Effects of High-Intensity Ultrasound & Supercritical Nitrogen on PP-MA Reactive Extrusion

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Introduction

Compatibilizers contribute many ways in the polymer industry, such as manufacturing polymer blends and composites. They are usually designed to be block or graft form which is combined in polar and non-polar parts in the first synthesis process level, for example, the general form of maleic anhydride (MA) as a compatiblizer is a grafted counterpart. However, the process of making compatibilizer is related to the first synthesis level and it has some problems, such as high cost, poor processability, limitation on use and properties, and so on. So, in order to improve its poor processability and overcome the limitation on use, we developed compatibilizers which have various chemical forms through high intensity ultrasound and super critical fluid nitrogen (SCF N_2) in polymer melt reactive extrusion.

Experimental

The polypropylene resins used in this study were PP-A (HP450J, Polymirae), whose density was 0.9g/cm^3 and MFR was 3.25g/10min, and PP-B (F400, Hyosung), whose density was 0.9g/cm^3 and MFR was 2.5g/10min. The organically modified MMT (Closite 20A; it will be called as clay) was obtained from Southern Clay Products. In addition, MA (TCI chemical) whose content of MA was 99% and SCF N_2 whose degree of purity was 99.99% were used to compound, and the commercial MA-grafted compatibilizer, PP-g-MA (PMD353D, DuPont) whose MA graft level was 3.2wt% used for comparison.

The extruder used in this study was a co-rotating, intermeshing twin screw extruder (TEK25, SM Platek) with a diameter of 25mm, total screw length of 1025mm and a ratio of screw length to diameter (L/D) of 41. The operating temperature of the extruder was 160℃ at the feed section and 180℃ at the rest of the sections and die. In all the experiments, the environmental condition of the extruder was the same. Ultrasound was imposed during mixing, with the ultrasound horn, which vibrated longitudinally at a frequency of 20 kHz, and barrel assembled with twin screw extruder. Besides ultrasound, SCF N_2 was injected by the metered N_2 injection system which had a N_2 cylinder, a syringe pump, and a back pressure regulator. Syringe pump (model 260D, ISCO, Inc.) was set to make the flow rate of N_2 gas constant. To define the properties of master-batched compatibilizer we developed our experiment to PP-clay nanocomposite in concept of final product. In this step, all kind of compatibilizer that we made in the previous step was used and the amount of use was 20wt%. In this second extrusion process, no effect was used.

Results and discussion

In this study, we prepared various kind of compatibilizers by simple mixing, SCF mixing, sonicated mixing and sonicated SCF mixing. To analyze these samples, we removed the unreacted component with a solvent. The samples were dissolved in hot xylene and precipitated by using anti-solvent (water). According to the FT-IR result, we could conclude that the chemical form of PP changed by ultrasound and SCF N_2 during the reactive process. We could find new peaks which related to nitrogen reaction from FT-IR and the result of element analysis (EA-CHNS method) indicated that the chemical reaction of N_2 occurred.

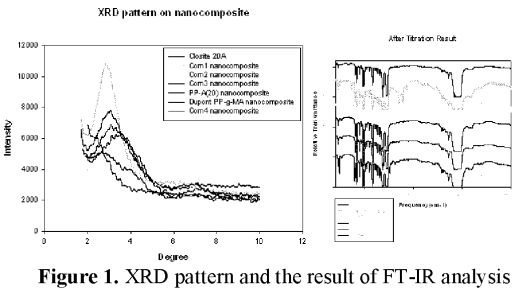

Figure 1. XRD pattern and the result of FT-IR analysis

We also analyzed these products with a plate-plate rheometer. According to the result of the rheometry, we saw that the properties of the compatibilizers affected the properties of the final product. During the melt reaction process, the viscosity of the compatibilizer influenced the shear stress of the whole system. We checked dispersion and distribution of clay after mixing for these products through SEM. According to the SEM images of fractured cross sections for these samples, the interaction between polymer and clay caused by transportation of shear stress to clay, and it made the morphology of these images different. By increasing the polarity of the compatibilizer, the pellet structure of the clay became smaller and its depth structure looked swollen because of the polymer chain intercalation into the clay pellet. However, in case of the commercial compatibilizer mixing, bad morphology has founded. It was caused by an inadequate melt temperature of the commercial compatibilizer (T_m=136℃). So it caused thermal degradation during extruder melt processing. The result of dispersity mixing was also founded in the XRD pattern. The small gallery distance of intercalated clay pellet, which was indicated by the XRD result, had a consistency with the small clay pellet structure in the SEM image, and the intensity was related to the regularity of the clay pellet gallery state. In the event, the XRD result also corroborated the fact of dispersion.

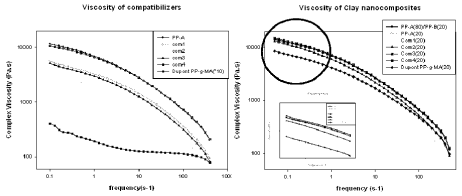

Figure 2. Complex viscosity of compatibilizers and nanocomposites

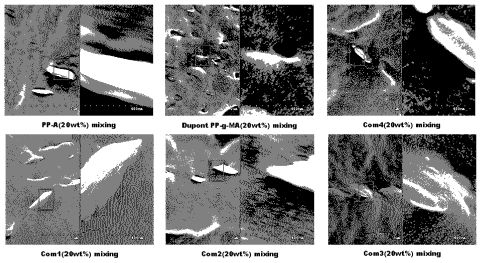

Figure 3. SEM images of various PP-clay nanocomposites

Table 1. Characterization of experiment samples

Sample name	Composition	Used effect
Com1	PP-A (96.8%)/MA (3.2wt%)	None
Com2		Ultrasound (120W)
Com3		SCF (N_2, 2wt%)
Com4		All the effects

Conclusions

The results of this work show that power ultrasound and SCF N_2 have a strong possibility of making various chemically formed compatibilizers which are suitable for the final use of product. Ultrasonic energy makes a chance of chemical transformation and SCF N_2 provides a new chemical source. From this mechanism, the reaction of PP and MA was successfully generated by imposition of ultrasonic energy and SCF N_2 during melt process.

Acknowledgement

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References

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