Study of preparation for co-polymer nanocomposites using PLA/LDPE/CTAB modified clay

Wisam H. Hoidy

Department of Chemistry, College of Education, University of AL-Qadisiya

Email : wisam92@yahoo.com

Emad A. Jaffar Al-Mulla

Department of Chemistry, College of Science, University of Kufa

Email : emadalmulla@yahoo.com

(NJC)

Abstract

Study of preparation involve the examination of the effects of operating variables on mechanical properties of polylactic acid /low density polyethylene (PLA/LDPE)/clay nanocomposites including tensile strength, modulus, and elongation at break. Thermal stability of these nanocomposites that's investigated.   Montmorillonite clay with alkyl ammonium ion of hexadecyl trimethylammonium bromide (CTAB) was examined. Among the parameters studied, PLA/ LDPE nanocomposites showed larger improvements in mechanical properties compared to PLA/ LDPE blend due to higher shear forces exerted by polymer blend matrix on clay aggregates during polymer-clay mixing. The original MMT with Na^+ cation results in weak improvements in mechanical properties compared to organoclays. It was observed that the tensile strength, modulus, and elongation at break of the nanocomposite samples can be optimized with 4% of clay loading. The morphology and chemical structure of the optimum sample were examined by X-ray diffraction and FT-IR spectroscopy, respectively.

الخلاصة

تتناول هذا البحث تحضير ودراسة تاثير المتغيرات على الخواص الميكانيكية للكوبوليمرالمتكون من حامض البولي لاكتيك / البولي اثيلين منخفض الكثافة (PLA / LDPE) مع الطين المعدل (organoclay) بطريقة النانوكومبوزت وتشمل هذه الخواص قوة الشد والمرونه واستطالة عند الكسر.ايضا تم دراسة الثباتية الحرارية للكومبوليمر بعد انتاجه بطريقة النانو . تم مفاعلة وفحص الطين من نوع مونتمورينوليت مع أيون هكساديسايل ثلاثي مثيل الامونيوم hexadecyl trimethylammonium (CTAB)لانتاج الايون (organoclay) الذي يعمل بطريقة النانو.

اضهرت النتائج على دراسة PLA/LDPE نانوكومبوزت ان هنالك تحسن كبير في الخواص الميكانيكية والحرارية كما ظهر في فحص TGA والتنسايل والمرونه مقارنة بمزيج PLA/LDPE لوحده حيث ان الطين المعدل(organoclay) المضاف حسن من قوة تحمل البوليمرللحرارة والشد . كما تمت ملاحظة ان قوة الشد التنسايل والاستطارة قد ازدادت بوجود الطين المعدل المضاف بمعدل 4% فيما قلت هذه الخواص عند زيادة النسبة عن 4% . ايضا تم فحص التركيب الكيميائي والمورفولوجي للناتج للعينة الامثل المضاف لها 4% من الطين المعدل بواسطة FTIR و XRD ايضا تم اخذ صور للناتج لاضهار النانو بواسطة SEM و TEM.

Introduction

Public attention has been increased into environmental problems, the research of biodegradable polymers has gained considerable momentum in recent years [1,2]. Polylactic acid (PLA) is the most popular commercial biodegradable polymers that have found wide applications, especially in the biomedical applications [3-5]. However, PLA has some disadvantages that restrict their practical applications. For instance, PLA has high strength. melting temperature, slow degradable, hard, and brittle [6].The main limitations of these biodegradable polymers towards their wider industrial application are their poor thermal, mechanical resistance and limited gas barrier properties, which limit their access to industrial sectors, such as packaging, in which their use would be justified when biodegradability is required [7,8]. Many attempts have recently been made to improve the mechanical properties of PLA through fabrication of blends with other polymers and composite materials with clay or natural fibers [9-11]. For example, Yuan and Ruckenstein found that toughness of PLA can be improved by blending a proper amount of polyurethane and a proper extent of cross-linking . Park and Im suggested that toughness of PLA/starch blend can be improved by using gelatinized starch as dispersed phases mainly owing to improvement of the interfacial adhesion. LLDPE improved the impact strength of PLA nanocomposites with a sacrifice of tensile and flexural strength. The tensile and flexural strength also decreased with increasing content of MMT in PLA/LLDPE nanocomposites. The impact strength and elongation at break of LLDPE toughened PLA nanocomposites also declined steadily with increasing loadings of MMT [12].

Previous researchers have shown that addition of plasticizers such as polyethylene glycol (PEG), glucosemonoesters and partial fatty acid esters had successfully overcome the brittleness and widen PLA's application [13]. Previous study also shown performed melt blending of PLA and LLDPE in an effort to toughen PLA showed that semicrystalline PLA has relatively good miscibility with LLDPE, hence these two materials are chosen as matrix and impact modifier. The researchers also reported a significant increase of impact strength in semicrystalline PLA with the addition of LLDPE and stated that they had successfully toughen PLA with LLDPE[14].

However, the researchers had only investigated the effect of 20 wt.% LLDPE with PLA and the study focused on the compatibility of LLDPE in semicrystalline PLA.

Polymer/clay nanocomposites have received significant attentions from both academic and industrial area in recent years due to the excellent enhancement in physical and/or chemical properties relative to the neat polymer matrix [15]. The polymer/clay nanocomposites is prepared by the intercalation of monomers or

polymers into swellable layered silicate hosts. In most cases, the synthesis involves either melt-direct polymer intercalation by using a conventional polymer extrusion process or intercalation of a suitable monomer and then exfoliating the layered host into their nanoscale elements by subsequent polymerization [16,17]. The high aspect ratio layered silicate affects the mechanical, physical and thermal properties of the synthesizing polymer/clay nanocomposites [18].

In this paper, we report the preparation and characterization PLA/LDPE-CTAB-MMT to produce nanocomposites using organoclay. CTAB was employed to modify Na-MMT. Characterization of nanocomposites was done by various apparatuses.

Experimental

Materials

Sodium montmorillonite was Kunimine Ind. Co. Japan. Cetyl trimethylammonium bromide was from Acros Organics, USA. Polylactic acid was purchases from Japan. Polyethylene was obtained from Solvay Caprolactone, Warrington, England. Hydrochloric acid HCl was from Sigma – Aldrich, Germany. (All experiments and tests were completed at the University of UPM in Malaysia)

Preparation of Organoclay

Organoclay was prepared by cationic exchange process where Na+ in the montmorillonite was exchanged with alkylammonium ion in an aqueous solution. Designated amount of sodium montmorillonite (Na-MMT) was stirred vigorously in 600 ml of hot distilled water for one hour to form a clay suspension. Subsequently, desired amount of surfactant (CTAB) which had been dissolved in 400 ml of hot water and desired amount of concentrated acid hydrochloride (HCl) was added into the clay suspension of (CTAB). After stirred vigorously for one hour at 80 °C. The organoclay suspension was filtered and washed with distilled water until no chloride was detected with 1.0 M silver nitrate solution. It was then dried at 60 °C for 72 hours. The dried organoclay (CTAB-MMT) was ground until the particle size was less than 100 μm before the preparation of nanocomposite.

Preparations of PLA/PE –clay nanocomposites by melt blending

The designed amount of PLA/LDPE ratio were prepared by an internal mixer (Haake Polydrive), using different conditions (temperature, speed and time) in order to obtain the optimum conditions which were 185 °C, 50 rpm and 12 minutes ,respectively. To prepare a sample of the composite, a specific amount of PLA was first melted and mixed thoroughly with appropriate amount of LDPE for 2 minutes. Various amounts of organoclays (1, 2, 3, 4, 5 and 6 phr) were incorporated into the blend in the third minute. The mixture was compress-moulded into sheet of 1 mm thickness sheets under a pressure of 100 kgcm^{-1} in a standard hot press at 150 °C for 15 min, and cooled pressed process for 10 minutes to obtain a good blend film. The amount of PLA,LDPE and the organoclays used are listed in Table 1

Table 1: The amount of PLA/PE and organoclay for melt blending

Sample Identity	Weight of PLA (g)	Weight of PCL (g)	Weight of Organoclay
8PLA 2LDPE	32.00	8.00	0.00
8PLA 2LDPE mod1	31.68	7.92	0.40
8PLA 2LDPE mod2	31.36	7.84	0.80
8PLA 2LDPE mod3	31.04	7.76	1.20
8PLA 2LDPE mod4	30.72	7.68	1.60
8PLA 2LDPE mod5	30.40	7.60	2.00
8PLA 2LDPE mod6	30.08	7.52	2.40
8PLA 2LDPE mod7	29.76	7.44	2.80
8PLA 2LDPE mod9	29.12	7.28	3.60

Characterization

The FTIR spectra were recorded on Perkin Elmer FTIR 1650 spectrophotometer at ambient temperature using a KBr disk method. The disk containing 0.0010 g of the sample and 0.3000 g of fine grade KBr was scanned at 16 scans at wavenumber range of 400-4000 cm^{-1}

Elemental analyser (LECO CHNS-932) was used for quantitative analysis of amount of intercalation agent present in the organoclay. A sample of approximately 2 mg of organocly burned at 1000°C under oxygen gaseous flow was used for this test. The sulfamethazine was used as standard.

X-ray Diffraction (XRD) study was carried out using shimadzu XRD 6000 diffractometer with Cu-K α radiation (λ = 0, 15406 nm). The diffractogram was scanned in the ranges from 2-10° at a scan rate of 1° min^{-1}.

TG analysis using Perkin Elmer model TGA 7 Thermogravimetric analyzer was used to measure the weight loss of the samples. The samples were heated from 30-800°C with the heating rate of 10°C min^{-1} under nitrogen atmosphere at the flow rate of 20 ml min^{-1}.

SEM the fractured surfaces of the nanocomposites were studied using a JEOL attached with Oxford Inca Energy 300 EDXFEL scanning electron microscope operated at 20 to 30 KV. The scanning electron micro photographs were recorded at a magnification of 1000X to 3000X. SEM analysis was carried out to investigate polymer splitting, polymer pull-out, debonding, matrix cracking and polymer matrix adhesion. Samples were dehydrated for 45 minutes before being coated with gold particle using SEM coating unit Baltec SC030 sputter coater.

The dispersion of clay was studied by using Energy Filtering Transmission Electron Microscopy (EFTEM). TEM pictures were taken in a LEO 912 AB Energy Filtering Transmission Electron Microscope with an acceleration voltage of 120 KeV. The specimens were prepared using a Utracut E (Reichert and Jung) cryomicrotome. Thin sections of about 100 nm were cut with a diamond knife at - 120 ºC.

Results and Discussion

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of PLA/LDPE blends are shown in Figure1 b. The peaks located at 2995, 2944, and 1749 cm^{-1}. The

FTIR spectra of the CTAB-MMT, PLA/PE and PLA/PE nanocomposites are shown in Figure 1. The spectrum of PLA/LDPE nanocomposites shows the peak at 3301 cm^{-1} is due to the N-H amide. The peaks at 2945 cm^{-1} and 2890 cm^{-1} are due to the C-H stretching. The peak for C=O bending absorbed at 1748 cm^{-1}. The peak for C-O bending is at 1183 cm^{-1}. The peak for Si-O stretching is at 400 cm^{-1}. Therefore, these indicate that CTAB-MMT are intercalated with polymers. [19].
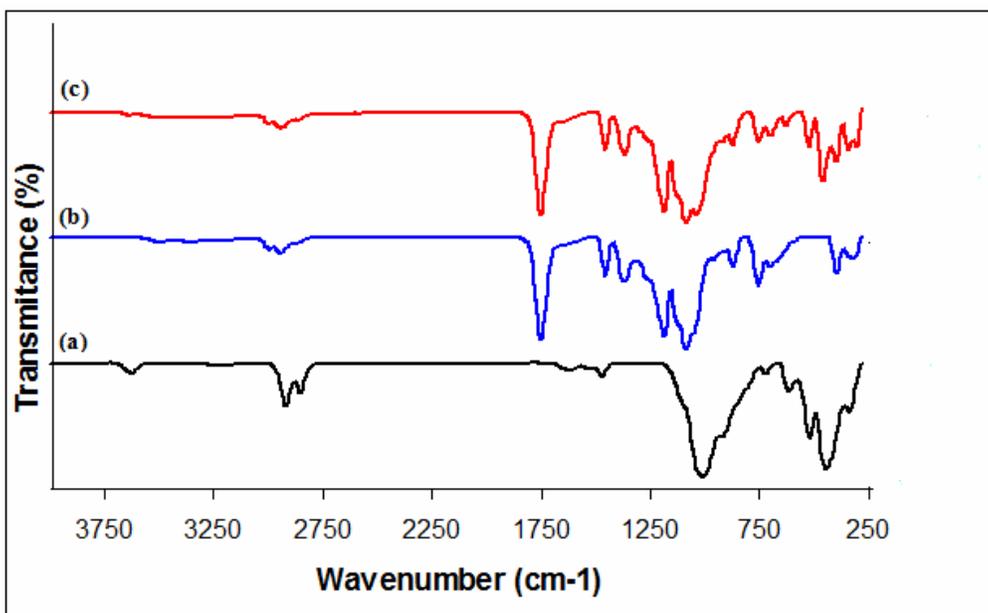
Figure 1. FTIR spectra of (a) CTAB-MMT, (b) PLA/LDPE and

(c) PLA/LDPE-CTAB-MMT

Thermogravimetric analysis TGA

Thermogravimetric analysis (TGA) is a quantitative measurement of mass change for a material exposed to a controlled temperature program. It also records the temperature of the weight loss region and the maximum temperature of decomposition. TGA detects single or multiple loss steps from room temperature to 1000 C. This measurement was done to determine the thermal stability of the sample. The sample mass loss due to the volatilizations of degraded by-product is monitored as a function of a temperature. Inorganic materials are more thermally stable and resistance compared to the organic material. Thus introduction of inorganic particles would greatly improve the thermal stability of organic materials [20].

Figure2 (a) shows the decomposition of PLA/LDPE starts at around 250.8ºC and completes at 299.1 ºC a single peak at 274.5°C

Figure2 b, shows the TGA thermogram of PLA/LDPE- MMT nanocomposites. The degradation temperature of the nanocomposites increase with the adding of MMT to the PLA/PE blend, the decomposition of PLA/LDPE - MMT nanocomposites starts at around 258.7°C and completes at 306.1°C the single peak at 282.2°C. Figure 2 c shows the TGA thermogram of PLA/LDPE-CTAB-MMT nanocomposites. The degradation temperature of the

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nanocomposites increase with the adding of CTAB-MMT to the PLA/LDPE blend, the decomposition of PLA/LDPE-CTAB-MMT nanocomposites starts at around 291.2°C and completes at 340.3 °C a single peak at 315.1 °C. The temperature of the main degradation is shifted towards a higher value when OMMT is used compare to the pristine composite, it could be observed that organophilic treatment improves the thermal stability of

PLA/LDPE nanocomposites due to better interaction between PLA/PE matrix and clay. Incorporated of the MMT, CTAB-MMT in PLA/LDPE improves slightly the composites thermal stability. The increase in thermal stability of PLA/LDPE-MMT and PLA/LDPE-CTAB-MMT nanocomposites may result from the dispersion of the clay and from a strong interaction between the clay platelets and the polymer matrix [21].
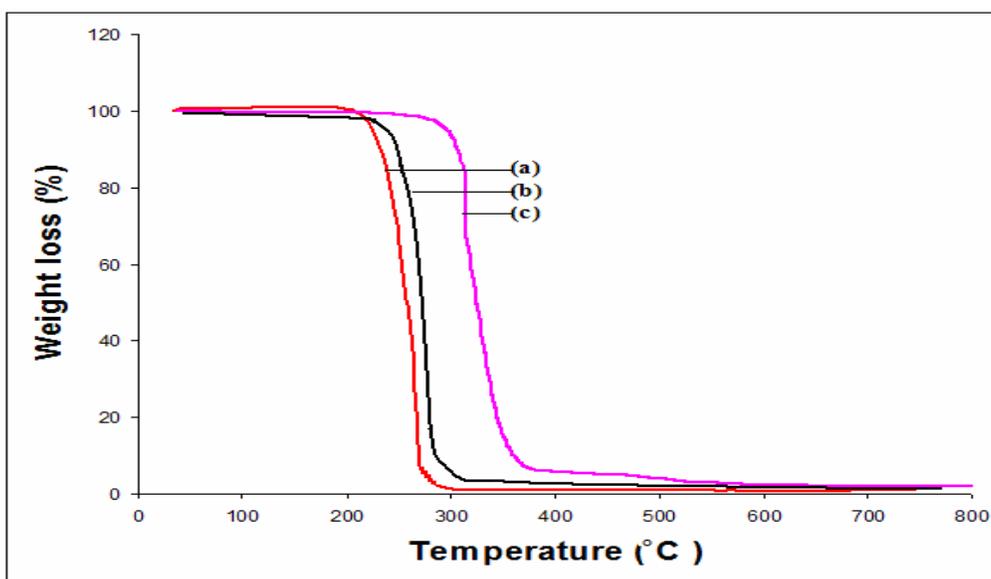
Figure2. TGA thermogram of (a) PLA/LDPE , (b) PLA/LDPE-MMT and
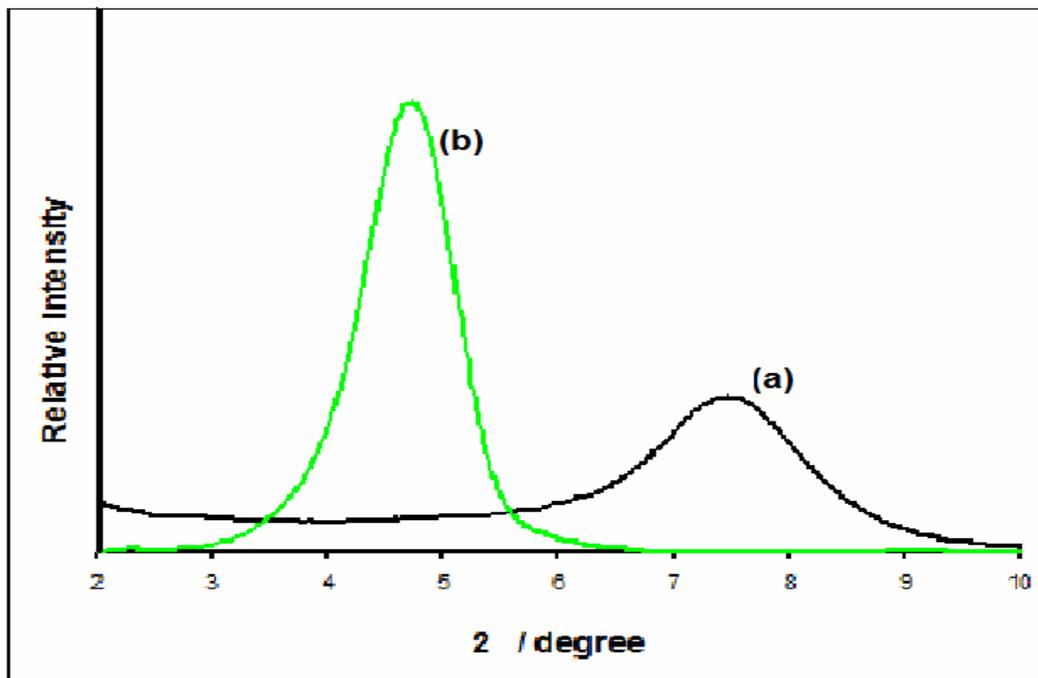
(c) PLA/LDPE-CTAB-MMT

X-ray diffraction XRD

The XRD pattern of MMT and CTAB-MMT show peak 2θ of 7.35 and 4.64 which correspond to the basal spacing 12.2 and 19.32 Å, respectively. (Figure3, Table2). XRD of PLA/LDPE-CTAB-MMT nanocomposites with 1,2,3,4,5and 6 phr of CTAB-MMT show shift to lower angles between 2θ of 3.73- 3.35 correspond to the basal spacing between 24.04 -26.76°A (Figure 4, Table 3). It is found that PLA/LDPE- CTAB-MMT nanocomposites with organoclay in melt blending loading 4% give the highest basal

spacing. The above findings indicate that there is intercalation of PLA/LDPE into the interlayers of the organoclay prepared melt blending. Increase the organoclay content decrease the basal spacing interlayer spacing this because increase the organoclay content will reduce the amount of the polymer intercalated in the galleries of the silicate layers [22]. These can be also related to the surface accessibility where the closer packing of the silicate layers is more difficult for the polymer chains to penetrate. Based on the above results, intercalated nanocomposites were prepared in this study.

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Table 2: Diffraction angle and basal spacing of montmorillonite and modified montmorillonite with CTAB

Sample	2θ (°)	d(001) spacing (Å)
Montmorillonite	7.35	12.2
CTAB modified	4.64	19.32

Figure 3. The XRD patterns of (a) Na-MMT (b) CTAB-MMT

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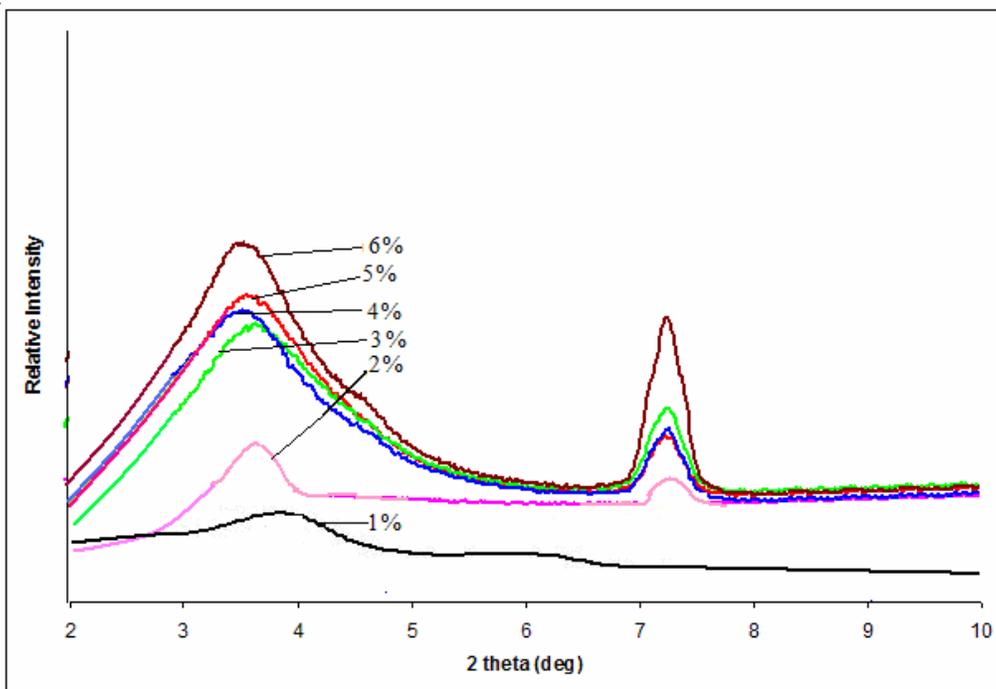
Figure 4. XRD patterns of PLA/LDPE with various ratio of CTAM-MMT

Table 3: XRD of PLA/PE- CTAB-MMT

Organoclay content	2θ (degree)	d_{001}-spacing (Å)
1%	3.73	24.04
2%	3.50	25.62
3%	3.47	25.84
4%	3.35	26.76
5%	3.45	25.99
6%	3.39	26.45

Tensile strength

The best ratio of tensile strength and modulus properties of PLA/LDPE blending was 80/20 [23]. Therefore, the ratio of 80/20 was used for further experiments.

The tensile properties of polymeric materials can be improved in different degrees if nanocomposites are formed with layered silicates. The tensile strengths of hybrid films with different OMMT contents are shown in Figure 5. The Figure shows that low contents of OMMT (4 wt%) was best ratio of organoclay. Further increase of the CTAB-MMT content does not significantly change the tensile strength of the blend. At the higher clay concentration, the organoclay is not homogenously distributed in the matrix. The agglomeration of the clay causes phase separation [24].

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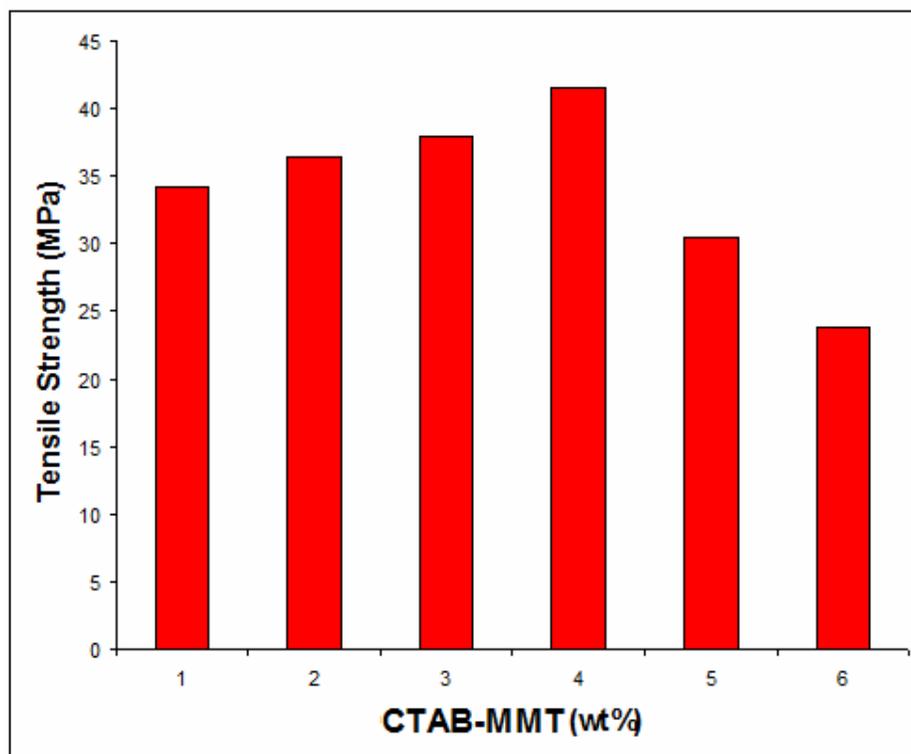
Figure 5. Tensile strength of 80PLA20LDPE, with various contents of CTAB-MMT

Scanning electron microscopy (SEM)

Figure 6 shows the SEM images of PLA/LDPE blends and PLA/LDPE with 4% CTAB-MMT in the same scale 10 μm. LDPE was located inside of the empty voids of the PLA continuous phase. It can be seen that the distribution of LDPE in the PLA matrix is homogenous and form single phase morphology (Figure 6a).

Figure 6b shows PLA/LDPE-CTAB-MMT morphology. The incorporation of CTAB-MMT strongly affects the morphology, and thus also the fraction behaviour of PLA/LDPE nanocomposites which indicate the OMMT flow homogenous in the matrix and form smaller void size. This reveals that the presence of OMMT as a filler enhanced the dispersion and interfacial adhesion of polymer matrix. This observation is agreement with the higher value of tensile strength during tensile test when OMMT is added into composites.

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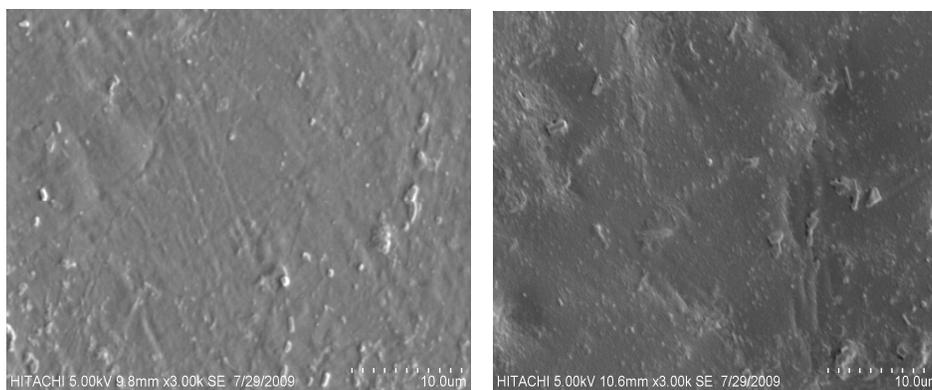
(a)   (b)

Figure 6. SEM micrographs of (a) PLA/LDPE, (b) PLA/LDPE 4% CTAB-MMT

Transmission electron microscope (TEM)

Figure 7a illustrates the TEM micrographs of PLA/LDPE pure while in Figure 7b The TEM images of PLA/LDPE/4% CTAB-MMT revealed that the OMMT layers had aggregated at 4 phr OMMT content consistent with XRD analysis

earlier. This could be the possible reason for the drop in the impact strength observed for PLA/LDPE with 4 phr of OMMT. The decrease in impact strength, however, was not severe due to the well dispersed LDPE particles which compensated the loss of toughness due to agglomeration of OMMT.
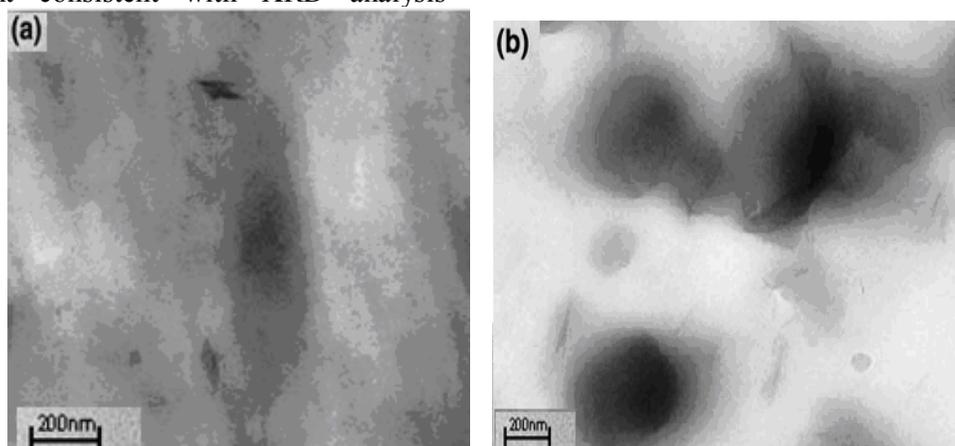
Figure7. TEM micrographs of (a) PLA/LDPE, (b) PLA/LDPE 4% CTAB-MMT

Conclusion

PLA/LDPE-OMMT nanocomposites were prepared by melt blending of PLA, LDPE and OMMT using CTAB as modifiers of clay. X-ray diffraction (XRD) shows that method

could be used to synthesize PLA/LDPE clay nanocomposites. The silicate layers of the clay were intercalated distributed in the matrix. The addition of OMMT to the PLA/LDPE blend significantly improved the tensile properties of nanocomposites. The highest values were obtained when the

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OMMT content was about 4% (CTAB-MMT). Further amount of organoclay could cause brittleness of nanocomposites. FTIR results indicate that CTAB-MMT is intercalated with polymer On other hand, layered silicate explicitly improved the thermal stability of PLA/LDPE blend. SEM images show the incorporation of OMMT strongly affects the morphology which indicate the OMMT flow homogenous in the matrix and form smaller void size.

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