전기활성화된 PP/Clay 나노복합체의 유변특성에 대한 연구

김도훈, 박준욱, 안경현, 이승종
서울대학교 응용화학부

Rheology of electrically activated PP/Clay nanocomposites

Do Hoon Kim, Jun Uk Park, Kyung Hyun Ahn, and Seung Jong Lee
School of Chemical Engineering, Seoul National University

Introduction

Nanocomposites are a novel class of polymeric materials that offers dramatic improvements in permeability, mechanical, thermal, and processing properties in various applications[1-5]. Polymer based nanocomposites may be produced by incorporating layered silicates in polymer matrices such as polypropylene, polystyrene, polyethylene, polyesters, polysiloxanes, epoxides, among others. From a structural point of view, three main types of composites may be obtained when a layered silicate is associated with a polymer depending on the nature of components used and the method of preparation.[4] They are microcomposite, intercalated and exfoliated (or delaminated) nanocomposite. The structure of nanocomposite plays an important role on the improvements of their properties.

Polyolefin-based nanocomposites can replace metals and high-performance engineering thermoplastics by lower cost. Especially, PP has great potential for nanocomposite applications because of their good processibility by conventional technologies and their possible applications in the automotive industry[1, 6]. Since Toyota group had reported PP/clay hybrid composites by melt intercalation of montmorillonite (MMT) organo-clays with PP modified with either MAPP or hydroxyl groups (HOPP)[7,8]. These additives improved the performance of the materials, however, relatively high contents of these additives cost a lot enough to prevent their commercial production.

In this study, we will propose a novel approach to make exfoliated PP/clay nanocomposites using electric field without adding the compatibilizers such as MAPP or HOPP. PP/clay nanocomposites under large electric field over 1 kV/mm do show the exfoliated structure, which is evidenced by the dramatic increase of storage modulus in rheological measurements and the absence of diffraction peaks in XRD patterns. Furthermore, the electric melt pipe equipped on twin-screw extruder was designed to produce PP/clay nanocomposites.

Experimental Methods

Materials. PP (MI: 6.0g/min, Mw:127000, Mn:13000) used for this study was donated by Polymirae Corp. of Korea. Organically modified MMT clay, that is Cloisite 20A (C20A), was purchased from Southern Clay Products Inc., USA. The C20A has a dimethyl hydrogenated-tallow ammonium as an organic modifier with a cation exchange capacity of 95 meg/100g. And its basal spacing (d_{001}) is 2.61 nm.

The melt compounding of PP/clay composites was performed in an intensive mixer (Haake Rheocord 90). The rotor speed was 50 rpm and mixing time was 10 minutes after clay feeding at 180°C. The clay and polymer samples were dried in a vacuum oven at 80°C for 8 hr prior to compounding. Then the specimens for rheological testing were molded in a heated press (Carver hot press CH 4386) at 180°C for 5 minutes. The molded samples were of disc shape with diameter 25mm and approximately 1 mm thickness.

Experiments. Rheometrics mechanical spectrometer (RMS 800) was used to assess the rheological performance of the PP/clay nanocomposites with parallel plate geometry(Fig.1). Two types of experiments were carried out: time sweep test and frequency sweep test. The time sweep tests were performed at a frequency of 1rad/sec and strain of 10%, which is in the linear region at 180°C. The a.c. electric field of 1kV/mm and 60Hz was applied after 10 minutes from the start of the test. The frequency sweep tests were performed at a 10% strain in a frequency range of 0.1 rad/sec to 100 rad/sec at 180°C. They were performed without electric field after time sweep tests. All the measurements took place under a nitrogen atmosphere. The electric melt pipe was used to produce a large amount of PP/clay nanocomposites at 180°C and 25 rpm(Fig.2).

The electric field was applied with a function generator (Tektronix AFG 310) and high voltage amplifier (Trek 677B), and it was detected by a digital oscilloscope (Tektronix TDS210).

To verify the process of the exfoliation in PP/clay nanocomposites, X-ray diffraction (XRD) was measured using Rigaku D/MAX-IIIC X-ray diffractometer (40kV, 45 mV) with Cu-Kα radiation in transmission mode. The samples were scanned at a scanning speed of 1°/min under the diffraction angle in the range of 1.2-10°. These samples had been obtained after rheological measurements by rapid quenching.

Results and Discussion

Understanding the rheological properties of polymer melt layered silicate nanocomposites is crucial to gain a fundamental understanding of the processibility and structure-property relations for these materials.[9,10] The result of time sweep tests (Fig. 3) shows the processes of the exfoliation under electric field in the case of PP composites with clay of 5% (PP-C20A5w). The a.c. electric field of 1kV/mm, 60Hz was applied perpendicular to the samples loaded. The storage modulus G' increases after electric field is applied, while they show no changes for 10 minutes before applying the electric field at the beginning of the measurements. Of course, pure PP does not show any change by applying electric field. The result of frequency sweep tests (Fig. 4) also shows the properties of the exfoliated PP/clay nanocomposites. At low frequencies, we can find a large increase of G' and the slope of the curve decreases as electric field was applied. The result is in good agreement with that of time sweep tests. Such a large increase indicates the formation of networks involving the assembly of individual platelets being composed of layered silicates [12].

XRD was measured to confirm the exfoliated structures in PP/clay nanocomposites. Figure 5 shows the XRD curves of the bulk organo-MMT C20A, PP-C20A5w and electrically treated PP-C20A5w, respectively. The bulk clay of C20A shows main peak at 3.37°, corresponding to the basal spacing of 2.61 nm, whereas the XRD curve of electrically treated PP-C20A5w shows no d_{001} peak of the silicate layers indicating that they become fully exfoliated under the electric field. And Figure 6 shows the improvement of rheological properties such as G' and dynamic complex viscosity for PP/clay nanocomposites using electric melt pipe.

Conclusions

We proposed a novel method of producing the exfoliated PP/clay system under large electric field. Rheological and XRD measurements were presented to confirm the process of the exfoliation and the electric melt pipe was designed for commercial applications.

Acknowledgement

The authors wish to acknowledge the Korean Science and Engineering Foundation (KOSEF) for the financial support through the Applied Rheology Center, and official engineering research center (ERC) in Korea.

References

[1] J. Garces, D.J. Moll, J. Bicerano, R. Fibiger and D.G. MeLeod, Adv. Mater. **12**(23) 1835 (2000).
[2] P.C. LeBaron, Z. Wang and T.J. Pinnavaia, Appl. Clay Sci. **15**, 11 (1999).
[3] E.P. Giannelis, Adv. Mater. **8**(1), 29 (1996).
[4] Alexandre, M. and P. Dubis, Mater. Sci. Eng. **28**, 1 (2000).
[5] P.B. Messersmith and E.P. Giannelis, J. Polym. Sci.: Polym. Chem. **15**, 11 (1995).
[6] P. Kodgire, R. Kalgaonkar, S. Hambir, N. Bulakh and J.P. Jog, J. Appl. Ploym. Sci. **81**, 1786 (2001).
[7] A. Usuki, M. Kato, A. Okata and T. Kurauchi, J. Appl. Polym. Sci. **63**, 137 (1997).
[8] M. Kato, A. Usuki and A. Okada, J. Appl. Polym. Sci. **66**, 1781(1997).
[9] M.J. Solomon, A.S. Almusallam, K.F. Seefeldt and P. Varadan, Ploym. Mater. Sci. Eng. **82**, 263 (2000).
[10] P. Reichert, B. Hoffmann, T. Bock, R. Thomann, R. Mulhaupt and C. Friedrich, Macromol. Rapid Commun. **22**, 519 (2001).

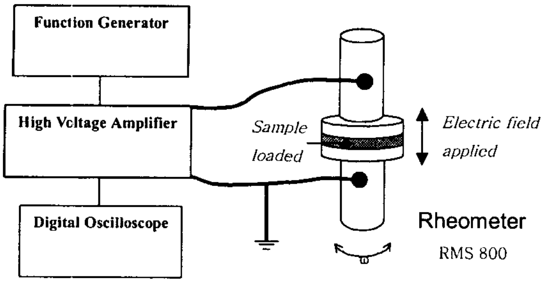

Fig. 1. Experimental apparatus.

Fig. 2. ENC melt pipe.

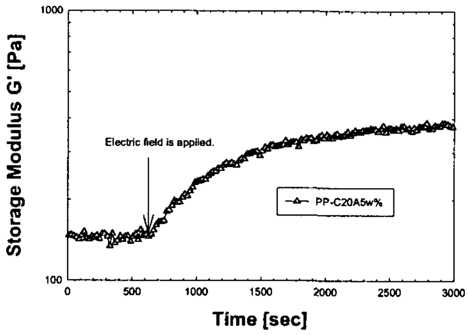

Fig. 3. Time sweep test.

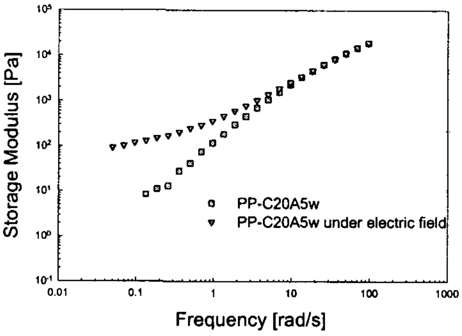

Fig. 4. Frequency sweep test.

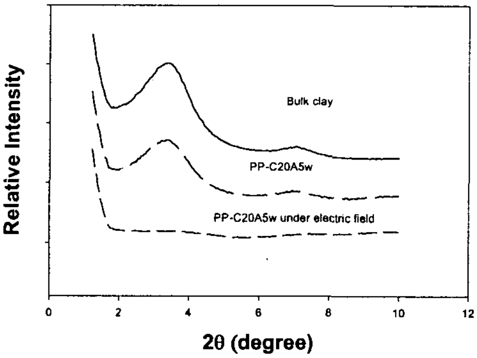

Fig. 5. XRD results.

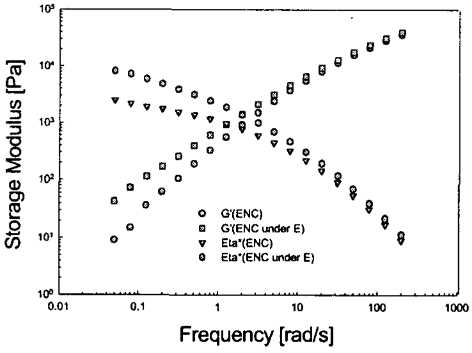

Fig. 6. Melt pipe effect.