

Sharkskin Mechanism of High-Impact Polystyrene (HIPS) and Rheological Behavior of HIPS/TiO₂ Composites

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Received 21 January 2004; accepted 9 August 2004

DOI 10.1002/app.21517

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The rheological behaviors of high-impact polystyrene (HIPS) and HIPS/TiO₂ composites were investigated by use of a rheometer in the present article. HIPS exhibited a constant critical stress of the sharkskin in various temperatures, and the analysis indicated that the mechanism of sharkskin of HIPS was wall-slip and its special temperature dependency was determined by weak wall-melt adsorption. The experimental results also showed that the introduction of TiO₂ into HIPS only slightly influenced the apparent viscosity (η_a) of the composites. Moreover, TiO₂ exhibited an unusual effect on the non-Newtonian index of

the composites at high shear rate. Both phenomena indicated the increase of inner free volume induced by TiO₂ in molecularly rigid HIPS. Moreover, it was noteworthy that a featured stress could be used to label the dispersion of TiO₂ in the HIPS matrix, and the numeric affinity of this featured stress and the critical stress of sharkskin revealed that both processes were relevant to the same molecular relaxation. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 802–807, 2005

Key words: agglomerates; composites; dispersions; rheology; unsteady flow

INTRODUCTION

The unsteady flow of linear polymers with high viscosity and high molecular entanglement, such as high-density polyethylene (HDPE)¹ and ultrahigh molecular weight polyethylene (UHMWPE),² has long been the focus of rheological researches. Now it is believed that the macroscopic unsteady flow behaviors, the heavy one as melt fracture and the slight one as sharkskin, are relevant to the substantial vibration between various boundary conditions in the melt-wall interface. Although appearing like a pure interfacial phenomenon, the process of “wall-slip” under slip boundary conditions involves the molecular relaxation of the polymer melt. Wang³ calculated in detail the period time of sharkskin from the regular surface distortion of low-density polyethylene (LDPE) extrudate, and found the period time was proportional to relaxation time of molecules in the bulk melt. The same magnitude of these two feature times provided sufficient evidence to prove the molecular mechanism of the sharkskin.

Filled polymer composites, another focus of rheological research, are characterized by the evolution of the structure of the dispersed phase in the melt flow.

A filler/polymer system displays a rather complex rheological behavior because both the dispersed phase (inorganic particle) and continuous phase (polymer) possess both independent flow structure and flow mechanism, as well as their complex interaction. The influence of filler agglomerate on rheological behavior usually showed as “solidlike” behaviors and “yielding” of the melts.⁴ Also, filler particles, particularly those in nanoscale,^{5–7} had a notable effect on the molecular mobility of polymer molecules. Until now, the segment and dispersion of filler agglomerates have long been investigated in the mesoscopic scale; for example, the effect of stress distribution on dispersion of fillers in the melt was studied in detail.^{8,9} However, the molecular mechanism of the dispersion of fillers in the melt has not yet been studied, although the dispersion of the fillers in nanoscale was obviously involved in the relaxation of molecular chains of the polymer.

In this article, the rheological behaviors of high-impact polystyrene (HIPS)/TiO₂ composites were investigated. Nanoscaled TiO₂, a functional filler attractive to industry for its promising properties in light catalyst and UV light shielding,¹⁰ was introduced into polymer to prepare the functional composites. However, the exhibition of the special properties of TiO₂ in the final products was determined by its dispersion status in the polymer matrix. In dual focus of our research was the influence on the viscosity of TiO₂ in nanoscale and its dispersion in the flow. In subsequent discussion, it was revealed that the sharkskin behavior

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Contract grant sponsor: Chinese National Foundation of Natural Science; contract grant number: 50273016.

of pure HIPS and the dispersion of TiO₂ in HIPS/TiO₂ composites possessed the same molecular mechanism.

EXPERIMENTAL

High-impact polystyrene [HIPS, 466F type; 5–10 wt % content of butadiene, melt flow index (MFI) 4.80 g/10 min] was commercially obtained from Yangzi-BASF Company (Nanjing, China). Polystyrene (PS; MFI 9.04 g/10 min) was supplied by Lanzhou Petrochemistry Co. (Lanzhou, China). LDPE (MFI 2.25 g/10 min) was commercially obtained from Qilu Petrochemistry Co. (Zibo City, China). Nano-TiO₂ was provided by Qingdao Haier-keda Nano Technology Co. (China), whose average primary particle size was 80 nm. A copolymer of ethylene and vinyl acetate (EVA, 334N type) was commercially obtained from Leuna GmbH (Leuna, Germany).

HIPS and TiO₂ were first subjected to high-speed mixing, after which the mixture was extruded in a two-screw extruder (ZKS-25 type; Krupp Werner & Pfleiderer GmbH, Stuttgart, Germany), to yield HIPS/TiO₂ composites.

Measurements of the Charpy and Izod impact strengths of the composites were conducted according to ASTM D256 on an API-type impact tester (Atlas Electric Devices Co., Chicago, IL). The rheological behaviors of the materials were measured using a Rosand Precision rheometer (now Bohlin Instruments, Cirencester, UK) in the double-bore experiment mode. The *L/D* ratio of the capillary in one bore was 16/1, and the orifice die in another bore was zero length capillary. The experiments were carried out at four temperatures, 190, 200, 210, and 220°C, respectively, while the piston velocities were maintained at constant levels. Experimental results were processed by the software provided by Bohlin Instruments, and all the rheological data obtained were subjected to calibration by use of Bagley and Rabinowitch corrections.

The glass-transition temperatures (*T_g*) of composites were measured on a DSC cell (Netzsch-Gerätebau GmbH, Bavaria, Germany), from room temperature to 200°C, in increments of 6 K/min, determined by the software provided by Netzsch-Gerätebau.

RESULTS AND DISCUSSION

Molecular mobility and sharkskin mechanism of HIPS

HIPS was a grafted copolymer with the flexible main chain of polybutadiene and the rigid branch chain of polystyrene. Commonly, it was prepared by the solution polymerization of styrene in the presence of polybutadiene. In the synthesis most of the polystyrene chains were grafted onto the polybutadiene main chains, to form a grafted molecular structure. In our

TABLE I
Comparison of Flow Active Energies

Material	LDPE	PS	HIPS
$E_{\eta}^{(\gamma)}$, kJ/mol	49.4	73.3	80.5
$E_{\eta}^{(\sigma)}$, kJ/mol	105.7	290.5	240.2

experiment, the molecular mobility of the HIPS, the polymer with a long branched chain, was characterized by its activation energy of the flow.

However, the zero-shear viscosity could not be determined directly in the rheological tests, and thus the activation energies were calculated from the apparent viscosities at different temperatures while keeping the shear rate or the shear stress constant, respectively. Values of activation energy under identical shear rate, $E_{\eta}^{(\gamma)}$, and the activation energy under identical shear stress, $E_{\eta}^{(\sigma)}$, are shown in Table I. From the comparison it was concluded that HIPS possessed a molecular mobility similar to that of PS. Compared to LDPE, the rather high activation energy of HIPS revealed that HIPS was a rigid polymer and its molecular mobility of HIPS was mainly affected by the long branched chains of polystyrene.

In capillary extrusion, the extrudate of HIPS exhibited a continuous change with shear rate. At low shear rates, the extrudate was smooth and transparent; a higher shear rate started the unsteady flow in the form of sharkskin. The onset of sharkskin was determined according to the surface of the extrudate. Figure 1 shows the dependency of these critical points on temperature. Obviously the critical stress remained almost the same under various experimental temperatures. As has been well established, stress initiation is the characteristic of wall-slip, and it was found in the study on the unsteady flow of HDPE that the critical stress of wall-slip was linearly correlated with the temperature.¹¹ Although dissimilar with each other in appearance, the analysis based on the single-layered Langmuir adsorption indicated that the HIPS sharkskin mechanism was also actually "wall-slip" and the difference between the dependencies on temperature of critical stress of HIPS and HDPE could be attributed to the disparate melt-wall adsorptions.

According to de Gennes' theory¹² on the sliding on the melt–solid interface, the critical stress of wall-slip may be expressed as

$$\sigma_c = \nu K_B T / N_e^{1/2} \alpha$$

where ν is the number density of molecular chains adsorbed in the interface and $N_e^{1/2} \alpha$ is the distance of disentanglement.

Wang³ believed ν of HDPE would remain unchanged with changes in temperature, which could be

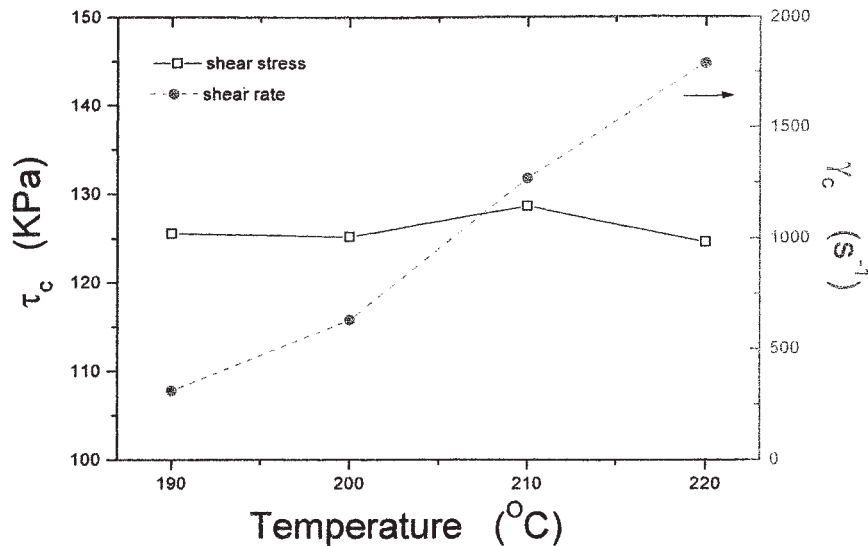


Figure 1 Critical points of the sharkskin of HIPS.

a reasonable hypothesis for the strong interface adsorption of HDPE on the capillary wall. Therefore the saturated adsorption of molecular chains could be maintained during increasing temperature. Thus HDPE showed a linear temperature dependency on critical stress.

Given the common case of single-layered adsorption, the percentage area occupied by the adsorbed chains in the wall–melt interface is expressed as

$$\theta = bv_0 / (1 + bv_0)$$

where v_0 is the number density of molecular chains in the bulk melt and b is the parameter indicating the intensity of adsorption.

In the case of strong interface adsorption, for example HDPE melt and capillary wall, it followed $bv_0 \gg 1$, so $\theta = 1$, indicating the saturated adsorption of molecular chains. Therefore the wall–slip under strong interface adsorption was characterized by the linear temperature dependency of the critical stress.

In the case of weak interface adsorption, $bv_0 \ll 1$, so $\theta = bv_0$. By substituting $\theta = bv_0$ and the Arrhenius equation into eq. (1), it follows that

$$\sigma_c = q_0 e^{-E_a/RT} v_0 K_B T / (N_e^2 \alpha) = K_0 T e^{-E_a/RT}$$

Because $e^{-E_a/RT}$ in eq. (3), the simple differential calculation revealed $d\sigma_c/dT = 0$. The above analysis indicated that the wall–slip under weak interface adsorption was characterized by the constant critical stress in the temperature change. The interface of HIPS melt and capillary wall in our study was a qualified example of weak adsorption.

The above analysis indicated that the sharkskin of HIPS was identical to that of HDPE, an interface phenomenon, but also influenced by the characteristic of bulk polymer. Although the absorption conditions were different, both the sharkskin of HIPS and HDPE were relevant to the desorption of molecular chains from the flow–wall (wall–slip) and the recovery of the absorbed molecular layer. The corresponding relaxation in the conformational level was the recycling between coil-like conformation and the stretched one of the polymer molecules. Such a molecular relaxation could occur not only in the bulk interface of flow–wall and polymer melt, but also in the inner interface of the melt of the multiphase polymer system. Thus the dispersion of fillers in the flow ought to be substantially influenced by the presence of this molecular relaxation.

Influence of nano-TiO₂ filler on the rheological behaviors of the composites

Recent research of nano/rigid polymer composites¹³ showed that the introduction of a nanoscaled dispersion phase into the rigid polymer matrix could promote the increase of inner free volume. Figure 2 shows the DSC curves of HIPS/TiO₂ composites and pure HIPS. The T_g of pure HIPS was 96.3°C, whereas the T_g of HIPS/TiO₂ composite with 1.0 wt % TiO₂ was 97.2°C. The 0.9°C difference in T_g provided sufficient proof of the increase of inner free volume in the HIPS/TiO₂ composite. Thus nano-TiO₂ was not a simple inert filler, and the molecular mobility of HIPS had been influenced by its introduction.

At the macroscopic level, the increase of inner volume resulted in the enhancement of the toughness of

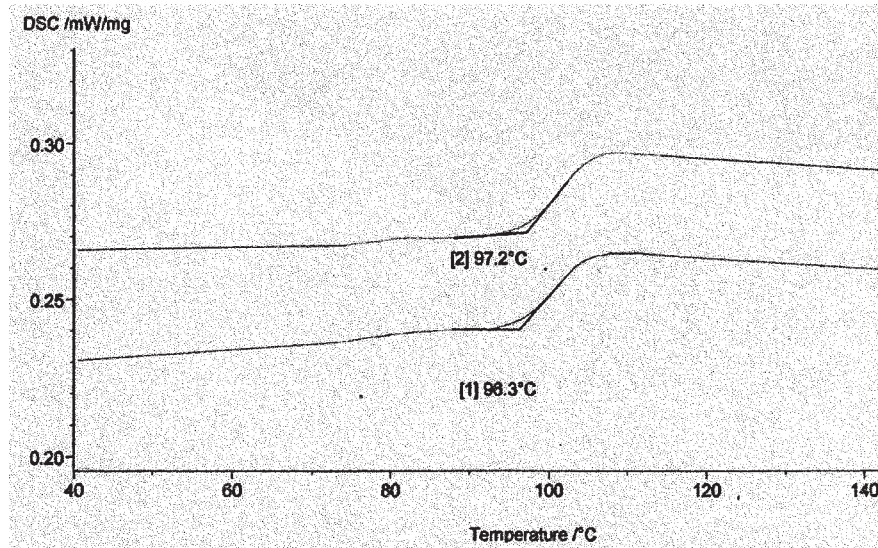


Figure 2 DSC curves of HIPS/TiO₂ composites to indicate the T_g : (1) for HIPS/TiO₂ composite with 1.0 wt % TiO₂; (2) for pure HIPS.

HIPS/TiO₂ composites. As shown in Figure 3, both the Charpy impact strength and the Izod impact strength of the composites with low nano-TiO₂ loadings were higher than those of pure HIPS. The toughening effect of the nano-TiO₂ verified again the increase of inner volume.

Therefore the rheological behaviors of nanoscale filler/rigid polymer composites were affected mainly by two factors. As the first, the introduction of inorganic fillers could induce the increase of inner free volume, which was the factor leading to the decrease of apparent viscosity. On the other hand, the inert volume effect of fillers could result in the increase of melt viscosity, provided that the melt of the composites was regarded as a suspending sys-

tem. These two volume effects could spontaneously influence the rheological behavior of the composites.

The flow curves of HIPS/TiO₂ composites are shown in Figure 4. All the melts exhibited typically pseudoplastic flow behavior; the linear regulation between the apparent viscosity and shear rate was distinct enough. Also, the apparent viscosities were influenced only slightly by nano-TiO₂ content. The flow curves overlapped with each other when nano-TiO₂ weight content varied within a wide range, from 0 to 28%. Thus a slight increase in viscosity was clearly attributed to the special inner free volume increase that resulted from the nanoscaled dispersion of TiO₂ in the rigid HIPS matrix.

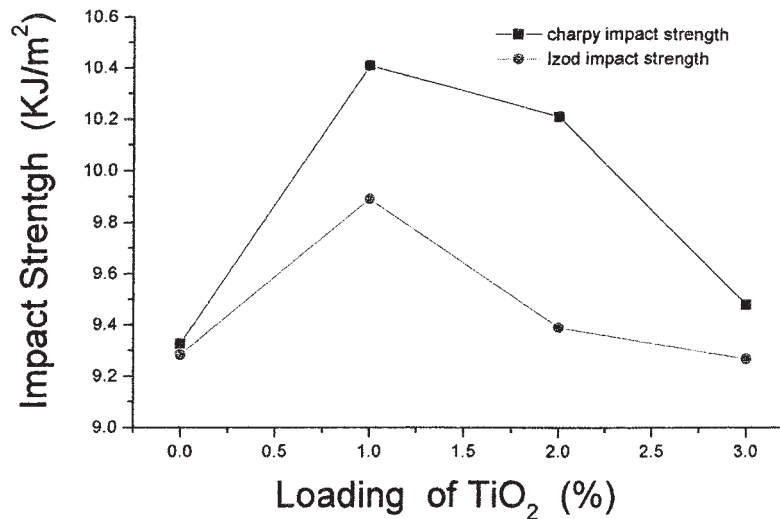


Figure 3 Impact strength of HIPS/TiO₂ composites.

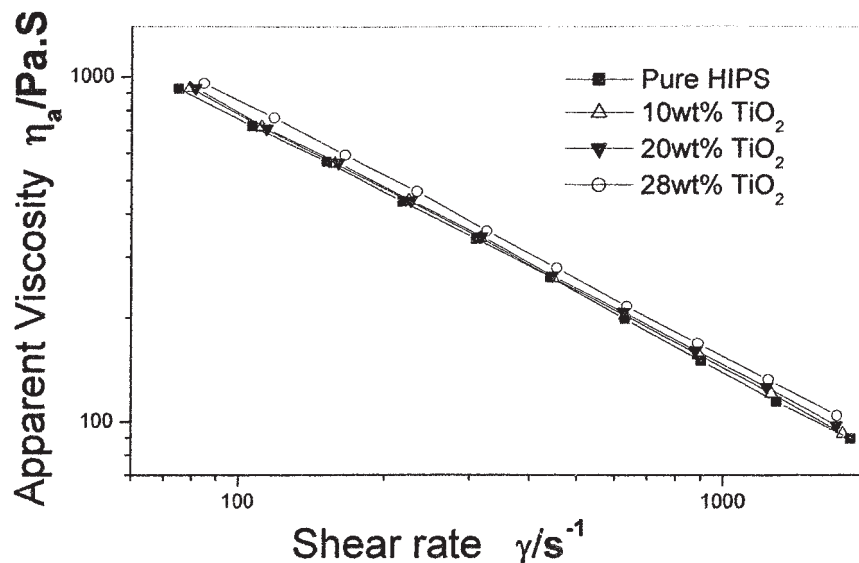


Figure 4 Flow curves of HIPS/TiO₂ composites.

The program provided with the Bohlin Instruments Rosand Precision rheometer could also provide the non-Newtonian indices at different shear stresses. As shown in Figure 5, the non-Newtonian indices of the composites decreased with shear stress, which is a normal phenomenon in pseudoplastic fluids. The non-Newtonian index of HIPS decreased from 0.31 to 0.21 with the shear stress, whereas the presence of nano-TiO₂ in composites lessened the variation range. There was an intersection point of the index curves at about 120 kPa. At low shear stress before the intersection point, the non-Newtonian indices of composites decreased with increasing nano-TiO₂ content, where the changing tendency of the index with filler loadings was the same as that with common filled polymer

system. However the nano-TiO₂ loadings exhibited an abnormal influence on the non-Newtonian indices at higher shear stress. The introduction of nano-TiO₂ could increase non-Newtonian index of the composites, and a continuous decrease of the non-Newtonian index with TiO₂ occurred. For the composite with high nano-TiO₂ content composites (28 wt %), the non-Newtonian index remained nearly constant over the whole range of shear stress.

Usually, the presence of inorganic filler in composites could increase the non-Newtonian rheological characteristic of the melt of a filled polymer system and lead to a decrease of the non-Newtonian index.⁴ The abnormal influence of nano-TiO₂ on the non-Newtonian index at high shear stress is likely attrib-

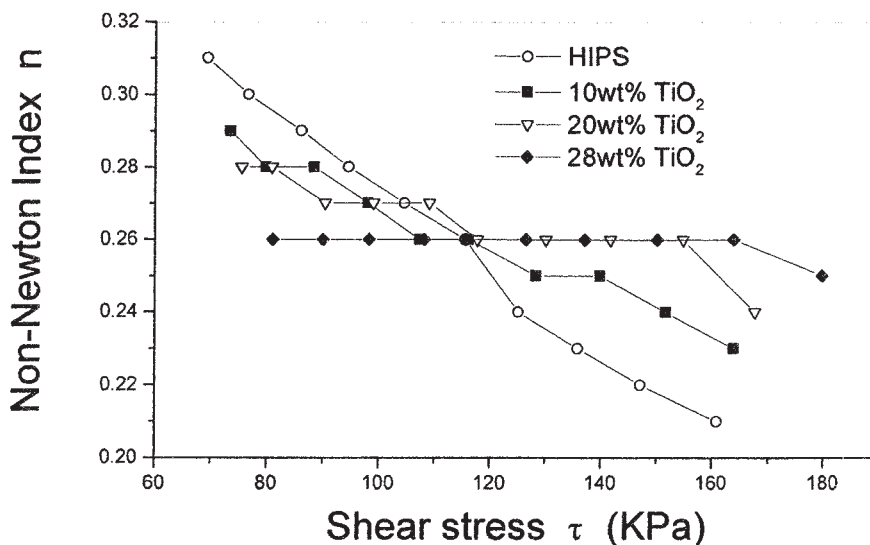


Figure 5 Dependency of non-Newtonian indices of HIPS/TiO₂ composites on shear rate.

utable to the increase of the inner free volume brought about by the nano-TiO₂ filler phase.

Before and after the intersection point in Figure 5, nano-TiO₂ exerted a contrary influence on the non-Newtonian indices of the composites, which was supposed to be a result of the quite different dispersed forms of nano-TiO₂. Because of the inadequate dispersive mixing, TiO₂ dispersed in the form of particle agglomerates in the HIPS matrix at low shear rate. With increasing shear rate, the agglomerates of TiO₂ were gradually destroyed by the shear in the flow. Concomitantly with the decreasing dimension of the dispersed units, nano-TiO₂ could exert its special effect of increasing inner free volume in molecular rigid HIPS, and so performed the abnormal influence on the non-Newtonian indices of the melts. The above analysis showed the point at 120 kPa could be used to label the fine dispersion of TiO₂.

Moreover, the numeric affinity between the intersection point and the critical point of wall-slip at 125 kPa indicated the filler dispersion was influenced by the same molecular mechanism with the wall-slip. The coil-stretch relaxation of the molecular chains would occur in the wall-melt interface, as well as the inner interface between filler particles and melt. Thus, the sharkskin and dispersion of fillers were both influenced by this molecular relaxation.

CONCLUSIONS

In the present article, the rheological behaviors of HIPS were investigated with a capillary rheometer and the temperature dependency of the critical stress for the sharkskin of HIPS was analyzed based on the single-layered Langmuir adsorption. It was demonstrated that the temperature dependency was determined by the weak wall-melt adsorption condition. In

further study, the rheological behaviors of HIPS/TiO₂ composites were investigated, and the results showed that the introduction of nano-TiO₂ into HIPS influenced the apparent viscosity of composites to only a slight extent, indicating that the nano-TiO₂ dispersion phase could promote the unique effect of increasing inner free volume. Compared to apparent viscosity, the index could be a more sensitive parameter to reflect the structure changing in the flow. Moreover, a featured stress in the non-Newtonian index curves was found to label the dispersion of TiO₂. The numeric affinity of the featured stress and the critical stress of sharkskin linked the sharkskin with the dispersion of TiO₂ together by the same molecular mechanism.

We thank the Chinese National Foundation of Natural Science (contract number 50273016) for financial support.

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