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# 전기활성화된 고분자-점토 나노복합체의 유변특성에 대한 연구

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# Rheology of electrically activated Polymer layered silicate nanocomposites

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## Introduction

Nanocomposites are a new class of polymeric materials exhibiting superior mechanical, thermal and processing properties in various applications compared with conventional micro-sized composites [1-4]. Polymer based nanocomposites may be produced by incorporating layered silicates in various polymer matrices. From a structural point of view, there are three main types of composites obtained when clay is associated with polymer depending on the components and the method of preparation. They are microcomposite, intercalated and exfoliated nanocomposite [3].

The focus of industrial research and development is on the in-situ polymerization and direct melt intercalation process. Whereas the degree of exfoliation and the correlated physical properties with the in-situ polymerization process is slightly greater than that with the melt intercalation process, the latter is much more attractive because of commercial feasibility as well as lower cost [4].

PP has great potential for nanocomposite applications because of their good processability by conventional technologies and their possible applications in the automotive industry. PP/clay nanocomposites have been investigated since Toyota group reported PP/clay hybrid composites by melt intercalation of montmorillonite (MMT) organo-clays with PP modified with either MAPP or hydroxyl groups (HOPP) [5]. Recently, Kim et al. [6] has reported that PP/clay nanocomposites under electric field show an exfoliated structure without any compatibilizer. We could regulate the degree of dispersion and exfoliation of materials by controlling the amount of clay loading, the strength of electric field, the time exposed to electric field, etc. However, this was accomplished by applying the electric field on a rheometer for a very long time.

In this study, we will present a new method to make PP/clay nanocomposites using electric melt pipe equipped on a twin-screw extruder for the continuous production. Rheological, XRD, and polarized optical microscope (POM) measurements were used to investigate the degree of dispersion and exfoliation of PP/clay nanocomposites.

## Experimental Methods

Electric melt pipe was used to apply the electric field. It was designed as an annular type and a diameter of inner stick for applying a high voltage was 18mm and the gap was 2mm. The input a.c. electric field of 1kV/mm and 60 Hz was applied. 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). The schematic diagram was pictured in Figure 1.

Rheometrics mechanical spectrometer (RMS 800) was used to assess the rheological performance of the nanocomposites. The time sweep tests were performed at a frequency of 1rad/sec and strain of 10%, which was in the linear region at 180°C. 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.

To verify the structures of PP/clay nanocomposites, 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°.

To investigate the degree of dispersion, an Olympus BX51 microscope with 20X lens coupled with a Linkam CSS-450 hot stage was used. Molten nanocomposites were observed at 180°C.

## Results and Discussion

It is well known that the rheological measurement gives us a good information about the formation of nano-sized structures because of its sensitivity to elastic properties of nanocomposites [7-8]. Kim et al.[6] reported that the increase of storage modulus under electric field indicates the process of exfoliation, and the decrease of terminal slope in the frequency sweep test shows the formation of nanocomposites. Figure 2 shows the improvement of rheological properties such as G and dynamic complex viscosity for PP/clay nanocomposites using electric melt pipe (ENC3). The solid line is reference data for PP/clay nanocomposite that is electrically treated during time sweep test in a rheometer for 40 minutes[6]. The storage modulus of ENC3 is greater than those of ENC1 and 2, but the terminal slope doesnt decrease to the level of reference. It means that the electrically treated PP/clay composite forms the microstructure in between intercalation and exfoliation.

XRD confirms the results. Figure 3 shows the XRD curves of the bulk organo-MMT C20A, ENC2, ENC3 and reference data, respectively. The bulk clay of C20A shows $d_{001}$ peak at 2 values of 3.37°, corresponding to basal spacing of 2.61 nm. But, the $d_{001}$ peak of ENC3 indicates the basal spacing of 3.10 nm and it verifies that the intercalated PP/clay nanocomposite is formed through the electric melt pipe.

Figure 4 shows the polarized optical microscopic results for ENC2 and ENC3. Molten nanocomposites are observed at 180 °C. Since PP is fully melted and clay particles are not melted at this temperature, polarized light can be used to observe the degree of dispersion of clay. Whereas aggregated clay particles are observed in ENC2 (a), clay particles are well dispersed in ENC3 (b). It means that the electric treatment enhances the dispersion of nanocomposites.

## Conclusions

We reported a new method for the formation of PP/clay nanocomposites with an electric melt pipe in this study. By applying the electric field on a melt pipe during the short residence time, we could control the nano structure in a single, continuous process. Rheological, XRD and POM measurements were also presented to confirm the formation of nanocomposites. As this method can be accomplished in a continuous extrusion process with little additional cost, it is expected to be applied for commercial applications.

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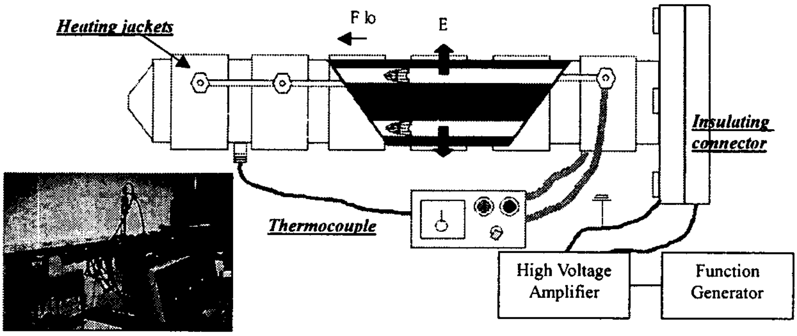

Figure 1. Experimental apparatus-Electric melt pipe equipped on a twin-screw extruder.

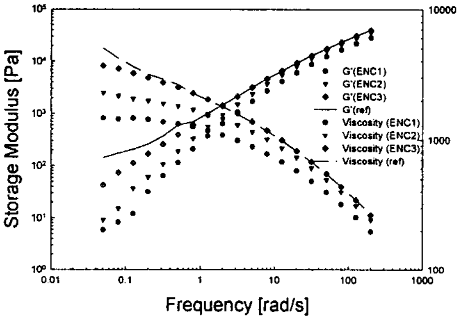

Fig. 2. Rheological properties.

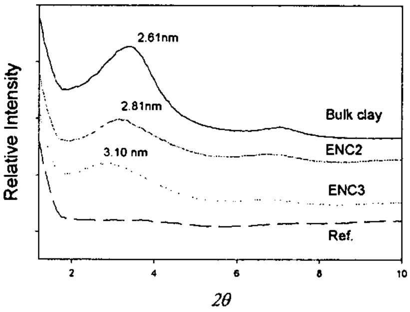

Fig. 3. XRD results.

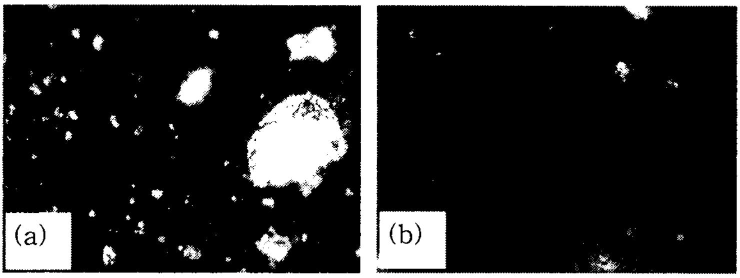

Fig. 4. Polarized optical microscope (180 oC, x200): (a) ENC2, (b) ENC3.