Rheological Properties of Modified Polypropylene by High intensity Ultrasound

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고강도 초음파로 제조된 Modified Polypropylene의 유변학적 특성

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Introduction

High intensity ultrasounds are widely employed in the areas of biology, cleaning, plastic welding, matching and chemical reactions, and the like. In addition to these conventional applications, numerous studies have been suggested to the new possibilities as a useful way to induce mechanochemical degradation in polymeric materials [1-2]. It was observed that if polymer solution was subjected to irradiation of high intensity ultrasonic waves, main-chain scission of polymer chains occurred and consequently the molecular weight is decreased.

Kim and Lee [3] studied the effect of sonication on the degradation in polypropylene melt without any solvents. It was found that the ultrasound-aided degradation was possible during melt processing of polypropylene in a batch mixer, and this process could be used to control the rheological properties of polypropylene in the absence of other chemical agents. In this study, based on these previous results, a novel approach was attempted to manufacture the long chain branched high melt strength polypropylene. Sonication process using high power ultrasonic wave was employed to lead the uniform degradation and radical generation compared to that of the peroxide-induced. To enhance the combination reaction during sonication, coupling agent was added.

Experimental

Materials used in this study were modified from linear-structured polypropylene. Homo polypropylene, grade name HY301, was supplied from Samsung General Chemicals (MI 3.3g/10min). Coupling agent was Trimethylolpropane triacrylate from Aldrich Chemical. In order to impose ultrasonic wave during melt 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 μm. A 1.5 kW power supply with a piezoelectric converter was used. Prior to mixing operation, homo polypropylene 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 210℃ 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, Rheometrics Scientific) was used to measure the dynamic viscosity and modulus of samples. Experiments were carried out with 25mm plate diameter, 1.2mm gap distance, 10% strain, and 0.1 ~ 500rad/sec frequency ranges. Torque data was collected during mixing.

Result and Discussion

Complex viscosities were measured to characterize the rheological properties of polypropylenes made by high intensity ultrasound, and the results are represented in Fig. 1 without anti-oxidant(AO) and Fig. 2 with AO. It can be seen from Fig. 1, complex viscosities of polypropylenes decrease in all frequency region by ultrasonic effect. When 3phr of coupling agent(CA) was added without sonication, though there was molecular weight increase, little yield behavior of complex viscosities in low frequency ranges was observed. With sonication, however, significant yield behavior was observed, which is the strong evident of long chain branch structure. With 0.2phr of AO in Fig. 2, the chain degradation was reduced. Also in this result, the sample with sonication and CA shows higher yield behavior.

To investigate the relationship between ultrasound effect and melt torque, torque data was compared for various cases in Haake mixer. Figure 3 shows the torque results for various samples. Sonication dosage decreases melt torque for neat polypropylene. Also 3phr of CA, sonication reduces the torque, which means the reduction of molecular weight, though combination reaction was occurred. When 3phr of CA and 0.2phr of AO, higher torque was

observed when sonication dosed. This is because of combination of long chain branches with reduced degradation. Figure 4 shows the cole-cole plot, which characterizes the viscoelastic behavior of a polymer particularly in low frequency region. The values of slop are similar in high frequency region. At low frequency region, however, G' values of modified polypropylenes by ultrasound deviate from the G' values of polypropylenes by general mixing. It indicates the increase of elasticity due to the long chain branching with sonication dosage.

Conclusions

By using high intensity ultrasonic wave, it was possible to induce chain scission of the polypropylenes in melt state without any peroxide or decomposer. The viscosities of polypropylenes were significantly decreased by sonication. Viscosities of modified polypropylenes with coupling agent showed yield behaviors, which indicated the presence of long chain branches grafted to the backbone chain. However, significant molecular weight decrease was observed. Addition of anti-oxidant prevents excess degradation with moderate grafting reaction. Melt torque results also showed that the sonication with adequate addition of CA and AO could induce the long chain grafting reaction successfully. This sonication process is expected to lead the uniform radical generation compared to the conventional peroxide-induced reactive extrusion process.

Acknowledgement

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Reference

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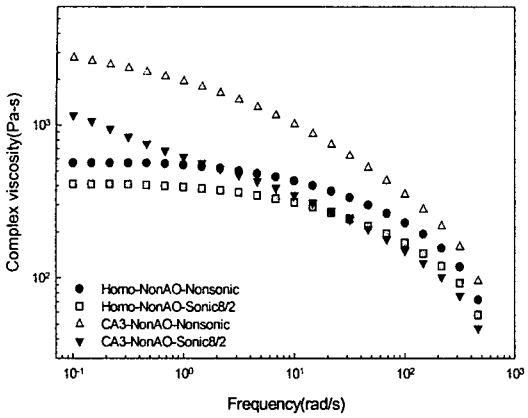

Fig1. Effect of sonication dosage on the complex viscosity of PPs. (a),(b) : neat PP, (c),(d) PP with coupling agent.

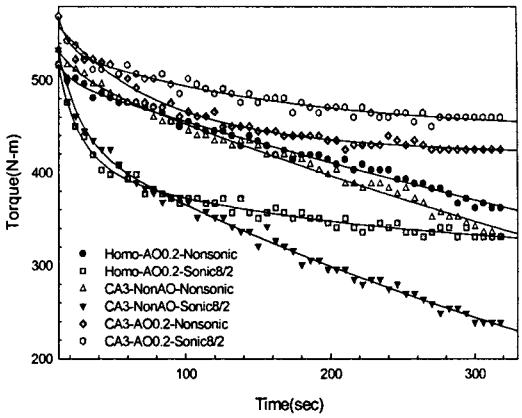

Fig3. Torque data of various samples.

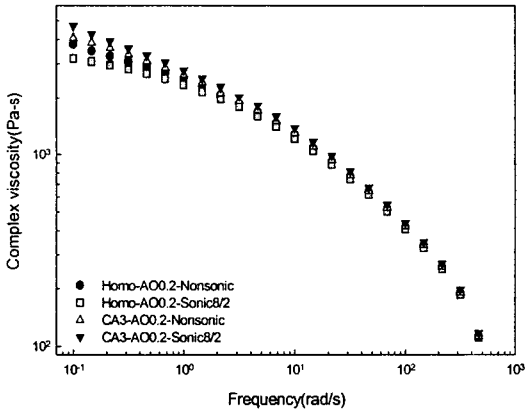

Fig2. Effect of anti-oxidant on the complex viscosity of PPs (a),(b) : neat PP with anti-oxidant, (c),(d) : PP with coupling agent and anti-oxidant.

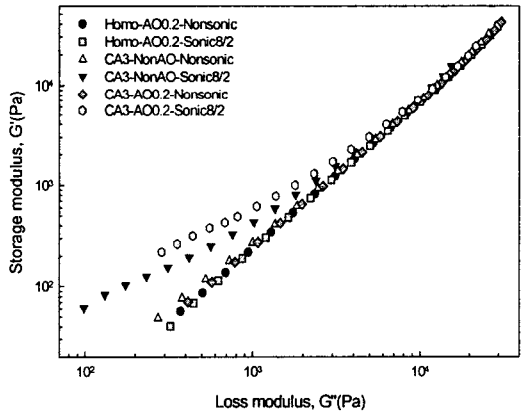

Fig4. Cole-cole plot of various samples