Water-assisted extrusion of polypropylene/clay nanocomposites in high shear condition

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Sangmook Lee [a], Jisoo Yoo [b,*], Jae Wook Lee [c,*]

[a] Division of Chemical Engineering, Dankook University, 126, Jukjeon-dong, Suji-gu, Gyeonggi-do 448-701, Republic of Korea
[b] Compound Development Team1, Kumho Tire R&D Center, 215-21, Saeun-ro, Giheung-gu, Yongin-si, Gyeonggi-do 446-909, Republic of Korea
[c] Applied Rheology Center, Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 121-742, Republic of Korea

ABSTRACT

Polypropylene (PP)/clay nanocomposites were prepared by water-assisted extrusion process at high shear rates. The effects of mixing methods of clay (with or without the use of water) and degree of shear rates on the properties of PP/clay nanocomposites were investigated by measuring their thermal, rheological, and tensile properties and morphology. The best properties were achieved when the clay was mixed in slurry state and the shear rates were high simultaneously. This was verified by both SEM and XRD showing a good dispersion status of the nano-clay in PP matrix for PP/clay nanocomposites. Expected mechanisms explaining the clay dispersions were proposed in this study. By these synergistic effects of water and high shear rates, the PP/clay nanocomposites would be promising materials for many applications where economic feasibility is needed as well as good mechanical properties.

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Introduction

Polymer nanocomposites have been extensively studied during last two decades. The studies have been focused mainly on the enhancement of properties such as mechanical, barrier, and thermal properties by mixing polymers with only a few percent of nano-fillers. To achieve the properties required, the good dispersion of clay in polymer matrix and the compatibility between clay and polymer were essential [1–5]. Among many kinds of clay, montmorillonite (MMT) clay has been used generally for the preparation of polymer/clay nanocomposites. MMT silicate layers have a high aspect ratio (one nanometer thick and hundreds nanometers long). Because layered silicates are stacked into aggregates, they should be separated to obtain a delaminated structure and dispersed into polymer matrix to achieve a polymer/clay nanocomposite [4–8]. Polypropylene (PP) is a low cost commodity polymer widely employed in various applications and thus PP/clay nanocomposites have attracted much interest. Works on PP/clay nanocomposites were initiated at Toyota Research Lab. and studied on the thermal and mechanical behaviors of these materials by many research groups [2]. To obtain the best properties of PP/clay nanocomposites, exfoliation of clays and their dispersion in PP matrix are essential during extrusion process. It has been reported that well-dispersion is greatly influenced by processing conditions [9,10].

To maximize exfoliation, the extrusion by using water was introduced for polyamide/clay nanocomposites system [11]. Without any further modification of clay, they obtained exfoliated polyamide/clay nanocomposites by melt mixing polyamide and clay in a twin screw extruder attached with a water injection and a degassing system. Recently, these water-assisted extrusions have been reported for other polymers, e.g. polyethylene terephthalate and polypropylene [6,12].

In this study, PP/clay nanocomposites were prepared through a water-assisted extrusion. Two different methods in introducing clay and water processes were used during melt extrusion. One was that PP and clay were melt-mixed first and then water was injected. The other was that PP was melt-mixed first and then clay–water slurry was introduced. The property changes of the nanocomposites processed at very high screw speeds were also investigated.

Experimental

Materials

Polypropylene (PP, HJ500, Melt index: 11 g/10 min at 230 °C/ 2.16 kg; density: 0.91 g/cm^3) was obtained from Samsung total. The

* Corresponding authors. Tel.: +82 2 705 8479.
  E-mail address: jwlee@sogang.ac.kr (J.W. Lee).

natural montmorillonite clay (Cloisite Na+, CNa+, Southern Clay Products, Inc.) was used as a nanoparticle. All materials were dried at 80 °C for 8 h in vacuum.

Nanocomposites preparation

Dried pellets of PP were melt mixed with clay in an intermeshing corotating twin screw extruder (KZW15, Technovel Corporation) with 15 mm in screw diameter and 45 in L/D ratio. The barrel and die temperature ranged from 190 to 200 °C. The screw speeds were 300 and 2000 rpm. The melt extrudates were cooled by water-bath and pelletized. The clay content in nanocomposites was fixed at 6 wt%. Nano-clay was mixed with PP in an extruder using two different ways.

One was that PP and clay were melt-mixed with water injected. In order to develop well-dispersed PP/clay nanocomposites successfully, metered water was injected by a piston pump into the twin screw extruder and removed in vacuum through a vent port at the end of the extruder.

The other one was that PP was melt-mixed with clay–water slurry as schematically shown in Fig. 1. First, aqueous Cloisite Na+ slurries were prepared by mechanical stirring at 600 rpm for 2 h. The clay content in the slurry was 5 wt% and the slurry level was kept constant while the flow rate was calibrated. Then the slurry was introduced using a separatory funnel into the extruder. The state of slurry was relatively stable while the experiment was performed. There was not any particular sign of flocculation or sedimentation. Water was fully removed through an open vent in vacuum at the end of the extruder. Compositions of samples and feeding methods of clay were summarized in Table 1.

After mixing, all specimens were compression molded using hot press (Laboratory Press Model M, Fred S. Carver Inc.) into disks and dog bone shapes for measurements of rheological and tensile properties. The molding temperature and load were 200 °C and 19,000 lb$_f$, respectively.

Instruments

Thermogravimetric analysis (TGA) was carried out employing TGA Q-series (TA, U. S. A.) to verify the thermal stability of the nanocomposites. Samples of approximately 10 mg were heated from 50 to 500 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

Stress-controlled rheometer (MCR500, Anton parr) was used to measure the complex viscosity and modulus. A parallel-plate

Table 1
Composition of samples and feeding method of clay.

Sample code	PP (wt%)	Clay (wt%)	Remark
p-PP	100	0	Processed PP
PP-C	94	6	Side feeding
PP-S	94	6	Feeding in slurry state (5 wt% in water)

fixture of 25 mm in diameter with 1 mm in gap was used. The frequency range was 0.05–500 rad/s and strain amplitude was kept enough value (5%) to ensure a linear viscoelastic response of the polymers. The measurement was performed at 200 °C.

Scanning electron microscope (SEM, JSM-6010LA, JEOL) was used to investigate the clay network structure in the nanocomposites. The cryo-fractured surfaces were gold coated before SEM observation.

Structural characterization was carried out utilizing X-ray diffraction (XRD) to evaluate the degree of delamination and dispersion. The XRD data was obtained by X-ray diffractometer (D/Max-A, Rigaku) using Cu Kα radiation (λ = 1.54056 Å) at room temperature. The 2θ angles were varying between 1.5 and 10° at a scanning rate of 1°/min in order to measure the d0 0 1-spacing between silicate layers. The generator was operated at 30 kV and 15 mA.

Tensile test was performed using a universal testing machine (UTM, LR-5K, Lloyd Instrument). The crossheads speed was fixed 20 mm/min for all of the specimens. The dimension of the test sample satisfied ASTM D638. Each tensile property was averaged over 8 tests.

Results and discussion

Thermal behavior

TGA results of the PP/clay nanocomposites were shown in Fig. 2. At early stage of degradation, when clay was incorporated in PP matrix, the degradation was delayed. Fig. 3 shows that the temperatures at 5 wt% degradation of PP/clay nanocomposites were higher than those of processed PP. And differences became more remarkable especially at high screw speed. The thermal stability of nanocomposites in inert atmosphere was correlated with their morphologies. It was reported that incorporation of clays, which are in a platelet form, improved considerably the initial thermal stability of the PP [13]. The initial thermal stability
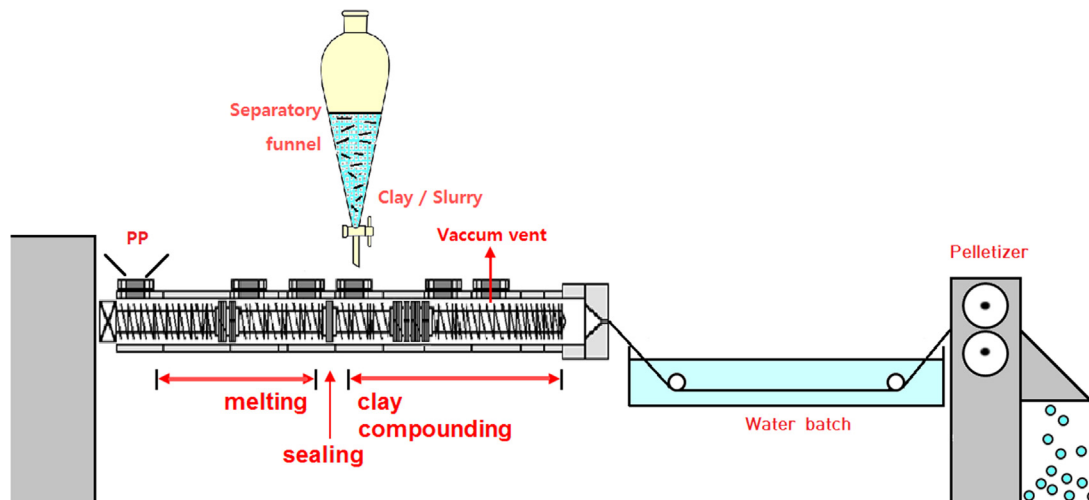
Fig. 1. Water-assisted extrusion with attached clay slurry injection system.