Effect of Ultrasonic Oscillations on the Rheological Behavior and Morphology of Illite-Filled High-Density Polyethylene Composites

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ABSTRACT: The effects of ultrasonic oscillations on the rheological and viscoelastic properties and morphology of high-density polyethylene (HDPE)/Illite (70/30) composites were studied. The experimental results showed that the die pressure and apparent viscosity of the HDPE/Illite (70/30) composites were reduced greatly, and so the mass-flow rate significantly increased in the presence of ultrasonic oscillations during the extrusion. Scanning electron microscopy and linear viscoelasticity tests showed that ultrasonic oscillations improved the dispersion of the Illite particles into the HDPE matrix. The aggregation of the Illite particles disappeared on the fractured surfaces of HDPE/Illite (70/30) composites extruded in the presence of ultrasonic oscillations, and this indicated that ultrasonic oscillations promoted the homogeneous dispersion of Illite particles into the HDPE matrix. Ultrasonic oscillations caused the permanent reduction of the dynamic viscosity and zero-shear viscosity of HDPE/Illite (70/30) composites. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 379–384, 2005

Key words: composites; morphology; rheology

INTRODUCTION

Inorganic fillers are being increasingly used to enhance the stiffness and reduce the dielectric loss of polymers.[1–4] They are also used to improve UV light absorption, electroluminescence, and drug delivery[5,6] and to improve thermal and aging stability, fire resistance,[7] and so on. To a great extent, the improvement of these properties depends on the morphology and dispersion of fillers in the matrix. The mechanical properties and processability of polymers will be significantly sacrificed because of the poor dispersion of fillers and weak interactions between fillers and polymer matrices. To achieve homogeneous dispersions of fillers in polymer matrices and to enhance the interactions between fillers and polymer matrices, several methods are generally applied: (1) the surface treatment of fillers with a coupling agent;[2,8,9] (2) the polar group functionalization of polymers with partial oxidation, γ-rays, electron beams, microwaves, UV irradiation, or polar grafting;[10,11] (3) the addition of a bifunctional component that can interact with both fillers and matrices;[12] and (4) the mechanochemical modification of fillers.[13–15]

The recent development of melt vibration technology has led to attempts to improve the processing behavior of polymers.[16–19] Superimposing oscillations upon a constant-pressure gradient flow of a viscoelastic liquid produces a more significant increase in the flow rate with respect to the stationary flow. Oscillations can also improve the mechanical properties of the extrudate and reduce the die pressure and die swell. Our previous work[20,21] has shown that the appearance of polystyrene (PS), high-density polyethylene (HDPE), and linear low-density polyethylene extrudates is greatly improved in the presence of ultrasonic waves. Ultrasonic oscillations can greatly enhance the compatibility and mechanical properties of PS/HDPE blends because of the *in situ* formation of interchain copolymers of PS and HDPE.

In this work, ultrasonic oscillations were introduced during the extrusion of Illite-filled HDPE composites. The effects of the ultrasonic oscillations on the processing behavior, linear rheological behavior, and dispersion of Illite fillers in HDPE/Illite composites were studied.

EXPERIMENTAL

Materials

HDPE [DGDA6098; melt-flow index = 0.1 g/10 min, number-average molecular weight = 3.18×10^4, polydispersity (molecular weight distribution) = 8.8] was

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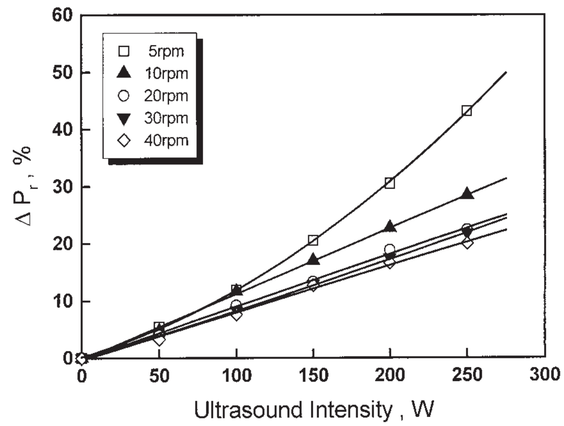


Figure 1 ΔP_r versus the ultrasound intensity for HDPE/Illite (70/30) composites at various extruder rotation speeds.

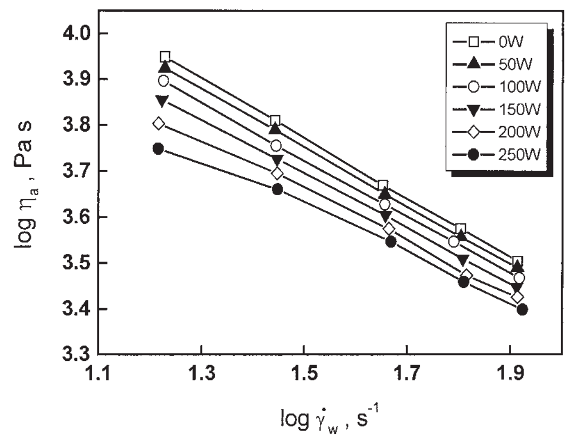


Figure 3 Apparent flow curves for HDPE/Illite (70/30) composites at various ultrasound intensities.

supplied by Qilu Petrochemical Co., Ltd. (Shandong, China). Illite powders were supplied by Zhejiang Wenzhou Mining Co. (Zhejiang, China).

Sample preparation

HDPE/Illite (70/30) composites were prepared in a single-screw extruder with a diameter of 25 mm and a length/diameter ratio of 28. The extrusion temperatures at different zones, from the hopper to the die, were set at 160, 180, 200, and 200°C. The screw speed was 30 rpm.

Rheological parameters

A special ultrasonic oscillation extrusion system,[22] developed in our laboratory, was used to investigate the processing behavior of the HDPE/Illite (70/30) composites. The measurements of the die pressure in the presence of ultrasonic oscillations were performed at a die melting temperature of 200°C, at screw rotation speeds of 5, 10, 20, 30, and 40 rpm, and at superimposed ultrasonic intensities of 0–250 W in steps of 50 W.

The shear stress on the capillary wall (τ_w) was determined as follows:

$$\tau_w = \frac{PR}{2L}$$

where P is the die pressure and R and L are the radius and length of the capillary, respectively.

The apparent shear rate ($\dot{\gamma}_w$) was obtained as follows:

$$\dot{\gamma}_w = \frac{4Q}{\pi R^3}$$

where Q is the volumetric flow rate. The apparent viscosity (η_a) was determined as follows:

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} = \frac{\pi P R^4}{8QL}$$

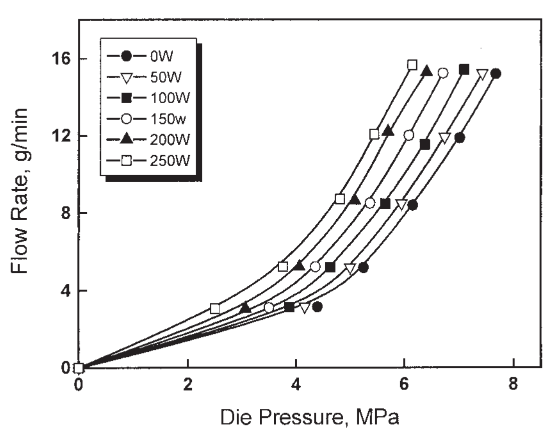


Figure 2 Flow rate versus the die pressure for HDPE/Illite (70/30) composites at various ultrasound intensities.

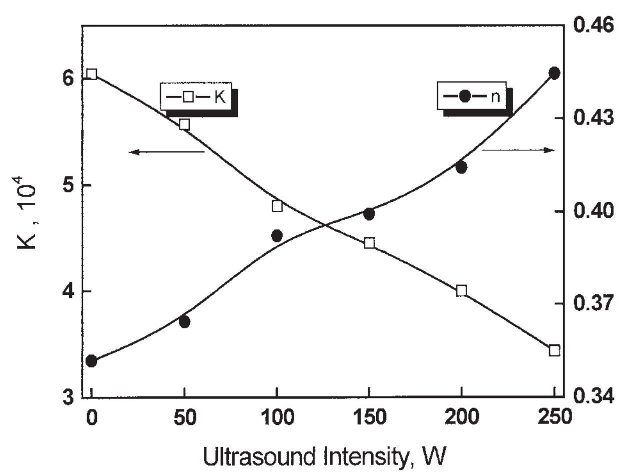


Figure 4 *k* and *n* versus the ultrasound intensity for HDPE/Illite (70/30) composites.

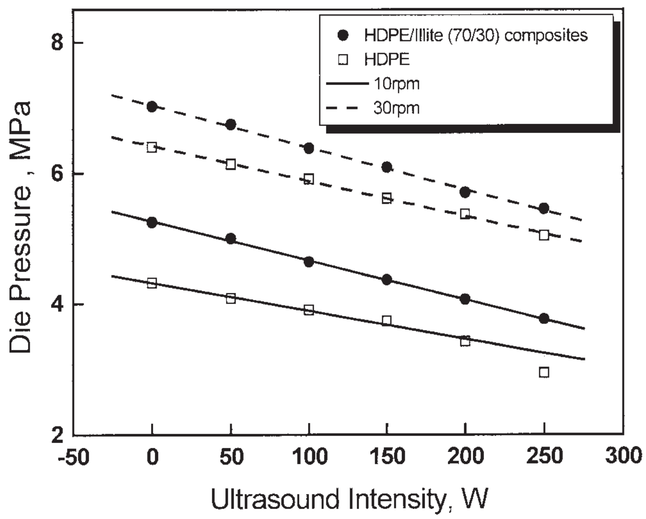


Figure 5 Die pressure versus the ultrasound intensity for HDPE/Illite (70/30) composites at various extruder rotation speeds.

The morphology of the composites was examined with a Hitachi X-650 scanning electron microscope (Hitachi Co., Japan). The impact-fractured surfaces, obtained at room temperature and the temperature of liquid nitrogen, were observed with scanning electron microscopy (SEM). Gold was sputtered on the surfaces before the SEM observations.

For the dynamic rheological behavior, the samples were compression-molded at 200°C into disks 25 mm in diameter and about 1.5 mm thick. The HDPE/Illite (70/30) composites were extruded at a die temperature of 200°C and an extruder rotation speed of 5 rpm in the absence and presence of ultrasonic oscillations. A 2ARES-9A rheometer (Rheometrics Co., United States) with parallel-plate geometry was used to measure the dynamic viscoelastic properties of the HDPE/Illite (70/30) composites with parallel-plate geometry. The measurements were performed in the frequency range of 0.01–10 Hz at various temperatures from 170 to 200°C. The tests were carried out in a nitrogen atmosphere to avoid the thermal degradation of the polymers at high temperatures. The strain was set to be small enough so that the rheological behavior was linear and viscoelastic. The zero-shear viscosity (η_0) was determined from Cole–Cole plots of the out-of-phase viscous component of the dynamic complex viscosity (η'') versus the dynamic viscosity (η').

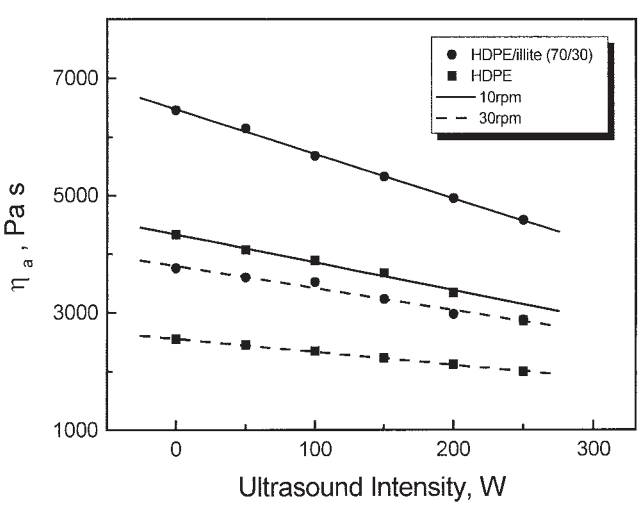


Figure 6 η_a versus the ultrasound intensity for HDPE/Illite (70/30) composites at various extruder rotation speeds.

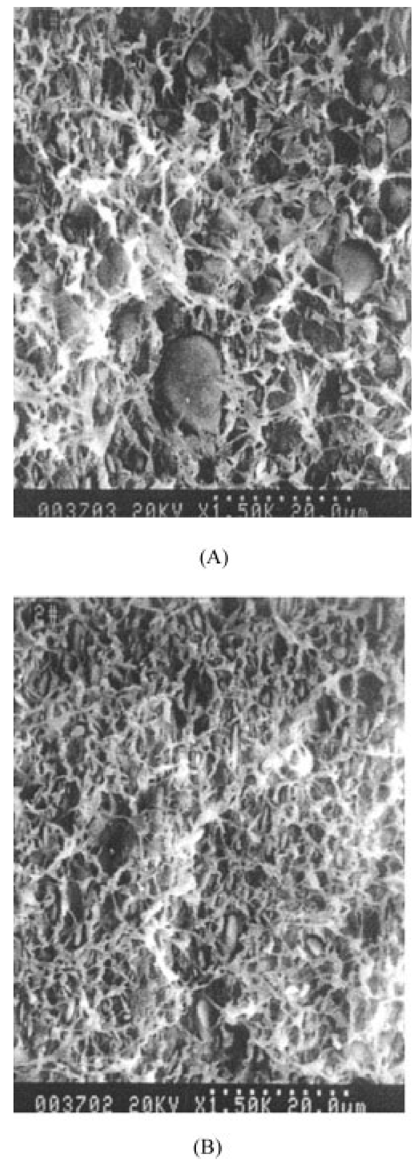


Figure 7 SEM images of the impact surfaces of HDPE/Illite (70/30) composites obtained at room temperature at ultrasound intensities of (A) 0 and (B) 250 W.

RESULTS AND DISCUSSION

Effect of the ultrasonic oscillations on the rheological behavior of the HDPE/Illite (70/30) composites during extrusion

The relative die pressure drop (ΔP_r) in the presence of ultrasonic oscillations can be written as follows:

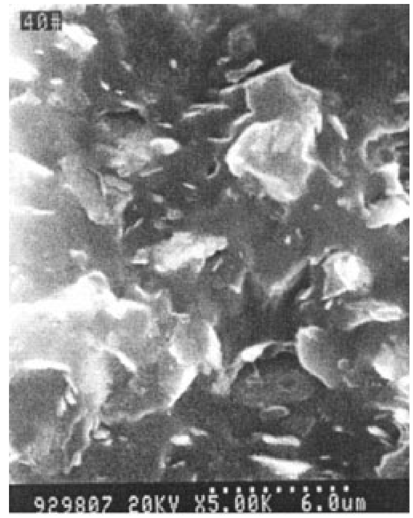
$$\Delta P_r = \frac{P_1 - P_2}{P_1} \times 100\%$$

where P_1 and P_2 are the die pressures in the absence and presence of ultrasonic oscillations, respectively. As shown in Figure 1, ΔP_r of the HDPE/Illite (70/30) composites increased with an increase in the ultrasound intensity but decreased with an increase in the screw rotation speed. At a given ultrasound intensity, ΔP_r was larger when the screw rotation speed was lower, and vice versa; this indicated that the die pressure of the HDPE/Illite (70/30) composites decreased during extrusion and the processability of the composites improved in the presence of ultrasonic oscillations.

Figure 2 shows the relationship between the mass-flow rate and the die pressure at different ultrasonic intensities during the extrusion of the HDPE/Illite (70/30) composites. The flow rate increased as the die pressure increased. The left shift shown on the curves of the flow rate versus the die pressure with increasing ultrasonic intensity indicates that the mass-flow rate of the HDPE/Illite (70/30) composites increased with increasing ultrasonic intensity at the same die pressure. Compared with that in the absence of ultrasonic oscillations, the mass-flow rate could be increased by a maximum of two times in the presence of ultrasonic oscillations.

Figure 3 shows the apparent flow curves of the HDPE/Illite (70/30) composites. The apparent viscosity behavior of the HDPE/Illite (70/30) composites followed a power-law equation, $\eta_a = k\dot{\gamma}^{n-1}$ (where k is the consistency coefficient and n is the power-law index), within the experimental range, and η_a decreased with an increase in the ultrasound intensity and screw rotation speed. η_a decreased more remarkably at a lower screw rotation speed. In the range of $\dot{\gamma}_w = 30-80\ s^{-1}$, linear regression was conducted for apparent flow curves of the HDPE/Illite (70/30) composites, and their k and n values were obtained. All relative coefficients of regression were greater than 0.99. The effect of the ultrasound intensity on k and n is shown in Figure 4. k decreased and n increased with an increase in the ultrasound intensity, and this indicated that the shear dependence of the melt viscosity was weakened and that the flow properties of the HDPE/Illite (70/30) composites improved in the presence of ultrasonic oscillations.

As shown in Figures 5 and 6, the die pressure and η_a of the HDPE/Illite (70/30) composites decreased more remarkably than those of HDPE in the presence of ultrasonic oscillations. Qu[23] observed analogous phenomena during a study of the effect of magnetic oscillations on PP/$CaCO_3$ and LLDPE/$CaCO_3$ systems, which were ascribed to the anisotropic diffusion of the instantaneous momentum of $CaCO_3$ particles. With the same filler volume portion of a composite system, the more aggregative the filler is, the higher the viscosity is of the system.[24] In the presence of ultrasonic oscillations, not only was the molecular motion of HDPE improved, but Illite particles were dispersed by the high-frequency oscillations of ultrasound, and this resulted in a smaller particle size and less aggregation of Illite particles in the composites. All of this reduced the viscosity of the composites.



(A)

(B)

Figure 8 SEM images of the impact surfaces of HDPE/Illite (70/30) composites obtained at the temperature of liquid nitrogen at ultrasound intensities of (A) 0 and (B) 250 W.

Figures 7 and 8 present SEM micrographs of impact-fractured surfaces of HDPE/Illite (70/30) samples extruded in the absence and presence of ultrasonic oscillations at the ambient temperature and the temperature of liquid nitrogen, respectively. In the absence of ultrasonic oscillations [Figs. 7(A) and 8(A)], large and aggregated Illite particles could be observed on the fractured surfaces of HDPE/Illite (70/30) composites. However, the Illite particles became smaller and the aggregation of the Illite particles disappeared [Figs.

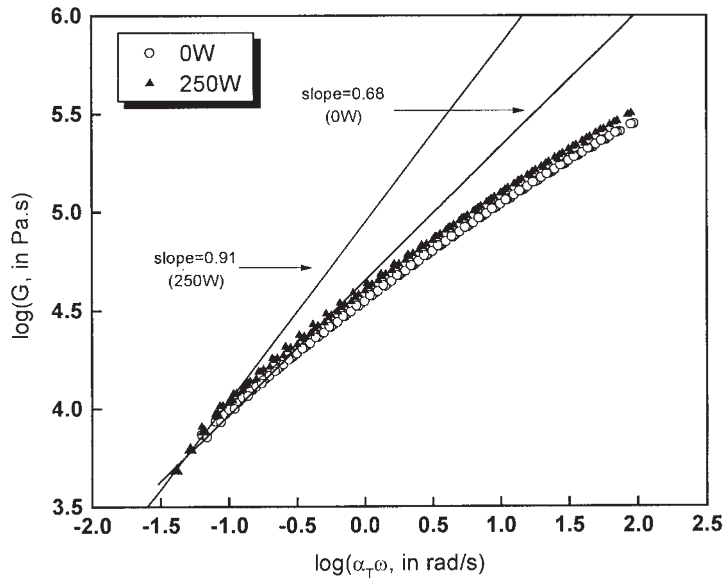


Figure 9 Master curve of G' for HDPE/Illite (70/30) composites at two ultrasound intensities.

7(B) and 8(B)] in the presence of ultrasonic oscillations. This confirmed that the relatively homogeneous dispersion of Illite particles into the HDPE matrix was achieved by the application of ultrasonic oscillations.

Effect of ultrasonic oscillations on the linear viscoelastic properties of the HDPE/Illite (70/30) composites

Master curves of log G' (storage shear modulus) versus log $\alpha_T\omega$ and log G'' (loss shear modulus) versus log $\alpha_T\omega$ (α_T is the only applied horizontal shift factor) for the HDPE/Illite (70/30) composites at 200°C were constructed with time–temperature superposition. The dynamic viscoelasticities of the polymer blends and composites were very sensitive to the variation of the morphological structures. At the terminal zone (i.e., the low-frequency zone), the slopes of the master curves were closely related to the variation of the composite morphology. The higher the slopes were, the better the composite compatibility was and the more uniform the particle dispersion was.[25–29]

Curves of log G' versus log $\alpha_T\omega$ and log G'' versus log $\alpha_T\omega$ of the HDPE/Illite (70/30) composites are shown in Figures 9 and 10. Ultrasonic oscillations during the extrusion of polymer composites increased the slope of the curve of log G' versus $\alpha_T\omega$. The slopes increased from 0.68 to 0.91 in the presence of ultrasonic oscillations. Within the low-frequency range, the

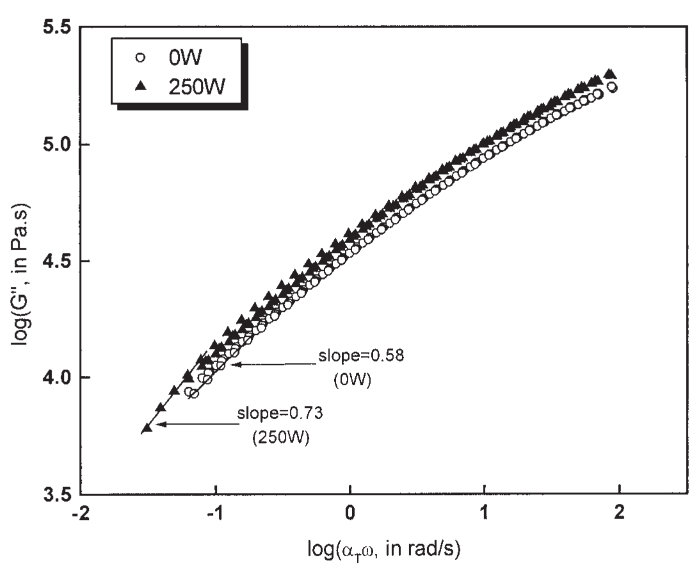


Figure 10 Master curve of G'' for HDPE/Illite (70/30) composites at two ultrasound intensities.

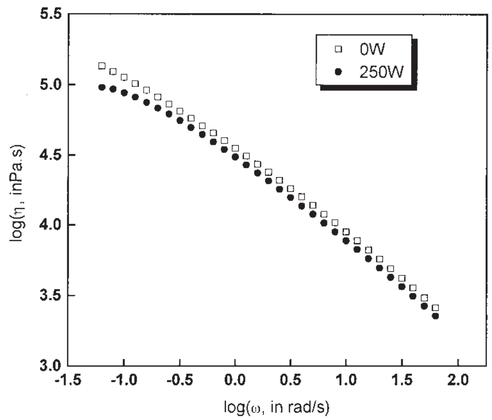


Figure 11 Log η' versus log ω for HDPE/Illite (70/30) composites at two ultrasound intensities.

slopes changed from 0.58 in the absence of ultrasonic oscillations to 0.73 in the presence of ultrasonic oscillations. As shown in Figure 11, ultrasonic oscillations caused a permanent reduction of η'. Meanwhile, the η_0 values were obtained by the extrapolation of Cole–Cole curves of experimental dynamic viscosities at 200°C.[30] η_0 of the HDPE/Illite (70/30) composites decreased from 11.62×10^5 in the absence of ultrasonic oscillations to 6.04×10^5 in the presence of ultrasonic oscillations. These results indicated that the particle dispersion of the HDPE/Illite (70/30) composites improved in the presence of ultrasonic oscillations; this was similar to the findings of our previous works.[22,31] The permanent reduction of the viscosity of the HDPE/Illite (70/30) composites was partially ascribed to the degradation of polyethylene.[32]

Ultrasonic oscillations could cause a reduction of the viscosity of the HDPE/Illite (70/30) composites and break up the aggregation of Illite particles. This benefited the homogeneous dispersion of Illite particles into the HDPE matrix.

CONCLUSIONS

The die pressure of the HDPE/Illite (70/30) composites decreased remarkably in the presence of ultrasonic oscillations during the extrusion. The higher the ultrasound intensity was, the lower the die pressure was. At a constant ultrasound intensity, the lower the extruder rotation speed was, the lower the die pressure was. η_a of the HDPE/Illite (70/30) composites decreased significantly and the flow rate increased to a maximum of about two times in the presence of ultrasonic oscillations during extrusion.

The apparent flow curves of the HDPE/Illite (70/30) composites followed a power law in the presence of ultrasonic oscillations during the extrusion. k decreased and n increased as the ultrasound intensity increased.

The Illite particles in the HDPE/Illite (70/30) composites became smaller and less aggregated in the presence of ultrasonic oscillations.

The dynamic viscoelastic properties of the HDPE/Illite (70/30) composites were changed remarkably in the presence of ultrasonic oscillations. Permanent reductions of η' and η_0 of the HDPE/Illite (70/30) composites were observed.

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