DOI: 10.1002/masy.200750440

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

*Chang Hee Sohn, Dong Chul Shim, Jae Wook Lee**

Summary: The reaction of polypropylene (PP) and maleic anhydride (MA) was successfully generated by imposition of ultrasonic energy during the mixing process of extrusion. The possibility of the various transformations by PP-MA reaction became stronger under the sonicated supercritical fluid mixing. The properties of the compatibilizer and the nanocomposites as the final products in the presence of ultrasound and supercritical fluid nitrogen were properly obtained without the addition of any solvents or additives.

Keywords: maleic anhydride; nanocomposites; polypropylene; reactive extrusion; supercritical fluid; ultrasound

Introduction

Compatibilizers are widely used in many processes in the polymer industry. They are usually designed to be attached to polymer in block or graft form. For example, the general form of maleic anhydride (MA), as a compatiblizing agent for polypropylene (PP), is a grafted counterpart in polymeric compatiblizer, PP-g-MA. In particular, it contributes to the spontaneous dispersion mixing of clay in the process of manufacturing nanocomposite.

The melt process for the maleation of PP has been used, where the molten polymer is mixed with MA and with a suitable initiator such as peroxide in the various mixers as well as the single and twin screw extruders.[1–5] The functionalization of PP with MA has also been achieved in the solution process, which makes the polymer dissolved in an appropriate solvent and MA is added with the initiator.[6–8]

In this study, a novel reactive extrusion process with ultrasound and supercritical fluid for developing polymeric compatibilizers was introduced. It is known that the ultrasound assisted melt processing is able to generate radical species via chemical route in polymer,[9–12] and the use of supercritical fluid CO_2 lead to improved grafting of MA to PP in reactive extrusion.[13] We developed polymeric compatibilizers which have various chemical forms by high-intensity ultrasound and supercritical fluid nitrogen (SCF N_2) in polymer melt reactive extrusion without the addition of any solvents or additives. Effects of ultrasound and SCF N_2 on PP-MA reactive extrusion were also studied.

Experimental Part

The polypropylene resins used in this study were PP-A (HP450J, Polymirae) and PP-B (F400, Hyosung). The density of the resins was 0.9 g/cm^3. The MFR of the resisns were 3.25 g/10 min for PP-A, and 2.5 g/10 min for PP-B. The organically modified MMT (Closite 20A; it will be referred to clay) was obtained from Southern Clay Products. In addition, MA (TCI chemical) and SCF N_2, whose degrees of purity were 99% and 99.99% respectively, were used to compound the resins.

In order to obtain MA-grafted polymeric compatibilizer successfully, a specially designed ultrasound horn and a 202 V

Applied Rheology Center, Dept. of Chemical & Biomolecular Engineering, Sogang University, Seoul, 121-742, Korea
E-mail: jwlee@sogang.ac.kr

power supply with a converter were used. Ultrasound was imposed during the mixing of the polymer melt, with an ultrasound horn, the horn vibrated longitudinally at a frequency of 20 kHz. A barrel, which was assembled with a twin screw extruder, transferred ultrasound from the horn to the polymer melt. Besides ultrasound, SCF N_2 was injected by a metered N_2 injection system which had a N_2 cylinder, a syringe pump, and a back pressure regulator. A syringe pump (model 260D, ISCO, Inc.) was set to make the flow rate of N_2 gas constant. In addition, the back pressure regulator was used to maintain constant pressure.

We used a co-rotating, intermeshing twin screw extruder (TEK25, SM Platek) in this study. Its diameter was 25 mm, the screw length was 1025 mm, and the ratio of screw length to diameter (L/D) was 41. The screw was arranged in a special combination of conveying, shearing, mixing, and reversing elements. The operating temperature of the extruder was 160 °C at the feed section and 180 °C at the rest of the sections and the die. In all of the experimental processes, the environmental condition of the extruder was the same.

In order to define the properties of polymeric compatibilizer, we developed our experiment into making PP-clay nanocomposite in the concept of the final product. In this step, all of the polymeric compatibilizers that we made in the first process were used and the amount of use was 20 wt%, as shown in Table 1. All of the compatibilizers were made up of 96.8 wt % of PP-A and 3.2 wt% of MA. The mass flow rate of the products was 40 g/min in the extrusion process. In cases of the sonicated mixing, the ultrasound was imposed by the high intensity ultrasonicator continuously during the process. When the SCF N_2 was used, the flow rate of the SCF N_2 was 0.82 g/min in mass, and 2.78 ml/min in volume. The pressure and the temperature of SCF N_2 were 125 atm and 2 °C respectively. In the second extrusion process of making the nanocomposite, no ultrasound and SCF N_2 effect was used.

Results and Discussion

In order to verify the effects of ultrasound and SCF N_2, we prepared various kinds of compatibilizers by simple mixing, SCF mixing, sonicated mixing, and sonicated SCF mixing. The thermal stabilities of the samples were determined by thermogravimetric analysis (TGA), as shown in Figure 2. The compatabilizers had inferior thermal stability to PP-A around 200 °C because of the decomposition of the unreacted MA. In the presence of the SCF N_2, the unreacted component is reduced by the SCF N_2 like the process of purification in making decaffeinated coffee using supercritical fluid; Com-S and Com-US showed better thermal properties than other compatabilizers, Com-N and Com-U. However, the properties were changed after the complete decomposition of the unreacted residual at the high temperature. Even though Com-U had the worst property among the samples at the temperature of the MA decomposition, it showed the superior property to PP-A and Com-N at the high temperature over

Table 1.
Characterization of the samples.

The 1st process (polymeric compatibilizers)		The 2nd process (PP-clay nanocomposites)	
Sample	Effect	Sample	Composition
Com-N	None	NC	PP-A(20%)/PP-B(80%)/Clay(3phr)
Com-U	Ultrasound(120 W)	NC-N	Com-N(20%)/PP-B(80%)/Clay(3phr)
Com-S	SCF(N_2, 2 wt%)	NC-U	Com-U(20%)/PP-B(80%)/Clay(3phr)
Com-US	Ultrasound(120 W) +SCF(N_2, 2 wt%)	NC-S	Com-S(20%)/PP-B(80%)/Clay(3phr)
		NC-US	Com-US(20%)/PP-B(80%)/Clay(3phr)

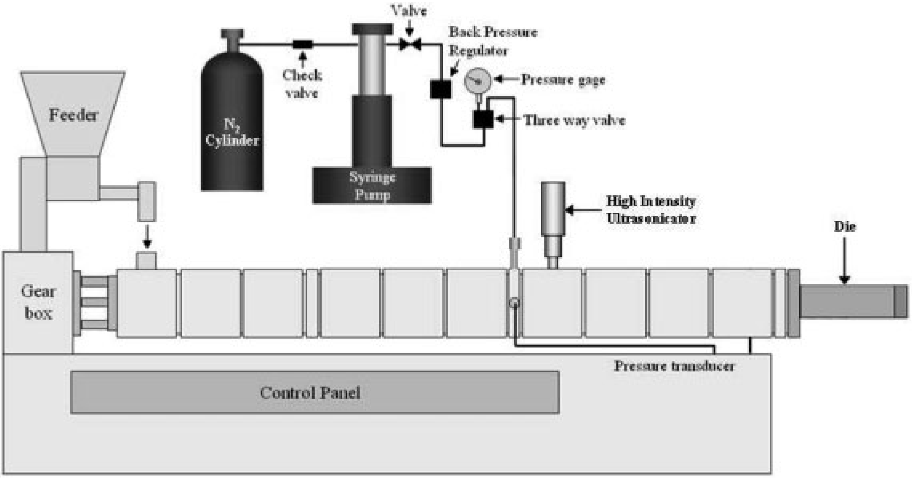

Figure 1.
Schematic diagram of the reactive extrusion system.

300 °C. The samples treated by ultrasound and SCF N_2 had the better thermal stability than non-treated compatabilizer (PP-N) and neat PP (PP-A) at the high temperature, for the change of molecular structures occurred by the chemical reaction due to the presence of ultrasound and SCF N_2.

The chemical reactions in the products were studied by FT-IR and element analysis. The unreacted component in the products was removed by solvent before the analysis. The samples were dissolved in hot xylene and precipitated by using anti-solvent (water).[14] According to the FT-IR result, we concluded that the chemical form of PP was changed by ultrasound and SCF N_2 during the reactive process. The sonicated process brought the chain scission and the generation of the macro-radical like peroxide. We found new peaks which related to nitrogen reactions from FT-IR (Figure 3). In case of the sonication, the carbonyl peaks at the range of 1840 to 1860 cm^{-1} were detected; this indicated that MA was transformed into grafted form in the presence of sonication. However, when the product of sonicated SCF process was analyzed, not only the carbonyl peaks but also C–N–H peaks at 480 cm^{-1} and N–H peaks at 1900 cm^{-1} were found.

The result of element analysis (EA-CHNS method) also showed that the

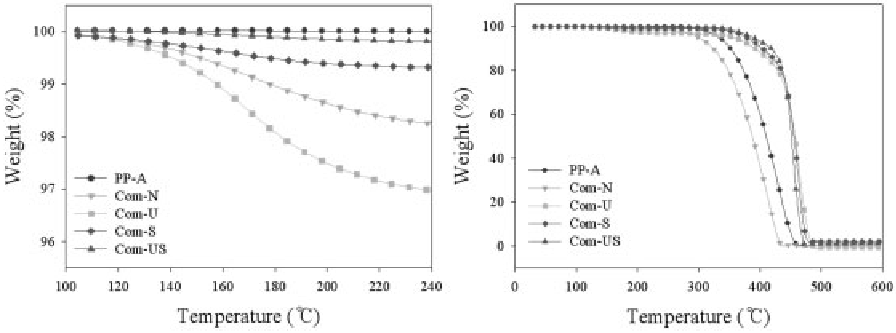

Figure 2.
The results of TGA.

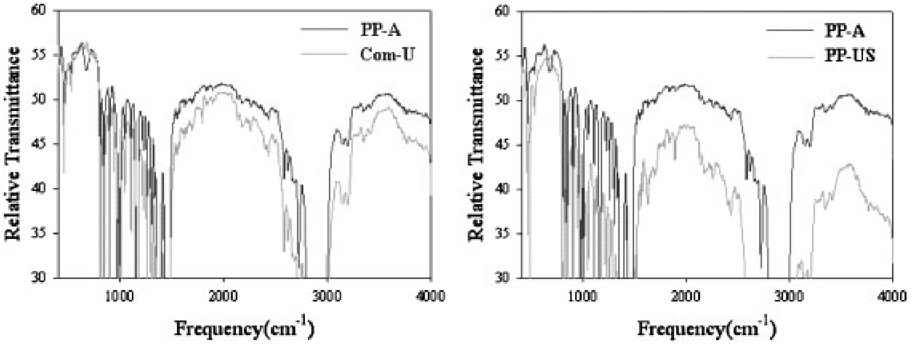

Figure 3.
The results of FT-IR analysis.

nitrogen reaction occurred most in the sonicated SCF process (Table 2). According to these results, the sonicated SCF process had a possibility to make various chemical reactions during extrusion process without any additives.

Rheological characterization of the products was performed by using a plate-plate rheometer. The frequency range was $0.05 \sim 500\ s^{-1}$ and the test temperature was 180 °C. According to the result of the rheometry, the process of ultrasound and SCF N_2 changed the rheological properties of the compatibilizers, which affected the properties of the final products (Figure 4). The sonicated compatabilizer, Com-U had the lowest complex viscosity because of the scission of polymeric chains caused by ultrasound. The rheological property of Com-S was similar to Com-N. However, the compatibilizer made by sonicated SCF mixing, Com-US showed the highest viscosity. Even though the process of sonication could make the PP chains short, the sonicated SCF mixing caused the change of molecular structure and rheological property, due to the high possibility of chemical reactions. In case of the nanocomposites, the rheological property of each compatibilizer was similar to others except NC-N. The reason why the composite, NC-N had the lowest viscosity was because the residual unreacted MA was thermally damaged and acted as the defect of the matrix after the second extrusion process. In the case of the nanocomposites made of other compatibilizers, it was deduced from the rheometry that the polarity was generated in the non-polar PP matrix by the reaction of MA, and it enhanced the interaction between the polar clay and the matrix. During the melt reaction process, the viscosity of the compatibilizer influenced the shear stress of the whole system.

A scanning electron microscope (SEM) was used to observe the dispersion and the distribution of the clay after mixing these products (Figure 5). According to the SEM images of the fractured cross sections of these samples, the interaction between polymer and clay caused by transportation

Table 2.
The Result of the elementary analysis (EA-CHNS method).

EA	C	H	N	S	Total
Com-N	85.36%	14.58%	–	–	99.94%
Com-U	84.72%	14.62%	–	–	99.34%
Com-S	85.23%	14.77%	–	–	100.00%
Com-US	84.71%	14.70%	0.05%	–	99.46%

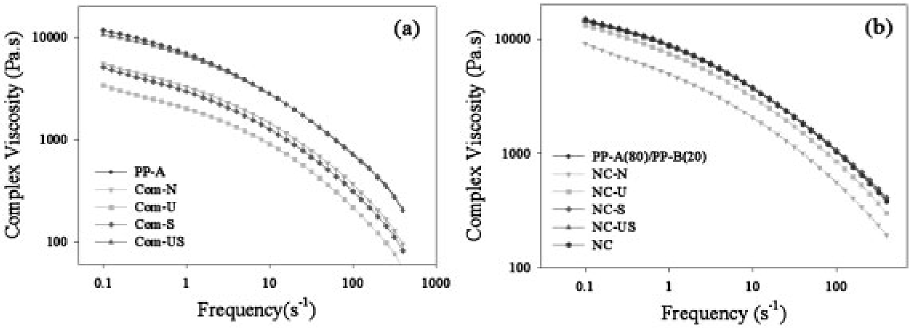

Figure 4.
Complex viscosities of (a) polymeric compatibilizers and (b) nanocomposites.

of shear stress to clay made the morphology of these images different. Increasing the polarity of the compatibilizer due to the chemical reaction in the presence of ultrasound and SCF N_2, the pellet structure of the clay became smaller and its depth structure looked swollen because of the polymer chain intercalation into the clay pellet.

The result of dispersity mixing was also found in the XRD patterns (Figure 6). The small gallery distance of intercalated clay pellet, which was indicated by the result of XRD, had a consistency with the small clay

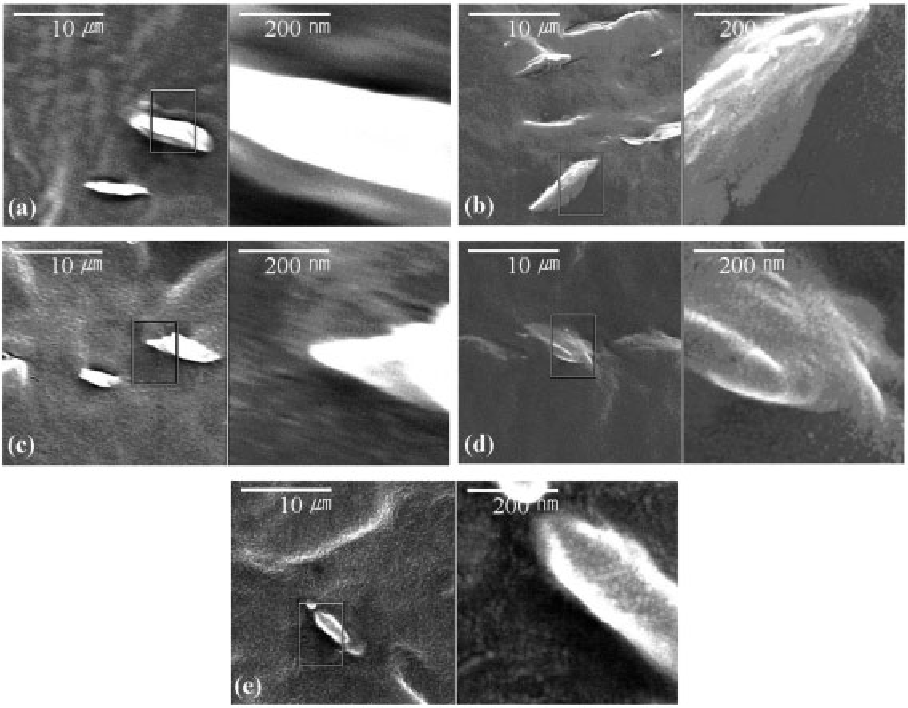

Figure 5.
SEM images of (a) NC, (b) NC-N, (c) NC-U, (d) NC-S, and (e) NC-US.

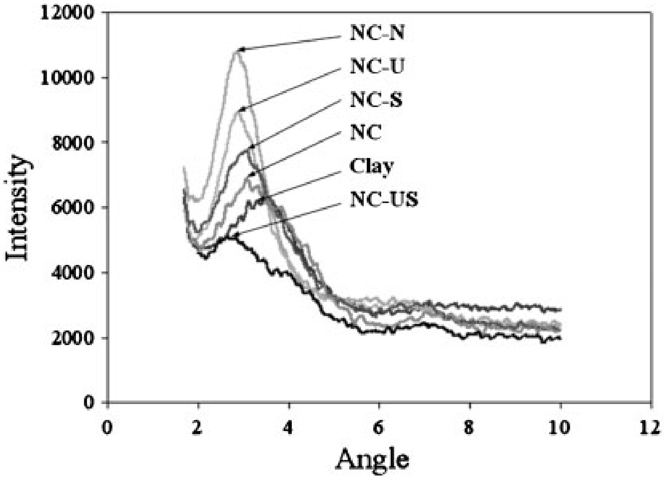

Figure 6.
XRD patterns of various PP-clay nanocomposites.

pellet structure in the SEM image; the nanocomposite obtained from sonicated SCF mixing, NC-US indicated the best dispersion. Finally, the result of XRD also corroborated the fact of dispersion.

Conclusion

The results of this study show that high-intensity ultrasound and SCF N_2 have the possibility to make various chemically formed compatibilizers. These results meet a case on the final use of the product. It was revealed that the reaction of PP and MA was successfully generated by the imposition of ultrasonic energy during the mixing process. The chemical form of MA was transformed into grafted form in the presence of sonication, and the possibility of the various transformations by PP-MA reaction became stronger under the environment of sonicated SCF mixing. The properties of the compatibilizer and the nanocomposites as the final products in the presence of ultrasound and SCF N_2 were properly obtained without adding any solvents or additives.

Acknowledgements: The authors gratefully acknowledge the Korea Research Foundation Grant for the financial support. (KRF-2006-005-J02302).

[1] F. Ide, K. Kamasa, A. Hasegawa, *Kobunshi Kagaku* **1968**, *25*, 107.
[2] I. Sasaki, F. Ide, *Kobunshi Ronbunshu* **1981**, *38*, 67.
[3] N. G. Gaylord, M. K. Mishra, *J. Polym. Sci.: Polym. Lett. Ed.* **1983**, *21*, 23.
[4] P. A. Callais, R. T. Kazmierczak, *ANTEC* **1990**, *48*, 1921.
[5] B. Kim, J. L. White, *ANTEC* **1995**, *53*, 242.
[6] R. Rengarajan, M. Vicic, S. Lee, *Polymer* **1989**, *30*, 933.
[7] S. N. Sathe, G. S. Srinivasa Rao, S. Devi, *J. Appl. Polym. Sci.* **1994**, *31*, 1447.
[8] E. Borsig, A. Fiedlerová, L. Hrčková, *J. Macromol. Sci., Pure Appl. Chem. A* **1995**, *32*, 2017.
[9] H. Kim, J. W. Lee, *Polymer* **2002**, *43*, 2585.
[10] J. G. Ryu, J. W. Lee, H. Kim, *Macromol. Research*, **2002**, *10*, 187.
[11] J. G. Ryu, H. Kim, M. H. Kim, J. W. Lee, *Korea-Australia Rheol. J.* **2004**, *16*, 147.
[12] K. Y. Kim, G. J. Nam, S. M. Lee, J. W. Lee, *J. Appl. Polym. Sci.* **2006**, *99*(5), 2132.
[13] B. M. Dorscht, C. Tzoganakis, *J. Appl. Polym. Sci.* **2003**, *87*, 1116.
[14] Lianchao Zhu, Jinghua Yin, *J. Polym. Sci.* **2006**, *44*, 134.