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AN IN-PROCESS ULTRASONIC APPROACH TO INVESTIGATING THE RELAXATION OF ORIENTATION AND DISORIENTATION OF POLYMER MELTS

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Abstract

The orientation and relaxation behaviors of a low density polyethylene melt after undergoing a shear flow in a restricted channel were investigated by using ultrasound. A capillary rheometer was used to force the polymer melt through a slit die equipped with pressure, temperature, and ultrasound sensors, and the variation of ultrasound velocity traversing the melt was measured. Experimental results revealed that due to different mechanisms involved, the relaxations of orientation and disorientation processes show different dependences on temperature and shear rate.

Introduction

It is well known that many properties, such as mechanical and optical properties, of polymer materials are strongly influenced by shear induced molecular orientation occurring under various polymer melt processing conditions. During such macroscopic deformation, the orientation of isotropic network of polymer chain segments becomes anisotropic with ability to adopt different conformations, from a coil to an extended chain. The disorientation is an opposite process to orientation by which the molecular chains recoil gradually after the cessation of shear. Apparently, the developments of molecular orientation and disorientation depend on the relaxation process due to the undergone great friction when macromolecular chains move. The relaxation phenomena in polymers have been the subject of research for many years, due to their importance in the modeling of polymer processing and analysis of processing experiments [1-3].

Traditionally, polymer relaxation is characterized by a spectrum of multiple relaxation times corresponding to various modes of relaxation a polymer chain can undergo. The longest relaxation time corresponds to the relaxation of a whole chain, while the shorter ones correspond to the relaxation of short parts of the macromolecules. In this paper, we are particularly interested in the relaxation behavior at molecular chain level. Dynamic rheometers are the most used means for providing relaxation time spectrum of polymer melts [4-6]. However, since they only generate small scale melt deformation during measurements, the relaxation time at macromolecular level

calculated from the terminal region of linear viscoelastic properties is not directly representative of the relaxation of the orientation or disorientation of molecular chains undergoing large deformation. The basic understanding of the mechanisms involved in orientation (disorientation) and its subsequent relaxation is based on the reptation theory by de Gennes and on the chain relaxation model developed by Doi and Edward [7]. Some computer simulations were performed to predict the relaxation behavior of polymer melts according to the concept of reptation [8, 9]. Recently, experimental characterization of molecular relaxation behavior is of particular interest for both industrial applications and fundamental understanding of the molecular mechanisms involved in polymer deformation. Several experimental techniques such as X-ray diffraction [10, 11], NMR spectroscopy [12, 13], and polarized infrared dichroism [11, 14, 15] have been applied extensively to measure the orientation (disorientation) and relaxation in polymers on a molecular scale in order to correlate the microstructure to the macrophysical properties. The studied objects were solid polymer samples, which were obtained by immediate quenching in the glassy state after being allowed to relax in the melt state for different time intervals in order to freeze the corresponding molecular orientation. These are off-line methods and cannot provide a continuous observation on the sample during melt deformation. The degree of orientation of injection-molded parts at the solidification stage has been studied by using ultrasonic shear wave transducers [16, 17]. Again, the method only applies to solid samples.

In this paper, we report a novel ultrasonic method for real-time study of the relaxations of orientation and disorientation of polymer melts. Ultrasonic technology offers the advantages of being non-invasive, non-intrusive, quick in response, and highly sensitive to micro-structural changes. These advantages make ultrasonic technology suitable for many real-time process diagnosis needs [18-21].

The velocity of ultrasound in a polymer melt can be expressed as a function of the bulk modulus, K , and the density, ρ , of the melt:

$$C = \sqrt{K/\rho} \quad (1)$$

When undergoing shearing stress, the macromolecular chains tend to align parallel to the direction of shear flow. The modulus in the direction perpendicular to shear flow decreases compared to an un-oriented polymer melt, resulting in a decrease in the velocity of ultrasound in the melt propagating perpendicularly to the shear flow direction. Similarly, the disorientation after the cessation of shear will result in an increase in the velocity of ultrasound propagated perpendicularly to the shear flow. This forms a theoretical basis for correlating the change of ultrasonic velocity to the relaxation of orientation or disorientation. The objective of this work is to establish a basic understanding of processing-orientation (disorientation)-relaxation-ultrasonic velocity relationships.

Experiments

The experimental setup is shown in Fig. 1. A slit die was fit to the barrel exit of a Rosand capillary rheometer. The slit die had a rectangular opening of 13.35 mm by 2.0 mm, a length of 140 mm, and was equipped with two ultrasound sensors located in cross-section I, one pressure sensor and a melt temperature sensor in cross-section II, and another pressure sensor and a die temperature sensor in cross-section III. The cross-sections I, II, and III were equidistantly located from the exit of the slit die. The slit die temperature was controlled with a wrapped-on heating jacket. The sensors and the thermocouple were flush-mounted in three cross-sections and perpendicularly to the wider surfaces of the slit. The ultrasound sensors were axially aligned, but on the opposite sides of the slit.

The material was a low density polyethylene (LDPE) with a melt index of 3.2 g/10min and density of 0.923 g/cc at 190 °C. The experiments were carried out at five set temperatures, namely, 166, 167, 200, 210 and 220 °C. For each test, the set temperatures for the rheometer barrel and the slit die were maintained at the same value. The polymer melt was forced through the slit die by means of a piston moving in the rheometer barrel. Nine piston speeds in the range of 10 to 90 mm/min were selected in this study. For ultrasonic measurements, one of the ultrasound sensors transmitted ultrasonic waves to the molten polymer. The transmitted ultrasonic waves were then received by the ultrasound sensor on the other side of the slit. By measuring the traveling time of ultrasound from the transmitter to the receiver, the ultrasound velocity in the molten polymer was obtained. The melt temperature was measured with the thermocouple. The melt pressure in the cross-section I probed by the ultrasound sensors was obtained through a second order polynomial fitting of pressure readings provided by the pressure sensors located in the cross-sections II and III and the pressure at the slit die exit (which was set to zero).

Results and Discussion

As can be seen from Eq. (1), the ultrasound velocity in a polymer melt is determined by the bulk modulus and mass density of the melt. When subjected to a shear flow, the molecular chains of a polymer melt can be forced to orient along the shear flow direction. After the cessation of flow, the macromolecules will undergo a disorientation process by which the molecular chains recoil with time. These changes in microstructure will affect the bulk modulus, and to a much lesser extent, the melt density, leading to a change in the velocity of ultrasound propagating in the polymer melt. However, variations in the temperature and pressure also affect sound velocity through their effects on bulk modulus and density. It has been observed that within the temperature and pressure variation ranges encountered during the tests, the effects of temperature and pressure on ultrasound velocity can be reasonably well factored into the following equation via a linear dependence of ultrasound velocity on temperature and pressure:

$$C(S, T, P) = C(S_0, T_0, P_0) + C_T(T - T_0) + C_P(P - P_0) + f(S_0, S) \quad (2)$$

where $C(S_0, T_0, P_0)$ is the ultrasound speed measured at temperature T_0 and pressure P_0 when the melt is in a static state denoted by S_0 , $C(S, T, P)$ is the sound speed measured at temperature T and pressure P when the melt is in a state S , C_T and C_P are the sensitivity coefficients of ultrasound velocity to temperature and pressure changes, and $f(S_0, S)$ is the variation of ultrasound velocity caused by the material structure change from state S_0 to state S that is not accounted for by the linear temperature and pressure dependences in Eq. (2). We use C_R to replace $f(S_0, S)$ in Eq. (2) with the subscript "R" denoting the velocity variation relative to the initial state and with pressure and temperature effects cancelled out, and we have

$$C_R = C(S, T, P) - C(S_0, T_0, P_0) - C_T(T - T_0) - C_P(P - P_0) \quad (3)$$

The coefficients C_T and C_P were obtained through a separate study in which the ultrasound speed in the polymer melt were measured under various temperatures and pressures and when the melt was in a static state.

As an example, Fig. 2 shows typical behaviors of melt temperature, pressure, ultrasound velocity C during a test carried out at set temperatures of 167 °C and a shear rate of 23.1 s⁻¹. The process is divided into three stages, namely, static stage (from 0 to 13.5 s), shearing stage (from 13.5 to 44.9 s) during which the piston was pushing the melt through the slit die, and post-shearing stage (from 44.9 s to the end) during which the movement of the piston was stopped. One can see that the melt temperature

increases slightly (about 0.5 °C) during the shearing stage due mainly to shear heating, then decreases gradually in the post-shearing stage. According to one of our separate studies, this temperature rise can lead to a small decrease of about 1 m/s in ultrasound speed. At the beginnings of shearing and post-shearing stages, the pressure changes sharply. Under the effect of pressure, the ultrasound velocity also changes sharply in the direction of pressure change. However, after the pressure stabilizes, the ultrasound velocity evolves in an opposition direction, due to the variation in the degree of molecular chain orientation. It should be pointed out that the ultrasound velocity carries almost the same value at the end of the post-shearing stage as that in the static stage, suggesting that the original molecular structure was completely recovered at the end of the process. The above analysis demonstrates clearly that the ultrasound velocity can reveal the structural information related to the relaxations of macular orientation and disorientation.

The effects of pressure and temperature on the ultrasound velocity displayed in Fig. 2 can be cancelled out after Eq. (3). The resulting C_R for the shearing stage is shown in Fig. 3. For easier presentation, the starting point of the shearing stage is taken as the origin of the time axis of the figure. The experimental data shown in Fig. 3 can be reasonably well described by the following relaxation model:

$$C_R(t) = C_\infty(1 - e^{-t/\tau}) \quad (4)$$

where τ is the relaxation time and C_∞ represents the chain orientation induced change of ultrasound velocity after the melt flow reaches a steady state. By using least squares fitting, we obtained $C_\infty = -8.92 \text{ m/s}$, and $\tau = 3.55 \text{ s}$.

Figure 4 provides a comparison among the values of C_∞ measured under different shear rates and different temperatures. The absolute value of C_∞ increases with increasing shear rate. Every increase in melt temperature results in a downward shift of the curve (i.e. an increase of the absolute value of C_∞). Molecular orientation is not a spontaneous process. The positive effects of shear rate and temperature on orientation can be well explained by the facts that a stronger shearing force increases the deformation of macromolecules in kinetics, and a higher temperature decreases the potential energy of molecular motion in thermodynamics.

Molecular orientation can also affect melt viscosity. Figure 5 displays corresponding melt viscosities measured at the same time of ultrasonic tests. The influence of shear rate and temperature on viscosity is totally reverse to that on C_∞ . The viscosity decreases with increasing

temperature and shear rate. Since at high melt temperatures as is the case of this study, a decrease in melt viscosity indicates a decrease in melt modulus, whereas an increase in the absolute value of C_∞ (or decrease of ultrasound speed) with increasing temperature and shear rate is also a consequence of reduced modulus, both ultrasonic and viscosity measurements point to the same direction.

Figure 6 reveals the effects of shear rate and temperature on orientation relaxation time. The relaxation time decreases moderately with increasing shear rate at different temperatures. The dependence of relaxation time on temperature is not obvious compared to that on shear rate. Overall, the relaxation process is faster at higher temperatures in the range from 167 to 220 °C. However, the influence of temperature on relaxation time is more pronounced at the lower end of shear rate. At high shear rates, all the relaxation times fall in the range between 2 and 3 s. The data seem to suggest a convergence of the relaxation curves to a limiting point at higher shear rates, independently of temperature. Obviously, this revelation cannot be explained by the classical WLF equation that predicts strong temperature dependence of relaxation time near glass transition temperature.

Molecular disorientation takes place in the post-shearing stage, after the cessation of shear flow. The molecular disorientation causes a slow increase in ultrasonic velocity as shown in Fig. 2. The relaxation process of disorientation was investigated through the same approach described earlier for the orientation process except that the following relaxation model is used to describe the experimental data:

$$C_R(t) = C_0 e^{-t/\tau} \quad (5)$$

where the starting point of the post-shearing stage was taken as the origin of time counter, and C_0 represents the chain orientation induced change of ultrasound velocity with respect to that after disorientation is completely relaxed. The evolution of C_R corresponding to the post-shearing stage displayed in Fig. 2 is shown in Fig. 7 in which the values of C_0 and τ are -6.76 m/s and 5.86 s, respectively. Note that the relaxation time of disorientation is greatly different from that of orientation. This is attributed to the fact that thermodynamically the molecular disorientation is a spontaneous process with distinct relaxation mechanisms from that of orientation.

Figures 8 and 9 show the influence of shear rate and temperature on C_0 and the relaxation time of disorientation, respectively. For the disorientation process, the evolutions of C_0 versus shear rate and temperature behave very similarly to those of C_∞ in the orientation

process. However, the temperature and shear rate dependence of the relaxation time appears negligible in the disorientation process compared to the orientation process. This coincides with the finding by G. Wiberg that the relaxation of thermotropic liquid crystalline copolyester was independent of temperatures above 275 °C [22]. This suggests that the relaxation time of the disorientation process of a polymer melt could be advantageously used as an intrinsic property of the polymer owing to its insensitiveness to shear rate and temperature. This needs to be confirmed by further studies.

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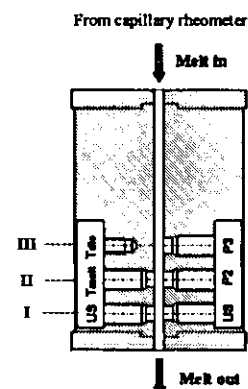


Figure 1. Instrumented slit die.

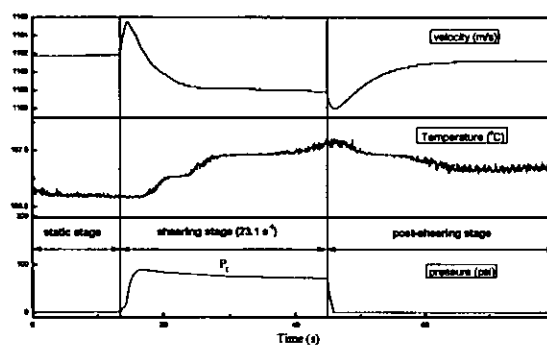


Figure 2. Evolution of ultrasound velocity, melt temperature, and melt pressure during a test carried out at set temperatures of 167 °C and a shear rate of 23.1 s⁻¹.

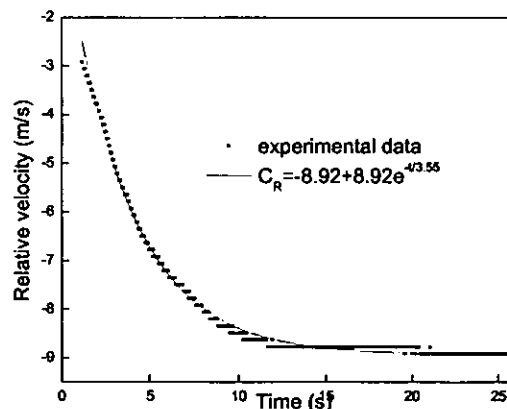


Figure 3. Modeling of the relation between relative velocity (C_R) and process time during orientation at a shear rate of 23.1 s⁻¹ and a temperature of 167 °C.

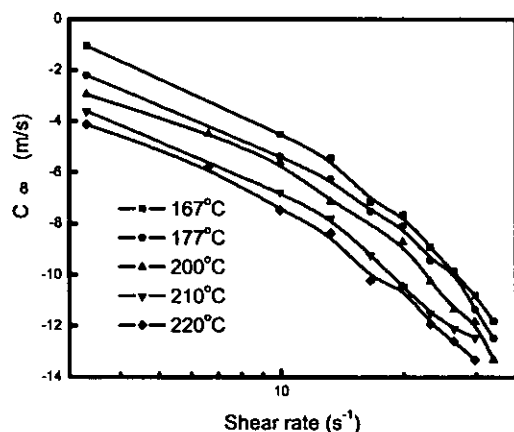


Figure 4. Shear rate and temperature dependences of C_∞ during orientation.

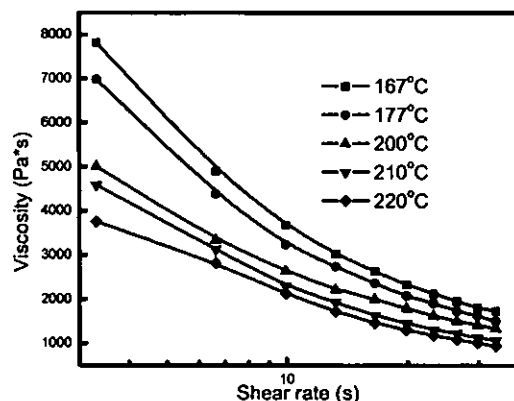


Figure 5. Apparent viscosity versus shear rate at different temperatures measured during the orientation stage.

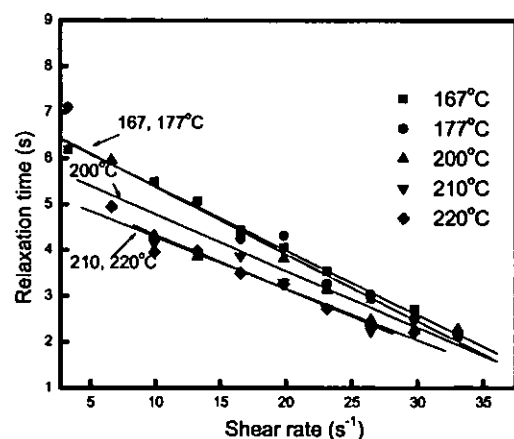


Figure 6. The shear rate and temperature dependences of relaxation time during orientation.

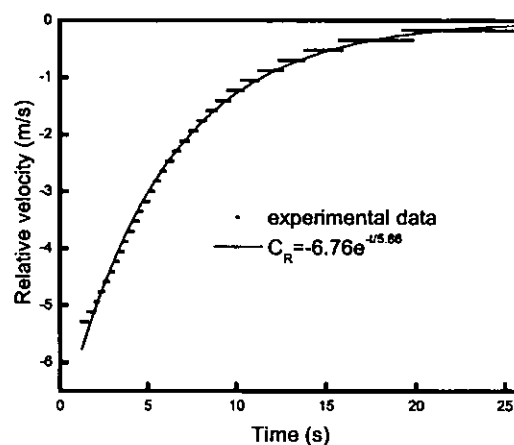


Figure 7. Modeling of the relation between relative velocity (C_R) and process time during disorientation at a shear rate of 23.1 s^{-1} and a temperature of 167°C .

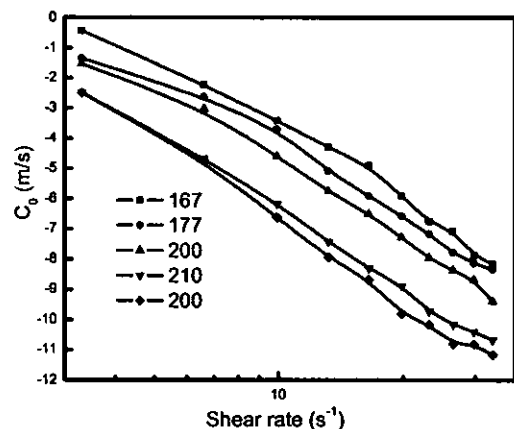


Figure 8. The shear rate and temperature dependence of C_0 during disorientation.

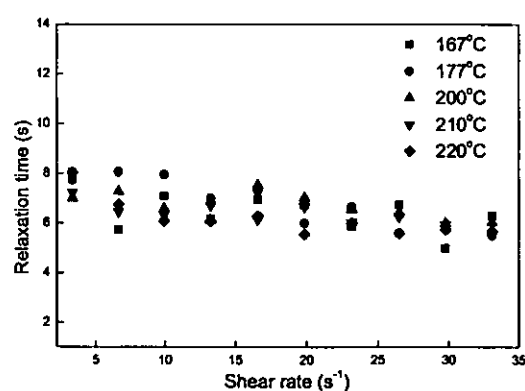


Figure 9. Shear rate and temperature dependences of relaxation time during disorientation.

Key Words: Ultrasound, Relaxation, Molecular chain orientation, Molecular chain disorientation.