초음파/초임계 효과를 이용한 PP/MA 반응압출을 통한 clay nanocmoposite

심동철, 손창희, 이재욱

서강대학교 화공생명공학과

PP-Clay nanocomposite by various maleic anhydride graft reactive extrusion

Dong Chul Shim, Chang Hee Sohn, Jae Wook Lee

Dept. of Chemical Engineering, Sogang University

Introduction

Generally, a newly developed technology in laboratory is hard to be applied immediately to actual industry applications. Because, the new developed technology usually requires special equipments, which make problems of economic feasibility. In this point of a view, our study concept was designed to 'master-batched' compatibilizer process to overcome this problems. Compatibilizers contribute to many processes in 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. In particular, it contributes to spontaneous clay dispersion mixing in the process of manufacturing nanocomposite. However, the process of making the 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 by high intensity ultrasound and super critical fluid nitrogen (SCF N2) in polymer melt reactive extrusion.

Experimental

The polypropylene resin used in this study was PP-A (HP450J, Polymirae) whose density was 0.9g/cm3 and MFR was 3.25g/10min, and PP-B (F400, Hyosung) whose density was 0.9g/cm3 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 N2 whose degree of purity was 99.99% were used to compound. We also used the commercial MA-grafted compatibilizer, PP-g-MA (PMD353D, DuPont) whose MA graft level was 3.2wt% for comparison.

In order to get MA-grafted compatibilizer successfully, a specially designed ultrasound horn and a 202V power supply with a converter were used. Ultrasound was imposed during mixing melt, as the effect for mixing, with the ultrasound horn, which vibrated longitudinally at a frequency of 20kHz, and barrel assembled with twin screw extruder. Besides ultrasound, SCF N2 was injected by the metered N2 injection system which had a N2 cylinder, a syringe pump, and a back pressure regulator. Syringe pump (model 260D, ISCO, Inc.) was set to make the flow rate of N2 gas constant. In addition, the back pressure regulator was used to maintain constant pressure. We made compatiblizers using PP-A and MA with various effect as master-batch. In order to define the properties of master-batched compatibilizer, we developed our experiment to PP-clay nanocomposite in the concept of final product. In this step, all kind of compatibilizer that we made previous step was used, and its amount of use was 20wt%. In this second extrusion process, no effect was used.

The extruder used in this study was a co-rotating, intermeshing twin screw extruder (TEK25, SM Platek) with diameter of 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. The operating temperature of the extruder was 160℃ at the feed section and 180℃ at the rest of the sections and die. In all case of the experiment process, the environment condition of extruder was same.

sample name	composition	effcet	sample name	composition
com1	PP-A(96.8wt%) /MA(3.2wt%)	no	PPCN0	PP-A(20wt%)/PP-B(80%)/Clay(3phr)
			PPCN1	commercial-compatibilizer(20wt%)/PP-B(80%)/Clay(3phr)
com2		ultrasonic(120W)	PPCN2	com1(20wt%)/PP-B(80%)/Clay(3phr)
com3		SCF(N2, 2wt%)	PPCN3	com2(20wt%)/PP-B(80%)/Clay(3phr)
com4		ultrasonic(120W) SCF(N2, 2wt%)	PPCN4	com3(20wt%)/PP-B(80%)/Clay(3phr)
			PPCN5	com4(20wt%)/PP-B(80%)/Clay(3phr)

Table.1 Characterization of experiment sample

Results and discussion

In this study, we prepared various kind of compatibilizers by simple mixing, SCF mixing, sonicated mixing and sonicated SCF mixing. To characterize these samples, we removed the unreacted component by solvent. The samples are dissolved in hot xylene and precipitated by using of anti-solvent(water). According to the result of FT-IR for these samples, we could conclude that the chemical form of PP has changed by ultrasound and SCF N2 during reactive process. We could find new peak which related to nitrogen reaction from FT-IR data, and the result of element analysis (EA-CHNS method) indicated that the chemical reaction of N2 was occurred.

We analyzed these products by a plate-plate rheometer. The frequency range was 0.05-500(s-1) and the test temperature was 180℃. According to the result of rheometry, we could see that the property of compatibilizer affected the property of the final product. Because, during the melt reaction process, the viscosity of compatibilizer influenced shear stress of the whole system. The result of rheometry indicated two different phenomena on these samples, which were shear thining behavior and yield behavior. From the first phenomenon, we could conclude that the low viscosity of compatiblizer has a problem with dispersion mixing, especially. Low viscosity of the compatibilizer make poor mixing stress. So whole shear thining behavior of the final product revealed poor dispersity mixing. Moreover, from the second phenomena, we could conclude that the interaction between polymer and clay related to the graft level of compatibilizer and the property of chemical element which related to the polarity of material, such as electro-negativity.

The dispersity of clay through mixing was verified from the result of XRD pattern. The result of XRD analysis indicated two structural information, the regularity and the gallery distance of clay pellet, which related to the structure between clay pellet and polymer chain. In the case of PPCN1 and PPCN5, XRD peak indicated low intensity and small angle. Thus, in these case, we could conclude that the good dispersion of clay pellet occurred in the polymer system. However, according to the result of rheometry, there are some defective properties in the case of PPCN1. In order to find the factor affected these properties, we checked dispersion and distribution condition of the final products by 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 make the morphology of these images different. By more increasing polarity of compatibilizer, pellet structure of clay became smaller and surface morphology of clay looks like swelled, because polymer chain intercalated into the clay pellet. This result also make the same sense with the result of XRD analysis. However, in the case of PPCN1, bad morphology was founded. It was caused by the poor melt temperature of commercial compatibilizer, which made thermal degradation during extrusion processing and leaded to all the bad properties of final product.

Conclusion

The results of this work showed that power ultrasound and SCF N2 have a possibility of making various chemically formed compatibilizer which meet a case on final use of product. It was also possible to induce the properties of compatibilizer and final product without adding any solvents or additives. It was revealed from the morphology analysis and plate-plate rhemometer test that the reaction of PP and MA was successfully generated by imposition of ultrasonic energy during mixing process. The chemical form of MA was transformed into grafted form under the given environment of sonication, and the possibility of the transformation by reaction became stronger under the environment of sonicated SCF mixing.

Reference

1. H. Kim and J. LEE, Polymer, 43, 2585 (2002)
2. P. G. Jessop and W. Leitner, Chemical Synthesis Using Supercritical Fluids, Weinheim: Wiley-VCH (1999).
3. B. M Dorscht, C. Tzoganakis, Applied Pol. Sci., Vol.87, 1116-1122 (2003)
4. Eduardo A. Gonzalez De Los Santos, Applied Pol. Sci., Vol.68, 45-52 (1998)
5. Lianchao Zhu, Jinghua Yin, reactive & functional polymers 21. January (2006)
6. C. W. Macosko, P. Marachel and T. Inoue, Macromolecules, 29, 5590 (1996)

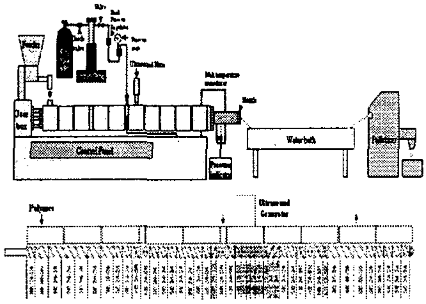

Fig. 1. SCF N2 and sonication associated extrusion system

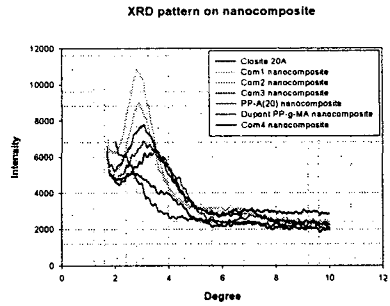

Fig. 2. XRD pattern of nanocomposite

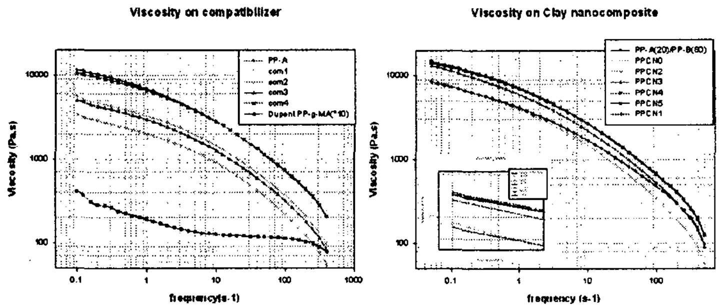

Fig. 3. Viscosity of compatibilizer & nanocomposite

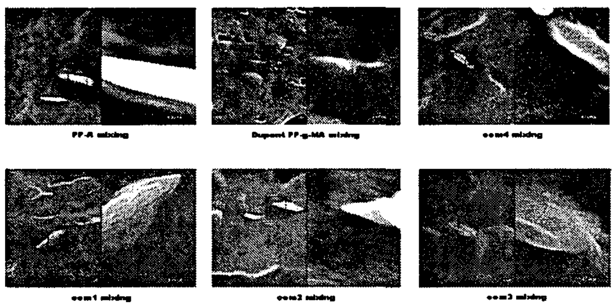

Fig. 5. SEM image of various PP-Clay nanocomposite

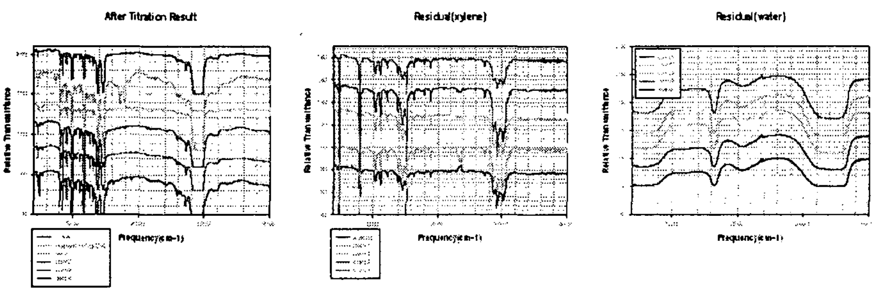

Fig. 6. FT-IR analysis of titration and residual