Real-time characterization of polymer-chain orientation

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Ultrasound is a powerful tool for monitoring orientation and disorientation behavior of polymer melts during processing.

A certain level of shear stress and rate during processing results in polymer chains melting along the direction of the external force, with the chains transforming from coils to extended configurations. When the shear is halted, the molecular chains recoil. The non-negligible friction between molecular chains affects the relaxation of both a chain’s orientation and disorientation. Orientation plays a key role in final product characteristics, such as mechanical, optical, barrier, and thermal properties.\(^1\),\(^2\) Therefore, many efforts have focused on measuring degrees of orientation. In the past decade, various approaches have been developed to characterize orientation, including wide-angle x-ray diffraction and scattering, optical birefringence, IR dichroism, and nuclear magnetic resonance.\(^3\),\(^4\)\(^5\) However, most of these methods operate off-line and are costly and time-consuming. They cannot be used to continually inspect orientation-relaxation behavior.

We have developed a novel ultrasonic technique to study in-process orientation and disorientation relaxation of polymer melts. Ultrasound has been widely applied to characterize injection molding and extrusion processes in real time\(^6\),\(^7\) because of its robustness, safety, simplicity, fast response, nondestructiveness, noninvasiveness, cost-effectiveness, and high sensitivity to material properties and processing conditions. However, research aimed at gaining a fundamental understanding of the relationship between ultrasonic measurements and orientation-relaxation behavior is relatively scarce.\(^8\),\(^9\) We have, therefore, investigated the effects of molecular weight, shear rate, and temperature on orientation and disorientation relaxation of polymer melts.

We designed and employed a special experimental apparatus (see Figure 1). An instrumental slit die (flow-channel dimensions: \(20 \times 2 \times 250\) mm\(^3\)) was fitted to the barrel exit of a capillary rheometer. (The latter is used to preheat samples and induce a certain level of shear stress.) We equipped the slit die with two ultrasonic sensors, two pressure/temperature transducers, and a die-temperature sensor.

The velocity of longitudinal waves (\(C\)) through the polymer material is a function of the bulk modulus (\(K\)) and density (\(\rho\)),

\[
C = \sqrt{\frac{K}{\rho}}
\]  

During orientation, a decrease in bulk modulus perpendicular to the shear flow results in a velocity decrease. (The opposite applies to

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Figure 2. Relaxation processes for JHC7260 (a type of high-density polyethylene resin) at a shear temperature of 185°C and a shear rate of 22.1 s⁻¹. (a) Orientation. (b) Disorientation. $C_R$: Relative ultrasonic velocity. $t$: Time.

disorientation.) The evolution of the ultrasonic velocity during orientation and disorientation obeys, respectively (see Figure 2),

$$C_{R1}(t) = C_1(1 - e^{-t/\tau_1})$$

(2)

and

$$C_{R0}(t) = C_0e^{-t/\tau_0},$$

(3)

where the subscripts $n = 1, 0$ represent orientation and disorientation, respectively, $C_n$ and $C_{Rn}$ are the maximum relative velocity and the relative ultrasonic velocity, respectively, $\tau$ is the relaxation time, and $C(t)$ is the maximum velocity at time $t$ with respect to that in the unoriented state, $C(t_0)$.

Figures 3 and 4 show the effects of shear rate, temperature, and molecular weight on orientation and disorientation. The maximum degree of orientation ($C_1$) and disorientation ($C_0$) increases with increasing shear rate and temperature, while the orientation-relaxation time simultaneously decreases. This can be explained by considering that the presence of an external force thermodynamically favors molecular-chain motion. (The interactions of molecular chains could be reduced by increasing the temperature.) Note that no pronounced variation in disorientation time is seen during disorientation because molecular disorientation is a spontaneous process. The sample characterized by a low melt index exhibits a significant increase in both the maximum degree of orientation and the relaxation times of orientation and disorientation.

In summary, we have demonstrated how orientation and disorientation relaxation behavior can be measured using ultrasound. Our results reveal that the ultrasonic velocity is sensitive to orientation and disorientation relaxation during processing. Our future work will focus on high-density polyethylene and other polymer composites to study the influences of compatibilizer concentration and component ratio on their orientation and disorientation relaxation behavior.

Figure 3. Effects of shear rate and molecular weight on the maximum degree of orientation, and on the relaxation time of orientation and disorientation. 5000S, DGDB2480: Types of high-density polyethylene resin. $C_1, C_0$: Maximum degree of orientation and disorientation.

Figure 4. Effects of temperature on the maximum degree of orientation, and on the relaxation time of orientation and disorientation for JHC7260.

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