전기 활성화된 PP/Clay 나노복합체의 유변특성 연구

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Electrically activated PP/clay nanocomposites

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Introduction

Polymer-based nanocomposites are a novel class of polymeric materials that offers dramatic improvements in permeability, mechanical, thermal, and processing properties in various applications[1-4]. Several strategies are currently proposed to prepare polymer/clay nanocomposites [2,3] and the melt intercalation method which was demonstrated by Giannelis group[5] is a quite effective technology for the case of polyolefin-based nanocomposites[6].

There are two classes of polymer/clay nanocomposites: One is intercalated nanocomposites and the other is exfoliated ones. Since Toyota group had reported PP/clay hybrid composites by melt intercalation of montmorillonite (MMT) organo-clays with PP modified with compatibilizer such as MAPP or hydroxyl groups (HOPP) [7,8], PP/clay nanocomposites are well known as exfoliated nanocomposites. 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 present a novel approach to make exfoliated PP/clay nanocomposites without adding MAPP. PP/clay systems under large electric field do show the exfoliated structure, which is evidenced by rheometer and XRD.

Experiments

PP (MI: 6.0g/min, Mw:127000, Mn:13000) used for this study was donated by PolyMirae Co., Ltd. of Korea. Organo-MMT, 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 composite was performed in an intensive Hakke mixer (Rheocord 90) with the rotor speed of 50 rpm and mixing time for 10 minutes after clay feeding at 180 °C. Then the specimens for rheological testing were molded in a heated press at 180 °C for 5 minutes. The molded samples were of disc shape with diameter 25mm and approximately 1.0 mm thickness.

The weight percent of C20A was changed from 5% and 10%; PP-C20A5w (5% by wt.) and PP-C20A7.5w (10% by wt.).

Rheometrics mechanical spectrometer (RMS 800) was used to assess the rheological performance of the PP/clay nanocomposites with parallel plate geometry. 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 10 minutes delay of external field is to investigate the changes of materials without electric field. 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.

The electric field was applied with a function generator and high voltage amplifier, and it was detected by a digital oscilloscope. The apparatus is schematically pictured in Figure 1.

X-ray diffraction (XRD) was measured using Rigaku D/MAX-IIIC X-ray diffractometer (40kV, 45 mV) with Cu-K 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

PP does not interact with organo-MMTs without the compatibilizer such as MAPP. After melt compounding of PP/clay composite without MAPP, the organo-MMT C20A behaves as a tactoid without indicating any sign of intercalation or exfoliation. It means that it shows no enhanced material properties as nanocomposites.

The rheological measurements give us good information of the three-dimensional suprastructure of silicate layers because of its sensitivity to elastic properties of nanocomposites described by Solomon et al. [9] and Reichert et al [10]. Figure 2 shows two results of rheological measurements. One is the result of time sweep tests (a) and the other is that of frequency sweep tests (b). The result of time sweep tests shows the processes of the exfoliation under electric field in the case of PP-C20A5w and PP-C20A10w, respectively. The high voltage 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. The result of frequency sweep tests 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 clay contents increases. 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 [10].

Figure 3 shows the XRD curves of the bulk organo-MMT C20A, PP-C20A5w and PP-C20A10w, respectively. The bulk clay of C20A shows two peaks at 2 values of 3.37° and 7.05°, corresponding to the basal spacing of 2.61 nm and 1.24 nm, respectively, whereas the XRD curves of other two samples show no d_{001} peak of the silicate layers indicating that they become fully exfoliated under the electric field.

Conclusion

We proposed the exfoliation of PP/clay nanocomposites under electric field without maleic anhydride functionalized polypropylene. To verify the process of exfoliation, rheological and XRD measurements were performed. From these results, we could suggest that applying electric field is a promising method of achieving the exfoliated structure in PP/clay systems.

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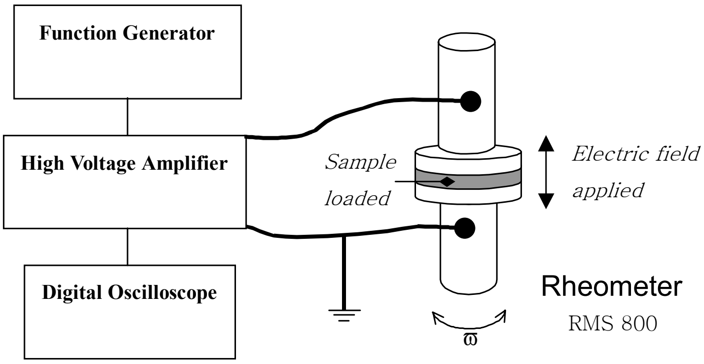

Figure 1. Experimental apparatus.

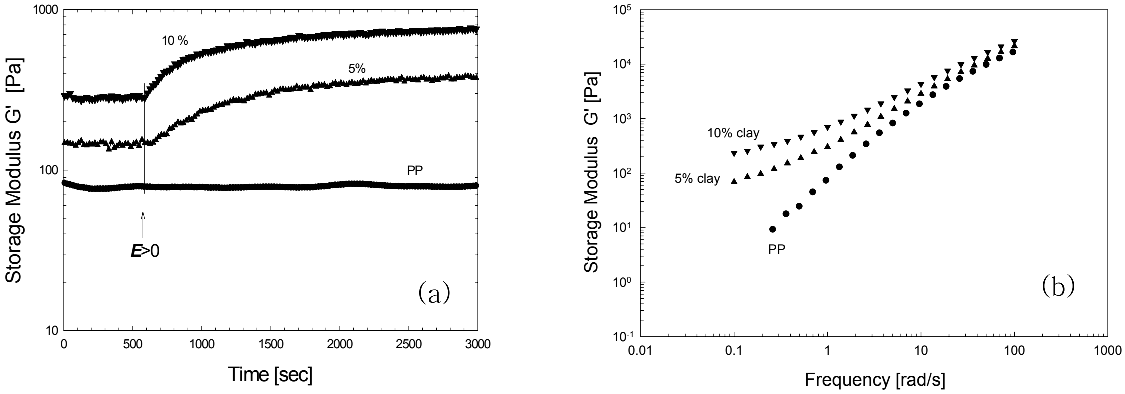

Figure 2. Rheological measuremetns: (a) time sweep test (b) frequency sweep test.

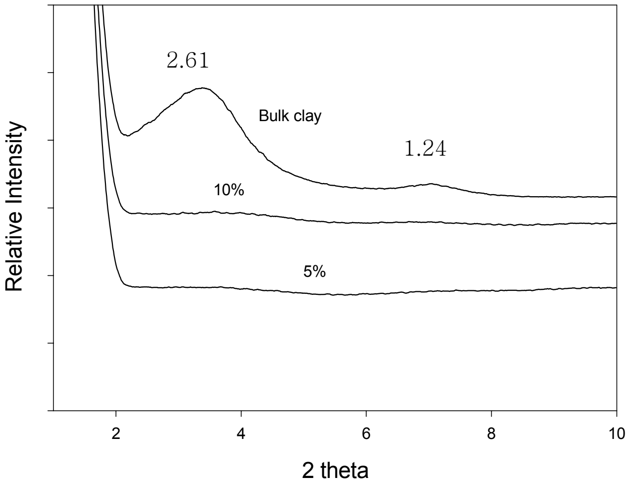

Figure 3. XRD results.