Research Article

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The optimization of Carreau model and rheological behavior of alumina/linear low-density polyethylene composites with different alumina content and diameter

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Abstract: The influence of alumina (Al_2O_3) content and diameter on the viscosity characteristics of the alumina/linear low-density polyethylene (Al_2O_3 /LLDPE) composites was discussed. The composites were fabricated by melt mixing with the two-rotor continuous mixer. The equivalent surface average particle diameter ($\bar{d}_A$) of Al_2O_3 was calculated by the scanning electron microscopic (SEM) images of samples. The steady-state and dynamic rheological measurements were used to study the evolution of viscosity parameters. With the Carreau model fitting to the steady-rate rheological data, zero-shear viscosity η_0 , time constant λ , and power law index n of composites were obtained. On this basis, an optimized Carreau model was established by studying the changes of these parameter values. The rheological result presented that the parameter values (η_0 , λ , and n) were linearly proportional to the filling content of Al_2O_3 particles for nano- Al_2O_3 /LLDPE

composites. However, these parameters were, respectively, related to $\bar{d}_A$, $\bar{d}_A^2$, and $\bar{d}_A^3$ for micron- Al_2O_3 /LLDPE composites.

Keywords: rheology, Carreau model, Al_2O_3 particle diameter, Al_2O_3 /LLDPE composites

1 Introduction

Adding fillers and additives is an important method for modifying the physical and rheological properties of polymers. Most advanced polymers are modified by adding inorganic or organic fillers to get better functionality, such as electrical conductivity, thermal conductivity, optical properties, and biological functions (1–3). The particle diameter and the content of the filler can affect not only the modification effect of the composites but also the rheological properties. Rheological behavior can be an indicator of the composites microstructure, which is an important factor affecting the final performance. Meanwhile, the addition of fillers will have a direct effect on the rheological behavior of the composites and affect the process. Therefore, the study of fillers' influence on the rheological behavior of the composites can optimize the processing technology and improve the properties of composites. It is of great significance for the intelligent control and online monitoring of the composite products preparation.

The rheological behavior of the composites reflects the molecular chain structure of the material. A series of studies (4–8) demonstrated that the rheological behavior of composites is mainly determined by the interaction between filler particles and polymer matrix and the interaction among filler particles. The surface tension between filler particles and polymer matrix is one of the main factors in forming the filler's network structure.

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Meanwhile, the relative distance between particles was also an important factor (9). The rheological behavior is not only related to the characteristics of the polymer matrix but also related to the physical and chemical properties of the filler particles. Many detailed influence factors on rheological behavior have been studied before, such as the content of particle filler (10–16), shape (17–19), particle diameter (20–24), surface treatment (25–30), and dispersion state in the composites (22). As a kind of rigid spherical particles, Al₂O₃ particles are widely used as fillers in functional composite materials because of their resistance to agglomeration and excellent thermal conductivity. However, most of the researches have focused on the performance of products (31–34). There were some researches that focus on the rheological behavior of the Al₂O₃/polymer matrix composites (35–37).

In this article, a series of Al₂O₃/LLDPE composites were prepared with different Al₂O₃ contents and particle diameters. Steady-state and dynamic rheological tests were used to reveal changes in the molecular chain internal structure of the composites. Then, influences of the particle diameter and the content of Al₂O₃ particles on the rheological behavior of the composites were analyzed. The content parameters and average surface particle diameter parameters were proposed to optimize the Carreau model, and the optimized model was verified. With the optimized Carreau model, the viscosity of the Al₂O₃ filled composites could be predicted. This article provides a research method for studying the rheological behavior of filled polymers, which can evaluate the processing properties of composites and provide guidance for the design of composite material formulations for new applications.

2 Experiment and characterization

2.1 Materials

Spherical Al₂O₃ (the diameters of Al₂O₃ particle are 1, 5, 10, 20, 40, and 70 μm, respectively) are supplied from Zhengzhou Sanhe New Material Co., Ltd. Linear low-density polyethylene (LLDPE), of 1,002 kW, density of 0.918 g·cm⁻³, and melting index of 2 g·10 min⁻¹, is supplied by Suzhou Renfa Plastic Chemical Co., Ltd. Antioxidant 1010 (1,178 g·mol⁻¹) is purchased from BASF (China) Co., Ltd.

2.2 Experiment and characterization

Al₂O₃ and LLDPE were vacuum dried at 80°C for 8 h. The Al₂O₃/LLDPE composites were prepared by two-rotor continuous mixer (rotor diameter is 30 mm). The rotor speed was 600 rpm, the orifice setting was 50%, and the feed rate was 4,000 g·h⁻¹. The barrel temperature of the solid conveying section and the melt mixing section were 55°C and 145°C, respectively. The samples for the measurement were made by a plate vulcanizer at 160°C.

SEM was used to characterize the dispersion and distribution of Al₂O₃ particles in the composites. The samples were cryo-fractured in liquid nitrogen and etched in concentrated hydrochloric acid. The etched surfaces of the samples were coated with gold before SEM observation. The surface morphologies under different magnifications were obtained by vacuum SEM (JSM-6300LV).

Eq. 1 is used to calculate the equivalent average surface diameter ($\bar{d}_A$) of Al₂O₃ particles. The Al₂O₃ particle diameter was obtained by the statistical analysis of the SEM images through the Image Pro Plus software. Then, $\bar{d}_A$ of the particles was obtained through Gaussian distribution fitting.

$$\bar{d}_A = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

To eliminate the statistical error and obtain the particle diameter accurately, five samples were prepared for each kind of the composites, and eight different regions were recorded for each sample. A comparison table of the original particle diameter d and $\bar{d}_A$ is presented in Table 1.

The viscosity tests versus the shear rate among shear rate of 0.01–10 s⁻¹ were measured by Malvern plate rheometer (Bohlin Gemini&CVO), and the viscosity versus shear rate among shear rate of 10–1,000 s⁻¹ was measured by capillary rheometer (Rosand RH10-D). The dynamic viscosity was conducted with frequency scanning by Malvern plate rheometer, and the strain amplitude was 5% (the composites in this strain amplitude range were always in the linear viscoelastic region).

Table 1: A comparison of the original particle diameter and equivalent average surface diameter of Al₂O₃

d (μm)	1	5	10	20	40	70
$\bar{d}_A$ (μm)	0.4	6.5	10.2	26.7	37.8	48.6

Figure 1: SEM micrographs of composite fracture surfaces with different $\bar{d}_A$: (a) 400 nm, (b) 6.5 μm , (c) 10.2 μm , (d) 26.7 μm , (e) 37.8 μm , (f) 48.6 μm , and enlarged view of 6.5 μm (g) and 48.6 μm (h).

3 Results and discussion

3.1 Micro morphology analysis

The fracture surface SEM morphologies of the Al₂O₃/LLDPE composites are illustrated in Figure 1. The spherical Al₂O₃ particles were indicated with white circles, and the holes where the Al₂O₃ particles were pulled out were indicated with red circles. It could be seen that spherical Al₂O₃ was uniformly dispersed in the composites, and Al₂O₃ particles with different particle diameters still maintained rigid spheres. Many Al₂O₃ particles were embedded in the LLDPE matrix, as shown in Figure 1a. When $\bar{d}_A$ of Al₂O₃ increased from 6.5 to 48.6 μm (Figure 1b–f), more voids spreading in the cross section of the matrix could be found. The reason for this phenomenon was that the interaction between the particles and the composites decreased with the increasing of the spherical Al₂O₃ diameter. Larger Al₂O₃ particles would lead to the reduction of specific surface area and the deterioration of the interfacial bonding between the particles and the composites. Therefore, the adhesion between the Al₂O₃ particles and the LLDPE matrix was weak, and the Al₂O₃ particles would be pulled out when preparing the sample for SEM testing. In Figure 1g and h, there was an apparent gap between the sphere particle and the matrix, and the particles were almost peeled off from the matrix.

3.2 Effect of Al₂O₃ content on rheological behavior of nano-Al₂O₃/LLDPE composites

A series of steady-state viscosity and dynamic viscosity measurements were conducted for the composites with

different Al₂O₃ contents, which varied from 4 to 20 wt% with a fixed particle diameter of Al₂O₃ ($\bar{d}_A$ is 400 nm). The steady-state rheological behavior of nano-Al₂O₃/LLDPE composites is shown in Figure 2. The steady-state viscosity of the composites showed a Newtonian plateau in the curve when the shear rate was below 10 s^{−1}, while the non-Newtonian properties became more obvious with the increasing content of Al₂O₃ particles. The addition of Al₂O₃ particles could cause the slip between molecular chains, and the slip effect was enhanced when the Al₂O₃ content was increased. At the same time, the zero-shear viscosity η_0 was increased with the increase in the Al₂O₃ content. The addition of Al₂O₃ increased the shear viscosity of the LLDPE as Al₂O₃ particles hindered the free motion of LLDPE molecular chains. With the increasing

Figure 2: Shear viscosity versus shear rate of the nano Al₂O₃/LLDPE composites with different Al₂O₃ contents.

filling content, the number of Al_2O_3 particles increased, and the hindrance effect was enhanced, which led to the increase of viscosity at low shear rates (10 s^{-1}). When the shear rate exceeded 10 s^{-1} , the viscosity curves of the composites almost overlapped and exhibited a typical shear thinning phenomenon. In addition, when the filling content of nano- Al_2O_3 particles increased from 8 to 12 wt%, the steady-state viscosity of the composites increased significantly. When the filling content of Al_2O_3 increased to 16 and 20 wt%, the steady-state viscosity continued to increase.

The dynamic frequency scanning test of nano- Al_2O_3 /LLDPE composites with different contents is presented in Figure 3. As shown in Figure 3a, the complex viscosity of the pure LLDPE sample showed a plateau around $10^4 \text{ Pa}\cdot\text{s}$ when the frequency was less than $10^{-1} \text{ rad}\cdot\text{s}^{-1}$. Besides, the complex viscosity of the composites increased with the addition of Al_2O_3 particles, and the platform

disappeared gradually. Meanwhile, the complex viscosity of the composites gradually increased with the increasing of the filling content. Similar to Figure 2, the complex viscosity curves of the composites had a significant upward shift when the nano- Al_2O_3 particles filling content increased from 8 to 12 wt%. When the filling content was lower, the blocking effect of Al_2O_3 particles on polymer melt mainly dominated the hindrance effect of Al_2O_3 particles on the movement of the polymer molecular chain. This blocking effect increased with the increasing filling content. When the content of Al_2O_3 particles increased to 12%, the distance among particles would be closer, and the particles no longer distributed individually in the composites. The interaction force among particles was strengthened, and the particle network structure began to form in the composites. Thus, the viscosity of the composites was affected by both the interaction force among particles and the interaction

Figure 3: Dynamic rheological properties of the nano Al_2O_3 /LLDPE composites with different Al_2O_3 contents: (a) complex viscosity, (b) storage modulus G' , (c) loss modulus G'' , and (d) Han plots.

force between particles and polymer molecular chain. As a result, the viscosity increased obviously at this stage.

Figure 3b and c show that the storage modulus (G') and loss modulus (G'') of the composites changed with the varying nano- Al_2O_3 filling content. The pure LLDPE exhibited typical end effect of linear high molecular polymers in the low-frequency range ($10^{-1} \text{ rad}\cdot\text{s}^{-1}$) because the ratio of $\lg G'$ to $\lg \omega$ was close to 2, and the ratio of $\lg G''$ to $\lg \omega$ was close to 1. When the Al_2O_3 filling content increased from 8 to 12 wt%, the storage modulus G' and loss modulus G'' showed an obvious increase in the low-frequency range. The ratio of $\lg G'$ to $\lg \omega$ and the ratio of $\lg G''$ to $\lg \omega$ were similar when the Al_2O_3 content increased to 12 wt%. In the low-frequency range, the ratio of $\lg G'$ to $\lg \omega$ gradually decreased with the increasing filling content, implying that the particle network structure started to form in the composites. When the content of Al_2O_3 increased to 20 wt%, the ratio of $\lg G'$ to $\lg \omega$ was less than 0.5, and the storage modulus G' of the composites was almost independent of the frequency in the low-frequency range. At the same time, the storage modulus curve appeared at an approximate platform region. Such response characteristic of storage modulus to the frequency indicated that the more complete internal particle network structure was formed, and the elastic characteristics were more obvious.

Figure 3d shows that the Han curves of the composites were significantly higher than that of pure LLDPE. The Han values became higher with the increase in the filling content, which meant that the composites would undergo a longer relaxation process. Meanwhile, an approximate platform region appeared in the low-frequency range when the Al_2O_3 content exceeded 12 wt%. This phenomenon revealed that the terminal effect was restrained in the composites. The longer relaxation process of the composites and the appearance of nonterminal effects proved that the Al_2O_3 /LLDPE composites transformed from the quasi-liquid state to the quasi-solid state, and the particle network structure was generated in the composites.

3.3 Effect of Al_2O_3 diameter on rheological behavior of micron- Al_2O_3 /LLDPE composites

A series of steady-state viscosity and dynamic viscosity measurements were conducted, and the $\bar{d}_A$ of Al_2O_3 particles varied from 6.5 to 48.6 μm with a fixed Al_2O_3 content (12 wt%). Figure 4 shows the steady-state rheological

Figure 4: Shear viscosity versus shear rate of the Al_2O_3 /LLDPE composites with different Al_2O_3 diameters.

curves of the composites with different $\bar{d}_A$ of Al_2O_3 . It presented that the addition of micron- Al_2O_3 particles also contributed to the increasing steady-state viscosity of the Al_2O_3 /LLDPE composites, but the degree of increase was lower than that of nano- Al_2O_3 particles shown in Figure 2. With the same filling content, the number of micron- Al_2O_3 particles was less than that of nanoparticles, and the specific surface area was also smaller. Thus, the interaction between filler particles and polymer molecular chain was weak, meaning that the hindrance to the melted polymer was inferior. It should be noted that the shear viscosity curves of the composites moved upward in the low shear rate range (10 s^{-1}) when the $\bar{d}_A$ increased from 6.5 to 26.7 μm . On the contrary, the shear viscosity curve shifted downward when the $\bar{d}_A$ continued to increase to 37.8 μm . When the $\bar{d}_A$ of Al_2O_3 particles reached 48.6 μm , the curve changed little and almost overlapped with the viscosity curve of 37.8 μm . In general, the steady-state viscosity curve increased at first and then decreased to a stable region with the increasing $\bar{d}_A$ in the lower shear range.

The dynamic frequency scanning rheological tests of Al_2O_3 /LLDPE composites with different $\bar{d}_A$ are presented in Figure 5. It could be seen that the evolution trend of complex viscosity in Figure 5a was the same as that of steady viscosity in Figure 4. In the low-frequency range (below $10^{-1} \text{ rad}\cdot\text{s}^{-1}$), the complex viscosity of the composites increased at first and then decreased when the $\bar{d}_A$ varied from 6.5 to 37.8 μm and finally tended to be stable at 48.6 μm . However, the change of $\bar{d}_A$ had little effect on the complex viscosity of the composites in the high-frequency range (above $1 \text{ rad}\cdot\text{s}^{-1}$), and all the curves almost overlapped. Here, the viscosity of the composites reached

Figure 5: Dynamic rheological properties of the Al_2O_3 /LLDPE composites with different Al_2O_3 particles diameters: (a) complex viscosity, (b) storage modulus G' , (c) loss modulus G'' , and (d) Han plots.

the maximum when the $\bar{d}_A$ of Al_2O_3 particles was 26.7 μm . The movement of molecular chains could be affected by the size and the number of rigid particles (38). When the content of particles was constant, the amount and the specific surface area would decrease with the increase of $\bar{d}_A$ of spherical particles. The increasing particle size would hinder the movement of molecular chains, while the corresponding decrease in the number and specific surface area would weaken the hindrance and reduce the viscosity accordingly (19,20). The previous data showed that when $\bar{d}_A$ varied from 6.5 to 26.7 μm , the viscosity of the composites increased. That was because the effect of particle size played a leading role in overall factors, highlighting the resistance to the movement of molecular chains. However, when the $\bar{d}_A$ varied from 26.7 to 48.6 μm , the number of Al_2O_3 particles decreased sharply. The factor of particle size was no longer dominated and had

a limited effect on the movement of LLDPE molecular chains, which made the steady-state viscosity of the composites decrease. A balancing effect of the mentioned factors led to the final stable trend of the viscosity.

In Figure 5b and c, the storage modulus (G') and loss modulus (G'') of the composites showed an increasing trend at first and then decreased in the low-frequency range (below $10^{-1} \text{ rad} \cdot \text{s}^{-1}$). When $\bar{d}_A$ was 26.7 μm , both the G' and G'' of the Al_2O_3 /LLDPE composites had the maximum value. When $\bar{d}_A$ continuously increased to 37.8 and 48.6 μm , the curves of both G' and G'' moved downward and overlapped. It was worth noting that there was no “platform effect” for the micron- Al_2O_3 particles, which was not similar to the G' curves for nanoparticles in the low-frequency range. It revealed that the various micron- Al_2O_3 /LLDPE composites with the same filling content (12 wt%) did not illustrate solid-state behavior

in the low-frequency range. In the high-frequency range, all the curves of G' and G'' tended to overlap, indicating that the effect of oscillating shear on the entangled polymer molecular chains was much greater than that of the Al_2O_3 particles.

Figure 5d shows that the Han curves of the composites with micron- Al_2O_3 particles were significantly higher than that of pure LLDPE. However, the change of $\bar{d}_A$ did not have an obvious effect on the Han curves. The Han curves of the composites with various $\bar{d}_A$ were overlapped, and the slope of the curves were almost the same. In addition, the Han curves did not illustrate the approximate platform area. It showed that the change of $\bar{d}_A$ did not affect the molecular chain internal structure of the composites when the filling content of micron Al_2O_3 was 12 wt%. This was mainly due to the large particle diameter and large specific surface area of micron Al_2O_3 particles, which mainly affected the movement of the polymer molecular chain in the composites. Due to the large particle diameter, the number of particles was much less than that of nanoparticles, and the distance between the particles was larger. Thus, there was almost no interaction effect among particles in the composites.

3.4 The optimization rheological model of Al_2O_3 /LLDPE composites

To analyze the influence of the nano Al_2O_3 content and the $\bar{d}_A$ of micron Al_2O_3 particles on the rheological behavior of the composites quantitatively, the Carreau model was applied to perform the nonlinear fitting for the steady-state viscosity curves of the Al_2O_3 /LLDPE composites. The fitting parameters including zero-shear viscosity η_0 , time constant λ , and power law exponent n are presented in Tables 2 and 3. The η_0 determined the height of the Newtonian platform region in the low shear rate range (below 10 s^{-1}), and the λ indicated the length of the

Table 3: Fitting results for the Al_2O_3 /LLDPE composites with different particle diameters via the Carreau model

Material	η_0 (Pa·s)	λ (s)	n	R^2
Pure LLDPE	9,572	0.86	0.54	0.99
6.5 μm –12 wt%	32607.51	11.37	0.57	0.98
10.2 μm –12 wt%	41021.37	12.38	0.51	0.99
26.7 μm –12 wt%	62577.27	14.63	0.44	0.98
37.8 μm –12 wt%	40726.74	12.43	0.53	0.98
48.6 μm –12 wt%	40974.63	12.94	0.53	0.98

relaxation time. The larger η_0 and the longer λ proved that the Al_2O_3 particles had a greater hindrance effect on the melt flow behavior for the composites. The formula of the Carreau viscosity model is presented in Eq. 2:

$$\eta = \frac{\eta_0}{(1 + \lambda^2 \dot{\gamma}^2)^{\frac{1-n}{2}}} \quad (2)$$

where η_0 is the zero-shear viscosity, Pa·s; λ is the time constant, s; $\dot{\gamma}$ is the shear rate, s^{-1} ; n is the power law index; and η is the shear viscosity, Pa·s.

Under the same pressure and the temperature condition, the main factors affecting the rheological behavior of the filler composites were surface modification, diameter, shape, and content of fillers. It was assumed that there was a certain relationship between the viscosity model of the composites and the viscosity model of the polymer matrix. The relationship is defined in Eqs. 3–5:

$$\eta_0 = f(s_c)f(\varphi_c)f(\phi)f(\omega)\eta_{\text{pure}} \quad (3)$$

$$\lambda = f(s_c)f(\varphi_c)f(\phi)f(\omega)\lambda_{\text{pure}} \quad (4)$$

$$n = f(s_c)f(\varphi_c)f(\phi)f(\omega)n_{\text{pure}} \quad (5)$$

where $f(s_c)$, $f(\varphi_c)$, $f(\phi)$, and $f(\omega)$ represented the adhesion coefficient, particle shape coefficient, filler particle diameter coefficient, and filler content coefficient, respectively. η_0 , λ , n , η_{pure} , λ_{pure} , and n_{pure} represented the zero-shear viscosity, time constant, and power law exponent in the Carreau model parameters of the composites and the polymer matrix under the same pressure and temperature, respectively.

In the previous section, the effects of Al_2O_3 content and particle diameter on the viscosity of composites were studied. The Al_2O_3 particles had a spherical structure and hence, the effects of the adhesion coefficient and the particle shape coefficient on the rheological properties of the composites could be simplified in Eqs. 6–8:

$$\eta_0 = f_1(\omega)f_1(\phi)\eta_{\text{pure}} \quad (6)$$

Table 2: Fitting results for the Al_2O_3 /LLDPE composites with different filling contents via the Carreau model

Material	η_0 (Pa·s)	λ (s)	n	R^2
Pure LLDPE	9,572	0.86	0.54	0.99
400 nm–4 wt%	31,790	10.85	0.52	0.98
400 nm–8 wt%	44,655	11.31	0.49	0.98
400 nm–12 wt%	75,306	14.53	0.43	0.98
400 nm–16 wt%	88,184	14.72	0.42	0.98
400 nm–20 wt%	98,743	15.48	0.39	0.98

$$\lambda = f_2(\omega)f_2(\phi)\lambda_{\text{pure}} \quad (7)$$

$$n = f_3(\omega)f_3(\phi)n_{\text{pure}} \quad (8)$$

where $f_{(1;2;3)}(\omega)$ and $f_{(1;2;3)}(\phi)$ represent the coefficients related to the filler content and the $\bar{d}_A$ of filler particles, respectively.

The Carreau viscosity model formula of Al₂O₃/LLDPE composites with different contents and particle diameters could be optimized as presented in Eq. 9:

$$\eta = \frac{f_1(\omega)f_1(\phi)\eta_{\text{pure}}}{(1 + f_2(\omega)f_2(\phi)^2\lambda_{\text{pure}}^2\gamma^2)^{\frac{1-f_3(\omega)f_3(\phi)n_{\text{pure}}}{2}}} \quad (9)$$

where $f_{(1;2;3)}(\omega)$ and $f_{(1;2;3)}(\phi)$ represent the coefficient of zero-shear viscosity, time constant, and power law index when the effect of the filling content and the diameter of the filler particle were considered. η_{pure} , λ_{pure} , and n_{pure} represent the zero-shear viscosity, time constant, and power law exponent of the matrix material, respectively; γ was the shear rate, s⁻¹; η was the shear viscosity, Pa·s.

As shown in Figure 6, the number of Al₂O₃ particles in the composites was proportional to the filling content with the same $\bar{d}_A$ in Al₂O₃/LLDPE composites, and the distance among particles was inversely proportional to the filling content. When the filling content of Al₂O₃ particles was consistent, the number of Al₂O₃ particles decreased with the increase of $\bar{d}_A$ and the distance between particles increased.

Combined with the aforementioned analysis, there were three kinds of interactions mainly affecting the rheological behavior (39). The first kind was the hydrodynamic effect of fillers. When the particle diameter of the filler and the content of filler increased, the hydrodynamic effect would be enhanced, as well as the viscosity of the composites. Therefore, the hydrodynamic effect was positively related to the number and content of Al₂O₃ particles. The second kind was the interaction between filler particles and polymer molecular chain, which mainly depended on the spherical surface area of Al₂O₃ particles. In another word, the interaction between filler particles and polymer molecular chain was related to the square of $\bar{d}_A$. Under the same content, this kind of interaction increased with the decreasing particle diameter. The third kind was the interaction among the particles, which occurred only when the network was formed in the composites.

For nano-Al₂O₃ composites with the same $\bar{d}_A$, it was assumed that the particles were uniformly dispersed in the composites, and the interaction among the particles could be ignored. Besides, the amount, the content, and the surface area of Al₂O₃ particles were proportional to the filling content. According to the aforementioned assumptions, $f_{(1;2;3)}(\omega)$ could be expressed as a linear relationship related to the filling content of Al₂O₃, as shown in Eqs. 10–12:

Figure 6: Diagrams of Al₂O₃ morphology with difference particle diameters and contents in the composites.

$$f_1(\omega) = a_1 + b_1\omega \quad (10)$$

$$f_2(\omega) = a_2 + b_2\omega \quad (11)$$

$$f_3(\omega) = a_3 + b_3\omega \quad (12)$$

where $a_{(1;2;3)}$ and $b_{(1;2;3)}$ represented the undetermined coefficients related to the filling content.

The black square points in Figure 7 represented the function values fitted by the Carreau viscosity model for the composites with different filling contents (Table 2). The straight lines in the figure were the curves fitted according to Eqs. 10–12. The fitting data and the R^2 are shown in Figure 7. It could be seen that three parameters exhibited excellent fitting accuracy ($R^2 > 0.99$). With the increase of the nano- Al_2O_3 content, the zero-shear viscosity η_0 and time constant λ increased proportionally, and the slope of the straight line was positive. While the power law index n decreased and the slope of the straight line was negative. This was due to the increase in the number of particles in the composites, leading to

the interaction between particles and the formation of the filler network structure. It was worth noting that the three functions deviated most from the fitting curves when the filling content of nano- Al_2O_3 particles was 12 wt%.

To verify the reliability of the equations, the steady-state rheological properties of nano- Al_2O_3 /LLDPE composites with 2 and 10 wt% filling contents were used. The three parameters were fitted according to the Carreau viscosity model, and the results are presented in Figure 7, with the red solid triangle. It could be seen that the five verification points were near the fitting line, and the error was acceptable. The fitting equations could reflect the evolution law of the three parameters of Carreau. At the same time, there was an error as Figure 7 illustrated when the filling content of Al_2O_3 was 10 wt%. Such variation might be due to the interaction between particles and the formation of the network structure.

According to the analysis for Figure 6, the effect of micron Al_2O_3 particles on the rheology of the composites

Figure 7: Carreau model parameters of the Al_2O_3 /LLDPE composites as a function of nano Al_2O_3 content: (a) $f_1(\omega)$, (b) $f_2(\omega)$, and (c) $f_3(\omega)$.

Figure 8: Carreau model parameters of the Al₂O₃/LLDPE composites as a function of mic-Al₂O₃ particle diameter: (a) $f_1(\phi)$, (b) $f_2(\phi)$, and (c) $f_3(\phi)$.

mainly depended on the diameter of Al₂O₃ particles, the surface area of the spherical particle, and the number of particles. The relationship between the number of Al₂O₃ particles and the equivalent average surface diameter ($\bar{d}_A$) is shown in Eq. 13:

$$z \propto \frac{1}{\bar{d}_A^3} \quad (13)$$

where z is the number of filler particles in the composites and $\bar{d}_A$ is the equivalent average surface diameter, μm.

Therefore, the function $f(\phi)$ of the particle diameter coefficient could be expressed as Eqs. 14–16:

$$f_1(\phi) = c_1\phi + d_1\phi^2 + e_1\phi^3 \quad (14)$$

$$f_2(\phi) = c_2\phi + d_2\phi^2 + e_2\phi^3 \quad (15)$$

$$f_3(\phi) = c_3\phi + d_3\phi^2 + e_3\phi^3 \quad (16)$$

where $c_{(1;2;3)}$, $d_{(1;2;3)}$, and $e_{(1;2;3)}$ represent the undetermined coefficients of the function, respectively.

The black square points in Figure 8 represent the values fitted by the Carreau viscosity model for the composites with different $\bar{d}_A$ (Table 3). In Figure 8, the zero-shear viscosity η_0 and time constant λ would increase and then decrease with the increasing Al₂O₃ particle diameter. While the evolution of power law index n decreased first and then increased. When $\bar{d}_A$ of the particles increased from 37.8 to 48.6 μm, the three parameters in the model tended to be unchanged. Therefore, the fitted values for the $\bar{d}_A = 48.6$ μm was ignored, thus, just fitting the parameter values with the rest particle diameter according to Eqs. 14–16. The obtained fitting curves and equations are shown in Figure 8. The fitted curves for zero shear viscosity and time constant in Figure 8 illustrated an increasing trend at first and then decreased with the increase in Al₂O₃ particle diameter. The change of the power law index was decreased. Besides, the fitted curve was very smooth as shown in Figure 8, and the data

points were just on the curves, proving that the equations proposed for fitting were very accurate and reliable.

4 Conclusion

The influences of the particle diameter and the filling content of spherical Al₂O₃ particles on the steady-state and dynamic rheological behavior of Al₂O₃/LLDPE composites were studied. For the nano-Al₂O₃/LLDPE composites, the viscosity of the composites increased greatly at the low shear rate range because of its large specific surface area and the interaction among filler particles. Meanwhile, the viscosity increased gradually with the increase in the filling content of Al₂O₃, and the filling content was proportional to the viscosity of the composites. For the micron-Al₂O₃/LLDPE composites, the effect of micron Al₂O₃ particle diameter on the rheological behavior of the composites mainly depended on the equivalent average surface diameter of the particles. Finally, the optimized Carreau viscosity model considering the two factors was established, and the model of nano-Al₂O₃/LLDPE composites with different filling contents was preliminarily verified. With the help of the optimized rheological model, the viscosity of Al₂O₃/LLDPE composites could be predicted quantitatively when the content of spherical Al₂O₃ particles was less than 20% and $\bar{d}_A$ of Al₂O₃ particles was less than 38.6 μm.

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