Evolution of Microstructure and Physical Properties of PMMA/MWCNTs Nanocomposites upon the Addition of Organoclay

Amir Rostami 1*, Forouzan Eskandari2, Mohsen Masoomi 2*, Mohsen Nowrouzi3

1 Department of Chemical Engineering, Faculty of Petroleum, Gas, and Petrochemical Engineering, Persian Gulf University, Bushehr, 75169, Iran.
2Department of Polymer Engineering, Islamic Azad University, Mahshahr Branch, Khuzestan-Iran.
3Department of Marine Environment, Faculty of Marine Science and Technology, Persian Gulf University, Bushehr, 75169, Iran

ARTICLE INFO
Article History:
Received 2 June 2019
Revised 9 July 2019
Accepted 30 July 2019

Keywords:
Polymer Modification
Nanocomposites
Hybrid system
Microstructure
Rheology
Thermal properties

ABSTRACT
The present investigation was carried out to evaluate the application of Cloisite 30B organoclay (C30B) on the rheological, structural, electrical, and thermal characteristics of poly (methyl methacrylate)/multiwalled carbon nanotubes nanocomposites (PMMA/MWCNTs) fabricated by the simultaneous melt mixing. The microstructure and the state of nanofillers dispersion were assessed by melt linear viscoelastic experiments, X-ray diffraction (XRD), and electron microscopy. The obtained results illustrated that the applied C30B nanofiller considerably altered the pattern of MWCNTs dispersion and reaggregation. The study of electrical properties of single filler and hybrid nanocomposites also showed that the percolation threshold almost remained intact with the addition of C30B (\(\phi_c\) ~0.18%), but an effective decrease in volume resistivity was observed at high MWCNTs loading levels. Finally, thermal analyses, employed as complementary experiments, confirmed that the MWCNTs dispersion was improved by the incorporation of C30B nanofillers. Upon the incorporation of nanofillers, a decrease in tanδ peak height and a small increase in Tg were observed. The Td,5%, Td,70%, and Tmax of the neat PMMA were 308, 342.9 and 335.2 °C, respectively while for the PMMA-0.5%MWCNTs-3%C30B, they stood at 314.7, 380.3 and 369.2 °C, respectively.

1. INTRODUCTION
Polymers produced in petrochemical plants are normally very basic materials of basic properties. The fabrication of more advanced polymers for the critical and high-tech applications has used several approaches including reinforcement via fillers, crosslinking reactions and crystallization. Among others, reinforcing was a preferred approach regarding its scale-up application, easy processability, and the considerable improvement properties [1, 2]. Polymer nanocomposites manufactured from the organoclays and/or carbon nanotubes have received considerable attention due to their vast application comprising flame retardancy, fuel cell applications, barrier and membrane separation, electrical conductivity and sensors, biomedical applications, and the compatibilization of polymer blends [3-6].

Two key determining parameters in achieving these goals are the microstructure of polymer

*Corresponding Author Email: arostami@pgu.ac.ir,
masoomi@aut.ac.ir

This work is licensed under the Creative Commons Attribution 4.0 International License.
To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.
nanocomposites and the state of dispersion. Proper nanofillers dispersion establishes the development of three dimensional (3D) networks with high efficiency to attain a combination of the enhanced properties. The interfacial interaction between the polymer matrix and the nanofillers plays an essential role in the state of nanofiller dispersion/exfoliation. Some methods to improve the interfacial interaction are to introduce the functionalized nanofillers or surfactants as a dispersing aid [7, 8].

Over the last decade, research investigations have demonstrated that the application of hybrid filler nanocomposites can be a promising approach in the development of advanced polymeric materials with improved characteristics, especially through synergistic effects [9-14]. In the following, some hybrid systems containing organoclay and carbon nanotubes or carbon black as the conductive filler are discussed. Feller et al. [15] showed that the electrical conductivity of carbon black filled polymer composites can be ameliorated by the simultaneous addition of clay nanofiller. They reported that clay has an important effect on the percolation threshold and rheological properties due to modifying the level of carbon black dispersion, even at very low contents. Konishi et al. [16] studied nylon6/carbon black composite and reported that the percolation threshold tends to the fractions of carbon black with lower volume in the optimum accessibility of organoclay, Sharma et al. [17] investigated nanoclay modified PC and PMMA/carbon black nanocomposites. Their results illustrated the positive effect of nanoclay application on the improvement of nanocomposites’ mechanical properties induced by the identical dispersion of reinforcing nanoparticles in the polymer matrix.

Liu et al. [18] demonstrated that the addition of clay significantly enhances the dispersion of CNTs and electrical properties in conductive epoxy nanocomposites. Lee et al. [19] studied the effects of nanoclays on the electrical and morphological characteristics of TPU/MWCNT nanocomposites. Their study showed that the coadition of clay changed the nanocomposites morphology and increased the electrical conductivity. Bilotti et al. [20] studied TPU/MWCNTs nanocomposites and demonstrated that the simultaneous use of a secondary nanofiller, not only changes the shape and electrical properties of the CNT in a polymeric matrix but also has a significant positive impact on its dynamic percolation. Zhang et al. [21] also showed that a nanoclay coaddition accompanied by a coupling agent could enhance the storage modulus and electrical conductivity of PVDF/MWCNT nanocomposites.

Rheological properties of nanofiller filled polymer nanocomposites are significantly dependent upon their microstructure, in specific, nanofillers dispersion state in the polymer matrix. Therefore, the rheology is known as a useful tool to investigate the polymer nanocomposites microstructure. In addition, rheological evaluations revealed the required information with respect to the optimized condition of melt processing to acquire the highest performance of the polymer nanocomposites [22, 23].

According to the aforementioned explanations, to provide a deep view on the fundamental changes in the structure of modified PMMA/MWCNTs nanocomposites caused by C30B addition, we studied the main nanocomposite characteristics including rheological, structural, electrical, and thermal properties. In other words, the study aimed to find out whether the simultaneous addition of these nanofillers could result in the desired properties.

2. Experimental

2.1. Materials and Sample Preparation

Poly (methyl methacrylate) (PMMA) with a melt flow rate of 2.5 g/10 min (230°C, 3.8 kg) from LG chemical Co., (Korea) was used as the matrix. The applied multiwall carbon nanotubes (MWCNTs), Nanocyl 7000, with average diameter of 9.5 nm and average length of 1.5 μm were purchased from Nanocyl Inc. (Belgium). Cloisite 30B organoclay (C30B) modified by 90 meq/100g of bis-(2-hydroxyethyl) methyl tallow alkyl ammonium cations, supplied by Southern Clay Products (USA) was utilized as the secondary nanofiller.

PMMA, C30B and MWCNTs were dried at 80 °C for 12 h prior to melt mixing. PMMA with different concentrations of MWCNTs (0, 0.25, 0.5 and 0.75 wt.%) and C30B (0, 1 and 3 wt.%) were melt mixed using simultaneous feeding in a laboratory Internal Mixer (Brabender, Germany) at 230°C for 15 minutes. Afterward, by using a Ceast compression molding machine (Italy), all these processed materials compression were molded into sheet form at a pressure of 35MPa at 230°C for 8 minutes. The stepwise process of sample preparation is schematically illustrated in Figure 1.
2.2. Characterization Methods

In order to evaluate the dispersion of the C30B nanofillers in the samples, X-ray diffraction (XRD, Philips model X’Pert, Netherlands) was performed at room temperature using Cu Kα radiation (λ=1.78897 Å) over an angular range (2θ) of 2 to 10°.

Viscoelastic behavior of the samples was studied using a stress-controlled rheometer (MCR301, PaarPhysica, Austria) with a parallel-plate (25 mm diameter, 1 mm gap) system. Different rheological experiments were carried out to determine the rheological properties of the samples. These included (1) dynamic strain sweep experiment from 0.05 to 1000% at constant angular frequency (1 rad/s) and temperature (230 °C), and (2) frequency sweep experiment in a range of angular frequency (0.05 - 628 rad/s) and at constant values of strain amplitude (1 %) and temperature (230 °C).

The samples morphology and nanofillers dispersion/distribution were studied by the field emission scanning electron microscopy (FE-SEM, S-4160, Japan) and transmission electron microscopy (TEM, Philips EM 208S, Netherlands) at 15 and 120 kV, respectively.

The volume resistivity of the samples was measured using a Ceast Teraohm meter (Italy). The samples for the analysis were cut into the rectangular shapes of 10×10 cm² in area and 2 mm in thickness.

Dynamic viscoelastic measurements were performed by a dynamic mechanical analysis (DMA, Perkin-Elmer, USA) instrument. The temperature range and frequency were set to 40 to 150 °C and 1 Hz, respectively. Thermal degradation properties of the samples were studied by Thermogravimetry Analyzer (TGA, Perkin-Elmer, USA) under an atmosphere of nitrogen at a heating rate of 10 °C/min over a temperature range of 50 to 500 °C.

3. Results and Discussion

3.1. XRD Results

Figure 2 shows the X-ray diffraction patterns of neat C30B and the corresponding nanocomposite samples.
The XRD pattern of C30B demonstrates a broad single peak at around 2θ=4.7° which can be attributed to d-spacing of 1.86 nm [24]. The strong diffraction peak is absent in the single filler and hybrid nanocomposites, indicating that the C30B platelets were exfoliated in the PMMA matrix even in the presence of MWCNTs [25]. The appropriate processing capability of the mixer and the polar nature of PMMA are responsible for the exfoliated structure of the nanocomposite samples.

3.2. Linear Viscoelastic Rheological Experiments

Strain amplitude sweep experiments were carried out to distinguish the extent of strain below which the viscoelastic behavior is in the linear regime. Therefore, the plot of normalized storage modulus was depicted as a function of strain for PMMA matrix and its single nanofiller and hybrid nanocomposites (Figure 3).

As can be seen, the critical value of strain indicating the alteration of viscoelastic behavior was shifted to the lower values. However, the mentioned change for the single and hybrid nanocomposite samples were more considerable compared with the neat samples. This observation can be related to the changes in microstructure induced by the nanofillers and the breakup of some of the crucial elastic links in the nanofillers 3D networks, whose existence is more predominant in the case of hybrid nanofillers [26]. To assure being in the linear region, further rheological experiments were conducted in the strain lower than 1%.

The microstructural changes of C30B and MWCNTs filled PMMA are demonstrated in Figures 4a to d. A typical terminal behavior following the Rouse-Zimm theory, i.e. $G' \sim \omega^{-2}$, was observed for neat PMMA. In comparison, single-filler filled PMMA nanocomposites feature a solid-like behavior and a viscosity upturn, induced by the 3D network formation [27]. It is noteworthy to mention that the networks formation is implied as an appropriate dispersion of nanofillers in the polymer matrix.

The results dealing with PMMA and its hybrid filler nanocomposites are illustrated in Figures 4e and f. It shows that the simultaneous application of C30B and MWCNTs enhances the elasticity and viscosity properties of the samples, indicating good dispersion of the applied nanofillers. However, the increment of the used C30B content intensified the viscosity upturn and solid-like behavior in the frequency sweep test. Similar findings were reported by Rostami et al. for the functionalized graphene/MWCNTs filled poly(lactic acid) [28].
Figure 4. Storage modulus and complex viscosity of PMMA/C30B (a, b), PMMA/MWCNTs (c, d), and hybrid nanocomposite systems (e, f)
3.3. Morphology Characterizations

3.3.1. FE-SEM Results

Figure 5 shows FE-SEM micrographs of the cryofractured surface of PMMA, single filler filled PMMA including 0.75 wt.% of MWCNTs and the hybrid system including 0.75 wt.% of MWCNTs and 3 wt.% of C30B, in which the MWCNTs appeared as the white spots. The cracks observed are due to the FE-SEM electron beams. As can be seen from Figure 5b, the single filler nanocomposite shows a suitable distribution of MWCNTs; however rich MWCNTs domains or aggregated morphology can be observed. Figure 5c shows that the hybrid system displays an appropriate dispersion/distribution of MWCNTs with no rich nanofiller regions and fine aggregates, which demonstrate that the mixing process was adequate. This suggests that exfoliated C30B prevent MWCNTs from the reaggregation, in favor of their dispersion. In other words, the PMMA has a better dispersing potential when both nanofillers are present simultaneously and therefore, hybrid filler systems conceive stronger three-dimensional networks. They are thus expected to have enhanced electrical and thermal properties. These results are in close agreement with those reported by Bilotti et al. [20].

3.3.2. TEM Results

To further investigate the nanofiller dispersion in the PMMA matrix, TEM micrographs for single-filler filled (0.75 wt.% of MWCNTs) and hybrid system (0.75 wt.% of MWCNTs and 3 wt.% of C30B) are shown in Figure 6. With no use of C30B, MWCNTs show an aggregated morphology and weak dispersion (Figure 6b). Moreover, by the application of C30B the dispersion of MWCNTs significantly improved as demonstrated in Figure 6c because of the geometrical characteristics of the exfoliated C30B. The same findings are addressed by Lee et al. [19]. According to the microscopy results, it can be proposed that the exfoliated C30B nanoplatelets are located between the MWCNTs and the aggregated structure of MWCNTs was considerably altered which can lead to the creation of well-organized 3D networks. The above results are in close agreement with the rheological and XRD results.
3.4. Electrical Properties

Electrical Properties test were conducted to figure out the effect of C30B addition on the electrical conductivity of the hybrid system (Figure 7). It is interesting to say that both nanofillers possess enough potential for the dispersion/distribution in the PMMA matrix.

A very keen decrease in the electrical resistivity of the nanocomposite samples was obvious at lower loading levels. For example, volume resistivity of the neat PMMA (1.4×10^{13} \text{ Ohm.cm}) reduced to 1.34×10^{6} \text{ Ohm.cm} when the conductive MWCNTs weight percentage was augmented to 0.25 wt.%.

At a loading level of 0.25 wt.% for MWCNTs, a nanofiller interconnected structure was formed and the aforesaid decrease (~10^7 orders of magnitude) was observed, demonstrating the electrical percolation phenomenon. However, at higher mentioned loading level, the electrical resistivity decreased more gradually. In the other words, in 0.25 wt.% of MWCNTs, the interconnecting conductive pathway was formed and allowed the continuous electron transmissions [29]. It is clearly visible that the addition of C30B does not change the percolation threshold strongly, but reduces the electrical resistivity, which is more apparent at higher MWCNTs contents. This increase may be potentially associated with the C30B assisted dispersion of MWCNTs and the reformation of an efficient conductive network. Similar results were reported by Lee et al. and Zhang et al. [19, 21].

To assess the electrical percolation threshold, a percolation model [26] can be expressed as Equation 1:

\[ \sigma = \sigma_0 (\phi - \phi_c)^t \]  

(1)
where $\sigma$ represents volume resistivity, $\phi$ is the MWCNTs weight percentage, $\phi_c$ is the percolation threshold fraction, and $t$ stands for a critical exponent. Regarding the above model, the value of $\phi_c$ and $t$ for the single and hybrid filled PMMA were predicted from the best linear fit of the log-log plot of $\sigma$ versus $\phi - \phi_c$, as depicted within Figure 7. With respect to the presented model, the value of $\phi_c$ and $t$ equal 0.17 wt % and -3.42) for MWCNTs filled PMMA, while the addition of 1 and 3 wt.% of C30B changed these values to (0.18%, -3.45) and (0.185, -3.84), respectively.

3.5. Thermal Analyses

3.5.1. Dynamic Mechanical Behavior of samples

The results of dynamic mechanical experiment are illustrated in Figure 8 for the neat PMMA and its nanocomposites. As shown in Figure 8a, the restricted movements of the polymer chains induced by the nanofillers originated from the additional cross-linking physical bonds and led to the increase of storage modulus. This increase is more pronounced for hybrid filler system due to the improved dispersion of MWCNTs by the addition of C30B [30]. As seen from Figure 8b, PMMA displays a single peak corresponding to its Tg at 124 °C. The incorporation of nanofillers into the PMMA matrix, especially for the hybrid system, has a strong influence on reducing the chains mobility and dissipating additional energy and consequently, a decrease in tanδ peak height and a small increase in Tg were observed [31]. These results validated that the MWCNTs dispersion enhanced by the coaddition of C30Bs, confirmed the results obtained from the rheology and microscopy experiments.

3.5.2. Thermal Decomposition Study

Thermal decomposition behavior of the nanocomposite samples was studied by TGA as shown in Figure 9. The temperature of 5%, 70%, and maximum rate of the samples’ weight loss (Td,5%, Td,70%, and Tmax), and the char yields at 500°C were utilized to compare the thermal decomposition of the samples. Table 1 exhibits TGA data with respect to the prepared samples. One-pot decomposition of PMMA matrix was observed for all the prepared samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Td,5% (°C)</th>
<th>Td,70% (°C)</th>
<th>Tmax (°C)</th>
<th>Char residue (%) at 500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>308</td>
<td>342.9</td>
<td>335.2</td>
<td>0.76</td>
</tr>
<tr>
<td>PMMA-0.5%MWCNTs</td>
<td>313.8</td>
<td>352.5</td>
<td>343.9</td>
<td>1.87</td>
</tr>
<tr>
<td>PMMA-3%C30B</td>
<td>308.1</td>
<td>370.6</td>
<td>361.5</td>
<td>4.21</td>
</tr>
<tr>
<td>PMMA-0.5%MWCNTs-3%C30B</td>
<td>314.7</td>
<td>380.3</td>
<td>369.2</td>
<td>5.17</td>
</tr>
</tbody>
</table>

Figure 8. DMA plots of (a) storage modulus and (b) damping factor of neat and modified PMMA
The Td,5% and Td,70% were shifted to higher temperatures by the addition of nanofillers, especially for the hybrid sample. Furthermore, Tmax is higher in case of the nanocomposites compared to that of neat PMMA, demonstrating that the incorporation of nanofillers has drastically enhanced the thermal stability of the samples. This indicates the positive effect of MWCNTs on the thermal stability of the hybrid nanocomposite.

The enhancement in the thermal stability of hybrid nanofiller filled PMMA is because of C30B assisted dispersion of MWCNTs and appropriate mass and heat barrier effect of the nanofillers against the decomposition process [32]. However, regarding the obtained results, for the nanocomposites a higher content of residual chars was accessed in comparison with the neat PMMA.

4. Conclusions

The single and hybrid nanofiller filled PMMA prepared by the simultaneous melt mixing showed differences in the rheological, structural, electrical and thermal properties. Concerning the samples, an appropriate nanofiller’s dispersion/distribution was observed with XRD, rheology, and electron microscopy methods. The strong interfacial adhesion between the C30B nanofiller and the PMMA matrix accompanied by a good degree of dispersion created strong hybrid 3D networks. It was concluded that C30B plays an essential role in determining the state of dispersion and the aggregation of MWCNTs. The electrical properties of the hybrid samples were enhanced by the incorporation of MWCNTs. The electrical percolation threshold almost remained intact with the addition of C30B, but the formation of conductive pathways was more efficient at high MWCNTs content, which resulted in a strong decrease in the volume resistivity. Moreover, it was found that the hybrid filler nanocomposites containing C30B did not show pronounced synergism effect compared to the hybrid systems previously reported in the literature containing a mixture of the carbon fillers. Regarding the DMA results, a remarkable reduce in the damping of PMMA constituent for the hybrid system was observed proposing the more restriction of the chain movement due to the well-dispersed nanofillers. In addition, the thermal stability, as well as char content of the single and hybrid nanocomposites were significantly improved by the application of the nanofillers as compared to the neat TPU matrix.

References


مقاله تحقیقاتی

تکامل ریزساختار و خواص فیزیکی نانوکامپوزیت‌های پلیمتیل متاکریلات/نانولوله‌های کربنی با افزایش نانورس آلی

امیر رستمی ۱، محسن مصوومی ۲، فر uomini اسکندری ۲، محسن معصومی ۱، امیر رستمی ۳

دانشکده مهندسی شیمی، هیئت علمی مهندسی نفت، گاز و پتروشیمی، دانشگاه خلیج فارس، بوشهر، ایران.

چکیده

تحقیق حاضر با هدف ارزیابی کاربرد نانورس آلی کلوزیت (C30B) بر میکروکامپوزیت‌های پلی متیل متاکریلات (PMMA/MWCNTs) با افزایش نانورس آلی بررسی شد. تغییرات ریزساختار و حالت پراکنش نانولوله‌ها با استفاده از آزمایشات ویسکوالاستیک خطی مذاب، پراش اشعه ایکس (XRD) و میکروسکوپ الکترونی در زمینه تحقیقات آینده استفاده شد. نتایج بدست آمده نشان داد که با افزایش نانورس آلی، مشخصات رئولوژیکی، الکتریکی و حرارتی نانوکامپوزیت‌ها تغییر کرد. مطالعه خواص الکتریکی نانوکامپوزیت‌ها نشان داد که تغییرات در حالت پراکنش نانولوله‌ها با افزایش نانورس آلی کلوزیت بهبود یافت. افزایش نانوزرات باعث افزایش درجه حرارتی و کاهش درجه حرارتی و کاهش درجه حرارتی و کاهش درجه حرارتی و کاهش درجه حرارتی و کاهش درجه حرارتی می‌شود.

کلمات کلیدی:
اصلاح پلیمرها، نانوکامپوزیت‌ها، سیستم هیبریدی، ریزساختار، رئولوژی، خواص حرارتی

 مشخصات مقاله

تاریخچه مقاله:
دریافت ۱۳۹۸ خرداد
دریافت پس از اصلاح ۱۳۹۸ تیر
پذیرش نهایی ۱۳۹۸ مرداد

کلمات کلیدی:
اصلاح پلیمرها، نانوکامپوزیت‌ها، سیستم هیبریدی، ریزساختار، رئولوژی، خواص حرارتی

نحوه استناد به این مقاله:


This work is licensed under the Creative Commons Attribution 4.0 International License.
To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.