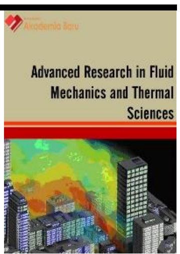
Penerbit Akademia Baru

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



Mechanical and Thermal Properties of Nylon-6/LNR/MMT Nanocomposites Prepared Through Emulsion Dispersion Technique

Ahmad Adlie Shamsuri[1,*], Rusli Daik[2]

[1] Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[2] School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

ARTICLE INFO

Article history:
Received 8 April 2020
Received in revised form 30 April 2020
Accepted 1 May 2020
Available online 4 July 2020

Keywords:
Nanocomposite; emulsion dispersion; nylon-6; montmorillonite; liquid natural rubber

ABSTRACT

In this research, nylon-6/liquid natural rubber/montmorillonite (nylon-6/LNR/MMT) nanocomposites were prepared through emulsion dispersion technique with contents of MMT from 2 to 10 wt.%. The mechanical, crystallographical, morphological, and thermal properties of the prepared nanocomposites were then characterised by using mechanical testers, XRD, TEM, DSC, and TGA. The mechanical test results showed that the tensile stress, tensile modulus, and impact strength of the nanocomposites improved with the incorporation of MMT. The XRD results displayed that there are no isotropic peaks were observed in the nanocomposites with 2, 4, and 6 wt.% of MMT. The TEM micrographs exhibited that the exfoliated state was achieved in the nanocomposites with less than 8 wt.% of MMT. The DSC and TGA results also indicated that the incorporation of MMT had increased the glass transition temperatures and degradation temperatures of the nanocomposites. In conclusion, the emulsion dispersion technique could prepare the nylon-6/LNR/MMT nanocomposites with improved mechanical and thermal properties.

1. Introduction

Polymer nanocomposite, a type of composite material with the dimension of the reinforcing filler is in nanometre. The use of polymer nanocomposites has received significant interest in recent years from industries and academics in order to overcome the disadvantages of polymer microcomposites. On the other hand, polymer/nanoclay silicate layers nanocomposites could be acquired via the dispersion of very high aspect ratio clay-type particles in a polymeric matrix [1]. Previous study has

---

[*] *Corresponding author.*
E-mail address: adlie@upm.edu.my

https://doi.org/10.37934/arfmts.73.1.112

exhibited that the dispersion of high aspect ratio nanoclay silicate layers caused the improvement of mechanical properties such as tensile and flexural strengths [2]. The gas permeability barrier, thermal properties, dimensional stability, and surface appearance also improved with the incorporation of the nanoclay silicate layers at very low content (between 2 and 5 wt.%) [3]. This is much better than conventional fillers, for instance, talc, glass fiber and carbon particles [4]. Moreover, incorporation of the nanoclay silicate layers into a transparent polymer matrix has slightly decreased the light transmittance, which allows the production of transparent nanocomposite materials [5]. Besides, nanoclay silicate layers are naturally abundant, inexpensive, and most importantly, it is an environmentally friendly material [6].

Nanoclay silicate layers, for example, montmorillonite (MMT), is an inorganic material that commonly disperses poorly in organic matrices [7]; this is because of strong electrostatic forces between the layers. Furthermore, the hydrophilic nature of MMT does not provide good dispersion in the hydrophobic polymer phase as well [8]. Thus, one of the ways to overcome this problem is by modifying the MMT through ion exchange reaction [9]. The reaction occurs when the interlayer sodium ions between silicate layers are replaced with organic cations, which could change the hydrophilic silicate surface to organophilic, which known as organosilicates. They are much more compatible with the hydrophobic polymer matrix as compared to the previous ones [10,11]. Typical organic cations selected are alkylammonium cations with one or more aliphatic chains of 12 or more carbon atoms as surfactants. However, organic modification has its disadvantages, whereby it requires an extra step in the production of polymer/clay nanocomposites. Moreover, the organic modifiers that are commonly used could degrade at a high temperature, which needed for the processing of nanocomposites; this causes the silicate layers to recover their hydrophilicity [12].

The nanocomposite researchers have prepared the polymer/clay nanocomposites with different techniques such as modification of MMT with long alkyl tail surfactants [13,14] as well as the addition of MMT slurry into the extruder machine during the processing of nanocomposites [15]. Therefore, in this research, the emulsion dispersion technique was applied to prepare the nanocomposites without an additional step and not consumed a lot of energy to process. The emulsion dispersion technique contains an organic solution of polymer, surfactant, and water. The technique was first introduced for the preparation of homogeneous blends [16,17]. The molecules of surfactant have polar and non-polar parts, which could act as an intermediary for providing intermolecular interactions between polymer matrix and filler [18]. By using the emulsion dispersion technique, MMT can be modified through ion exchange reaction by a surfactant to become organophilic; this could increase the interlayer or basal spacing of MMT. Additionally, the presence of water could exfoliate MMT [19] and increase the diffusion of individual silicate layers in the polymer matrix.

The purpose of this research is to demonstrate that the emulsion dispersion technique could prepare polymer/clay nanocomposites. As far as we are concerned, there are little published articles pertaining to the application of the emulsion system as a technique for preparation of the nanocomposites. Thus, in this research, the preparation of nylon-6/LNR/MMT nanocomposites through emulsion dispersion technique was described, and the mechanical, crystallographical, morphological, and thermal properties of the prepared nanocomposites were studied.

2. Methodology

2.1 Materials

Nylon-6 was supplied by Ube Nylon in granules form [20]. 2,2,2-trifluoroethanol was purchased from Fluka (density 1.38 g/cm^3) and chloroform (density 1.48 g/cm^3) was supplied by Sigma Aldrich. The surfactant used was hexadecyltrimethylammonium bromide (purity >99%), abbreviated as HTAB, it was purchased from Sigma Aldrich as well. Pristine sodium montmorillonite (Na-MMT) with a cation exchange capacity of 100 mequiv/100 g was supplied by Fluka. All chemicals were used as received without any modifications.

2.2 Preparation of Nylon-6/LNR/MMT Nanocomposites

The preparation of LNR has been described elsewhere [21]. The Na-MMT clay was dispersed and stirred in 90 wt.% organic solution (2,2,2-trifluoroethanol + chloroform) of nylon-6 for 1 hour at ambient temperature. The contents of Na-MMT were varied from 2 to 10 wt.%. Then 2 wt.% of HTAB was added slowly into the mixture, and 8 wt.% of deionized water was poured. They are kept stirred for another 1 hour to obtain emulsion [17]. After that, the LNR was added drop wise into the emulsion with stirring at ambient temperature. The composition of the nylon-6/LNR matrix was fixed to 85:15 (wt./wt.). The mixture was then kept under the stirring condition for 3 hours. After dispersion, the emulsion of nylon-6/LNR/MMT was precipitated by pouring into methanol. The white sediment was also filtered and washed with methanol. The nanocomposites were dried in a vacuum oven at elevated temperatures (50°C) for 12 hours. The dried nanocomposites were then pressed between plates by using a hot press machine [22] with 1- and 3-mm moulds under pressure of 30 kgf/cm^2 at 200°C for 10 minutes.

2.3 Characterisation

The samples of 1 mm thickness were cut into dumbbell shape following ASTM D638-10 (Type V). The tensile tests were conducted at room temperature by using a universal testing machine, Instron (model 5575), with standard test method ASTM D638-10. The loadcell and crosshead speed were 1 kN and 50 mm/min, respectively. The results of tensile stress, tensile modulus, and tensile strain were recorded. The readings were taken from an average of five samples [23].

The samples of 3 mm thickness were cut into a rectangular shape with a dimension of 13 x 3 x 63 mm. The impact test was carried out by using a universal digital pendulum fractoscope, Ceast (model 6546/100), according to ASTM D256-88. The tests were conducted at room temperature. Five samples were taken for the readings.

The crystallographic character specifically interlayer or basal spacing [24,25] of the pristine Na-MMT powder and the nanocomposite samples, was determined by using an X-ray diffractometer (XRD), Bruker (model D8 Advance) with monochromatized CuKα radiation (λ=0.154 nm). The samples were then scanned at a rate of 1°/min, and the range of 2θ was from 2° to 12° in 0.02° steps at room temperature. All samples were dried in a vacuum oven for at least 24 hours [26].

The morphology of the samples was observed by using a transmission electron microscope (TEM), Philips (model HMG 400) operated at an accelerating voltage of 100 kV. The ultra-thin sections of the nanocomposite samples were obtained by using a cryo ultramicrotome equipped with a diamond knife and sliced at -80°C. The samples with a thickness of around 100 nm were viewed on a 300-mesh copper grid [27]. The TEM micrographs of the samples were taken at room temperature at a magnification of 125000 X.

The thermal analysis was conducted by using a differential scanning calorimeter (DSC), Mettler Toledo (model DSC 823^e) under nitrogen flow. All samples were subjected to the following procedures: the samples were first heated to 200°C to eliminate the thermal history. The analysis was carried out in a temperature range from -60 to 200°C at a heating rate of 10°C/min to obtain the glass transition temperature, T_g (midpoint value) of the nanocomposites.

The thermal stability was studied by using a thermogravimetric analyser (TGA), Mettler Toledo (model TGA 851^e) under the air atmosphere at a scan rate of 10°C/min, and the temperature range was from room temperature to 700°C. The ASTM D3850 was applied as a standard to determine the initial degradation temperature of the nanocomposites (10% of weight loss).

3. Results

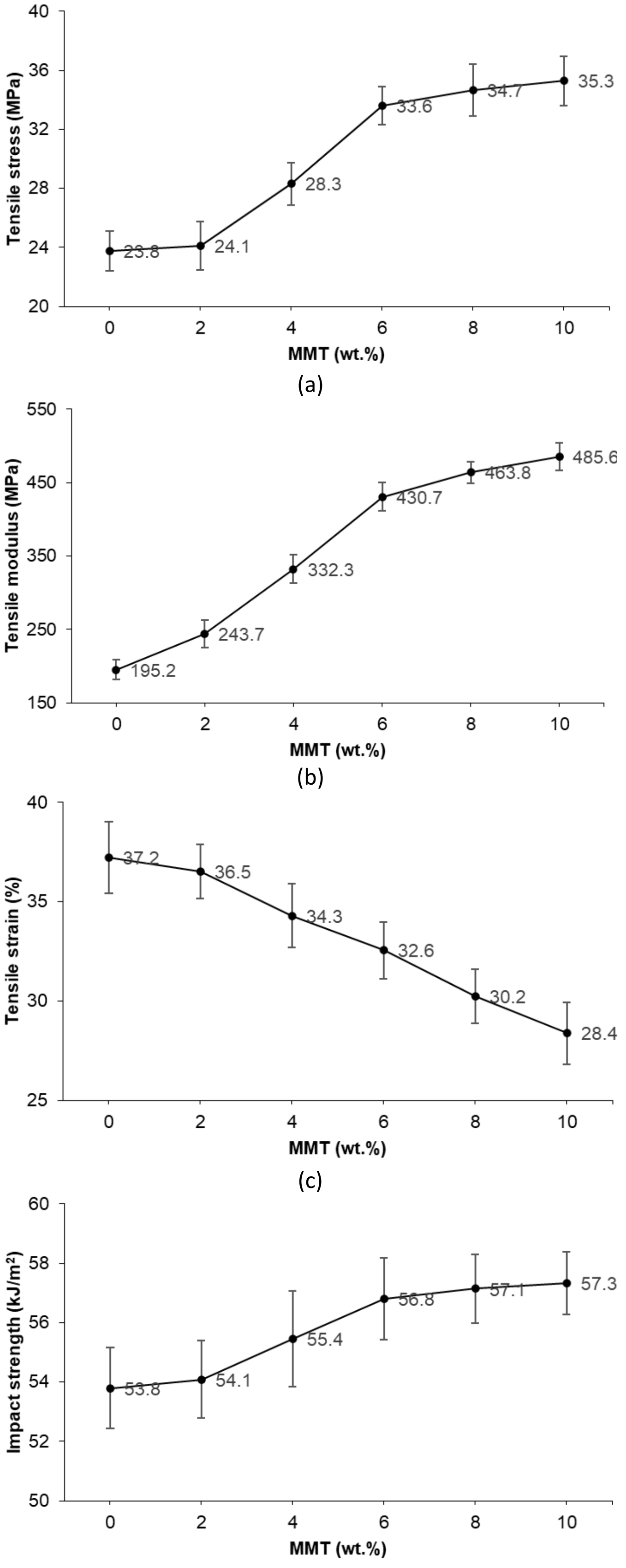
3.1 Mechanical Properties

Figure 1 shows the tensile stress, tensile modulus, tensile strain, and impact strength of the nylon-6/LNR/MMT nanocomposites with different contents of MMT. It is observed that the tensile stress, tensile modulus, and impact strength properties of the nylon-6/LNR/MMT nanocomposites are higher than nylon-6/LNR without incorporating MMT. Hence, the incorporation of MMT provided a reinforcing effect on the nanocomposites since the tensile stress and tensile modulus increased simultaneously. Conversely, the incorporation of MMT into the nylon-6/LNR decreased the tensile strain of the nanocomposites, as shown in Figure 1(c), this is as expected. However, the impact strength of the nanocomposites unexpectedly increased as seen in Figure 1(d), the strain-related properties, especially impact strength, relatively decreased at high content of MMT [28]. On the other hand, the tensile stress, tensile modulus, and impact strength properties also increased as the contents of MMT increase from 2 to 10 wt.%. Therefore, the incorporation of MMT has improved the mechanical properties of the nanocomposites.

Nevertheless, after incorporation of 6 wt.% of MMT, there is no significant improvement of the tensile stress, tensile modulus, and impact strength properties of the nanocomposites. The percentage of water used for exfoliating the modified MMT was fixed to 8 wt.% of the overall nylon-6 emulsion because it was the optimum percentage [17]. Any changes in the percentage of water could certainly modify the emulsion system. If the percentage of water more than 8 wt.%, it would interrupt the compatibility between nylon-6 and LNR due to the excess of water, which could decrease the interfacial area and increase the interfacial tension between them. On the contrary, if the percentage of water less than 8 wt.%, it would impede the exfoliation of the modified MMT because of the negative charge of silicate layers could electrostatically attract with counterions in the gallery of MMT. Consequently, the nanocomposites with less than 8 wt.% of MMT have a more significant improvement in mechanical properties compared to the others.

3.2 Crystallographical Properties

Figure 2 displays the XRD patterns of pristine Na-MMT and nylon-6/LNR/MMT nanocomposites with different contents of MMT. The XRD pattern of the pristine Na-MMT in Figure 2(a) with characteristic diffraction peak (001) around 8.9° of 2θ attributed to 1.00 nm of basal spacing. The XRD patterns of the nanocomposites in Figure 2(b) to (f) with characteristic diffraction peak (001) around 8.9° of 2θ, which belonged to pristine Na-MMT has completely disappeared, this is due to the absence of pristine Na-MMT in the nanocomposites. On the other hand, the XRD patterns in Figure 2(b), (c), and (d) demonstrate there are no isotropic peaks in the range from 2° to 12° of 2θ were observed in the nanocomposites prepared through emulsion dispersion technique. The absence of isotropic peaks is due to the silicate layers of MMT have lost their structural gallery. Moreover, the absence of Bragg diffraction peaks in the nanocomposites revealed that the MMT had been completely exfoliated.



(a)

(b)

(c)

(d)

Fig. 1. (a) Tensile stress, (b) tensile modulus, (c) tensile strain, and (d) impact strength of the nylon-6/LNR/MMT nanocomposites

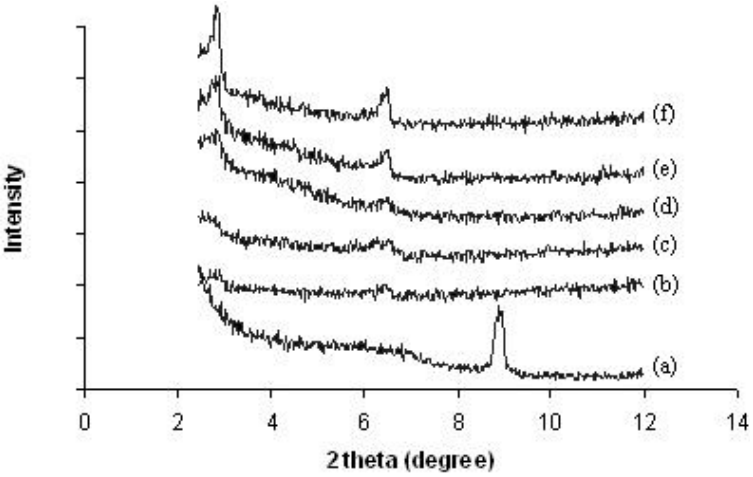


Fig. 2. XRD patterns of (a) pristine Na-MMT, nylon-6/LNR/MMT nanocomposites (b) 2 wt.% of MMT, (c) 4 wt.% of MMT, (d) 6 wt.% of MMT, (e) 8 wt.% of MMT, and (f) 10 wt.% of MMT

The XRD patterns of the nanocomposites in Figure 2(e) and (f) present the existence of the new characteristic diffraction peaks around 7.4° and 2.8° of 2θ that corresponded to 1.20 and 3.16 nm of basal spacing, respectively; this is due to the expansion of the basal spacing of MMT silicate layers since ion exchange reaction [29] occurred between Na-MMT and HTAB surfactant which has long alkyl chain (16 carbon atoms). Two sizes of basal spacing indicated that there are two phases in the nanocomposites, namely HTA-MMT and nylon/LNR phases. The hydrophobic interaction between long alkyl chains of HTA-MMT increased the expansion of the basal spacing, and the presence of nylon/LNR has formed the intercalated structure. Although the basal spacing increased, the high content of MMT hindered the silicate layers to exfoliate entirely. Therefore, there is limitation in term of MMT content for emulsion dispersion technique on diffusion of silicate layers in the polymer matrix. Nevertheless, the diffusion of silicate layers in the nylon-6/LNR/MMT nanocomposites was further observed by using a TEM.

3.3 Morphological Properties

Figure 3 indicates the TEM micrographs of the ultra-thin sections of the nylon-6/LNR/MMT nanocomposites with different contents of MMT. It is visible in Figure 3(a), (b), and (c) the individual silicate layers were dispersed randomly in the nylon-6/LNR matrix; this exposed that the MMT was exfoliated thoroughly in the matrix which was a similar trend with the XRD pattern results. If the silicate layers of MMT in the nanocomposites are not exfoliated, the obvious peaks could be perceived in XRD patterns [30]. On the other hand, a few pieces of MMT silicate layers in the matrix are owing to the microtoming direction, which is not rightly vertical to the surface of the silicate layers. Additionally, the silicate layers are flexible, and, hence they appeared with some curvatures. The TEM micrograph in Figure 3(d) revealed that the less exfoliated and more intercalated silicate layers exist in the nanocomposite with 8 wt.% of MMT. The intercalated state caused by the polymer matrix inserted within the interlayer of silicates. The TEM micrograph in Figure 3(e) showed that the wholly intercalated silicate layers were obtained in the nanocomposite with 10 wt.% of MMT compared to 8 wt.% of MMT. These observations are consistent with the XRD pattern results shown in Figure 2. Therefore, it also proved that the 8 wt.% of water could exfoliate 2 to 6 wt.% of the modified MMT. If the MMT content is greater than 6 wt.% in the emulsion dispersion system, the efficiency of water to exfoliate is unsatisfactory. Thus, the exfoliated and intercalated states of the nylon-6/LNR/MMT nanocomposites were confirmed by the XRD and TEM results. In addition, the TEM results also demonstrated that the nanocomposites with exfoliated state could be prepared through emulsion dispersion technique. The results are in line with the mechanical test results as well, whereby the exfoliated state nanocomposites have significant improvement in the tensile stress, tensile modulus, and impact strength properties as compared to the nanocomposites with intercalated state.

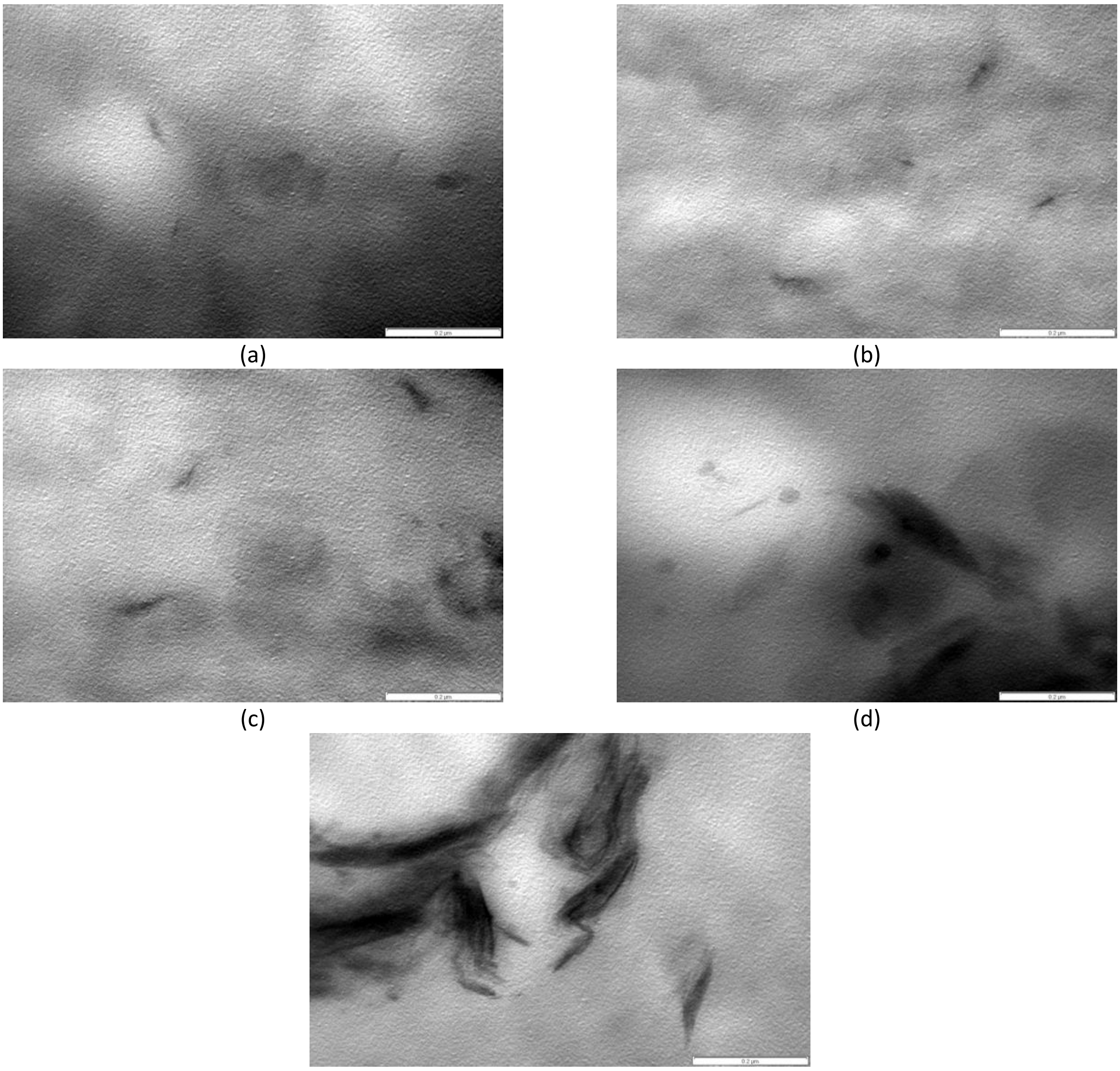

(a) (b) (c) (d) (e)

Fig. 3. TEM micrographs of ultra-thin sections of the nylon-6/LNR/MMT nanocomposites (a) 2 wt.% of MMT, (b) 4 wt.% of MMT, (c) 6 wt.% of MMT, (d) 8 wt.% of MMT, and (e) 10 wt.% of MMT

3.4 Thermal Properties

Figure 4 demonstrates the DSC thermograms of the nylon-6/LNR/MMT nanocomposites with different contents of MMT. The glass transition temperatures, T_gs (midpoint value) of the nanocomposites are showed in Table 1. It can be observed that the T_gs of the nanocomposites are higher than T_g of the nylon-6/LNR without incorporating MMT. The results displayed that the incorporation of MMT silicate layers has increased the restriction of the polymer matrix chain movement. Moreover, the T_gs of the nanocomposites drastically increased as the contents of MMT increase from 2 to 10 wt.%. Nonetheless, the effect of the nanocomposites structure on T_g is very significant, especially for the exfoliated state, which varies from an intercalated state. The increment of the T_g for the exfoliated state (4 and 6 wt.% of MMT) is considerably large compared with the increment of the T_g for the intercalated state (8 and 10 wt.% of MMT). However, the nanocomposites containing more MMT have slightly higher T_g than the lesser ones, thus the MMT content has also influenced the thermal properties of the nanocomposites. The DSC results of the nylon-6/LNR/MMT nanocomposites are consistent with the mechanical, crystallographical, and morphological results. Furthermore, the interaction inside the nanocomposites is probably exist between polymer matrix and MMT due to the presence of nylon-6 [31].

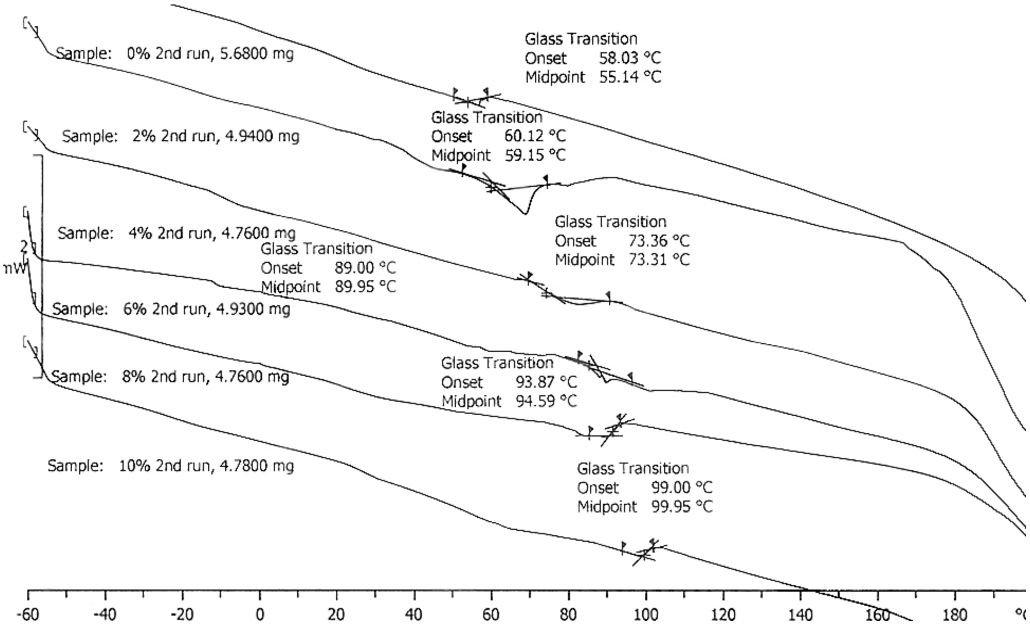


Fig. 4. DSC thermograms of the nylon-6/LNR/MMT nanocomposites

Table 1
Glass transition temperatures of nylon-6/LNR/MMT nanocomposites obtained from DSC thermograms

MMT (wt.%)	Glass transition temperature (°C)
0	55.1
2	59.2
4	73.3
6	90.0
8	94.6
10	100.0

Figure 5 exhibits the TGA thermograms of the nylon-6/LNR/MMT nanocomposites with different contents of MMT. The initial degradation temperatures at 10% of weight loss of the nanocomposites are presented in Table 2; it exhibited that the nanocomposites have higher thermal stability than nylon-6/LNR without incorporating MMT; this is because silicate layers could avert vaporisation of the volatile decomposition products. Additionally, the enhancement of the thermal stability of the nanocomposites is also related to the uniform diffusion of silicate layers in the polymer matrix [32]. It can be seen that the nanocomposites with the exfoliated state (2, 4, and 6 wt.% of MMT) have more raise of thermal degradation; this is due to their barrier effect [33]. On the contrary, the nanocomposites with the intercalated state (8 and 10 wt.% of MMT) have less raise of thermal degradation. However, they still have high thermal stability due to their high content of MMT. It is clear that the MMT content as well as interaction between polymer matrix and MMT have also increased the thermal stability of the nanocomposites. The TGA results are in good agreement with the results obtained from mechanical tests, XRD patterns, TEM micrographs, and DSC thermograms. The nylon-6/LNR/MMT nanocomposites that have excellent mechanical and thermal properties could potentially be applied in production of automotive interior parts [34].

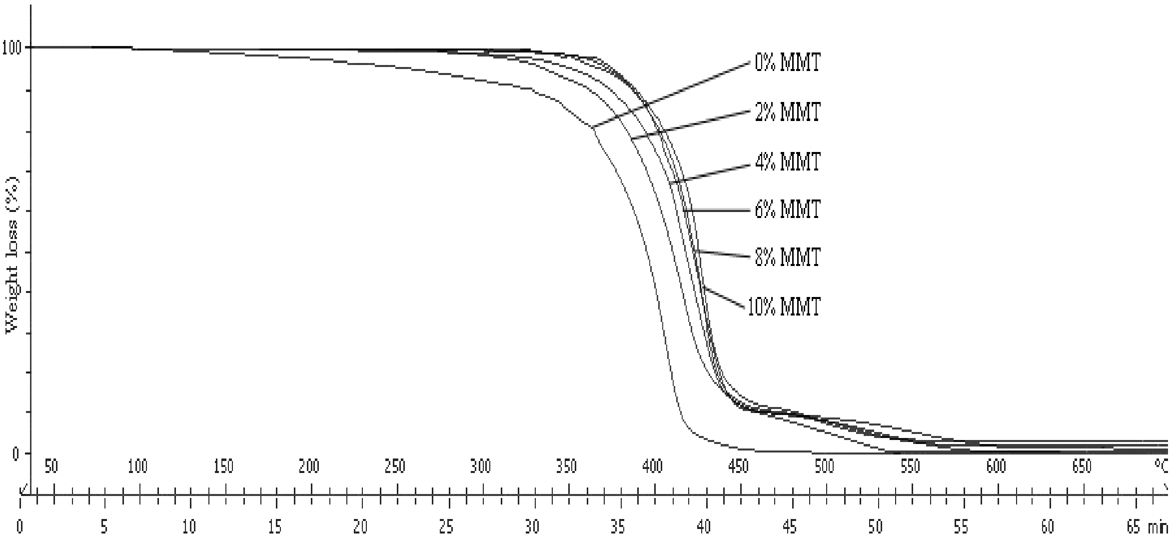


Fig. 5. TGA thermograms of the nylon-6/LNR/MMT nanocomposites

Table 2
The initial degradation temperatures of nylon-6/LNR/MMT nanocomposites obtained from TGA thermograms

MMT (wt.%)	Initial degradation temperature (°C)
0	328.1
2	363.3
4	376.2
6	386.5
8	387.7
10	390.3

4. Conclusions

From the obtained results, the incorporation of MMT has improved the tensile stress, tensile modulus, and impact strength of the nanocomposites. There are no isotropic peaks observed in the nanocomposites with 2, 4, and 6 wt.% of MMT based on the XRD results. The exfoliated state was achieved in the nanocomposites with less than 8 wt.% of MMT as perceived in the TEM micrographs. The incorporation of MMT has increased the glass transition temperatures and degradation temperatures of the nanocomposites, as indicated in the DSC and TGA results. It could be concluded that the nylon-6/LNR/MMT nanocomposites with improved mechanical and thermal properties could successfully be prepared through emulsion dispersion technique. Moreover, this technique is not only limited to the nylon-6/LNR/MMT nanocomposites, but also possible to be applied in preparation of other polymer/clay nanocomposites without using plastic compounding machines such as internal mixer and extruder.

Acknowledgement

The authors are thankful to the School of Chemical Science & Food Technology, Faculty of Science & Technology, Universiti Kebangsaan Malaysia for providing the materials and facilities.

References

[1] Zare, Yasser. "Estimation of material and interfacial/interphase properties in clay/polymer nanocomposites by yield strength data." *Applied clay science* 115 (2015): 61-66. https://doi.org/10.1016/j.clay.2015.07.021

[2] Samariha, Ahmad, Amir Hooman Hemmasi, Ismail Ghasemi, Behzad Bazyar, and Mohammad Nemati. "Effect of nanoclay contents on properties, of bagasse flour/reprocessed high density polyethylene/nanoclay composites." *Maderas. Ciencia y tecnología* 17, no. 3 (2015): 637-646. https://doi.org/10.4067/S0718-221X2015005000056

[3] Akelah, Ahmed, Ahmed Rehab, Mohamed Abdelwahab, and Mohamed A. Betiha. "Synthesis and thermal properties of nanocomposites based on exfoliated organoclay polystyrene and poly (methylmethacrylate)." *Nanocomposites* 3, no. 1 (2017): 20-29. https://doi.org/10.1080/20550324.2017.1316599

[4] Marinoni, Laura, Sarah Montes, Elena Jubete, Jesus Palenzuela, Gabriel M. Cid, Daniel Aguilera, and Giorgia Spigno. "Incorporation of nanoclay and orange peels extract into pla for food applications: Migration assessment." *Journal of Applied Packaging Research* 10, no. 2 (2018): 5.

[5] Othman, Siti Hajar, Hee Nyia Ling, Rosnita A. Talib, Mohd Nazli Naim, Nazratul Putri Risyon, and Md Saifullah. "PLA/MMT and PLA/Halloysite Bio-Nanocomposite Films: Mechanical, Barrier, and Transparency." *Journal of Nano Research* 59, (2019): 77-93. https://doi.org/10.4028/www.scientific.net/JNanoR.59.77

[6] Hossain, Zahid, Biswajit Bairgi, Musharraf Zaman, and Rifat Bulut. "Prediction of the stripping resistance of nanoclay-modified asphalts using their surface chemistries." *Geo-Chicago* 2016, (2016): 477-487. https://doi.org/10.1061/9780784480120.049

[7] Ilyin, S. O., T. V. Brantseva, I. Yu Gorbunova, S. V. Antonov, Yu M. Korolev, and M. L. Kerber. "Epoxy reinforcement with silicate particles: Rheological and adhesive properties–Part I: Characterization of composites with natural and organically modified montmorillonites." *International Journal of Adhesion and Adhesives* 61, (2015): 127-136. https://doi.org/10.1016/j.ijadhadh.2015.05.008

[8] Osman, Azlin F., Tuty Fareyhynn M. Fitri, Md Rakibuddin, Fatimah Hashim, Syed Ahmad Tajudin Tuan Johari, Rajakumar Ananthakrishnan, and Rafiza Ramli. "Pre-dispersed organo-montmorillonite (organo-MMT) nanofiller: Morphology, cytocompatibility and impact on flexibility, toughness and biostability of biomedical ethyl vinyl acetate (EVA) copolymer." *Materials Science and Engineering: C* 74, (2017): 194-206. https://doi.org/10.1016/j.msec.2016.11.137

[9] Liu, Jiajia, Keqing Zhou, Panyue Wen, Bibo Wang, Yuan Hu, and Zhou Gui. "The influence of multiple modified MMT on the thermal and fire behavior of poly (lactic acid) nanocomposites." *Polymers for Advanced Technologies* 26, no. 6 (2015): 626-634. https://doi.org/10.1002/pat.3497

[10] Al-Mosawy, Manar Ghyath Abd-Almutalib, Emad Abbas Jaffar Al-Mulla, and Majed Jari Mohamad. "Bentonite-based nano organic clay using chalcone and azo dye as organophilic reagents." *Nano Biomed Eng* 9, no. 2 (2017): 124-128. https://doi.org/10.5101/nbe.v9i2.p124-128

[11] Hsieh, Wen Yen, Kuo Bing Cheng, and Chang Mou Wu. "Compatibilizer effect on Organosilicate reinforced NBR nanocomposites." *Journal of Polymer Research* 24, no. 11 (2017): 205. https://doi.org/10.1007/s10965-017-1380-7

[12] Triantou, M. I., E. M. Chatzigiannakis, and P. A. Tarantili. "Evaluation of thermal degradation mechanisms and their effect on the gross calorific value of ABS/PC/organoclay nanocomposites." *Journal of Thermal Analysis and Calorimetry* 119, no. 1 (2015): 337-347. https://doi.org/10.1007/s10973-014-4152-1

[13] Yan, Huiqiong, Xiuqiong Chen, Yuhong Feng, Fei Xiang, Jiacheng Li, Zaifeng Shi, Xianghui Wang, and Qiang Lin. "Modification of montmorillonite by ball-milling method for immobilization and delivery of acetamiprid based on alginate/exfoliated montmorillonite nanocomposite." *Polymer Bulletin* 73, no. 4 (2016): 1185-1206. https://doi.org/10.1007/s00289-015-1542-x

[14] Di Pasquale, Giovanna, and Antonino Pollicino. "PMMA/o-MMT nanocomposites obtained using thermally stable surfactants." *Journal of Applied Polymer Science* 132, no. 5 (2015): 41393.

https://doi.org/10.1002/app.41393

[15] Lee, Sangmook, Jisoo Yoo, and Jae Wook Lee. "Water-assisted extrusion of polypropylene/clay nanocomposites in high shear condition." *Journal of Industrial and Engineering Chemistry* 31, (2015): 317-322. https://doi.org/10.1016/j.jiec.2015.07.004

[16] Rusli, Daik, and Lee Ching Yee. "Preparation of LDPE/LNR blend via emulsion dispersion." *Sains Malaysiana* 36, no. 2 (2007): 183-188.

[17] Shamsuri, Ahmad Adlie, Rusli Daik, Ishak Ahmad, and Mohd Hafizuddin Hj Jumali. "Nylon-6/liquid natural rubber blends prepared via emulsion dispersion." *Journal of Polymer Research* 16, no. 4 (2009): 381-387. https://doi.org/10.1007/s10965-008-9239-6

[18] Shamsuri, Ahmad Adlie, Muhammad Kamarul Azroy Azid, Azmah Hanim Mohamed Ariff, and Ahmad Khuzairi Sudari. "Influence of surface treatment on tensile properties of low-density polyethylene/cellulose woven biocomposites: A preliminary study." *Polymers* 6, no. 9 (2014): 2345-2356. https://doi.org/10.3390/polym6092345

[19] Zhao, Yunliang, Hao Yi, Feifei Jia, Hongliang Li, Changsheng Peng, and Shaoxian Song. "A novel method for determining the thickness of hydration shells on nanosheets: A case of montmorillonite in water." *Powder Technology* 306, (2017): 74-79. https://doi.org/10.1016/j.powtec.2016.10.045

[20] Kumar, S., and K. Panneerselvam. "Optimization of friction and wear of nylon 6 and glass fiber reinforced (GFR) nylon 6 composites against 30 wt.% GFR nylon 6 disc." *Journal of Advanced Research in Materials Science* 19, no. 1 (2016): 14-32. https://doi.org/10.1016/j.protcy.2016.08.228

[21] Abdullah, Ibrahim, and Zuriati Zakaria. "Pendepolimeran fotokimia getah asli." *Sains Malaysiana* 18, no. 2 (1989): 99-109.

[22] Shamsuri, A. A. "Compression moulding technique for manufacturing biocomposite products." *International Journal of Applied Science and Technology* 5, no. 3 (2015): 23-26.

[23] Shamsuri, Ahmad Adlie, Muhamad Imran Awing, and Mohd Lufti Mohd Tawil. "Calculation of Measurement Uncertainty for Tensile Strength and Flexural Strength of Thermoplastic." *Asian Research Journal of Mathematics* 1, no. 3 (2016): 1-11. https://doi.org/10.9734/ARJOM/2016/28947

[24] Zhu, Xinzhe, Daoyi Chen, and Guozhong Wu. "Insights into asphaltene aggregation in the Na-montmorillonite interlayer." *Chemosphere* 160, (2016): 62-70. https://doi.org/10.1016/j.chemosphere.2016.06.041

[25] Marini, Juliano, and Rosario Elida Suman Bretas. "Optical Properties of Blown Films of PA6/MMT Nanocomposites." *Materials Research* 20, (2017): 53-60. https://doi.org/10.1590/1980-5373-mr-2017-0280

[26] Darus, Siti Atiqa Al Zahra Mat, Mariyam Jameelah Ghazali, Che Husna Azhari, Rozli Zulkifli, and Ahmad Adlie Shamsuri. "Mechanical properties of gigantochloa scortechinii bamboo particle reinforced semirigid polyvinyl chloride composites." *Jurnal Teknologi* 82, no. 2 (2020): 15-22. https://doi.org/10.11113/jt.v82.13693

[27] Ali, Z. I., O. A. Ghazy, G. Meligi, H. H. Saleh, and M. Bekhit. "Radiation-induced synthesis of Copper/Poly (vinyl alcohol) nanocomposites and their catalytic activity." *Advances in Polymer Technology* 37, no. 2 (2018): 365-375. https://doi.org/10.1002/adv.21675

[28] Chuayjuljit, Saowaroj, Suwasin Hosililak, and Anankran Athisart. "Thermoplastic cassava starch/sorbitol-modified montmorillonite nanocomposites blended with low density polyethylene: Properties and biodegradability study." *Journal of Metals, Materials and Minerals* 19, no. 1 (2009): 59-65.

[29] Liao, Chien-Yi, Jau-Yu Chiou, and Jiang-Jen Lin. "Phase change materials of fatty amine-modified silicate clays of nano layered structures." *RSC advances* 7, no. 38 (2017): 23530-23534. https://doi.org/10.1039/C7RA02876H

[30] Raheel, Muhammad, Kun Yao, Jiang Gong, Xue-cheng Chen, Dong-tao Liu, Yi-chao Lin, Dong-mei Cui, Muhammad Siddiq, and Tao Tang. "Poly (vinyl alcohol)/GO-MMT nanocomposites: Preparation, structure and properties." *Chinese Journal of Polymer Science* 33, no. 2 (2015): 329-338. https://doi.org/10.1007/s10118-015-1586-2

[31] Lin, Jia-Horng, Yi-Jun Pan, Chien-Teng Hsieh, Chen-Hung Huang, Zheng-Ian Lin, Yueh-Sheng Chen, Kuan-Hua Su, and Ching-Wen Lou. "Using multiple melt blending to improve the dispersion of montmorillonite in polyamide 6 nanocomposites." *Polymer Testing* 56, (2016): 74-82. https://doi.org/10.1016/j.polymertesting.2016.09.016

[32] Zhao, Min, Deqi Yi, Giovanni Camino, Alberto Frache, and Rongjie Yang. "Interdigitated crystalline MMT–MCA in polyamide 6." *RSC Advances* 7, no. 2 (2017): 861-869. https://doi.org/10.1039/C6RA26084E

[33] Al-Samhan, Meshal, Jacob Samuel, Fatema Al-Attar, and Gils Abraham. "Comparative effects of MMT clay modified with two different cationic surfactants on the thermal and rheological properties of polypropylene nanocomposites." *International Journal of Polymer Science* 2017, (2017): 5717968. https://doi.org/10.1155/2017/5717968

[34] Veličković, Sandra, Blaža Stojanović, Lozica Ivanović, Slavica Miladinović, and Saša Milojević. "Application of nanocomposites in the automotive industry." *Mobility & Vehicle Mechanics* 45, no. 3 (2019): 51-64. https://doi.org/10.24874/mvm.2019.45.03.05