고강도 초음파 믹서로 제조된 가지구조 Polycarbonate의 유변학적 특성

김형수, 이후석*, 이재욱*
단국대학교 화학공학과
*서강대학교 화공생명공학과

Rheological properties of branched polycarbonate prepared by an ultrasound-assisted intensive mixer

Hyungsu Kim, Hooseok Lee* and Jae Wook Lee*
Department of Chemical Engineering, Dankook University
Department of Chemical and Biomolecular Engineering, *Sogang University

Introduction

In our previous studies(1-3), we intended to induce degradation of polymer melts in a sonicated intensive mixer. An important consideration was to investigate whether the ultrasound-aided degradation is possible during melt processing of polymer in a batch mixer. It was found that the process can be used to control the rheological properties of various polymers in during the melt processing. In addition, since cleaving bonds can create reactive macromolecules (or macro-radicals), it was confirmed that direct mutual coupling between different macro-radicals is possible, thereby successful in-situ compatibilization of immiscible polymer blends based on styrenics, polyolefins, and polycarbonate(PC) was achieved. In this study, we intended to apply the previous idea to the transformation of molecular structure from linear to branched one during melt processing of polycarbonate.

Experimental

The PC used was a low viscosity grade of Teijin in powder form. A multifunctional agent(MFA) was Trimethylolpropane triacrylate purchased from Aldrich in liquid form. In order to impose ultrasonic wave during melting mixing, a

specially designed ultrasonic horn was assembled with a Haake mixer(Haake Rheocord 600). The horn vibrated longitudinally at a frequency of 20 kHz with an amplitude of 15㎛. A 1.5kW power supply with a piezoelectric converter was used. Prior to mixing operation, homo polycarbonate was dried in a vacuum oven at 80℃ for 24 hours. Each sample was prepared on a fixed volume basis of 70% and mixing temperature was 230℃ with 50rpm. Before irradiation of ultrasound, preliminary mixing was carried out for 1min to reach the molten state. Sonication time was set to 5 min. Plate-plate rheometer (ARES, Rheometric Scientific) was used to measure the dynamic viscosity and modulus samples. Experiments were carried out with 25mm plate diameter, 1.5mm gap distance, 10% strain, and 0.1 ~ 400rad/sec frequency ranges.

Result and Discussion

In order to induce chain scission of polymer molecules, it is important to concentrate adequate level of ultrasonic energy on the mixing region. This requirement was examined here by carrying out acoustic analysis to find pressure profile of the sonicated mixer. As shown in Fig.1, ultrasonic energy was well focused on the mixing volume at a filling percent of 70. Thus, by combining ultrasound and a multifunction agent having double bonds at its ends, we were able to modify a linear chain into a branched structure.

The rheological property measurements confirmed that the modified PC had a nonlinear branched structure. Unlike a typical PC or simply mixed PC with a multifunction agent, the sonicated PC with a multifunction agent showed shear thinning behaviors in its viscosities at low frequencies, as shown in Fig.2. From a Cole-Cole plot of the three cases mentioned in viscosity comparison, it was shown in Fig.3 that at a given G", G's of the modified PC are higher than those of the others, reflecting the existence of branched structure.

Since, in principle, we generate radical species to achieve transformation of molecular structure, such radicals may affect somewhat adverse effect in the thermal

stability of the modified PC. It was found from TGA analysis that the thermal stability of the modified PC is even superior or at least comparable to that of neat PC. Extensional behaviors of the modified PC are being investigated and the relevant results will be compared with those of a commercial branched PC.

Conclusions

By using intensive ultrasonic wave, it was possible to generate macroradicals of PC and subsequent coupling between macroradicals and MFA was proceeded. Rheological measurements revealed that melt viscosities of the sonicated PC with MFA were increased and its shear sensitivity was also higher compared to that of neat PC. Formation of the branched structure was further confirmed from the tendency found in Cole-Cole plot. It is suggested that ultrasound-assisted process can provide an effective route to transform the molecular structure of polymers during melt processing.

Acknowledgement

This study was supported by the research grants from the Korea Science and Engineering Foundation (KOSEF) through the Applied Rheology Center (ARC), Korea.

References

1. Kim, H., J.G. Ryu and J. W. Lee, **2002**, Evolution of phase morphology and in-situ compatibilization of polymer blends during ultrasound-assisted melt mixing, *Korea-Australia Rheol. J.*, **14**, 121-128.
2. Ryu, J.G., H. Kim, M.H. Kim and J.W. Lee, Morphology and mechanical properties of LDPE/PS blends prepared by ultrasound-assisted melt mixing, 2004, *Korea-Australia Rheol. J.*, **16**, 147-152.
3. Kim, H., 2004, Compatibilization of PC/SAN blends via ultrasound-irradiated melt mixing, *Polymer (Korea)*, 28, 225-231.

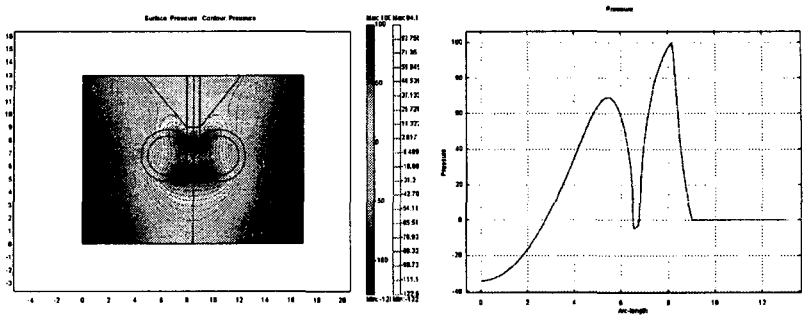

Figure 1. Pressure profile of a sonicated mixer

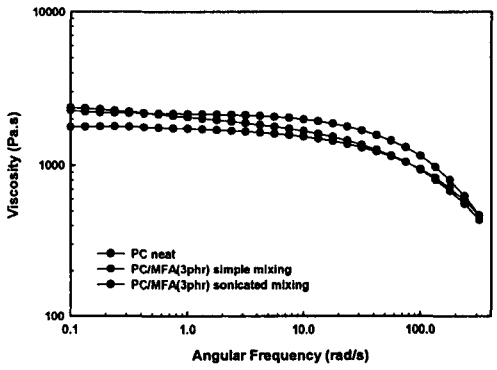

Figure 2. Complex viscosities for neat PC and modified PC with multifunctional agent

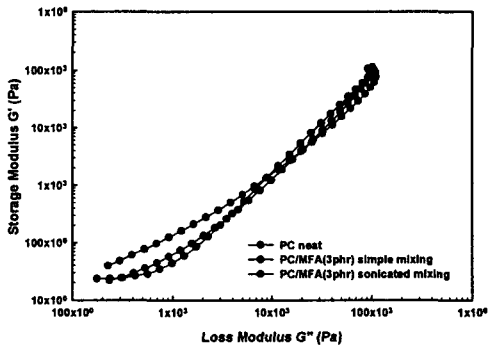

Figure 3. Cole-Cole plot for neat PC and modified PC with multifunctional agent