Effect of Compatibilizer on Properties of Polypropylene Layered Silicate Nanocomposite

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Abstract

Polypropylene layered silicate nanocomposites based on muscovite clay were prepared via melt compounding using Thermo Haake internal mixer. Muscovite was organically modified with cetyltrimethylammonium bromide (CTAB). Poly(propylene-g-maleic anhydride) copolymer (PP-g-MAH) and polypropylene-methyl polyhedral oligomeric silsesquioxane (PP-POSS) were used as a compatibilizer in the nanocomposite system at concentration of 3.0 wt% based on muscovite content. Consequently effect of compatibilizer on the mechanical properties of the nanocomposites was characterized. It was found that the PP-g-MAH compatibiliser possess better overall mechanical properties than the nanocomposites with PP-POSS compatibilizer. The reason was partly due to better adhesion provided by compatibilization effect of PP-g-MAH than PP-POSS as exhibited in scanning electron micrographs.

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Keywords: polymer layered silicate nanocomposite; muscovite; compatibilizer.

1. Introduction

Polymer layered silicate nanocomposites (PLSNs) are new class of composite materials composed of hybrid organic polymer-inorganic materials. In most cases, the layered silicate structure is finely dispersed and incorporated into the polymer [1]. In recent years, PLSNs have attracted great interest of researchers around the world due to its remarkable improvement in term of engineering properties of low filler loading, typically less than 5 wt% and better dispersion via intercalation and exfoliation mechanisms.
as compared to conventional nanocomposite. Simultaneous improvements in strength and modulus under tensile and flexural loading conditions have also been reported by several researchers [2-8]. Apart from mechanical properties, increase in other properties such as thermal stability [3, 9-11] and gas impermeability was also reported [12-13].

Despite of these improvements, PLSNs still suffer from the issues such as poor compatibility and miscibility [11, 14]. In order to overcome this problem, layered silicate structure is often treated using ion exchange treatment. The ion exchange treatment of layered silicate are influenced by several factors, such as the density of layer charge, the degree of exchange, the length of the alkyl chain, and the host–guest and guest–guest interactions [14-15]. In previous study, organic cationic surfactants, which are primary, secondary, tertiary and quaternary alkylammonium have been widely used in ion exchange treatment. Shimizu et al. [16-17] have used alkaline earth metal cations and transition metal ions as the exchange cation. Bracke et al. [18] and Suter et al. [19-20] have used Li as exchange cations for biotite, muscovite and phlogopite. However, the improvements are not significant to fully enlarge the basal spacing of muscovite through ion exchange treatment. Based on those studies, we have used two-step ion exchange treatment in order to enlarge further the basal spacing of muscovite. First, layered silicates were treated using lithium nitrate and followed by quaternary alkylammonium cations.

Layered silicates are clay minerals, built of two structural units. The simplest form of layered silicate is the 1:1 structures (example: kaolinite) where a tetrahedral silica sheet is fused to an aluminium octahedron with sharing the oxygen atoms. Kaolinite and montmorillonite (MMT) are among the most commonly used clays in producing PLSNs due to their ion exchange properties and swelling behaviour. However, there are also other types of clays which are equally potential such as Vermiculite and Muscovite. These clays have 2:1 layered structure of layer charge density, layer charge site, and charge distribution. Muscovite has the highest layer charge density and homogeneous charge distribution. In addition, it has high aspect ratio and much cheaper than MMT. The general formula of Muscovite is KAl₃(AlSi₃)O₁₀(OH)₂. It is composed of monoclinic structure with a very high layer charge density, close to 1.0 equivalent per O₁₀(OH)₂.

In the present study, Muscovite was used as reinforcement filler in the polymer matrix and the ion exchange treatment or the organically modified clay (organoclay) was prepared using lithium nitrate and cetyltrimethylammonium bromide (CTAB). The PLSNs was prepared by melt compounding and poly(propylene-g-maleic anhydride) copolymer (PP-g-MAH) and polypropylene-methyl polyhedral oligomeric silsesquioxane (PP-POSS) were used as compatibilizers. The effect of compatibilizer on the final nanocomposite structure was also investigated.

2. Experiment
2.1. Materials

Polypropylene (TITANPRO PM-255) was supplied by Titan PP polymers (M) Sdn. Bhd. and used as the base matrix for the present study.Compatibilizers, poly(propylene-g-maleic anhydride) copolymer (PP-g-MAH) with 8-10 wt% maleic anhydride (MA) and polypropylene-methyl polyhedral oligomeric silsesquioxane (PP-POSS) and cetyltrimethylammonium bromide (CTAB) were acquired from Sigma Aldrich. The Muscovite clay was provided by Bidor Mineral (M) Sdn. Bhd. with a cation exchange capacity (CEC) of 82 meq/100 g.
2.2. Ion exchange treatment of clays

The ion exchange treatment of muscovite was prepared using lithium nitrate (LiNO₃) followed by alkylammonium cations, cetyltrimethyl ammonium bromide (CTAB) under hydrothermal reaction method. The mixtures was placed in hydrothermal reactor (100 mL) of Teflon-lined stainless-steel autoclave and heated at 170 °C for 12 h. After the reaction completed, all the resulting organoclay products were filtered, washed three times with ethanol, and dried in a vacuum oven at room temperature.

2.3. Preparation of nanocomposite

PLSN containing 5 wt% organo muscovites was fabricated via melt blending method. PP, PP-g-MAH, PP-POSS and organo muscovite were mixed in internal mixer Thermo Haake Polydrive R600 fitted with cam blades at 180 °C for 8 min. Cam blade speed was set at 50 rpm. PP granulates and organo muscovite was dried prior to blending in a vacuum oven for 24 h at 80 °C in order to remove moisture.

2.4. Characterization

The interlayer distance of organoclay in the nanocomposites was analyzed by using wide angle X-ray diffraction (WAXD, Bruker) with a Cu target (Kₑ λ = 1.5405 Å) at a generator voltage and current of 35 kV and 30 mA. The experiments were performed in the range of 2θ =1-10° with a scanning rate of 2°/min. The interlayer distance of organoclay in composite was calculated from the (001) peak by using the Bragg Equation, \(2d \sin \theta = n\lambda\). The nanostructure of nanocomposites and the dispersion of muscovite were attempted by high-resolution transmission electronic microscopy (HRTEM, LIBRA 120) at an acceleration voltage of 120 kV equipped with energy dispersive X-ray spectroscopy (EDX). The morphology was observed by Phillips field emission scanning electron microscopy (model S-36; Leica Cambridge Ltd. With Leo Supra 35VP system) and Hitachi S-900 field emission scanning microscopy at an accelerating voltage of 15 kV. The mechanical properties of the nanocomposite samples were tested using Instron Universal model 5533 according to ASTM D638 for tensile test and ASTM D790 for flexural test. All tests were performed at room temperature and five replicate specimens from each modifier/muscovite ratio were prepared for the tests. The notch Izod impact test was conducted using an impact pendulum tester (Zwick Model 5101) according to the ASTM-D256. The hammer used to strike the specimen was 7.5 J.

3. Results and Discussion

3.1. The X-Ray Diffraction (XRD) diffractogram

The X-ray diffractograms of muscovite clay and PP nanocomposite with and without compatibilizer are shown in Figure 1 and the basal spacing value is summarized in Table 1. The X-ray diffractogram of muscovite and organo muscovite revealed a shift in (001) plane from 8.94° to 7.25°, corresponding to the increasing in the basal spacing of this plane, Table 1. Use of lithium nitrate and cetyltrimethyl ammonium bromide (CTAB) increases the opening of the interlayers spaces by 0.23 nm, corresponding to 23% of increment which confirm the existence of intercalation between muscovite clay layers by surfactant molecules. The X-ray diffraction pattern of the PP-OM nanocomposite showed that the addition of compatibilizer increases the basal spacing, as the \(d_{001}\) peak shifted to lower angle [21-22]. This indicate that the PLSN is successfully formed using PP as a matrix [23]. The improvement in the properties can be
attributed to the intercalation of clay platelets in the PP matrix. PLSN with MAH compatibilizer demonstrates highest increment as compared to PLSN with POSS as a compatibilizer with $d$ spacing of 1.93 nm and 1.39 nm respectively.

Table 1. The result of XRD of the OM and the corresponding polymer-OM nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d$(001) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovite(M)</td>
<td>0.99</td>
</tr>
<tr>
<td>Organo Muscovite (OM)</td>
<td>1.22</td>
</tr>
<tr>
<td>Polypropylene/ Organo Muscovite (PP/OM)</td>
<td>1.31</td>
</tr>
<tr>
<td>Polypropylene/ Organo Muscovite/PP-g-MAH (PP/OM/POSS)</td>
<td>1.39</td>
</tr>
<tr>
<td>Polypropylene/ Organo Muscovite/PP-g-MAH (PP/OM/MAH)</td>
<td>1.93</td>
</tr>
</tbody>
</table>

3.2. Mechanical properties

Figure 2 presents the tensile modulus and tensile strength of nanocomposite as a function of composite system with and without compatibilizer. All composites show an enhancement of the stiffness as compared to the neat PP. The enhancement of modulus varied with the types of compatibilizer. The nanocomposites compatibilized with PP-g-MAH compatibilizer show the highest tensile strength and modulus among the nanocomposites. In terms of percentages, both tensile strength and modulus recorded an increase of 36%. The significant and simultaneous improvement in the strength and modulus of nanocomposite can be directly related to the improvement in compatibility and miscibility after the ion exchange treatment. The result also highlighted the significant influence of compatibilizers in improving the mechanical performance of nanocomposite.

Fig. 1. XRD diffractograms of muscovite clay and PP nanocomposite with and without compatibilizer
Figure 4 shows the variation of flexural strength and modulus of organo muscovite/PP layered silicate as function of different compatibilizer. From the figure, it is clear that the addition of PP-g-MAH and PP-POSS promote less significant increase in flexural strength as compared to flexural modulus. The PP-g-MAH compatibilized PLSN showed better flexural properties as compared to PP-POSS compatibilized PLSN and uncompatibilized PLSN.

The results of notched Izod impact strength measurement for the PLSN are presented in Figure 5. Apparently, the impact strength is reduced for uncompatibilized PLSN system. This can be related to the agglomeration and nonuniform dispersion of clay in the polymer matrix. In all nanocomposite specimens considered, maximum impact strength was recorded for PP-g-MAH compatibilized PLSN. The increment reaches almost 23% as compared to the neat PP. This is possibly due to the better adhesion between clay particle and PP matrix as a result of better compatibility when compatibilizer is added. In addition, it is also probably due to the inter-diffusion of polymer matrix through the interlayer galleries of the muscovite.
3.3. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) allows for the direct imaging of the filler dispersion. Therefore, the dispersion of the organoclays within the PP matrix is further corroborated with TEM images. A series of TEM images for PLSN with 5 wt% clay content outlined in Figure 6. The dark line represents the intersection of the silicate layers while the white background corresponds to PP matrix. PP-g-MAH compatibilized PP nanocomposites, Figures 6a-b show a higher degree of disordered structures and exfoliated layers than PP-POSS compatibilized PP nanocomposite, Figures 6c-d. The presence of large aggregates indicates that the clays are not well dispersed in PP-POSS nanocomposite. MAH nanocomposite undergoes better intercalation and dispersion than the PP-POSS nanocomposite and uncompatibilize nanocomposite.

4. Conclusion

In this study, polypropylene layered silicate nanocomposite was successfully prepared using PP-g-MAH and PP-POSS as compatibilizers. Addition of compatibilizer into PLSN has been proven not only enhances the degrees of intercalation but also at the same time improves the mechanical properties. PP-g-MAH compatibilized PLSN exhibited better mechanical properties than PP-POSS compatibilized PLSN. This indicates that the PP-POSS compatibilizer has lower polarity than PP-g-MAH, and promotes
less effective interaction between organoclay and polymer matrix. Furthermore, this factor influences the interfacial adhesion.

![TEM images](image1)

Fig. 6. TEM images of (a) PP/OM; (b) PP/OM/MAH; (c) PP/OM/POSS nanocomposite

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**References**


