Development of polypropylene-clay nanocomposite with supercritical CO\textsubscript{2} assisted twin screw extrusion

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(Received October 8, 2008; final revision received November 21, 2008)

Abstract

The aim of this study is to explore the possibility of incorporating supercritical carbon dioxide (scCO\textsubscript{2}) into twin screw extrusion process for the production of polypropylene-clay nanocomposite (PPCN). The CO\textsubscript{2} is used as a reversible plasticizer which is expected to rapidly transport polymeric chains into the galleries of clay layers in its supercritical condition inside the extruder barrel and to expand the gallery spacings in its sub-critical state upon emerging from die. The structure and properties of the resulting PPCNs are characterized using wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), rheometry, thermogravimetry and mechanical testing. In the processing of the PPCNs with scCO\textsubscript{2}, optimum scCO\textsubscript{2} concentration and screw speed which maximized the degree of intercalation of clay layers were observed. The WAXD result reveals that the PP/PP-g-MA/clay system treated with scCO\textsubscript{2} has more exfoliated structure than that without scCO\textsubscript{2} treatment, which is supported by TEM result. ScCO\textsubscript{2} processing enhanced the thermal stability of PPCN hybrids. From the measurement of linear viscoelastic property, a solid-like behavior at low frequency was observed for the PPCNs with high concentration of PP-g-MA. The use of scCO\textsubscript{2} generally increased Young’s modulus and tensile strength of PPCN hybrids.

Keywords: polypropylene clay nanocomposite, supercritical fluid, twin screw extrusion

1. Introduction

Composite materials that contain a nanometer scale filler have been appeared over the last 15 years to afford remarkable property enhancements relative to conventionally-sized composites (Schmidt, 1985; Novak, 1993; Mark, 1996). A polymer layered silicate nanocomposite where layered silicates of nano-scale dimensions are dispersed as a reinforcing phase in an engineering polymer matrix is one of the most important forms of “hybrid organic-inorganic nanocomposites” (Okada and Usuki, 1995; Gnanellis, 1996; Ogawa and Kuroda, 1997). The composite with well dispersed silicate layers exhibit a significant improvement in thermal, mechanical, barrier properties with the use of minimal amount of filler. Many polymeric systems have been investigated in this field, such as polyamide 6 (Gnanellis, 1996; Kojima et al., 1993), polyethylene (Zax et al., 2000; Vaia et al., 1993), polyethylene terephthalate (Ke et al., 1999; Davis et al., 2002), polycaprolactone (Messersmith and Gnanellis, 1995; Jimenez et al., 1997), and epoxy resin (Messersmith and Gnanellis, 1994; Lan et al., 1995), etc. It was found that the exfoliated/intercalated dispersion of the clay layers could be achieved in certain polymers, which have polar functional groups compatible with the polar hydroxyl groups on the silicate clay layers.

Polypropylene is one of the most widely used thermoplastic materials in the plastics industry. A successfully developed PP/clay nanocomposite has a great potential being applied in the diverse areas of industry such as automobile, bottle, film, and package, etc. However, because of the non-polar nature of the polypropylene, it is difficult to exfoliate silicate layers and to have homogeneous dispersion of the silicate layers in PP matrix. This is because the organophilic clays have polar hydroxyl groups and are compatible only with polymers containing polar functional groups. To resolve the incompatibility between nonpolar polymer and polar clay, compatibilizers such as PP-g-MA and hydroxyl groups grafted polypropylene were used. These compatibilizers contain polar functional groups which enhance the interface interaction between the PP matrix and the clay layers (Usuki et al., 1997; Fischer and Gielgds, 1999).

Supercritical fluids have the characteristics of gas-like diffusivity, liquid-like density, low viscosity and surface tension. Supercritical fluids have received a great deal of attention as an efficient processing aid for the synthesis and processing polymeric materials Tae Yong Hwang, Sang...
Tae Yong Hwang, Sang Myung Lee, Youngjoon Ahn and Jae Wook Lee. The supercritical fluids can plasticize most of polymers efficiently and can be easily removed after depressurization acting as a “reversible plasticizer” (Brennecke, 1997). Among the supercritical fluids, scCO\textsubscript{2} has been used in a wide range of applications due to its environmentally friendliness, low critical point (31.1°C, 73.8 bar), relatively low cost, non-toxic nature, and non-flammability.

There have been various attempts to incorporate scCO\textsubscript{2} into continuous processing system to enhance the dispersion of clay layers of nanocomposite. Manke \textit{et al.} (2002) patented a method to delaminate a layered silicate material by supercritical fluid treatment. The method includes contacting the layered silicate with the supercritical fluid and catastrophically depressurizing the contacted layered silicate particle to exfoliate the layered particles. The supercritical treated particles were mixed with a polymer to form a reinforced nanocomposite. Mielewski \textit{et al.} (2002) patented a method of preparing a reinforced polymer by supercritical fluid treatment. In the method the layered silicate was mixed with a polymer to form a treatable silicate-polymer mixture and the mixture was contacted with supercritical fluid to exfoliate the silicate particles so that the particles disperse within the polymer. Garcia-Leiner (2004) recently reported data for a polyethylene-MMT nanocomposite processed in a modified single screw extruder equipped with scCO\textsubscript{2} injection near the feed hopper. Their results show a 40 – 100% increase in basal spacing and suggest that scCO\textsubscript{2} processing plays a significant role in facilitating melt intercalation and clay dispersion. Treece and Oberhauser (2007) investigated two different melt-blending strategies which are conventional TSE and single-screw extrusion capable of direct scCO\textsubscript{2} feed to extruder barrel. They concluded that the high shear of the twin screw process is vastly superior to the single-screw with in-line scCO\textsubscript{2} addition in generating well-exfoliated, percolated PP-clay nanocomposites.

The twin screw extruder is generally less advantageous in building up the high pressure required to provide the supercritical condition compared to single screw extruder. However, through a judicious design of screw configuration, a significant build up of pressure can be achieved before and after the supercritical fluid injection point and the melt seal to prevent leakage of scCO\textsubscript{2} can be formed. Referring to numerous solubility studies, it is expected that only a limited amount of CO\textsubscript{2} is required to plasticize polymeric melt and to enhance the diffusion of polymer chains. Furthermore twin screw extruder is an excellent mixer which is well suited to dissolve scCO\textsubscript{2} into the PP melt in relatively short distance of the barrel.

In this study we introduced scCO\textsubscript{2} directly into the midstream of twin screw extruder to produce the PP/clay nanocomposite with enhanced dispersion of clay layers. The scCO\textsubscript{2} was used as a reversible plasticizer which is

Fig. 1. Schematic of scCO\textsubscript{2} assisted twin screw extrusion process.
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expected to enhance the diffusion of polymer chains into the galleries of silicate layers in the extruder barrel and expand the gallery spacing by significant depressurization at the exit of die. The effects of concentrations of scCO₂, clay, and PP-g-MA and screw speed on the properties of the nanocomposite are studied. A comparison between conventional nanocomposite and the nanocomposite processed with scCO₂ was made.

2. Experimental

2.1. Materials

The matrix polymer used was polypropylene (HP602N, Polymira) with density of 0.9 g/cm³, MFR of 12.5 g/10 min, $M_w=222,400$ and $M_w/M_n=5.23$. Maleic anhydride modified polypropylene (Fusabond MD 353D, Dupont) with MA content of 3.2 wt% was used as a compatibilizer. A processing antioxidant (Irganox 8225, Ciba Specialty Chemicals) was used. The organically modified montmorillonite (Cloisite 20A, Southern Clay Products) was used as a nanoscale filler. The Cloisite 20A(C20A) was a montmorillonite ion-exchanged with dimethyl dehydrogenated tallow ammonium ions, where tallow was composed predominantly of octadecyl chains with smaller amount of lower homologues. The approximate composition was C18 (65%), C16 (30%), and C14 (5%). All materials were dried under vacuum at 80°C prior to the processing.

2.2. Procedure

The melt extrusion was performed in a co-rotating, intermeshing twin screw extruder (SM TEK25, SM Platek Korea) with a diameter of 25 mm and a ratio of screw length to diameter (L/D) of 41. The extruder setup and screw configuration are shown in Figs. 1 and 2. For precise scCO₂ feeding into the extruder barrel, a metered scCO₂ injection system shown in Fig. 1 was devised. It is composed of a CO₂ cylinder, a syringe pump (Model 260D, ISCO, Inc.) and a back pressure regulator. The Syringe pump was set to have a constant flow rate and the back pressure regulator was used for the stable supply of scCO₂ into the extruder barrel. The processing of PP/clay nanocomposite was performed by two step extrusion process (see Fig. 1). In the first step, PP and clay were blended in the extruder with scCO₂ injected into the middle of the extruder barrel and the foamed PP/clay mixture was obtained. In order to build up the pressure above the critical pressure (73.8 bar) of CO₂, a nozzle was used in a slit die. The resulting highly foamed extrudate was cooled and pelletized. In the second step, the foamed PP/clay was re-extruded with venting enabled to remove bubbles and to further disperse clay layers in the matrix. The operating temperature profile for the extruder varied from 140°C at the feed section to 180°C at the die. The screw was arranged in a special combination of conveying, shearing, mixing, and reversing elements as shown in Fig. 2. Reverse screw elements were inserted before and after the scCO₂ injection point to provide melt sealing. The PP/clay nanocomposite without scCO₂ was extruded at the same processing condition. The compositions of PP/clay hybrids tested are shown in Table 1. For brevity, the composition of the PPCN hybrid will be designated as (part PP/part PP-g-MA/part C20A).

2.3. Characterization of PP/clay nanocomposite

Structural characterization was carried out utilizing X-ray diffraction (XRD) and transmission electron microscope (TEM).

X-ray diffraction experiments were performed using Rigaku D/Max-A diffractometer (Cu Kα radiation with $\lambda=1.5406$ 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 d_{001}-spacing between silicate layers. The generator was operated at 40 kV and 40 mA. Test specimens

Table 1. Compositions of polypropylene nanocomposite

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP (part)</th>
<th>PP-g-MA (part)</th>
<th>C20A (part)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPCN1</td>
<td>100</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>PPCN2</td>
<td>100</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>PPCN3</td>
<td>98</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>PPCN4</td>
<td>95</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>PPCN5</td>
<td>90</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>PPCN6</td>
<td>85</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>PPCN7</td>
<td>75</td>
<td>25</td>
<td>5</td>
</tr>
</tbody>
</table>
were prepared by compression molding at 180°C.

Transmission electron microscope (TEM), Carl Zeiss LEO 912AB, was used to observe the dispersion of silicate in nanocomposites at an acceleration voltage of 160kV. Nanometer sections are prepared from the pellets via melt compounded on the twin-screw extruder. Ultrathin sections of 100 nm in thickness, mounted on a 200 mesh copper grid, are cut using a microtome (Leica EM FCS) procedure with a diamond knife where the sample is held at room temperature to produce the uniform thin sections required to obtain clear reproducible images.

The thermal gravimetric analyzer (TGA, TGA2950 from TA Inc.) was used to evaluate the thermal stability of the PP/clay nanocomposites. The chamber was purged with nitrogen. The temperature range was between 40 and 700°C, and the heating rate was 20°C/min.

Tensile test of nanocomposite was carried out using a universal testing machine (UTM, LR-5K from Lloyd Co.) with 500 kg load cell. The crosshead speed was fixed at 50 mm/min for all of the specimens and measurements for each case were performed more than at least 5 times. The dimension of the test sample corresponds to ASTM D638 (type V).

3. Results and discussion

3.1. Effect of scCO₂ on silicate layer dispersion

Fig. 3 shows the XRD patterns for organoclay C20A and PPCN1 (100/0/3) hybrids extruded with various loadings of scCO₂. The (001) plane peak of PPCN1 extruded with-
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noclay in the nanocomposite extruded without seCO$_2$. But further increase of seCO$_2$ content decreased the basal spacing. The XRD result can be complemented or confirmed by TEM analysis. Fig. 4 shows TEM images of PPCN1s processed without seCO$_2$ and with 2 wt% seCO$_2$. From low magnification TEM images, Figs. 4(a) and 4(c), it is seen that compared with those of PPCN1 samples processed without seCO$_2$, tactoids of PPCN1 samples processed with seCO$_2$ become smaller in size and larger in number. To observe detailed clay layer arrangement within a tactoid, high magnification TEM images are presented in Figs. 4(b) and 4(d). For PPCN1 processed without seCO$_2$, individual tactoid is composed of tightly bound silicate layers. For PPCN1 processed with 2% seCO$_2$, layer spacings are enlarged and some exfoliated silicate layers can be seen. This TEM result indicates that seCO$_2$ can be an effective dispersant for the dispersion of clay layers in PP matrix. It seems that seCO$_2$ enhances the diffusion rate of PP-seCO$_2$ mixture into the galleries of silicate layers and lower the surface tension between the polymer and the clay. Furthermore, the mixture of PP-clay-seCO$_2$ will experience significant pressure depression and volume expansion as it passes through a die, and this may help the clay layers fall apart. A similar result as shown in Fig. 4 was obtained for the PPCN2 (100/0/5) hybrid. The increase of seCO$_2$ concentration in PP melt results in the enhanced diffusion and thus intercalation of PP molecules into the galleries of clay layers but also makes it difficult to maintain melt seal within the seCO$_2$ dissolution screw zone due to the seCO$_2$ plasticated low pressure melt. The lowered viscosity of the seCO$_2$ dissolved PP melt is certainly not a favorable condition to break larger tactoids to smaller ones and exfoliate tactoids to individual clay layers. It seems that because of the two competing effects, there exists an optimum seCO$_2$ concentration of 2 wt% where the intercalation of clay is maximized.

3.2. Effects of screw speed on silicate layer dispersion

Figs. 5(a) and 5(b) show XRD patterns of PPCN1 extruded without seCO$_2$ and with 2 wt% seCO$_2$, respectively, as a function of screw speed. In case of PPCN1 without CO$_2$, as screw speed is increased, gallery distance was increased due to the increased stress level which promotes the dispersion of clay layers. But interestingly, in case of PPCN1 with 2 wt% CO$_2$, the degree of intercalation for PPCN1 was maximized at screw speed of 55 rpm. The decreasing degree of intercalation for PPCN1 at screw speed of 70 rpm can be attributed to the reduction of the residence time, which is not enough for the PP chains to diffuse into galleries of silicate layers.

3.3. Effects of PP-g-MA on clay exfoliation

Using seCO$_2$ it was possible to produce PP/organoclay nanocomposite with intercalated structure. To overcome the incompatibility of the polar hydroxyl groups on the surface of the clay layers and the non-polar PP and thus to achieve an improved dispersion state in the PPCNs, PP-g-MA is commonly used as a compatibilizer. Therefore, to further enhance the dispersion state of PP/clay hybrids and to have possible synergetic effect, seCO$_2$ and PP-g-MA was used together. Fig. 6(a) shows XRD patterns of PPCNs extruded without seCO$_2$ for various PP-g-MA concentrations. The (001) plane peak of clay is reduced and is shifted to the lower angle as PP-g-MA concentration is increased. PPCN2 having no PP-g-MA exhibits small peak angle shift and no significant intensity change indicating that limited intercalation of silicate layers has occurred in PPCN2. From PPCN3 (98/2/5) to PPCN5 (90/10/5) as PP-g-MA concentration increases the peak shifts to lower angle and the peak intensity is decreased which means the gallery spacing is increased and more disordered/exfoliated structure is created. In XRD curves of PPCN6 (85/15/5)
and PPCN7 (75/25/5) the peak was almost disappeared and this can be attributed to the highly disordered or exfoliated structure of silicate layers in the hybrids. Fig. 6(b) shows XRD patterns of PPCNs extruded with 2 wt% CO\textsubscript{2} as a function of PP-g-MA concentration. The peak was almost disappeared for PPCN5, PPCN6 and PPCN7. Note that whereas PPCN5 hybrid with no scCO\textsubscript{2} treatment was intercalated, the same hybrid with scCO\textsubscript{2} treatment was almost exfoliated.

Figs. 7(a)-(f) show TEM photomicrographs of PPCNs extruded with and without scCO\textsubscript{2}. Note the different magnifications for PPCN hybrids; 12000 for (a), 24000 for (b) through (e), and 37500 for (f). In Fig. 7(a) even larger clusters of clay are observed in PPCN2 with scCO\textsubscript{2} and without scCO\textsubscript{2} indicating poor dispersion of clay layers in PP matrix without PP-g-MA. From Figs. 7(b) and 7(c), the size of the clusters for PPCN3 and 4 became considerably

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**Fig. 6.** XRD pattern of PPCN as a function of PP-g-MA concentration. (a) processed without CO\textsubscript{2}, (b) processed with 2 wt% CO\textsubscript{2}.

**Fig. 7.** TEM images of PPCNs as a function of PP-g-MA concentration. (a),(b): PPCN2, (c),(d): PPCN3, (e),(f): PPCN4, (g),(h): PPCN5, (i),(j): PPCN6, (k),(l): PPCN7; left side: processed without CO\textsubscript{2}; right side: processed with 2 wt% CO\textsubscript{2}. 
smaller compared with that for PPCN2. But the difference between scCO₂ treated and untreated is not clear. In Figs. 7(d)-7(f), we can observe the improved dispersion of the PPCN hybrids processed with scCO₂ compared with those without scCO₂. A few of clusters or tactoids can be encountered but majority of the clay exists as exfoliated layers. Generally, as the PP-g-MA concentration increases it is observed that the dispersion state of silicate layers is improved especially at high concentration of PP-g-MA. Also, while the big clusters of clay appear in the PPCNs extruded without scCO₂ the clusters are broken to smaller ones in the PPCNs extruded with scCO₂. This indicates that scCO₂ is effective when it is applied with high concentration of PP-g-MA.

3.4. Linear viscoelastic properties

From the storage modulus vs. frequency plots for pure PP and PPCN hybrids processed without and with scCO₂, a significant enhancement of the storage moduli of the PPCN hybrids at low frequency as the PP-g-MA concentration was increased and the non-terminal behavior which is typically attributed to the three dimensional percolated network structure (Galgali et al., 2001; Solomon et al., 2001) at the high concentration of PP-g-MA were observed (data not shown for brevity). A cross-plot is constructed from the result of the small amplitude oscillatory measurement and is shown in Fig. 8 for PPCNs without CO₂ and PPCNs with CO₂. The cross-plot for PPCN7 processed with scCO₂ shows the divergence of η' at finite values of G' which is indicative of the solid-like nature exhibited by some exfoliated nanocomposites with good polymer-clay interactions (Xu et al., 2005).

3.5. Thermal stability of PPCNs

The thermal stability of nanocomposites is studied by thermogravimetric analysis (TGA). When the heating occurs under an inert gas flow, a non-oxidative degradation occurs, while the use of air or oxygen allows oxidative degradation of the samples. In general thermal stability of nanocomposites is enhanced by physical protective barrier created by the reassembling of silicate layers on the surface of nanocomposites and delayed volatilization due to the labyrinth effect of silicate layers dispersed in the matrix polymer (Gilnian et al., 1998). Fig. 9 represents the result of TGA analysis for PPCN2 as a function of scCO₂ concentration compared with neat PP. It is seen that PPCN2 hybrids processed with scCO₂ have superior thermal stability compared with neat PP and PPCN2 with 2 wt% scCO₂ has the highest thermal stability. As mentioned previously in XRD result, PPCN2 had a maximum interlayer distance when scCO₂ concentration was 2 wt%. Although the most desirable structure of the nanocomposites for a good thermal stability may be the exfoliated structure, intercalated structure may contribute to the enhancement in thermal stability of the nanocomposite. Thus this TGA
result is well correlated with XRD result in which the layer spacing was maximized at 2 wt% scCO$_2$ concentration. Figs 10(a) and 10(b) show the TGA results for neat PP and for PPCNs as a function of PP-g-MA concentration processed without CO$_2$ and with 2 wt% CO$_2$. Clearly the thermal stability improvement can be seen for the scCO$_2$ treated hybrids. As seen in Fig. 10(a), PPCN composites processed without scCO$_2$ shows progressive increase in thermal stability. But most of the PPCN hybrids (from PPCN3 through PPCN6) processed with scCO$_2$ have the almost the same thermal stability. Note that PPCN7 composite has the highest thermal stability which is well correlated with the previous rheometry result. The fact that the PPCN composites processed with scCO$_2$ have improved thermal stabilities compared with the counterparts without scCO$_2$ can be attributed to the disordered and/or exfoliated structure of the PPCN composites processed with scCO$_2$. 

Table 2. Mechanical properties of PPCNs measured by UTM

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus (MPa)</th>
<th>Stiffness (N/m)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPCN2</td>
<td>369 (1.26)</td>
<td>12751 (0.93)</td>
<td>28.8 (0.91)</td>
</tr>
<tr>
<td>PPCN3</td>
<td>394 (1.35)</td>
<td>130742 (0.96)</td>
<td>31.5 (1)</td>
</tr>
<tr>
<td>PPCN4</td>
<td>380 (1.30)</td>
<td>173410 (1.27)</td>
<td>31.4 (0.99)</td>
</tr>
<tr>
<td>PPCN5</td>
<td>406 (1.39)</td>
<td>138333 (1.01)</td>
<td>29.5 (0.94)</td>
</tr>
<tr>
<td>PPCN6</td>
<td>418 (1.43)</td>
<td>137906 (1.01)</td>
<td>32.4 (1.03)</td>
</tr>
<tr>
<td>PPCN7</td>
<td>430 (1.47)</td>
<td>145636 (1.07)</td>
<td>30.4 (0.97)</td>
</tr>
<tr>
<td>PPCN2 (2 wt% CO$_2$)</td>
<td>423 (1.44)</td>
<td>180829 (1.32)</td>
<td>33.1 (1.05)</td>
</tr>
<tr>
<td>PPCN3</td>
<td>455 (1.55)</td>
<td>167863 (1.23)</td>
<td>37.5 (1.19)</td>
</tr>
<tr>
<td>PPCN4</td>
<td>436 (1.49)</td>
<td>140894 (1.03)</td>
<td>30.1 (0.96)</td>
</tr>
<tr>
<td>PPCN5</td>
<td>435 (1.49)</td>
<td>158293 (1.16)</td>
<td>28.1 (0.89)</td>
</tr>
<tr>
<td>PPCN6</td>
<td>421 (1.44)</td>
<td>142649 (1.04)</td>
<td>32.0 (1.02)</td>
</tr>
<tr>
<td>PPCN7</td>
<td>446 (1.52)</td>
<td>165643 (1.21)</td>
<td>36.3 (1.15)</td>
</tr>
<tr>
<td>pure PP</td>
<td>293 (1)</td>
<td>136785 (1)</td>
<td>31.5 (1)</td>
</tr>
</tbody>
</table>

3.6. Mechanical properties of PPCNs

Mechanical properties of PPCNs were evaluated by universal testing machine. Table 2 shows the results of the tensile test of PPCNs processed without and with scCO$_2$. The effect of scCO$_2$ is not profound but it is observed that Young’s modulus and tensile strength for the PPCN hybrids processed with scCO$_2$. The main reason for the improvement in Young’s modulus and tensile strength in PPCNs processed with scCO$_2$ is due to the high aspect ratio of the clay dispersed in polymer matrix and the strong interaction between matrix and silicate layers via formation of hydrogen bonds.

4. Conclusions

The feasibility of producing PPCN hybrid with enhanced dispersion was explored by employing a method which injected scCO$_2$ directly into the midstream of twin screw extruder. In the processing of the PPCNs with scCO$_2$, optimum scCO$_2$ concentration and screw speed which maximized the degree of intercalation of clay layers were observed. From WAXD result of the PPCN hybrids, an optimum scCO$_2$ concentration at 2 wt% and an optimum screw speed of 55 rpm which give maximum interlayer distance of organoclay in PP matrix were observed. We
could find some positive results for the production of PPCNs with enhanced dispersion property using scCO\(_2\). A significant intercalation was achieved for PPCN1 (100/0/3) with 2 wt% scCO\(_2\), which was also confirmed by TEM result. The XRD result shows that when scCO\(_2\) is used in the PP/PP-g-MA/clay system, more exfoliated structure was observed at high PP-g-MA concentration compared with PP/PP-g-MA/clay system without scCO\(_2\) processing. This is supported by TEM result. The thermal stability of PPCN hybrid was improved when it is processed with scCO\(_2\). From the measurement of linear viscoelastic property, the PPCN with high concentration of PP-g-MA shows the solid-like nature exhibited by some exfoliated nanocomposites with good polymer-clay interactions. In summary, for the PP/organoclay hybrid the use of scCO\(_2\) mainly increased the interlayer distance of the hybrid but for the PP/PP-g-MA/organoclay hybrids the use of scCO\(_2\) improved the dispersion state and even enhanced the exfoliation of the hybrid in some cases.

Acknowledgements

Authors are gratefully acknowledging the support by Defense Acquisition Program Administration and Agency for Defence Development. The authors also gratefully acknowledge the Korea Research Foundation Grant for the financial support (KRF-2006-005-302302).

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