Preparation and Performance of High-Impact Polystyrene (HIPS)/Nano-TiO_2 Nanocomposites

Jinzhu Zhang, Xin Wang, Lude Lu, Dan Li, Xujie Yang

Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China

Received 14 May 2001; revised 12 April 2002; accepted 12 April 2002

ABSTRACT: High-impact polystyrene (HIPS)/nano-TiO_2 nanocomposites were prepared by surface pretreatment of nano-TiO_2 with special structure dispersing agent (TAS) and master batch manufacturing technology. The results show that when the nano-TiO_2 content is 2%, the notched impact strength, tensile strength, and elastic modulus of HIPS/nano-TiO_2 nanocomposites increased to a maximum. This result indicates that nano-TiO_2 has both toughening and reinforcing effects on HIPS. The heat-deflection temperature and flame-retardance of HIPS/nano-TiO_2 nanocomposites are also obviously improved as the nano-TiO_2 content is increased. The nanocomposites manufactured by the two-step method have better mechanical properties than that made by a one-step method. HIPS/nano-TiO_2 nanocomposites are also non-Newtonian and pseudoplastic fluids. J Appl Polym Sci 87: 381–385, 2003

Key words: high-impact polystyrene (HIPS); nano-TiO_2; nanocomposites; dispersions; performance

INTRODUCTION

High-impact polystyrene (HIPS) is a thermoplastic that is widely used in packaging, toys, bottles, housewares, electronic appliances, and light-duty industrial components because of its good rigidity and ease of coloring and processing. However, its application is somewhat limited because of its relatively poor impact strength, heat deflection, and flame retardancy. Modifications with rubber, elastomer, or polymer alloy can improve the impact strength of HIPS but, at same time, will sacrifice the rigidity of HIPS. Mineral fillers enhance the Young's modulus or the heat-deflection temperature of HIPS, but adversely affect the impact strength of HIPS.

With "little size effect," "surface effect," and "quantum effect," the nanoparticle has many special properties that are different from those of other particles. Modification of the polymer with inorganic nanoparticles results in polymer/inorganic nanoparticle composites with excellent performance due to the combination of higher rigidity and heat resistance of the inorganic filler and the good toughening and process ability of the polymer.[1–5] However, in the process of preparation, there are the great number of factors affecting the properties of the resultant polymer/inorganic nanoparticle composites.[6–8] The main factors are the nanoparticle size and volume fraction, the nature of the matrix and its adhesion to the nanoparticle, the nanoparticle dispersing into the matrix, and manufacturing technology. Among these factors, the interfacial adhesion and dispersing are of cardinal importance and markedly influence the properties of nanoparticle-filled polymers. In this work, by surface pretreatment of nano-TiO_2, by selecting a special structure dispersing agent (TAS), and by using master batch manufacturing technology, high-performance HIPS/nano-TiO_2 nanocomposites were prepared.[1]

EXPERIMENTAL

Materials

Materials are listed in Table I. HIPS and nano-TiO_2 were dried for 4 h at 80°C and 100°C, respectively, before blending.

Specimen preparation

The procedure for preparation of HIPS/nano-TiO_2 nanocomposites is indicated in Scheme 1. These composites (with different contents of nano-TiO_2) were injection molded in a BOY 225 dipronic injection molding machine at 220°C.

Impact testing

Notched specimens were tested with a Zwick 4 impact Tester, according to the ISO179 standard. The tests were carried out at room temperature, and the data obtained represent the average value from 10 test specimens.

TABLE I
Materials Used and Their Characteristics

Material	Source	Properties
HIPS 466-F	BASF Company Ltd.	Density, 1.05 g/cm^3 MFI, 3.8 g/10min
Nano-TiO_2	JiangSu TaiXing Nanometer Material Factory	Particle size, 40 nm Specific surface area, 80 m^2/g
TAS	JiangSu Guoguang Chemical Agent Factory	Density, 0.9 g/cm^3 Mb, 75 °C

Tensile testing

Tensile specimens were tested on Zwick 1464 universal test machine, according to the ISO 527 standard. Testing was done at room temperature, and tensile stress and elasticity modulus were determined at a deformation speeds of 100 and 10 mm/min, respectively. The mean value of five measurements was taken.

Thermal property

The heat deflection temperature was measured according to Chinese standard GB1634-79 Rate B(120°C/h)on a RV-300V heat-deflection temperature apparatus.

Rheology

The rheology properties were investigated with XLY-II capillary theology viscosity.

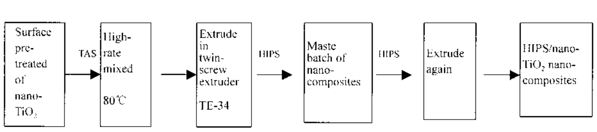
The L/D ratio of capillary was 20.

Flammability testing

The tests were carried out according to ASTM D 635-91, and the data obtained were the rate of burning of the material.

Scanning electron microscopy (sem)

Scanning electron microscopic (SEM) observations were carried out on fracture surfaces. The fracture surfaces were coat with gold under vacuum and then examined using a JEOL JSM-6300 apparatus.



Scheme 1

RESULTS AND DISCUSSION

Impact properties

The relationship of nano-TiO_2 content and notched impact strength of HIPS/nano-TiO_2 nanocomposites is shown in Figure 1. When TiO_2 content is 2%, the notched impact strength of nanocomposites increased to a maximum and then decreased with the addition of nano-TiO_2. This variation in notched impact strength can be attributed to two things. First, when nano-TiO_2 content is <2%, there is seldom agglomerated nano-TiO_2 in the matrix. As Nakagawa and Sano[9] have shown, the presence of fine particles dispersed within the matrix makes plastic deformation easier. So, during the fracture of a composite in which the nanoparticle is well dispersed, the stress will have to be bigger to start the microcrack on a nanoparticle, and the impact energy will largely be absorbed by the exhibited plastic deformation, which occurs more easily around the nanoparticles. Hence, the good nano-TiO_2 dispersion resulting from no agglomeration led to a better impact strength of the nanocomposites.

A second reason for the variation in the notched impact strength is that when nano-TiO_2 content is >2%, nano-TiO_2 easy agglomerates into large agglomerated particles, which will become the site of stress concentration and can act as a microcrack initiator. So, a large aggregate is a weak point that lowers the stress required for the composite to fracture and thus the notched impact strength of nanocomposites would be decreased.[10]

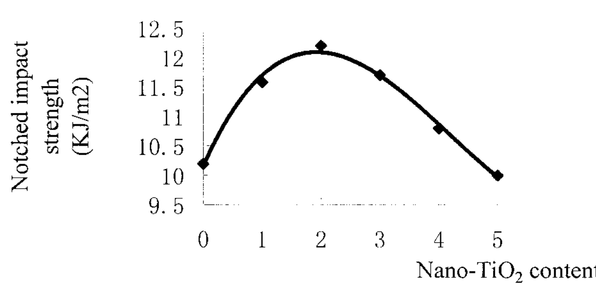


Figure 1 Effect of nano-TiO_2 content on notched impact strength of HIPS/nano-TiO_2 nanocomposites.

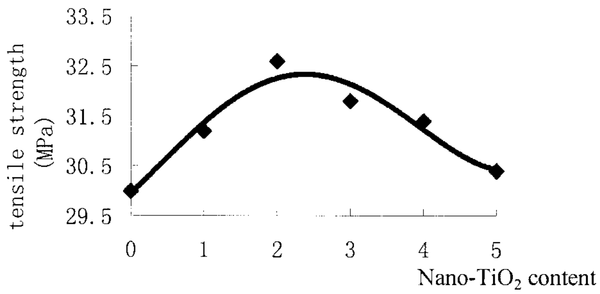


Figure 2 Effect of nano-TiO_2 content on tensile strength of HIPS/nano-TiO_2 nanocomposites.

Tensile properties

The relationship between nano-TiO_2 content and tensile strength of HIPS/nano-TiO_2 nanocomposites is shown in Figure 2. The relationship indicates that the tensile strength of the nanocomposites is higher than that of HIPS when nano-TiO_2 content is 1–5%, and reaches a maximum when nano-TiO_2 content is 2%.

The surface energy of nano-TiO_2 decreased when nano-TiO_2 was pretreated with coupling agent. In addition, the dispersing agent (TAS) has a group that is reactive with nano-TiO_2 and a group (solvolytic and oilphilic) that acts as a solvent wit HIPS. So, pretreated nano-TiO_2 will have good interfacial adhesion to HIPS because of the presence of the TAS.

Tensile strength of nanocomposites is enhanced when interfacial adhesion is improved. This result can be ascribed to better stress transfer at the interface between the matrix and nano-TiO_2. The improvement of interfacial adhesion can prevent dewetting at the HIPS/nano-TiO_2 interface during tensile deformation. Therefore, well-adhering nano-TiO_2 can bear on part of the load applied to the matrix and contribute to the tensile strength of the nanocomposites.[11]

The effect of nano-TiO_2 content on tensile elastic modulus of HIPS/nano-TiO_2 nanocomposites is shown in Figure 3. The tensile elastic modulus of nanocomposites increased to a maximum when nano-TiO_2 content is 2% and then decreased with the addition of more nano-TiO_2. This result can be explained

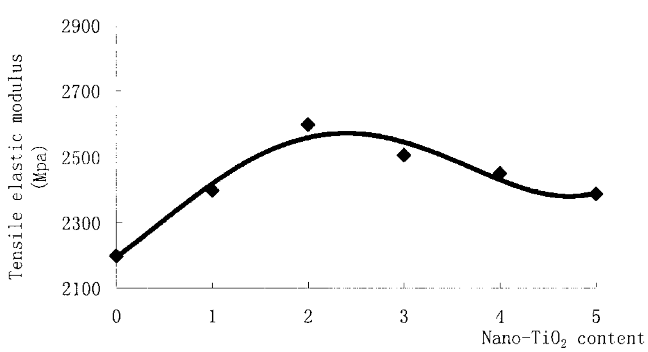


Figure 3 Effect of nano-TiO_2 content on tensile elastic modulus of HIPS/ nano-TiO_2 nanocomposites.

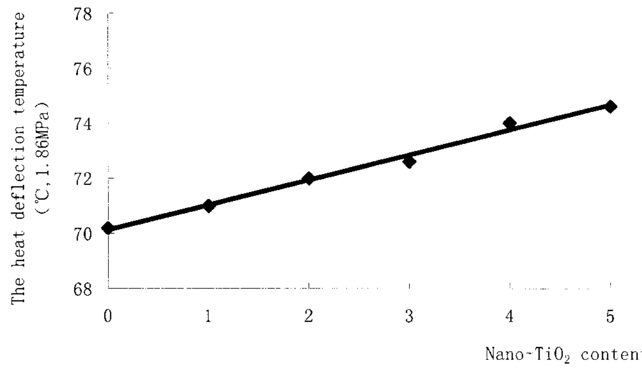


Figure 4 Effect of nano-TiO_2 content on the heat deflection temperature of HIPS/nano-TiO_2 nanocomposites.

as follows: When nano-TiO_2 is <2%, the high modulus of nano-TiO_2 plays major role and increased the tensile elastic modulus of the nanocomposites. When the nano-TiO_2 content is >2%, the volume fraction of soft interfacial layer of nanocomposites increases, resulting in lower stress for the nanocomposites.[12,13] Therefore, the tensile elastic modulus of the nanocomposites is somewhat decreased.

Thermal resistance

The heat deflection temperature may be taken as the material ultimate use point for a short period of time. The heat deflection temperatures for HIPS/nano-TiO_2 nanocomposites with different nano-TiO_2 contents are reported in Figure 4. A significant enhancement of the heat deflection temperature occurs with increasing nano-TiO_2 content. This behavior was expected because inorganic nano-TiO_2 has high thermal stability.[14]

Flammability

HIPS itself is not a flame-retardant material, so its application is limited. The rates of burning obtained for pure HIPS and nanocomposites with 3% nano-TiO_2 are shown in Table II. The presence of nano-TiO_2 reduced the HIPS rate of burning to ~30%.

Rheology

The relationship between viscosity and shear rate of HIPS/nano-TiO_2 nanocomposites is shown in Figure 5. The rheological behavior of HIPS/nano-TiO_2 nano-

TABLE II
Effect of Nano-TiO_2 on the Burning Rate of HIPS

Sample	Burning Rate (cm/min)
HIPS	11.0
HIPS/nano-TiO_2	8.0

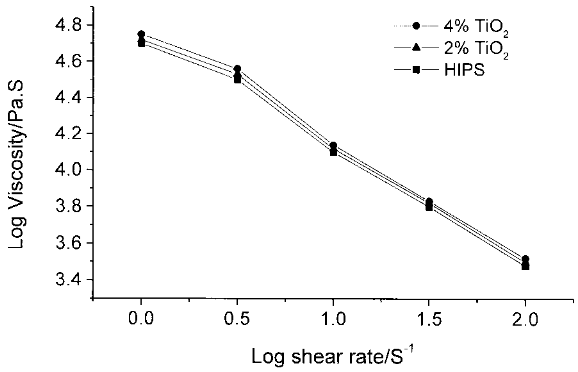


Figure 5 The relation between viscosity and shear rate of HIPS/nano-TiO_2 nanocomposites: (A) one-step method; (B) two-step method.

composites is similar to that of HIPS. All polymers exhibit pseudoplastic characteristics because the viscosity of these polymers decreases with shear rate. The addition of nano-TiO_2 promotes a slightly higher viscosity of HIPS.

Manufacturing technology

With very small size and very high surface energy, nano-TiO_2 easily agglomerates to large particles. If nano-TiO_2 did not disperse into the HIPS matrix effectively and evenly, we would only get microscale composites and achieve HIPS with poor mechanical properties. There are many factors that influence nanoparticle dispersing into the matrix. In this paper, the effect of one-step manufacturing (directly blend) and two-step (nano-TiO_2 master batch prepared first and then blended with HIPS again) technology on the properties of HIPS/nano-TiO_2 nanocomposites was studied. HIPS/nano-TiO_2 nanocomposites prepared by the two-step method have better mechanical properties than those prepared by the one-step method, as shown in Table III.

SEM photograph of HIPS/nano-TiO_2 nanocomposites prepared by the different manufacturing methods are shown in Figure 6. Comparison of the results in Figures 6A and 6B indicate that the size of the TiO_2 particle is smaller and the distribution of TiO_2 is more uniform with the two-step than with the one-step method.. Because of the agglomeration noted with the one-step method (Figure 6A), the size of TiO_2 is large and the distribution of TiO_2 is uneven. Agglomerated particles and uneven dispersion do not improve the mechanical properties of composites.[15] It is clear that the composite manufactured by the two-step method will have better mechanical properties than that prepared by the one-step method.

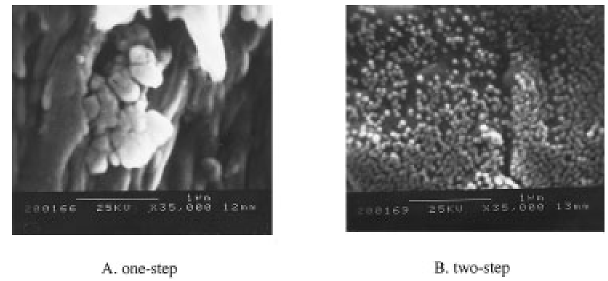


Figure 6 SEM photograph of HIPS/nano-TiO_2 nanocomposites.

CONCLUSIONS

HIPS/nano-TiO_2 nanocomposites were prepared by pretreating the surface of nano-TiO_2, selecting a special structure dispersing agent (TAS), and using two-step manufacturing technology. The notched impact strength., tensile strength, and tensile elastic modulus of HIPS/nano-TiO_2 nanocomposites increased to its maximum when nano-TiO_2 content was 2% and then decreased with addition of more nano-TiO_2. The nano-TiO_2 has both toughening and reinforcing effects on HIPS when nano-TiO_2 content is 2%. The heat deflection temperature and flame retardancy of HIPS/nano-TiO_2 nanocomposites are also obviously improved as nano-TiO_2 content is increased. Manufacturing technology also has obvious effects on the mechanical properties of HIPS/nano-TiO_2 nanocomposites; that is, the nanocomposites manufactured by the two-step method have better mechanical properties than those prepared by the one-step method. Analysis of the rheological behavior of HIPS/nano-TiO_2 nanocomposites indicates that the nanocomposites are still non-Newtonian and pseudoplastic fluids. The comprehensive performance of HIPS/nano-TiO_2 nanocomposites is better than that of HIPS alone, so the nanocomposites are useful for a wide range of applications.

TABLE III
Effect of Manufacturing Technology on Mechanical Properties of HIPS/Nano-TiO_2 Nanocomposites

Mechanical Properties / Manufacturing Technology	Notched Impact Strength (KJ/m^2)	Tensile Strength (MPa)	Tensile Elastic Modulus (Gpa)
One-step	10.8	29.6	2.4
Two-step	12.2	32.6	2.6

References

1. Grocela, T. A.; Nauman, E.B. Polymer 1993, 34, 2315.
2. Gleiter, H. Adv Mater 1992, 4, 474.
3. Novak B.M. Adv Mater 1993, 5, 422.
4. Komarmaerni, S. J Mater Chem 1992, 2, 1219.
5. Kornmann, X.; Berglung, L.A.; Sterte, J.; Glannelis, E. P. J Polym Eng Sci 1998, 8, 1351.
6. Calvert, P.; Burdon, J. Polym Mater Sci Eng 1994, 70, 224.
7. Karokawa, Y.; Yasuda, H.J. Mater Sci Lett 1996, 15, 1481.
8. Sumita, M.; Tsukumo, Y. J Mater Sci 1993, 18, 1758.
9. Nakagawa, H.; Sano, H. Polym Prep (Am Chem Soc, Div Polym, Chem) 1992, 26, 249.
10. Mareri, P.; Bastide, S.; Binda, N.; Crespy, A. Compos Sci Technol 1998, 58, 747.
11. Shang, S.W.; Willams, J.W.; Soderholm, K.J.M. J Mater Sci 1994, 29, 2406.
12. He, D.; Jiang, B. J Appl Polym Sci 1993, 49, 617.
13. Sahnouh, E.F.; Lopez-Cuesta, F.; Crespy. A. J Mater Sci 1999, 34, 535.
14. Pastouini, M. T. Nunes, R. C. R. J Appl Polym Sci 1999, 74, 1361.
15. Cook, D. G. Rudin, A. Plumtree, A. J Appl Polym Sci 1993, 48, 75.