이축압출기에서의 초음파/초임계 효과의 PP/PS blend 공정효과 연구

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PP/PS blend on twin screw extruder by ultrasonic & SCF CO2 effect

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Introduction

Polymer blending is a useful approach for the preparation of new materials with specially tailored or improved properties that are often absent in the single component polymers. Enhanced properties of polymeric materials are achieved by developing multi-component systems in the form of polymer blends composed of two or more homopolymers. However, many polymer pairs are incompatible or immiscible with each other and exhibit either very low or no interface adhesion and phase separate on blending.

The addition of pre-made block copolymers can lead to a reduction of domain size and interfacial tension. However, these methods are likely to be limited to the use of available polymers and the synthesis of block copolymers cannot use for most polymer pairs of interest.

High intensity ultrasounds, as compared with diagnostic ultrasounds, are generally at lower frequency where greater acoustic energy can be generated to induce cavitation in liquids. In this study, It was observed that if polymer solution is subjected to the irradiation of high intensity ultrasounds, main-chain scission of polymer chains occurs and consequently molecular weight is decreased. In addition, since cleaving bonds can create reactive macromolecules, it was also expected and confirmed that direct mutual coupling between different polymer.

And, in this study we used ScCO2 effect in polymer blending process. It can plasticize most of them very efficiently. Due to its high compressibility, these solvent properties can be controlled by small changes in processing conditions, acting as a "reversible plasticizer" that can be easily removed after depressurization. Also, ScCO2 is affect ultrasound efficiency. ScCO2 gas bubble make cavitation phenomena, and this make high efficiency in polymer melt processing.

Experimental

The polymer resin used in this study was PP(HP450J, Polymirae) whose density was 0.9 g/cm3, and whose MFR was 3.25 g/10min and PS(20HR(E), LG Chem) whose density was 1.05 g/cm3, and whose MFR was 17g/10min.

In order to develop PP/PS blend successfully, ultrasound was imposed during melt mixing with a specially designed ultrasound horn and barrel assembled with twin screw extruder. Ultrasound horn vibrated longitudinally at a frequency 25kHz. 202V power supply with a converter was used. Development process of PP/PS blend was composed of two step extrusion processes. And, The metered CO2 injection system has a CO2 cylinder, syringe pump, and back pressure regulator. Syringe pump (model 260D from ISCO, Inc.) was set to have CO2 gas flow with a constant flow rate. Additionally, the back pressure regulator was used to maintain constant pressure. The twin-screw extruder was a co-rotating, intermeshing twin screw extruder, SM Platek TEK25 with diameter 25mm, total screw length of 1025mm and a ratio of screw length to diameter (L/D) of 41. The screw was arranged in a special combination of conveying, shearing, mixing, and reversing elements.

In first step, CO2 was injected into metering zone of extruder by CO2 metered injection system and ultrasound was imposed. After that the foamed extrudate was pelletized after solidification in a water bath. In order to build up over critical pressure (73.8bar) of CO2, Slit die and nozzle was attached at extruder. In second step, CO2 or air in the foamed product was vented by vacuum pump. The orifice die was equipped to depressurize die exit. Finally, the non-foamed PP/PS blends were obtained. The operating temperature profile for the extruder varied from 150℃ at the feed section to 230℃ at the die.

Results and discussion

We prepared PS/PP blends by simple mixing, SCF mixing, sonicated mixing and SCF & ultrasound assisted mixing. It is well known that mechanical properties depended on the morphology of polymer blends; therefore compatibility that controls morphology should be the dominant factor. Micrographs of brittle fractured surfaces of PS/PP blends in liquid nitrogen. PP particles are smaller in PS/PP blends with SCF & sonicated mixing than in that others. It indicates a good dispersed PP phase is obtained through SCF & sonicated mixing. When SCF & ultrasound is applied, its powerful vibration, shatter, and cavitations help to shear, cut, and disperse PP in PS matrix. When blend melt goes into ultrasound zone, ultrasound vibration leads to disentanglement of molecular chins and inter-penetration of the two phases by dynamic controlling process. Once the melt flows out of the zone, the thermodynamics process become dominant, and the chains get entangled again. This gives a chance to PS and PP molecules near the interfacial tension of PS/PP blend is improved by applying ultrasound vibration, which means compatibility of PS and PP matrix is improved.

Influence of this improvement, the toughness and structural changes of the PP and PS chains. To verify this hypothesis, sample was analyzed by DSC and WAXD. This result shows the graph obtained from DSC thermograms. It was found that with use of ultrasound vibration in extrusion processing of PS/PP blends. PP is the minor component, it is dispersed in the immiscible PS matrix, and so the nucleation mechanism changes from being predominantly heterogeneous to being predominantly homogeneous as long as the size of the dispersed PP droplets is below a critical value (ca.1-2μm). Determined crystallization kinetic parameters, such as spherulitic growth rates and nucleation densities. The crystallization of i-PP has been found to be strongly influenced by the presence of PS. With increasing PS concentration in a blend, the nucleation densities decrease, whereas the spherulitic growth rates and the positions of the thermal peaks remain independent of the sample composition.

In order to verify that the β-form exists in sample SCF & sonicated mixing, WAXD patterns of PS/PP blends were taken. It can be seen from the X-ray diffraction patterns that samples with ultrasound treatments are different. In X-ray diffraction patterns of the sample SCF & sonicated mixing, a new peak at $\theta \fallingdotseq 16°$ appear, which correspond to plane. These undoubtly indicate the formation of the β-form of polypropylene. It special effects can be induced by ultrasound, such as strong stress, shatter, and vibration, which alter the growth of PP crystals and may favor a special crystal transformation(αβ). β-form has unusual performance characteristics, including improved elongation at break and impact strength. In this study, the β-form of PP is also induced to form by applying ultrasound irradiation in PS/PP blend.

Conclusion

The results of this work show that power ultrasound addition decreases both particle size and interfacial tension. Also, it was possible to induce chain scission of PP and PP in melt state without any solvents or additives. It was revealed from the morphology analysis and mechanical testing that the blend of PS and PP was successfully compatibilized by imposition of ultrasonic energy during melt mixing process. Under the given sonication environment, maximum mechanical properties of SCF & sonicated blends were obtained. Also, it is stabilize the phase morphology and prevent phase growth (or coalescence). And, interfacial tension of the PS/PP blends with sonication revealed similar compared to the using compatibilling agents in the incompatible polymer blends.

This result also can be confirmed that macroradical to be created by sonicated mixing was acted to the compatibilizer. DSC analysis indicated that the glass transition temperatures of PS and PP phases all change and approach each other.

Reference

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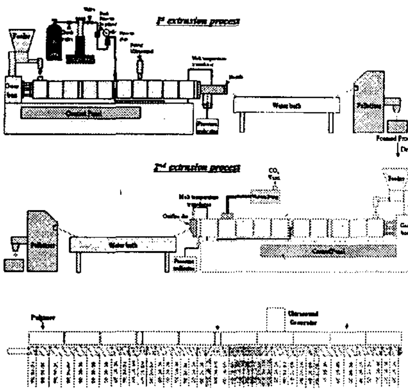

Fig.1. ScCO2 and Sonicated associated Extrusion System

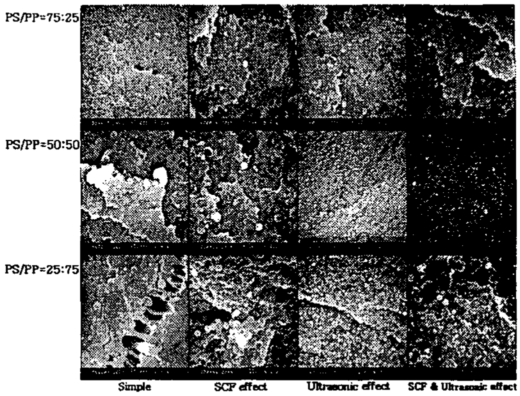

Fig.2. SEM images of PS/PP Blends

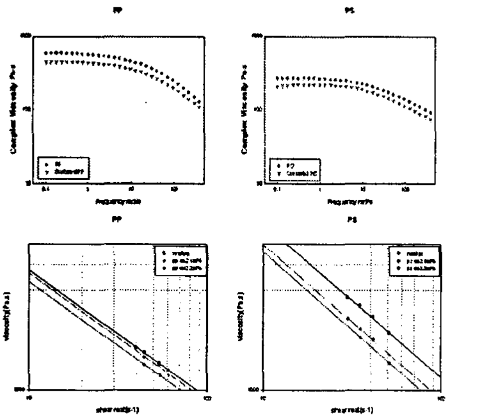

Fig.3. SCF & Ultrasonic effect on PS/PP single system

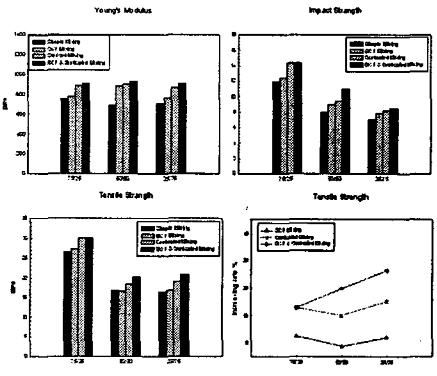

Fig.4. Mechanical properties of PS/PP Blends

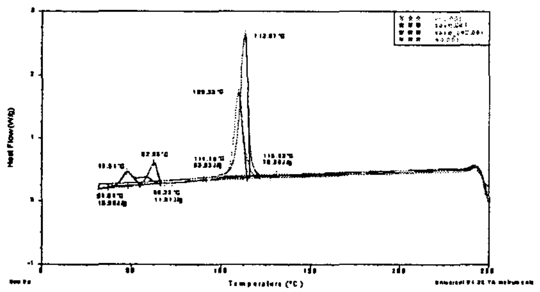

Fig.5. Tc curve of PP/PS Blend using DSC

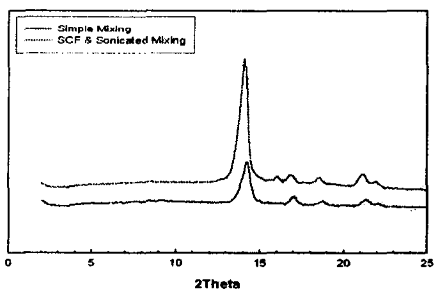

Fig.6. WAXD patterns of PP/PS =75/25 blend