

Rheological Properties of Polypropylene Modified by High-Intensity Ultrasonic Waves

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ABSTRACT: A new method using high-intensity ultrasonic waves, instead of peroxide-aided reactive extrusion, was applied to modify a linear polypropylene into a branched structure. The ultrasonic waves induced chain scission and created reactive macromolecules of polypropylene successfully in the melt state without any peroxide. To enhance and control the recombination reaction during sonication, a multifunctional agent and an antioxidant were used. The rheological property measurements clearly confirmed that the modified polypropylene had a nonlinear branched structure. It showed shear-thinning behaviors in its viscosities at low frequencies, high elastic behaviors in

Cole–Cole plots, and a high rheological polydispersity index in comparison with a linear polypropylene. The degradation or recombination of polypropylene was adequately controlled by an antioxidant, which stabilized the structure during sonication. Also, the use of an antioxidant was quite effective in improving the extrusion processability by delaying the instability of the extrudate to a higher shear rate.

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INTRODUCTION

Polypropylene (PP) is one of the most widely used commercial polymers. The advantages of PP are its economy, good thermal stability, mechanical properties, chemical resistance, wide processing window, and environmentally friendly nature. With these advantages, PP is greatly appreciated by the food and automotive industries. The application of PP to the foam and thermoforming industries has been limited, however, because of its weak melt strength and melt elasticity. When the melt strength and melt elasticity are weak, the cell walls separating the bubbles cannot be strong enough to keep the extensional force, and they are apt to rupture easily in the foaming process. Also, a high degree of sagging makes it difficult to control the product quality in the thermoforming process. The addition of long-chain branches to the PP backbone is an alternative for improving its melt strength and, as a result, its foaming or thermoforming processability. Several methods have been introduced to change the structure of PP from linear to

branched. Widely used methods include high-energy irradiation and reactive extrusion with a multifunctional agent (MFA) and peroxide.^{1–10}

In this study, a new method using high-intensity ultrasonic waves was applied to make long-chain-branched PP. High-intensity ultrasonic waves are generally employed in the areas of cleaning, plastic welding, machining, and so forth. In addition to these conventional applications, when a polymer solution is subjected to the irradiation of high-intensity ultrasonic waves, main-chain scission of the polymer occurs, and consequently the molecular weight (MW) decreases.^{11,12} Also, according to previous result, it is possible to induce the chain scission of PP in the melt state by high-intensity ultrasonic waves without any solvent or additives.¹³ This can be explained by the interaction of ultrasound and component molecules. High-intensity ultrasound, in comparison with diagnostic ultrasound, is generally at a lower frequency at which greater acoustic energy can be generated to induce cavitation in liquids. In a liquid, upon ultrasound irradiation, molecules are expected to alternate between compression and expansion modes, by which bubbles are formed and eventually collapsed. At the molecular level, this implies a rapid motion of solvent molecules to which the macromolecules embedded in the solvent cannot adjust. Thus, friction is generated and eventually causes bond rupture in the macromolecules.¹⁴

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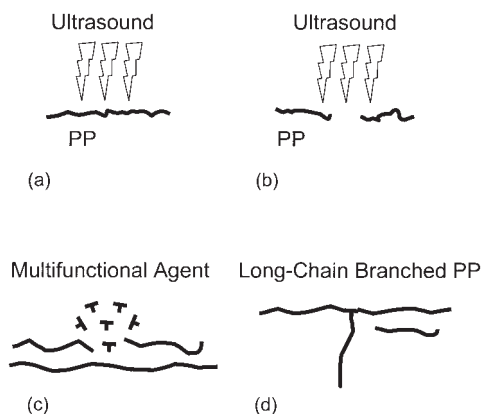


Figure 1 Schematic description of long-chain-branched PP by ultrasonic wave.

Uniform degradation and radical generation in PP were produced by a sonication process in this study. The created reactive macroradicals were expected to lead the recombination reaction, and as a result, a long-chain-branched structure was obtained. This peroxide-free method has advantages in comparison with the peroxide-aided method. The absence of peroxide could eliminate the possibility of unreacted peroxide remaining after processing and, as a result, lead to long-term stability of the mechanical and rheological properties. Figure 1 shows the expected mechanism of long-chain-branched PP by ultrasonic waves. To enhance or control the recombination reaction during sonication, an MFA and an antioxidant (AO) were used. The rheological and thermal properties were measured to characterize the effect of MFA and AO on the performance of long-chain-branched PP. Finally, the processabilities of the linear and modified PPs were compared. The first limiting factor on the production rate or processability during polymer processing is the onset of sharkskin or melt fracture.^{15,16} The effect of long-chain branches of PP on the onset of melt fracture was observed from the extrudate appearance.

EXPERIMENTAL

Sample preparation

Homopolypropylene (melt index = 3.3, 230°C, 2.16 kg) from Samsung–Atofina Co. (Seosan, Korea) was used in this study. The MFA was trimethylolpropane triacrylate from Aldrich Chemical Co. (St. Louis, MO). The AO was Songnox-11B from Songwon Industrial Co. (Ulsan, Korea); it was a blend of primary and secondary AOs with the same ratio.

To impose ultrasonic waves during melt mixing, a specially designed ultrasonic horn was assembled with a Rheocord 600 mixer from Haake (Karlsruhe, Germany). The details of the mixer are found in ref. 13. The horn vibrated longitudinally at a frequency of 20

kHz with an amplitude of 15 μm . A 1.5-kW power supply with a piezoelectric converter was used. For a durable operation, an effective cooling accessory was necessary. Before the mixing operation, PP was dried in a vacuum oven at 80°C for 24 h. Each sample was prepared on a fixed volume basis of 70%, and the mixing temperature was set to 210°C with 50 rpm. Before the ultrasonic irradiation, preliminary mixing was carried out for 1 min to reach the melt state. The sonication time was fixed to 5 min, and the on/off ratio of the ultrasonic irradiation was varied (5 : 5, 8 : 2, and 10 : 0). The 10 : 0 ratio means the highest sonic intensity, whereas the 5 : 5 ratio is the lowest.

Rheological property measurements

The samples obtained from the internal mixer were compression-molded at 230°C for 5 min. Disk-shaped specimens with a thickness of 2 mm and a diameter of 25 mm were prepared. An ARES rotational rheometer (TA Instrument, New Castle, Delaware) was used to measure the complex modulus and the complex viscosities as linear viscoelasticities and the time-dependent viscosities after the startup of steady shearing as nonlinear viscoelasticities of PPs. The measurements of the dynamic viscosities were performed with a parallel-plate fixture (diameter = 25 mm), with a gap distance of 1.2 mm, and the strain was kept at 10% to ensure linear viscoelasticity. The frequency range was 0.1–500 rad/s, and the temperature was 230°C. The work was conducted under a nitrogen atmosphere to prevent degradation.

Thermal property measurements

The thermal properties were measured with a TA Instrument 2910 differential scanning calorimeter. The temperature and heat flow area were calibrated with indium before the analysis. The samples (ca. 10 mg) were sealed in an aluminum pan and heated or cooled in a nitrogen atmosphere. Initially, the samples were heated from room temperature to 230°C at a rate of 10°C/min and cooled at a rate of 10°C/min to obtain the crystallization temperature (T_c). They were reheated to 230°C to obtain the melting temperature (T_m).

Extrudate appearance measurements

To observe the extrudate appearance, a Goettfert (Buchen, Germany) Rheograph 2003 capillary rheometer was used. A capillary die with a diameter of 2.0 mm, an entrance angle of 180°, and a length/diameter ratio of 15 was used. The test temperature was set to 210°C. Samples were obtained by rapid quenching to avoid gravity effects. A cooling solution was made via the mixing of water and ethanol to keep the specific

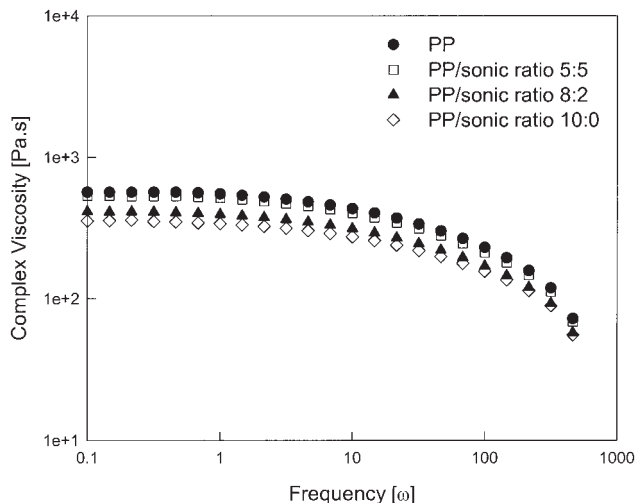


Figure 2 Ultrasonic degradation of PP as sonic intensities.

gravity of the solution to that of the extrudates. The extruded samples were observed by optical microscopy (Optiphoto 2-POL, Nikon, Tokyo, Japan).

RESULTS AND DISCUSSION

Rheological properties

Figure 2 shows the complex viscosities of PPs with various sonication degrees. The complex viscosities decreased with the sonic intensities, and this was clear evidence of the chain scission of PP by ultrasonic waves during melt processing. Also, the long Newtonian plateau behaviors of the viscosities at low frequencies showed that the main reaction was scission instead of recombination. To accelerate the recombination reaction, the MFA was introduced. The effects of 3 phr MFA on the complex viscosities are presented in Figure 3. When 3 phr MFA was added without sonication, MW increased because the complex viscosities increased, whereas the plateau regions decreased. As the ultrasonic waves were dosed, the viscosities decreased, and there were significant shear-thinning behaviors at low frequencies. Also, the shear-thinning degree was pronounced as the sonic intensity increased. The double bonds of the MFA were thought to act as sites for trapping macroradicals of PP. In particular, when the macroradical of PP was tertiary alkyl, the MFA reduced the disproportionation reaction significantly and augmented the recombination efficiency.¹⁷

Figure 4 shows the effect of AO on the viscosities of PPs. For clarity in the explanation, the samples are named as follows:

- Case 1. PP/0.2 phr AO.
- Case 2. PP/0.2 phr AO (sonic ratio = 8:2).
- Case 3. PP/3 phr MFA.

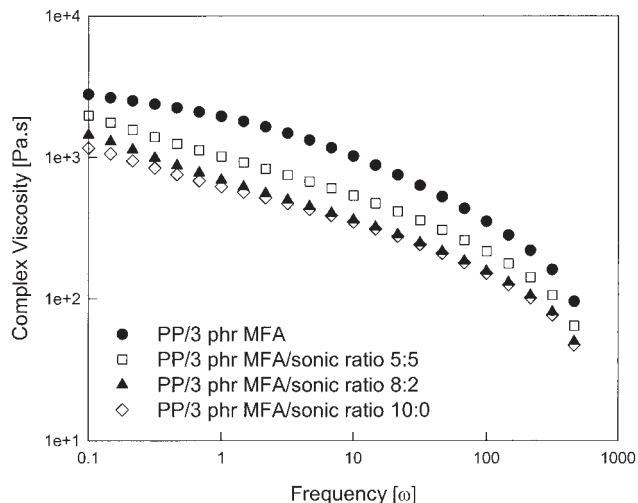


Figure 3 Effect of MFA on the viscosities of PPs with various sonic intensities.

Case 4. PP/3 phr MFA (sonic ratio = 8 : 2).

Case 5. PP/3 phr MFA/0.2 phr AO.

Case 6. PP/3 phr MFA/0.2 phr AO (sonic ratio = 8 : 2).

Cases 1 and 2 show the effect of sonication when 0.2 phr AO was added. There were increases in the viscosities in case 1, whereas the plateau regions decreased in comparison with neat PP in Figure 2. Even when the sonic ratio of 8 : 2 was irradiated, in case 2, there was little change in the viscosities. Also, when 3 phr MFA was added without sonication in case 3, there were increases in the complex viscosities. As the ultrasonic ratio of 8 : 2 was irradiated in case 4, there were significant shear-thinning behaviors with the reductions of the viscosities. In case 6, in which the MFA

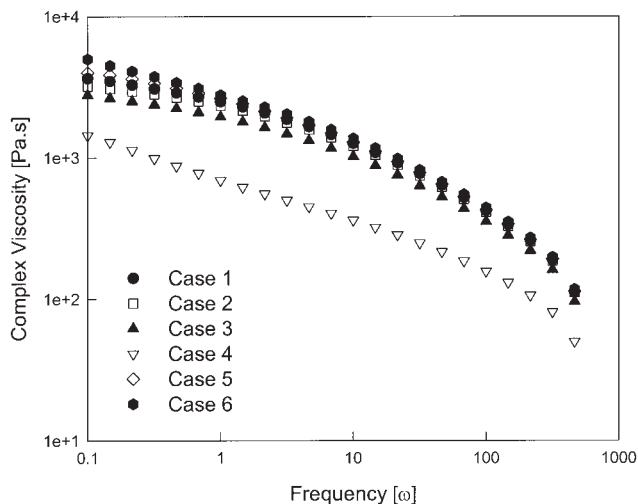


Figure 4 Effect of AO and MFA on the viscosities of PPs with various sonic intensities.

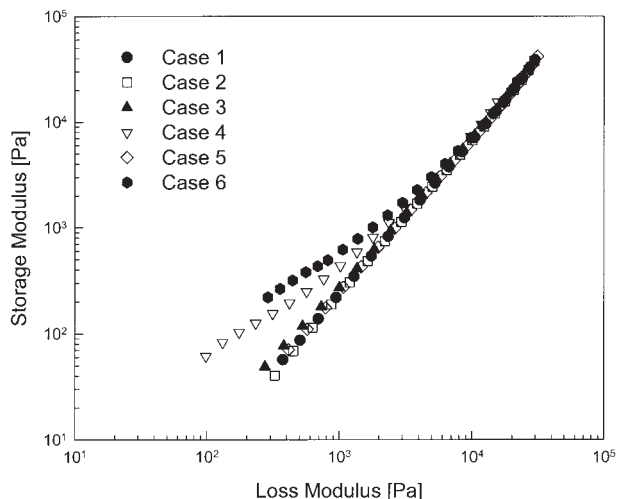


Figure 5 Cole-Cole plots for various PPs.

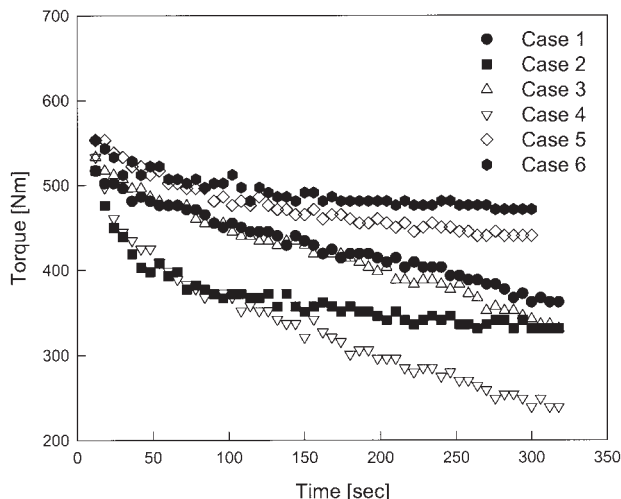


Figure 7 Mixer torque data for various conditions.

and AO were added together with the ultrasonic ratio of 8:2, on the other hand, there were shear-thinning behaviors at low frequencies without any reduction of the viscosities.

Figure 5 shows Cole-Cole plots for six cases. The data for all PP samples, except cases 4 and 6, show no plateau behaviors and lie in a single straight line. Cases 4 and 6 showed high elastic behaviors. It is believed that a physically connected structure increases the relaxation time and the dynamic storage modulus.¹⁸ Therefore, this result clearly showed that cases 4 and 6 had a long-chain-branched structure.

The time-dependent viscosities after the startup of steady shearing, $\eta^+(t, \dot{\gamma})$, for cases 1, 4, and 6 are presented in Figure 6. In case 1, $\eta^+(t, \dot{\gamma})$ below a shear rate of 1 s^{-1} was nearly in the linear viscoelastic regime, in which the viscosities became independent of

the shear rate. As the shear rate increased, $\eta^+(t, \dot{\gamma})$ decreased. When the sonic wave was dosed (cases 4 and 6), the viscosities deviated from the linear viscoelastic response even at low shear rates because of the nonlinear structure of PP. In case 4, $\eta^+(t, \dot{\gamma})$ did not reach the steady-state value even after a long time and at a low shear rate.

The mixing torque data of the samples are presented in Figure 7. A higher torque value meant the recombination reaction or the retention of the MW during mixing. Case 4 showed a low torque value because of the reduction of the MW, although it had a branched structure, as shown in Figure 5. Also, the high torque value of case 5 was not from a branched structure but from the retention of the MW. Case 6 showed the highest torque value, which was due to both the maintenance of the MW and the long-chain branches.

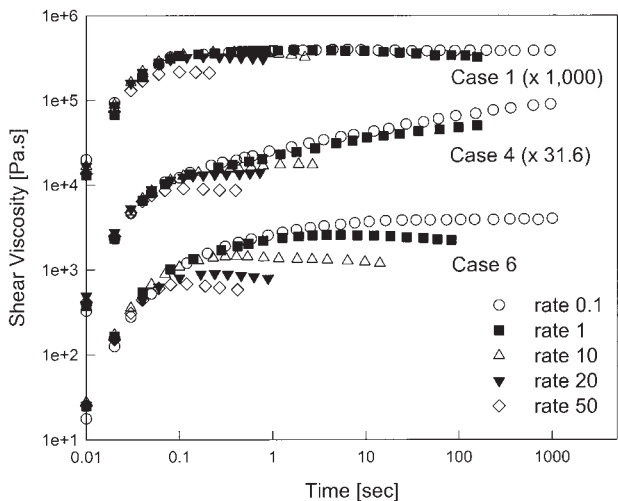


Figure 6 Growth of the shear viscosity as a function of time after the startup of steady shearing at various shear rates.

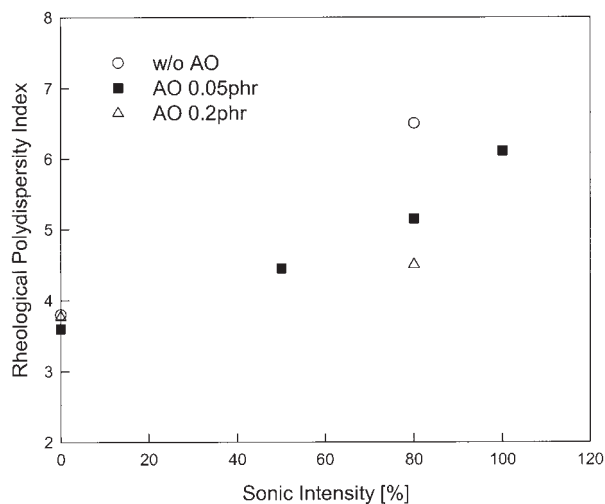


Figure 8 RPI for various sonic intensities and AO contents.

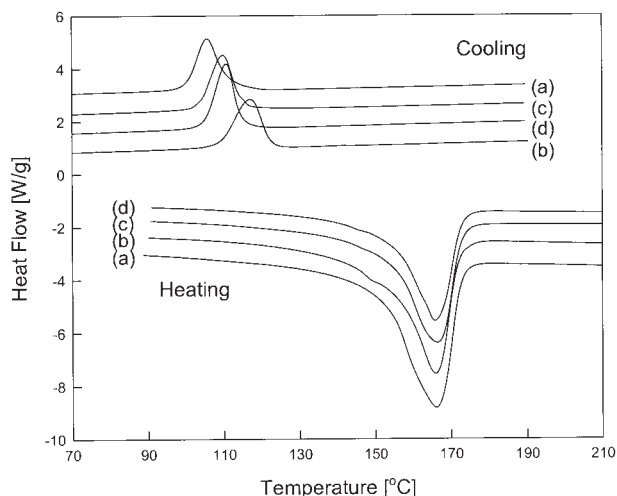


Figure 9 DSC melting and cooling behaviors of four PPs: (a) neat PP, (b) PP/3 phr MFA (sonic ratio = 8 : 2), (c) PP/3 phr MFA/0.05 phr AO (sonic ratio = 8 : 2), and (d) PP/3 phr MFA/0.2 phr AO (sonic ratio = 8 : 2).

The rheological polydispersity index (RPI) can be defined as $10^5/G_c$, where G_c is the crossover modulus (Pa; storage modulus = loss modulus).¹⁹ RPI is proportional to the MW distribution or the degree of long-chain branching. Figure 8 shows the RPI results as the sonic intensity with or without AO. MFA (3 phr) was added to all samples. The RPI increased with the sonic intensities. Also, the degree of the RPI increase was reduced with the AO contents. The addition of AO was an effective way of controlling the degree of branching and MW at the same time.

Thermal properties

Figure 9 presents the results for the melting and cooling behaviors of four different PPs. The T_m and T_c values are listed in Table I. The four PPs had similar T_m values, whereas the modified PPs had higher T_c values than linear PP. The branching or crosslinking unit considerably increased the nucleation density of PP and accelerated the crystallization.²⁰ When the AO was added, T_c lay between that of the linear PP and the sonicated PP without the AO.

Extrusion processability

Photographs of three extrudates at a shear rate of 28.8 s^{-1} are shown in Figure 10. At this shear rate, only

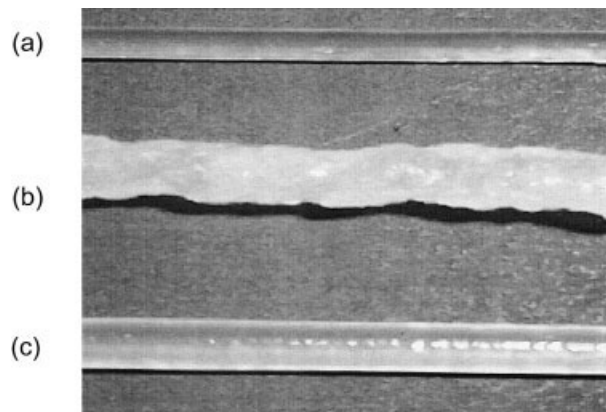


Figure 10 Photographs of the extrudates of three PPs: (a) neat PP, (b) PP/3 phr MFA (sonic ratio = 8 : 2), and (c) PP/3 phr MFA/0.05 phr AO (sonic ratio = 8 : 2).

sample B, PP/3 phr MFA (sonic ratio = 8 : 2), showed gross instability. In the case of linear PP (A), the flow instability appeared at a shear rate above 950 s^{-1} . In the case of sample C, PP/3 phr MFA/0.05 phr AO (sonic ratio = 8 : 2), the instability started at about 100 s^{-1} , whereas it began at 20 s^{-1} in the case of sample B. The branched structure showed poor processing performance from the viewpoint of flow instability. This was due to the high melt strength of long-chain-branched PPs with an increase in the elasticity. High elasticity led to higher end-pressure losses and eventually led to a deterioration of the processability. When we compared samples B and C, we found that the extrusion processability was improved by the degree of branching being controlled by the AO.

CONCLUSIONS

A new method, irradiation with high-intensity ultrasonic waves, was applied to change a linear PP into a branched structure. With these ultrasonic waves, it was possible to induce chain scission, and with the aid of an MFA, reactive macroradicals of PP in the melt stage were created without any peroxide or decomposing agent. The structure of the long-chain branch was confirmed by the measurement of the rheological and thermal properties. Long-chain-branched PP showed shear-thinning behaviors in its viscosities at low frequencies, plateau behavior in Cole–Cole plots, and a higher RPI than linear PP. The processability of

TABLE I
Thermal Properties of Four Different PPs

	Neat PP	PP/3 phr MFA (sonic ratio = 8 : 2)	PP/3 phr MFA/ 0.05 phr AO (sonic ratio = 8 : 2)	PP/3 phr MFA/0.2 phr AO (sonic ratio = 8 : 2)
T_m (°C)	166.1	165.9	166.5	165.9
T_c (°C)	105.8	117.1	110.0	110.8

long-chain-branched PP was compared by the measurement of the extrudate appearance. The long-chain-branched structure degraded the extrusion appearance because of its high elasticity, which caused high end-pressure losses in the extrusion die. The addition of AO was effective in controlling the MW and the degree of branching. As a result, it improved the extrusion performance by delaying the instability to a higher shear rate.

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