yoshihiko, H. Kazuhito, and F. Akira, *J. Photochem. Photobiol.*, A, **53**, 137 (2003).
5. G. B. Sun, G. Wu, R. F. Xu, and D. Z. Wu, *China Plastics*, **16**, 47 (2002).
6. Y. C. Dong, W. Meng, X. Wei, Y. J. Yang, L. D. Lu, and X. Wang, *China Plastics Industry*, **27**, 37 (1999).
7. A. Hagfeldt and M. Gratzel, *Chem. Rev.*, **95**, 49 (1995).
8. Y. Gao and H. Liu, *J. Mater. Sci. Lett.*, **22**, 1821 (2003).
9. K. Iketani, R. Sun, M. Toki, K. Hirota, and O. Yamaguchi, *J. Phys. Chem. Solids*, **64**, 507 (2003).
10. Q. Zhang, M. Tian, Y.-P. Wu, L. Liu, Y.-Q. Tong, W.-K. Hu, and L.-Q. Zhang, *Acta Materiae Compositae Sinica*, **20**, 88 (2003).
11. A. N. Gent, S. Kawahara, and J. Zhao, *Rubber Chem. Technol.*, **71**, 668 (1998).
12. A. N. Gent and L. Q. Zhang, *J. Polym. Sci., Part B: Polym. Phys.*, **39**, 811 (2001).