

Effects of Nano TiO₂ on the Light Reflectivity, Morphology, and Rheological Behavior of LLDPE-Glass Bead Composites

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ABSTRACT: Heat-shield composites based on linear low density polyethylene (LLDPE) filled with micro-hollow glass beads (HGB) and TiO₂ nanoparticles were prepared through melt compounding. Two kinds of LLDPE were used as the matrix of these composites with a fixed weight ratio of 60 : 40. HGB loadings were fixed at 28 wt % of LLDPE matrix while TiO₂ content varied between 8 and 28 wt % of LLDPE matrix. Interestingly, the results show with addition of TiO₂ to LLDPE-HGB composites, both the light reflectivity and the flow ability of composites show great enhancement. Especially when the TiO₂ loading is 14 wt % of LLDPE, UV, and infrared reflectivity of the composites are more than 90%, showing a optimal heat-shielding performance, and the rheo-

logical responses including the storage modulus, G' and the complex viscosities, $|\eta^*|$ of this composite are the lowest among all LLDPE/HGB composites. When TiO₂ content is more than 14 wt %; however, ultraviolet radiation resistance is almost unchanged while that two dynamic rheological parameters increase gradually. It is proposed that the TiO₂ loading of 14 wt % should be taken as the optimal value of a light reflectivity in LLDPE matrix, which is helpful in improving the processing ability by reduction in melt viscosity. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E644–E650, 2012

Key words: polyethylene; nanoparticles; composites; light reflectivity; dynamic rheological behavior

INTRODUCTION

Heat-shield materials with outstanding resistance to infrared and UV light are often composed of a large percentage of organic or inorganic reflecting materials, heat insulating materials, and the polymer matrix. Because of the important practical significance and wide application prospects in heat preservation, energy conservation, and emission reduction, those materials have attracted great interest recently. Polymer composites are the most popular heat-shield materials due to its excellent processability and low cost.

TiO₂ is a kind of widely-used filler in polymer heat-shield composites because it has a higher refractive index than any other white pigment, as well as good chemical stability. Several studies have reported the optical performance of TiO₂ in some fields.^{1–4} Liu et al.⁵ has reported that the incorporation of nano-TiO₂ can effectively improve the resistance to heat and ultraviolet irradiation of the nano SiO₂ and TiO₂ filled linear low density polyethylene (LLDPE)/low density polyethylene (LDPE) composites.

Hollow glass beads (HGB) are also used widely as fillers in some cellular composites with environmental functions (e.g., thermal insulation, vibration-proof, and sound insulation) for its many advantages such as relatively low density, heat and sound insulation, relatively even distribution in the matrix, and large surface area.⁶ Polymer/hollow microsphere composites can generally provide good thermal and sound insulation, low-density, and good mechanical properties.⁷

However, the introduction of normal light reflectivity fillers and heat insulating materials not only improves the optical and thermal properties, but greatly increases the viscosities of these systems, which makes it difficult for processing. Therefore, the melt rheological behavior and processing characteristics of polymer heat-shield material are very different from conventional compounds and the polymer matrix. Additionally, melt rheological behavior and processing characteristics primarily depend on the nature, formula and dispersion states of various components in the polymer matrix.

In this article, for the first time, we report the preparation of nano TiO₂ and micro hollow glass bead filled LLDPE heat-shield composites with outstanding resistance to infrared and UV light by melt compounding method. The correlativity between light reflectivity, morphology, and rheological behavior was brought forward and we obtained an

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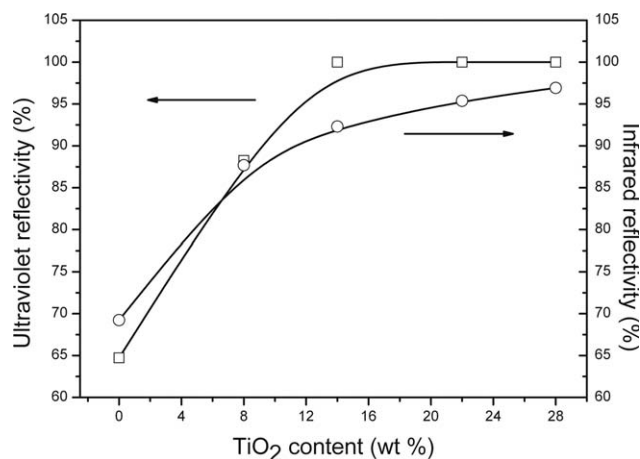


Figure 1 Ultraviolet and infrared reflectivity versus TiO₂ content for LLDPE-HGB-TiO₂ composites.

optimal value of TiO₂ loading for LLDPE matrix with excellent light reflectivity and low viscosity.

EXPERIMENTAL

Material

LLDPE-1 (DNDA-7042, density 0.922~0.928 g/cm³, melt flow rate 20.2~20.4 g/10 min) and LLDPE-2 (DNDA-7144, density 0.918~0.922 g/cm³, melt flow rate 1.6~2.4 g/10 min) were both purchased from Maoming Petroleum Chemical Industry. Commercially available TiO₂ (VK-T06S) with an average particle diameter of 20~25 nm was purchased from Hangzhou Wan Jing New Material and micro hollow glass bead (QH-550) with a diameter of 20–85 μm and a volume weight of 0.10–0.12 g/cm³ was purchased from Qinhuangdao Qinhuang Glass Microsphere. Titanate coupling agent (SG-BTP) was produced by Nanjing Shuguang Chemical Factory of China.

Sample preparation

The micro hollow glass bead (HGB) and nano titanium dioxide (nano TiO₂) were, respectively, treated with 2 wt % titanate coupling agent in a mixer and then dried in a vacuum oven overnight. Titanate coupling agent was prepared like this: (1) About 3 g titanate was added to 100 g ethyl alcohol and the solution was stirred until titanate was equably dispersed; (2) then ethylic acid was used to adjust the PH value of the solution to 4~6 to obtain the final titanate coupling agent. Then, the pretreated HGB and TiO₂ particles were compounded with LLDPE in a Haake chamber at 190°C, 50 rpm for 8 min. After that, obtained materials were hot pressed by compress machine at 190°C for 5 min at 0.5 MPa to obtain sheets with a size of 100 × 100 × 0.8 mm³. Samples used for dynamic rheological behavior test

were prepared at the same condition with a diameter of 25 mm and a thickness of 1.8 mm. For all the LLDPE-HGB-TiO₂ composites, the weight ratio of LLDPE-1/LLDPE-2 was fixed at 40/60. TiO₂ contents varied between 8 and 28 wt % of LLDPE matrix and HGB contents were fixed at 28 wt % of LLDPE matrix. In the following part of this article, the unfilled matrix is labeled as LLDPE while the composites are denoted as LLDPE followed by the name of filler and corresponding mass fraction of the LLDPE (wt %). For example, LLDPE-HGB-TiO₂ (8 wt %) indicates a LLDPE composite filled with 8 wt % TiO₂ and 28 wt % HGB of LLDPE.

Measurements

After cryogenic fracture in liquid nitrogen, the fracture surfaces were sputter-coated with a thin gold layer to make samples electric conductive and avoid the charge accumulated, and then observed in a JEOL JSM-5900LV SEM instrument, with an acceleration voltage of 20 kV.

UV and infrared reflectivity tests were conducted by using a recorder for the measurement of material refraction, temperature and radiation which was gained from Ningbo Dongnan Instrument. The size of samples size was 100 × 100 × 0.8 mm³. Three ultraviolet light lamps ZWSZ30 (10 W, wavelength 250 nm, Xiangcheng District Innovation Lightening Electrical Appliance Factory, Suzhou) were used as the UV radiation source. Samples were placed at a distance of 250 mm to the radiation source. An infrared lamp (150 W, wavelength 850 nm, Dongguan Yimai Science and Technology) was used as the infrared light radiation source, and the samples were placed at a distance of 200 mm to it.

Dynamic rheological tests were conducted by a Rheometer (AR 2000EX, TA Instruments, USA) in parallel plate configuration at a temperature of 190°C. Plates with a diameter of 25 mm and a thickness of 1.8 mm were chosen for these tests. Strains between 0.1 and 10% were imposed to the samples while the frequency range was varied between 0.01 and 100 Hz.

RESULTS AND DISCUSSION

Light reflectivity

Figure 1 shows the ultraviolet and infrared reflectivity versus TiO₂ content for sheet samples of LLDPE-HGB-TiO₂ composites. It shows that nano TiO₂ has a significant effect on the light reflectivity of the composites, especially when the TiO₂ loading is less than 14 wt % of the LLDPE matrix, and both ultraviolet reflectivity and infrared reflectivity increase sharply to above 90%. After that, both kinds of reflectivity increase slowly with TiO₂ contents, especially for

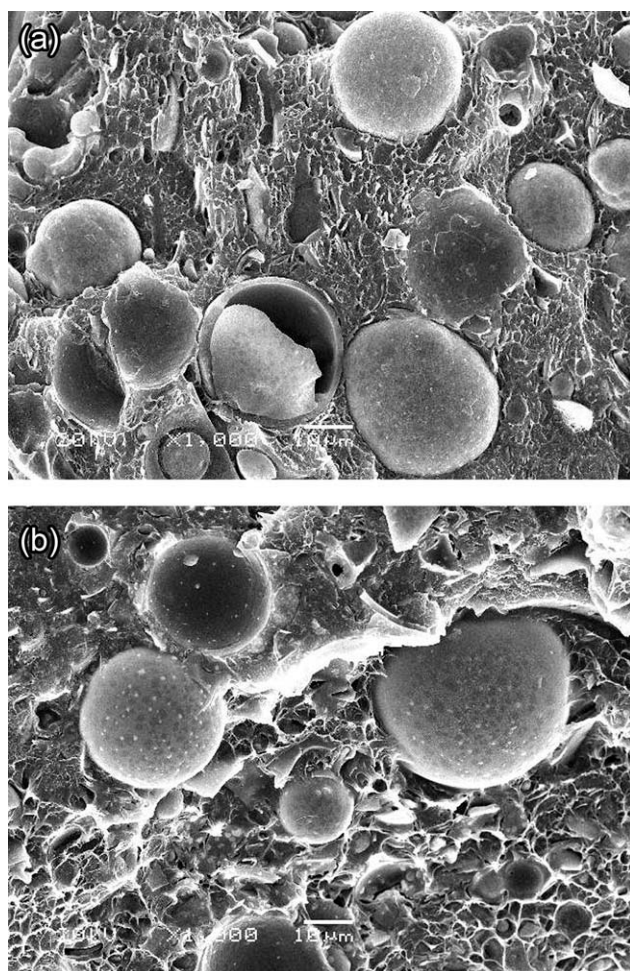


Figure 2 SEM images of the fractured surface of the HGB and nano TiO₂ filled LLDPE composites ($\times 1000$): (a) LLDPE-HGB (28 wt %); (b) LLDPE-HGB (28 wt %)-TiO₂ (8 wt %).

ultraviolet reflectivity. For the LLDPE-HGB-TiO₂ composites of interest here, the reflectivity of UV and infrared increase greatly when TiO₂ content is less than 14 wt % of the LLDPE matrix, which should be attributed to the addition of TiO₂ and the increasing concentration and dispersion of TiO₂ aggregates. With increasing in particle size, the ability of the particle to scatter light increases up to a maximum and then decreases.⁸ When TiO₂ content is up to 14 wt %, the size and dispersion of TiO₂ aggregates come to an optimal value for light reflectivity, as shown in Figure 3. When TiO₂ content is higher than 14 wt %, TiO₂ aggregates tend to increase in size but show no obvious increase in the dispersion state in the matrix. Therefore, both kinds of reflectivity tend to level off. Thus, the TiO₂ loading of 14 wt % can be taken as the optimal value for light reflectivity of LLDPE.

Morphology

Figure 2 shows the SEM images of LLDPE-HGB and LLDPE-HGB-TiO₂ (8 wt %) composites. Clear differ-

ences in the dispersion and surface texture of HGB particles between the two composites are seen. For LLDPE-HGB composites shown in Figure 2(a), the surface of HGB particles is smooth and some HGB particles are crushed. Besides, gaps between HGB particles and the matrix in LLDPE-HGB composites are not obvious, which indicates a good interfacial interaction between them owing to the interfacial treatment by titanate coupling agent.⁵ From Figure 2(b), however, visible white spots can be seen on the surface of HGB particles for LLDPE-HGB-TiO₂ composites. Additionally, relatively more concaves than Figure 2(a) resulting from the shedding of HGB are observed. It can be inferred that a certain amount of TiO₂ particles adhere to the surface of HGB particles, restricting the interactions between HGB particles and the polymer matrix.

In Figure 3(a), since the microscope is on a magnification of 30,000, the viewing range is far smaller than that of the volume of HGB particles, thus only a homogeneous matrix phase is observed. The white spots in Figure 3(a) are slightly stretched polymer

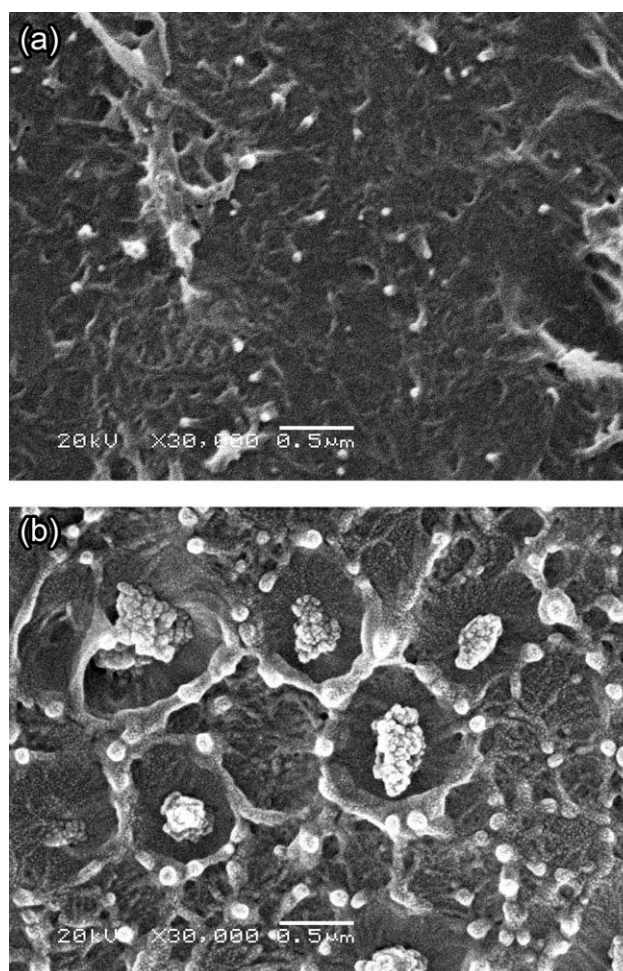


Figure 3 SEM images of the fractured surface of HGB and nano TiO₂ filled LLDPE composites ($\times 30,000$): (a) LLDPE-HGB (28 wt %); (b) LLDPE-TiO₂ (14 wt %).

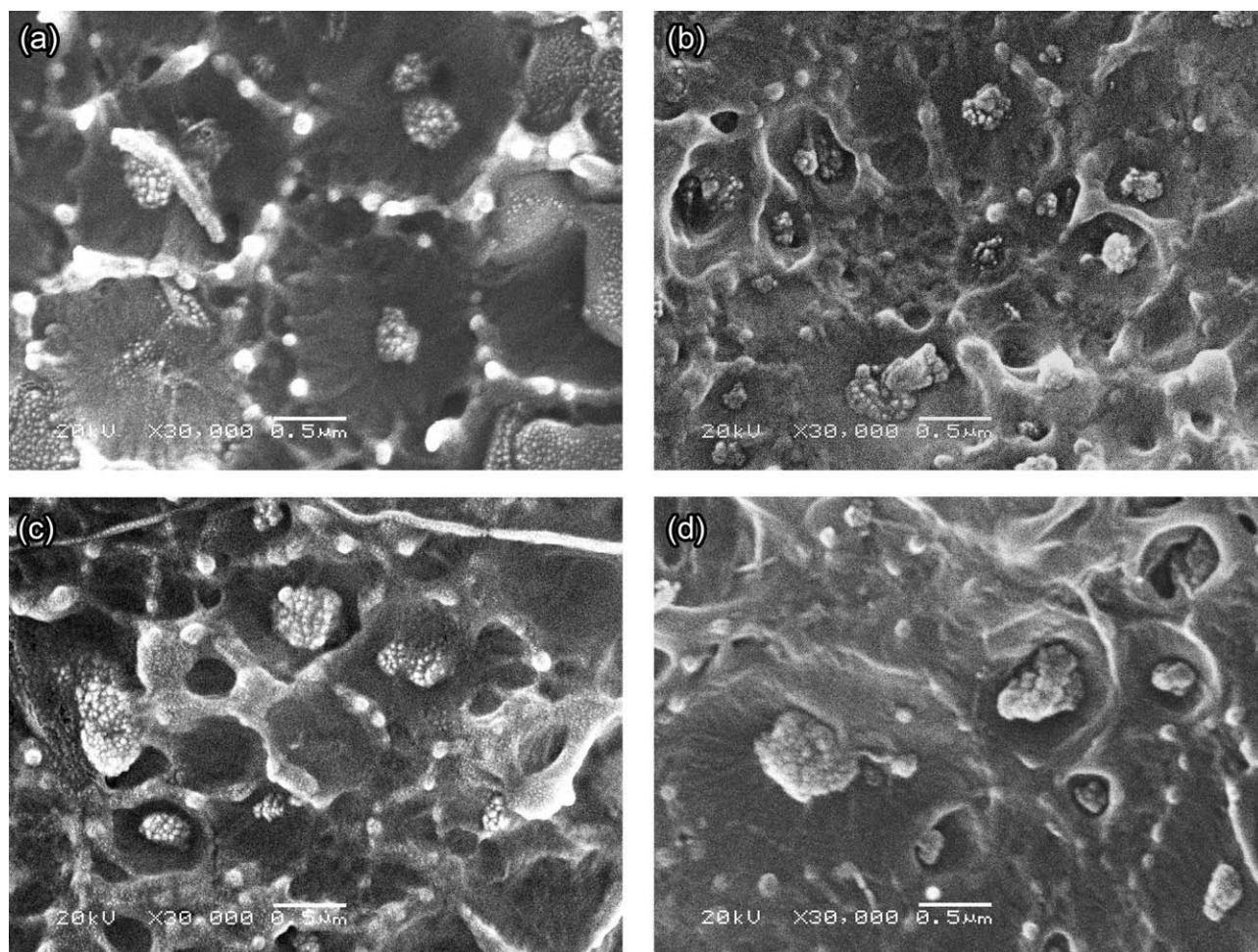


Figure 4 SEM images of the fractured surface of the LLDPE-HGB-TiO₂ composites ($\times 30,000$): (a) LLDPE-HGB-TiO₂ (8 wt %); (b) LLDPE-HGB-TiO₂ (14 wt %); (c) LLDPE-HGB-TiO₂ (22 wt %); (d) LLDPEHGB-TiO₂ (28 wt %).

matrix. Basically, the LLDPE-HGB composites present a brittle fracture surface. However, for the LLDPE-TiO₂ composite shown in Figure 3(b), TiO₂ aggregates with a mean diameter of about 500 nm disperse homogeneously in the matrix and the intervals between particles are larger than 1000 nm. Additionally, relatively much more stretched polymer matrix can be observed around TiO₂ aggregates, indicating a better toughness for LLDPE-TiO₂ composites.

The SEM micrographs of LLDPE-HGB-TiO₂ composites with various TiO₂ contents are shown in Figure 4. LLDPE-HGB-TiO₂ composites are characterized by the presence of the stretched polymer matrix and TiO₂ aggregates homogeneously dispersed in the matrix. Compared with Figure 3(a), it can be inferred that the molecular movement is greatly enhanced with addition of TiO₂, resulting in a ductile fracture surface. Besides, the size of TiO₂ aggregates and the interval between TiO₂ aggregates vary as TiO₂ content increasing. The TiO₂ aggregates with a diameter of less than 500 nm are observed when the content of TiO₂ is less than 14 wt % of the LLDPE matrix. When

TiO₂ loadings are more than 14 wt %, aggregates greater than 500 nm in diameter and the interval between TiO₂ aggregates small enough in comparison with the particle size are seen.

It has been reported that with increasing of particle size the ability of the particle to scatter light increases up to a maximum and then decreases.⁸ Comparing the four images in Figure 4, the sizes of TiO₂ aggregates are relatively small when TiO₂ content is no more than 14 wt %. When it is higher than 14 wt %, TiO₂ aggregates tend to increase in size but show no obvious increase in the dispersion state in the matrix. That is to say, it is the good dispersion and appropriate sizes of TiO₂ aggregates at 14 wt % that lead to an optimal light reflectivity. Additionally, one of the most important consequences of the incorporation of nano fillers in molten polymers is the significant change in their viscoelastic properties.⁹

Dynamic rheological properties

The effect of filler contents on the isothermal (at 190°C) frequency dependence of the dynamic

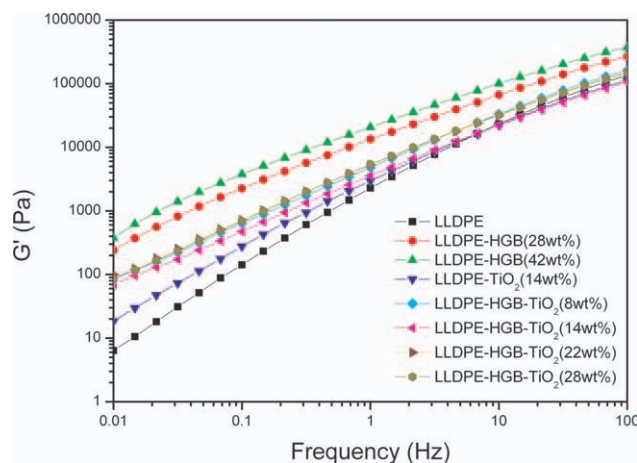


Figure 5 Storage modulus, G' , of LLDPE-HGB-TiO₂ composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

storage modulus (G') of the composites is given in Figure 5. It is shown that G' of LLDPE-HGB composites shows a great augment in the frequency range tested compared to that of LLDPE and increases with HGB content, which indicates a great enhancement in elasticity of the matrix. Complex viscosity, storage modulus and loss modulus usually increase several orders of magnitude in a filled system (especially in low frequency region).^{10–12} However, from Figure 5, when nano TiO₂ particles are introduced into the LLDPE-HGB composites, the G' of LLDPE-HGB-TiO₂ composites becomes lower than that of LLDPE-HGB composites for the same loading of HGB, especially in the low frequency region and at 14 wt % TiO₂ loading of LLDPE. In fact, polymer composites reinforced with submicron fillers generally show significant enhancements in the viscoelastic properties compared to microcomposites at similar filler contents, associated to the appearance of a secondary plateau for the dynamic storage modulus (G') in the low frequency regime.^{13–18} La Mantia et al.¹⁹ prepared a series of polyethylene/clay nanocomposites, finding a marked increase in dynamic modulus at all frequencies with increasing the filler loading. Dorigato et al.²⁰ prepared linear low-density polyethylene/silica macro- and nanocomposites by melt compounding and revealed a strong G' enhancement even at relatively low silica content ($\Phi > 2$ vol%), especially in the low frequency region. For the LLDPE-HGB-TiO₂ composites of interest here, the storage modulus show no increase but decrease to some degree compared to LLDPE-HGB composites. From SEM images, it can be seen that TiO₂ aggregates disperse homogeneously in the polymer matrix and on the surface of HGB for all composites. Besides, LLDPE matrix transfers from a brittle fracture surface to a ductile fracture surface with addition of TiO₂. Thus we conclude that the

interaction between TiO₂ and HGB which inhibits the restriction of HGB to the movement of LLDPE chains, as well as self-lubricity between nano TiO₂,⁵ results in the decrease of storage modulus.

The curves of loss factor, $\tan(\delta)$, as a function of frequency are shown in Figure 6. It shows that the $\tan(\delta)$ of these composites decreases in various degrees. For LLDPE-HGB composites, the $\tan(\delta)$ shows a monotonically decrease as many other reported fillers which have been mentioned above. Additionally, the $\tan(\delta)$ of LLDPE-TiO₂ (14 wt %) system shows the same trend as that for LLDPE-HGB system. However, it is interesting to note that the loss factor values of LLDPE-HGB-TiO₂ composites are higher than that of LLDPE-HGB composites at the same loadings of HGB, which is quite different from normal phenomena that the loss factor values of mono-filler based composites decrease as filling content increases. It can be concluded that the movement of polymer chains is enhanced with the addition of TiO₂ but show no obvious change as TiO₂ loading varies.

The complex viscosities of the composites are shown in Figure 7. LLDPE, LLDPE-TiO₂, and LLDPE-HGB composites show a trend of Newtonian plateau at low frequencies and obvious shear thinning at high frequencies. But, for the LLDPE-HGB composites, they show dramatically increased viscosities and great shear thinning compared to that of LLDPE. When TiO₂ is added into LLDPE-HGB composites, the viscosity shows an obvious decrease in all the frequency range tested compared to that of LLDPE-HGB, and presents no obvious Newtonian plateau. Except for that of LLDPE-HGB-TiO₂ (14 wt %) composite, the variation of the complex viscosities of LLDPE-HGB-TiO₂ composites are similar to

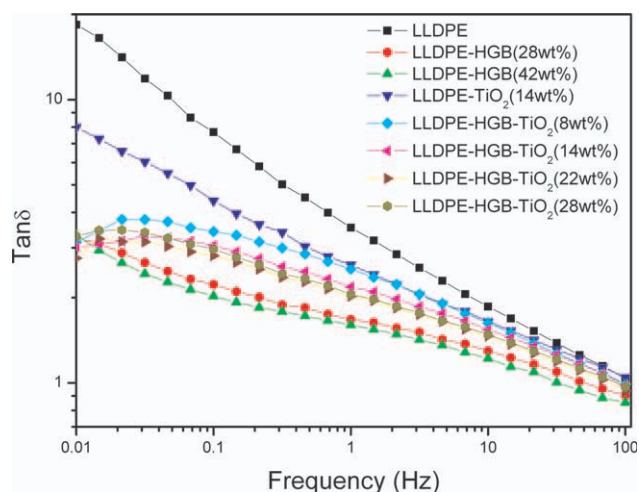


Figure 6 $\tan(\delta)$ curves of LLDPE-HGB-TiO₂ composites with different TiO₂ loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

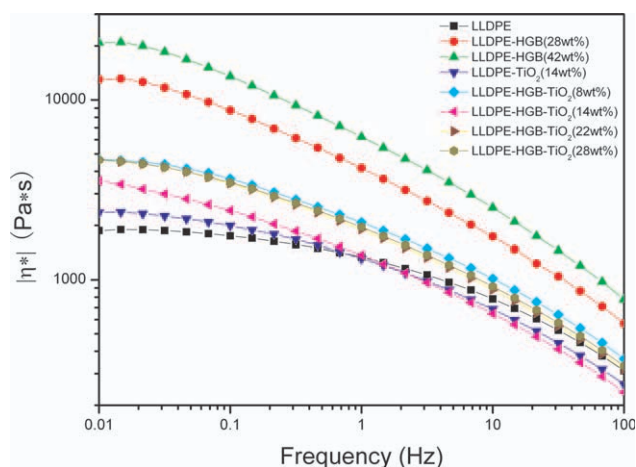


Figure 7 Complex viscosity, $|\eta^*|$, curves of LLDPE-HGB-TiO₂ composites with the contents of TiO₂ between 8 and 28 wt %.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

each other. The complex viscosity of LLDPE-HGB-TiO₂ (14 wt %) is the lowest among LLDPE-HGB-TiO₂ composites and even lower than that of LLDPE at the frequency higher than 1 Hz. From SEM images, we can see TiO₂ adhering to the surface of HGB particles, as well as homogeneously dispersing in the matrix. Thus, it can be implied that the restriction of HGB particles to polymer chains is greatly reduced by TiO₂ resulting in a great decreased complex viscosity. Besides, self-lubricity of TiO₂ is another factor that reduces complex viscosity of the system. When TiO₂ loading is 14 wt % of LLDPE, the dispersion of TiO₂ aggregates comes to an optimal value, leading to a LLDPE-HGB-TiO₂ composite with a lowest viscosity.

To analyze the relationship between the complex viscosities and the frequency more directly, the curves of complex viscosities versus nano TiO₂ content at different frequencies are shown in Figure 8. It is obvious that complex viscosities decrease with increasing TiO₂ content before TiO₂ content comes to 14 wt %, especially in the low frequency region. For the composites containing more than 14 wt % nano TiO₂, their viscosities just increase slightly and tend to level off. Combining the light reflectivity versus TiO₂ loading curves, it is reasonable to conclude that TiO₂ loading of 14 wt % can be taken as a critical value of the experimental systems.

CONCLUSION

The light reflectivity and rheological behavior of the LLDPE blends filled with micro HGB and nano TiO₂ particles have been investigated. The results show that it is feasible to improve the light reflectivity, heat insulating property, and melt flow property of LLDPE-HGB composites by adding TiO₂ to proper

proportions. Both UV and infrared reflectivity of the LLDPE composite with 28 wt % HGB and 14 wt % TiO₂ of LLDPE increase sharply up to more than 90%, which provides a kind of composite based on LLDPE with a high heat insulating property. The LLDPE composite with 14 wt % TiO₂ can be taken as the optimal value for light reflectivity of LLDPE.

From SEM images, gaps between HGB and the matrix in LLDPE-HGB composites are not obvious due to titanate coupling agent. For HGB and TiO₂ complex filled system, there are TiO₂ particles on the surface of HGB particles and relatively more HGB particles shedding from polymer matrix. Besides, polymer matrix transfers from a brittle fracture surface to a ductile fracture surface with addition of TiO₂.

The rheological behavior of the HGB and TiO₂ complex filled LLDPE composites is different from that of mono-filler LLDPE based composites. The storage modulus, G' , and the complex viscosities, $|\eta^*|$, of LLDPE-HGB composites increase significantly as HGB loadings increase. Adding nano TiO₂ is available to reduce the storage modulus, G' , and the complex viscosities, $|\eta^*|$, of LLDPE-HGB systems, especially at 14 wt % TiO₂ of LLDPE.

Based on an overall consideration of the light reflectivity, SEM images and rheological behaviors, it is proposed that nano TiO₂ aggregates not only homogeneously disperse in the matrix but adhere to the surface of HGB particles, which inhibit the restriction of HGB particles to polymer chains and act as solid lubricants in the composite, hence greatly reduce the viscosity of LLDPE-HGB composites. Besides, as TiO₂ loading increases, the sizes of TiO₂ aggregates in the matrix come to optimal values for light reflectivity when it comes to 14 wt %.

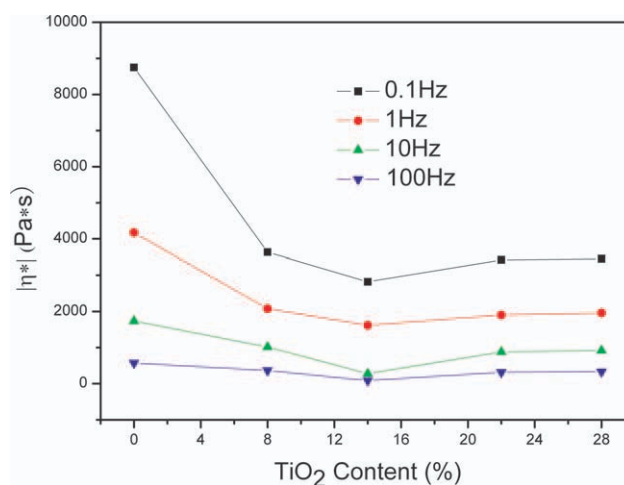


Figure 8 Complex viscosity as a function of TiO₂ loadings of LLDPE-HGB-TiO₂ composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, a composite with outstanding light reflectivity and optimal processing flow property can be obtained through adjusting the proportion of HGB and nano TiO₂.

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