

New biopolymer nanocomposites-based epoxidized palm oil/polybutylene succinate modified clay: preparation and characterization

Emad Abbas Jaffar Al-Mulla¹ · Manar Ghyath Abd-Almutalib Al-Mosawy² · Majed Jari Mohamad²

Received: 21 June 2017 / Accepted: 13 September 2017
© Accademia Nazionale dei Lincei 2017

Abstract Biodegradable polymers, such as polybutylene succinate (PBS), have attracted a lot of attention in the scientific community recently due to a rapid growth of intensive interest in the global environment for alternatives to petroleum-based polymeric materials. Chalcone (CH), hexadecylamine (HDA), and tetradecylamine (TDA) were used as one of organic compounds to modify natural clay (sodium montmorillonite). The clay modification was carried out by stirring the clay particles in an aqueous solution of CH-MMT, HDA-MMT and TDA-MMT increases from 1.27 to 1.51, 1.57 and 1.78 nm, respectively. The modified clay was then used in the preparation of the PBS/epoxidized palm oil (EPO) blend nanocomposites. They were prepared by incorporating 0.5–5% of CH-MMT, HDA-MMT and TDA-MMT. The interaction of the modifier in the clay layer was characterized by X-ray diffraction (XRD) and Fourier transform infrared (FTIR). The nanocomposites were synthesized by solution casting of the modified clay and a PBS/EPO blend at the weight ratio of 80/20, which has the highest increase in the tensile strength of the blend. The XRD, scanning electron microscopy and transmission electron microscopy results confirmed the production of nanocomposites. PBS/EPO modified clay nanocomposites show higher thermal stability and significant improvement of comparison with those of the PBS/EPO blend.

Keywords Sodium montmorillonite · Nanocomposites · Surfactants · Organic cations · PBS · EPO

1 Introduction

One of the most promising candidates for biodegradable synthetic polymers is PBS (Oishi et al. 2006; Al-Mulla 2011a). Accordingly, many efforts have been made by materials scientists and engineers to discover, develop and modify of biodegradable polymers derived from renewable resources (Reddy et al. 2012).

The PBS is one of the biodegradable thermoplastic polyesters which can be prepared from butanediol and succinic acid produced by fermentation process (Cho et al. 2010; Sugihara et al. 2006). In addition to its applications in textile industry and medical fields, PBS is a promising candidate to produce disposable packaging. However, low-molecular weight and low stiffness and high cost restrict its applications (Liu et al. 2009). Many studies have been conducted to enhance the properties by blending of biodegradable polymers with other polymers or using low-molecular weight plasticizers (Al-Mulla et al. 2010a, b; Dean et al. 2007; Al-Mulla 2011b, c; Radhi and Al-Mulla 2015; Shemmari and Rabah 2014). The morphologies and phase behaviors of polylactic acid/PBS blend have been investigated by Park and Im (2002), while the structures and properties of this blend were studied by Yokohara and Yamaguchi (2008).

Kim et al. (2001) reported that physical, thermal properties and biodegradation of PBS were evaluated by modifying it with peroxide. The EPO was used to improve properties and biodegradation of PBS. The EPO is produced from esters of glycerol in palm oil containing different of saturated and unsaturated fatty acids. It offers many advantages in chemical industries field because it is derived from

✉ Emad Abbas Jaffar Al-Mulla
almullaemad@gmail.com

Manar Ghyath Abd-Almutalib Al-Mosawy
manarghyath@yahoo.com

¹ College of Health and Medical Techniques, Al-Furat Al-Awsat Technical University, 54003 Al-Kufa, Iraq

² Department of Chemistry, Faculty of Science, University of Kufa, P.O. Box 21, An-Najaf 54001, Iraq

renewable, biodegradable and abundant raw materials (Al-Mulla et al. 2010b, c; Al-Mulla 2011d). The incorporation of organoclays in the polymer to produce a nanocomposite is another means to modify the property balance of a material. The improvements in thermal stability, physical and mechanical properties can be achieved by the addition of 0.5–5% weight of organoclays in comparison to the neat polymer (Kulinski and Piorkowska 2005; Ren et al. 2006a).

The modification of natural clay (montmorillonite) may carry out via exchanging the original interlayer cations by organic cations where they are transformed from organophobic to organophilic materials and significantly increase the basal spacing of the clay layers (Giannelis 1998). It is generally accepted that the extent of swelling depends on the length of the alkyl chain and the cation exchange capacity of the clay (Zidelkheir and Abdelgoad 2008).

Organoclays are mainly obtained by exchanging cations in the clay minerals, which contain hydrated Na^+ ions with alkylammonium (Giannelis et al. 1999). Processing and properties of PBS/EPO montmorillonite nanocomposites were investigated and characterized using X-ray diffraction and transmission electron microscopy (Arroyo et al. 2003). Plasticized PBS-based nanocomposites were prepared and characterized with epoxidized palm oil and montmorillonite. It is reported that the organo-modified montmorillonite-based composites have shown the possible competition between the polymer matrix and the plasticizer for the intercalation between the aluminosilicate layers (Paul et al. 2003).

In this study, three different ammonium compounds, CH, HDA and TDA, were used to modify montmorillonite clay to prepare nanocomposites-based EPO-plasticized PBS.

This is important for many biochemical industries as they are derived from renewable, biodegradable, environmentally friendly and easily available raw materials.

2 Materials and methods

2.1 Materials

Sodium montmorillonite, HDA and TDA were from obtained Sigma-Aldrich, Germany. EPO was provided by Advanced Oleochemical Technology Division (AOTD), Malaysia. PBS and chloroform were purchased through local suppliers from Nagoya, Japan and Merck, Germany, respectively. *p*-Aminoacetophenone and *p*-chlorobenzaldehyde were from obtained Fluka. Sodium hydroxide was obtained from B.D.H. Hydrochloric acid was from J.T. Baker, USA.

2.2 Preparation of CH (Sadiq et al. 2015)

0.5 g (1 mmol) of *p*-aminoacetophenone with 1 mmol *p*-chlorobenzaldehyde was mixed, then 0.5 mL of 10% NaOH aqueous solution and 5 mL of 99% EtOH were added to the mixture. The mixture was stirred at room temperature for 4 h. The crude mixture was poured into ice water and then acidified the product with 10% HCl solution. The solid formed was filtered and then washed with ethanol and water at a ratio of 10:5 mL. Recrystallization from 99% ethanol afforded (67% yield, yellow solid, m.p 160–165 °C).

2.3 Preparation of organoclay

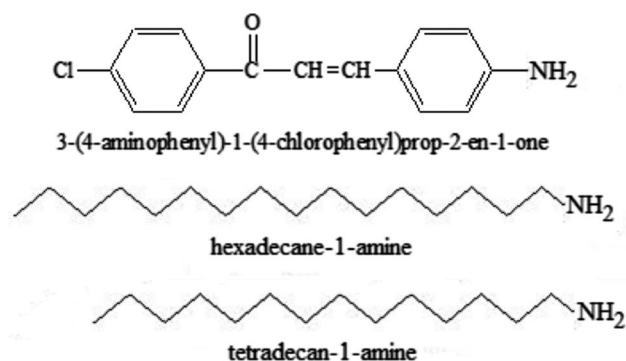
Organoclay was prepared with a cationic exchange process, where Na^+ in the montmorillonite was exchanged with alkylammonium ion from CH, HDA, and TDA, which were reported in our previous papers (Al-Mulla et al. 2011), in an aqueous solution. 4.00 g of sodium montmorillonite (Na-MMT) was stirred vigorously in 600 mL of hot distilled water for 1 h to form a clay suspension. Subsequently, a designated amount of CH, HDA, and TDA compounds, which had been dissolved in 400 mL of hot water and the desired amount of concentrated hydrochloric acid (HCl), was added into the clay suspension of CH, HDA, and TDA compounds. After being stirred vigorously for 1 h at 80 °C, the organoclay suspension was filtered and washed with distilled water until no chloride was detected.

With a 1.0 M silver nitrate solution. It was then dried at 60 °C for 72 h. The dried organoclay was ground until the particle size was less than 100 m before the preparation of the nanocomposite.

Structure of CH, HDA and TDA were shown in Scheme 1.

2.4 Preparation of PBS/EPO–clay nanocomposites

The required amounts of PBS and EPO were dissolved in 50 mL of chloroform, separately. The EPO solution was then transferred into the PBS solution with a dropper and



Scheme 1 Structures of the CH, HAD and TDA

Table 1 Amounts of PCL/EPO and the modified clay

Sample	Weight of PBS (g)	Weight of EPO (g)	Weight of organoclay (g)
1	0.9	0.1	0.00
2	0.86	0.09	0.05
3	0.82	0.08	0.1
4	0.78	0.07	0.15
5	0.74	0.06	0.2
6	0.50	0.25	0.25

continuous stirring. After all the EPO solution was transferred into the PBS solution, the resultant mixture was then stirred for 1 h. The required modified clay (CH-MMT, HDA-MMT, and TDA-MMT) was then added into the dissolved PBS/EPO in the small portion. The mixture was then refluxed for 1 h and then ultrasonically stirred using the Ultra Sonic Cathode for 10 min to make sure that the clay was fully dispersed in the PBS/EPO solution. The nanocomposite was then poured into a Petri dish and left to dry. The amount of PBS/EPO and the modified clay used in this study is listed in Table 1.

2.5 Characterization

2.5.1 Measurements of tensile properties

The tensile strength was measured using an Instron Universal Testing Machine 4301 at 5 mm/min of crosshead speed, in accordance with ASTM D638 (Al-Mulla 2011a). Seven samples were used for the tensile test and an average of five results was taken as the resultant value.

2.5.2 X-ray diffraction (XRD) analysis

X-ray diffraction study was carried out using a Shimadzu XRD 6000 diffractometer with Cu K α radiation (= 0.15406 nm). The diffractogram was scanned in the ranges from 2° to 10° at a scan rate of 1°/min.

2.5.3 Fourier transform infrared (FTIR)

The FTIR spectra of the samples were recorded by the FTIR spectrophotometer (Perkin Elmer FTIR-Spectrum BX, USA) using the KBr disc technique.

2.5.4 Thermogravimetric analysis (TGA)

The thermal stability of the samples was studied using the Perkin Elmer model TGA 7 Thermogravimetric Analyzer. The samples were heated from 35 to 500 °C with a heating

rate of 10 °C/min under a nitrogen atmosphere with a nitrogen flow rate of 20 mL/min.

2.5.5 Scanning electron microscopy (SEM)

SEM was recorded by Scanning Electron Microscopy, Angstrom (model AIS-2300C) USA.

2.5.6 Transmission electron microscopy (TEM)

The dispersion of clay was studied using energy filtering transmission electron microscopy (EFTEM). TEM pictures were taken in a LEO912AB Energy Filtering Transmission Electron Microscope with an acceleration voltage of 120 keV. The specimens were prepared using a Ultracut E (Reichert and Jung) cryomicrotome. Thin sections of about 100 nm were cut with a diamond knife at - 120 °C.

3 Results and discussion

3.1 Mechanical properties

The weight ratio of the PBS/EPO blend was fixed at 80:20 according to preliminary investigation which gave the highest tensile strength of the blend. Therefore, this ratio was chosen in subsequent experiments.

Table 2 shows the effect of clay content on the tensile strength properties of the PBS/EPO/HAD-OMMT, PBS/EPO/TAD-OMMT and PBS/EPO/CH-OMMT nanocomposite. The tensile strength of the PBS/EPO blend decreases to 11.89 MPa. The addition of 0.5, 1 or 2 php of OMMT into the PBS/EPO blend increases the tensile strength. The

Table 2 Tensile properties of PBS/EPO blend, PBS/EPO/HAD-OMMT, PBS/EPO/TADOMMT and PBS/EPO/CH-OMMT nanocomposites

Sample	Tensile strength, MPa		
	HAD-MMT	TAD-MMT	CH-MMT
PBS/EPO	11.89 ± 0.29	12.56 ± 0.31	10.81 ± 0.14
PBS/EPO/0.5 php OMMT	13.15 ± 0.31	14.25 ± 0.43	13.12 ± 0.32
PBS/EPO/1.0 php OMMT	16.29 ± 0.92	17.23 ± 0.72	16.05 ± 0.71
PBS/EPO/2.0 php OMMT	24.51 ± 1.25	23.38 ± 0.92	22.15 ± 0.62
PBS/EPO/3.0 php OMMT	19.35 ± 1.09	18.15 ± 0.81	17.69 ± 0.52
PBS/EPO/4.0 php OMMT	13.22 ± 0.80	13.10 ± 0.61	14.15 ± 0.49
PBS/EPO/5.0 php OMMT	11.61 ± 0.41	12.17 ± 0.56	11.61 ± 0.37

Table 3 Diffraction angle and basal spacing of natural clay (Na-MMT) and modified clays with the CH-MMT, HDA-MMT, and TDA-MMT

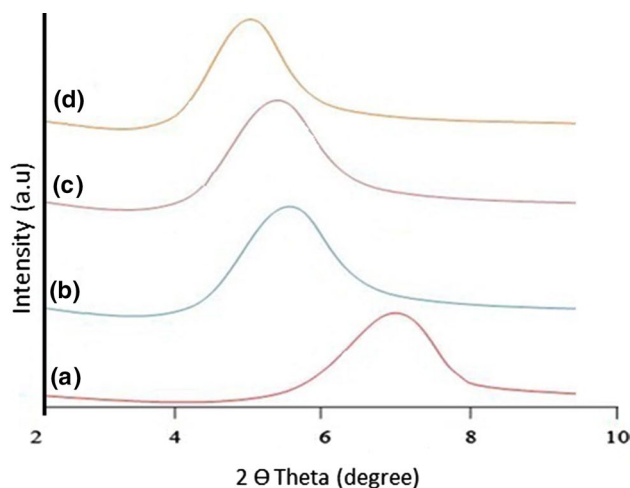
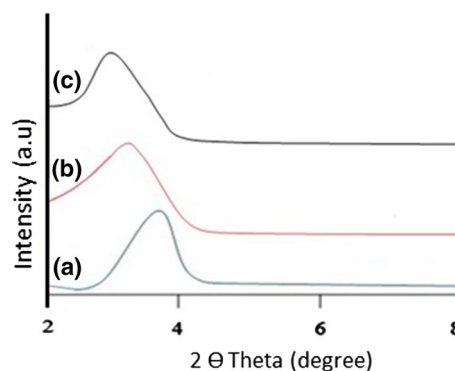
Sample	Exchanged cation	2θ ($^\circ$)	D(001) spacing (nm)
MMT	Na^+	6.91	1.27
CH	$\text{C}_{15}\text{H}_9\text{ClONH}_3^+(\text{CH}^+)$	5.86	1.51
HDA	$\text{C}_{16}\text{H}_{32}\text{NH}_3^+(\text{HDA}^+)$	5.64	1.57
TDA	$\text{C}_{14}\text{H}_{28}\text{NH}_3^+(\text{TDA}^+)$	4.96	1.78

highest tensile strength (24.51 MPa) is observed with 2 php of HAD-OMMT, tensile strength 23.38 is observed with 2 php of TAD-OMMT and tensile strength 22.15 is observed with 2 php of CH-OMMT.

3.2 XRD analysis

According to Bragg's law ($n\lambda = d \sin \theta$), d refers to the distance of two consecutive clay layers, where λ is the wavelength of the incident X-rays at the incident angle θ . The presence of CH-MMT, HDA-MMT and TDA-MMT chains in the galleries turns the original hydrophilic silicate to an organophilic silicate, and thus increases the layer-to-layer spacing of Na-MMT (Ren et al. 2006b). Using X-ray diffraction, Na-MMT shows a d001 diffraction peak at $2\theta = 6.91^\circ$, which assigns the interlayer distance of the natural montmorillonite with a basal spacing of 1.27 nm.

Na-MMT was surface treated with CH, HDA, and TDA, an intercalation agent through a cation exchange process. The cationic head groups of the intercalation agent molecule would preferentially reside at the surface layer and the aliphatic tail will radiate a way from the surface.

**Fig. 1** The XRD patterns of **a** Na-MMT, **b** CH-MMT, **c** HDA-MMT, and **d** TDA-MMT**Fig. 2** XRD patterns of **a** PBS/EPO/CH, **b** HDA and **c** TDA modified clay nanocomposites**Table 4** Diffraction angle and basal spacing of PLA/EPO/CH, HDA, and TDA modified clay nanocomposites

Sample	2θ ($^\circ$)	d-spacing (nm)
80PBS20EPO/CH-MMT	3.99	2.21
80PBS20EPO/HDA-MMT	3.37	2.62
80PBS20EPO/TDA-MMT	3.12	2.83

The maximum basal spacing of CH-MMT, HDA-MMT and TDA-MMT increases from 1.27 to 1.51, 1.57 and 1.78 nm, respectively (Table 3), indicating that these CH, HDA, and TAD were successfully intercalated into the Na-MMT galleries (Fig. 1).

Monolayer arrangement of CH, HDA and TDA is formed in the interlayer spacing of Na-MMT (Pospisil et al. 2004).

Figure 2 shows the XRD patterns of the nanocomposites prepared using three different CH, HDA and TDA (alkylammonium groups) modified of the montmorillonite

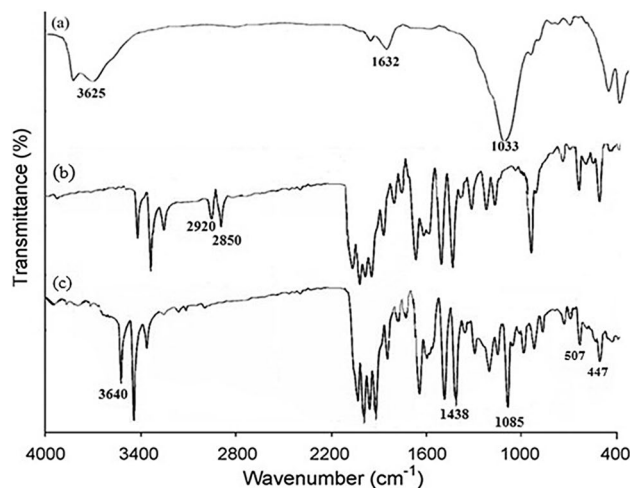
**Fig. 3** FTIR spectra of **a** Na-MMT, **b** CH and **c** CH-MMT

Fig. 4 FTIR spectra of **a** Na-MMT, **b** HDA and **c** HDA-MMT

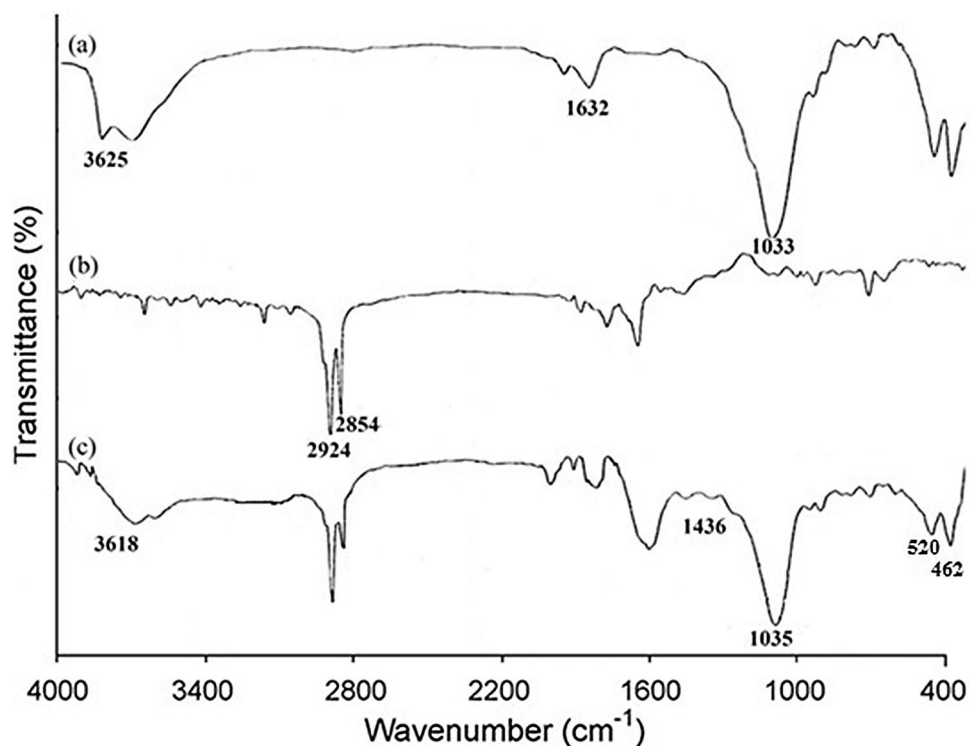
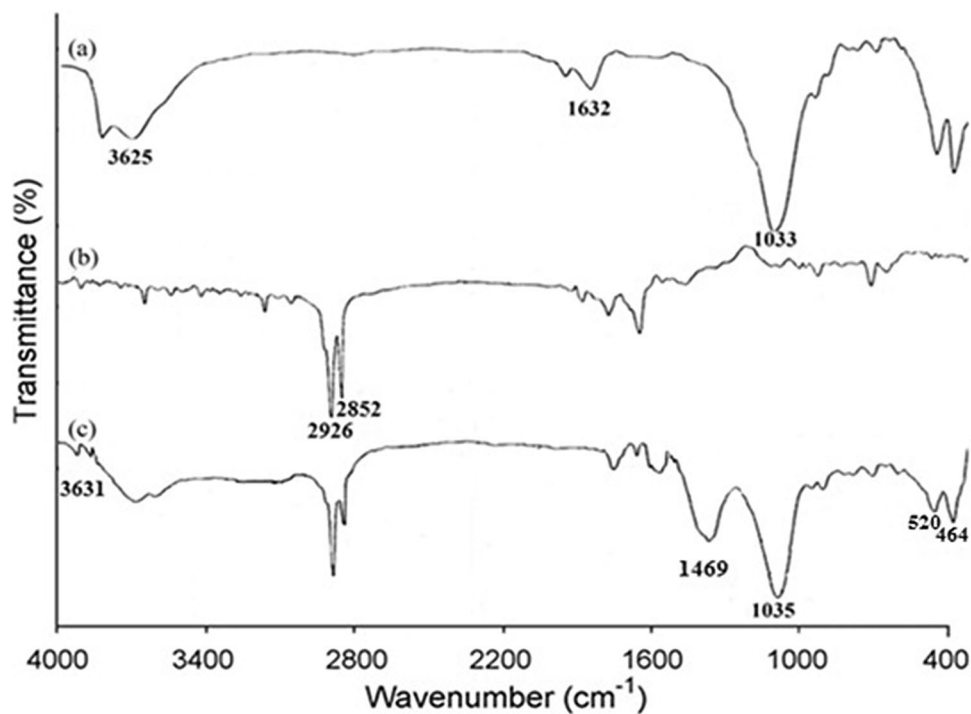


Fig. 5 FTIR spectra of **a** Na-MMT, **b** TDA and **c** TDA-MMT



nanocomposites. Table 4 illustrates increase basal spacing of the clay increased to 2.21, 2.62 and 2.82 nm for 80PBS20EPO/CH-MMT, 80PBS20EPO/HDA-MMT and 80PBS20EPO/TDA MMT, respectively.

This clearly shows that the basal spacing of organoclay in the polymer matrix increases with the increase in the size

of the surfactant as was observed by (Agag and Takeichi 2000). These XRD patterns also suggest that all the nanocomposites produced are intercalated compounds and some exfoliated. Scheme 1 shows schematic drawing of the clay modification of ammonium ion from their nanocomposites.

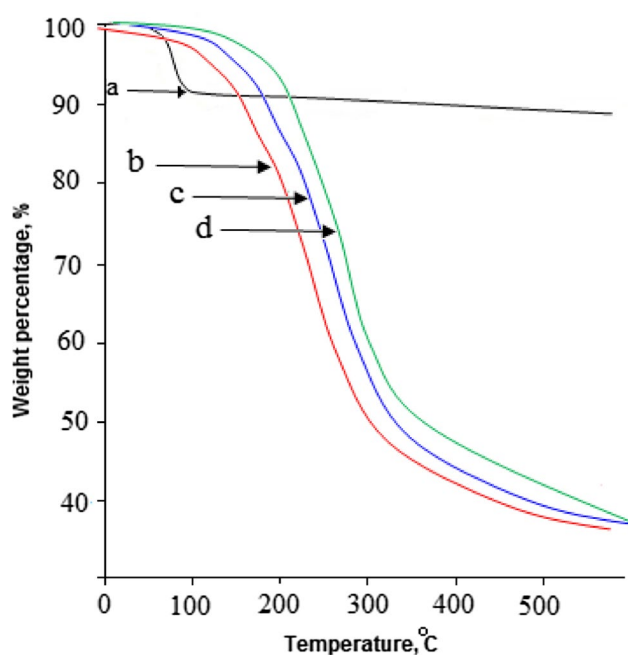


Fig. 6 TGA of **a** Na-MMT, **b** HDA-MMT, **c** TDA-MMT and **d** CH-MMT

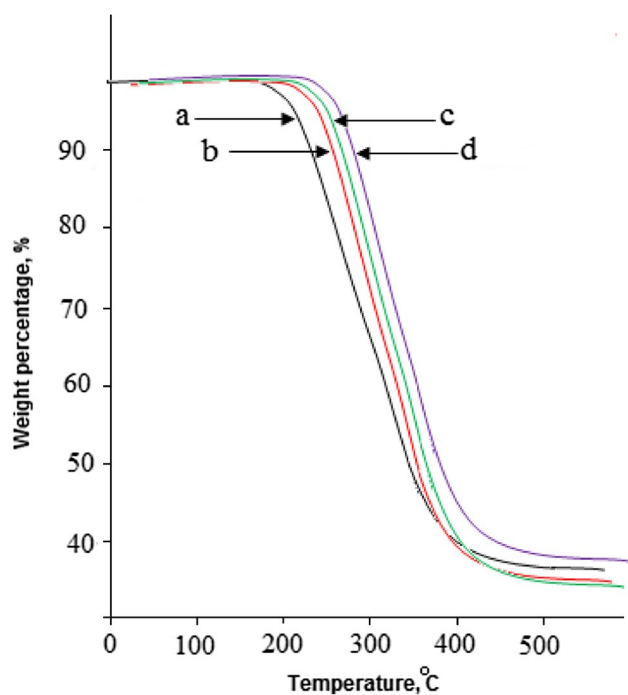


Fig. 7 TGA **a** PBS/EPO blends, **b** PBS/EPO/HDA-MMT, **c** PBS/EPO/TDA-MMT and **d** PBS/EPO/CH-MMT

3.3 FTIR

The FTIR spectra of Na-MMT, CH-MMT, HDA-MMT, and

TDA-MMT are shown in Figs. 3, 4 and 5. In the spectra of Na-MMT, the peaks at 3625, 1632 and 1033 cm^{-1} are due to the O–H stretching, interlayer water deformation and the Si–O stretching vibration, respectively.

The other strong band absorption from 507 to 462 cm^{-1} indicates the presence of Al–O stretching and Si–O bending, respectively, in the clay. The CH-MMT, HDA-MMT, and TDA-MMT spectra show the major bands of CH, HDA, and TDA spectra (Al-Mulla et al. 2009, 2010b; Hoidy et al. 2010) in addition to the bands of the original Na-MMT. The bands from 1438, 1436 and 1469 cm^{-1} suggest the existence of the ammonium ion. Therefore, these indicate that the CH, HDA, and TDA were intercalated in the silicate layers.

3.4 TGA

Most thermoanalytical studies reveal new insights into the structure of intercalated clays (Xi et al. 2005). TGA gives information on the structure of the intercalating molecules by the weight loss steps. Thermal degradation of MMT shows two steps (Arroyo et al. 2003). The first one is before 200 $^{\circ}\text{C}$ because of the volatilization of water adsorbed on the external surfaces of the MMT and water inside the interlayer space. Decomposition of the surfactant takes place in the second step between 200 and 500 $^{\circ}\text{C}$.

The weight loss curves (TGA) of the MMT, CH-MMT, HDA-MMT, and TDA-MMT are illustrated in Fig. 6. MMT contains water due to hydrated sodium (Na^+) cations intercalated inside the clay layers. The presence of alkylammonium groups within the MMT interlayer spacing lowers the surface energy of the inorganic structure and will transform organophobic to organophilic materials.

The major difference between the thermogram of the unmodified clay and that of the organoclay is that the organic constituents in the organoclay decompose in the range from 200 to 500 $^{\circ}\text{C}$, as the organic constituent in the organoclay decomposes in this range. That the C decomposed as the temperature increased from 180 to 370 $^{\circ}\text{C}$. The decomposition process ended at 370 $^{\circ}\text{C}$.

The CH started decomposing at higher temperatures than that of the TDA, which started at 198 $^{\circ}\text{C}$ and ended at 352 $^{\circ}\text{C}$. HDA had decomposition temperature (starting at 155 $^{\circ}\text{C}$ and ending at 305 $^{\circ}\text{C}$). There was a strong intermolecular interaction between the alkylammonium cations and the clay due to observation of higher decomposition temperatures of the CH-MMT, HDA-MMT and TDA-MMT compared to neat MMT. In other words, after ion exchange, the CH, HDA, and TDA are intercalated and attached to the silicate layers of the clay and hence their decomposition temperatures increase.

Thermogravimetric analyses were done on PBS/EPO/HDA-MMT nanocomposites to determine the effect of modified clay content in the polymer matrix on thermal

Fig. 8 SEM micrographs of fracture surfaces of **a** MMT, **b** neat PBS, **c** PBS/EPO blends, **d** PBS/EPO/HDA-MMT, **e** PBS/EPO/TDA-MMT and **f** PBS/EPO/CH-MMT

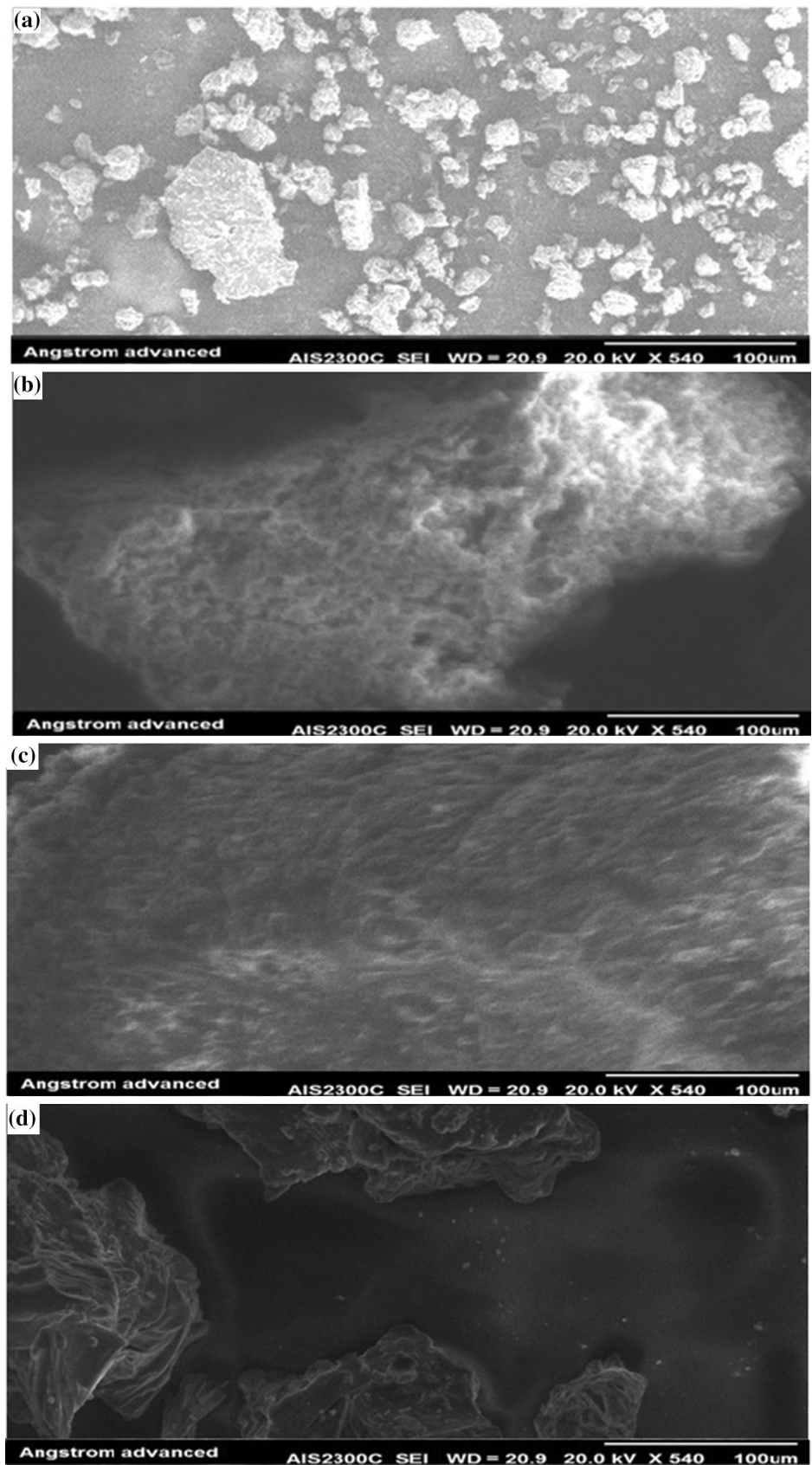


Fig. 8 (continued)

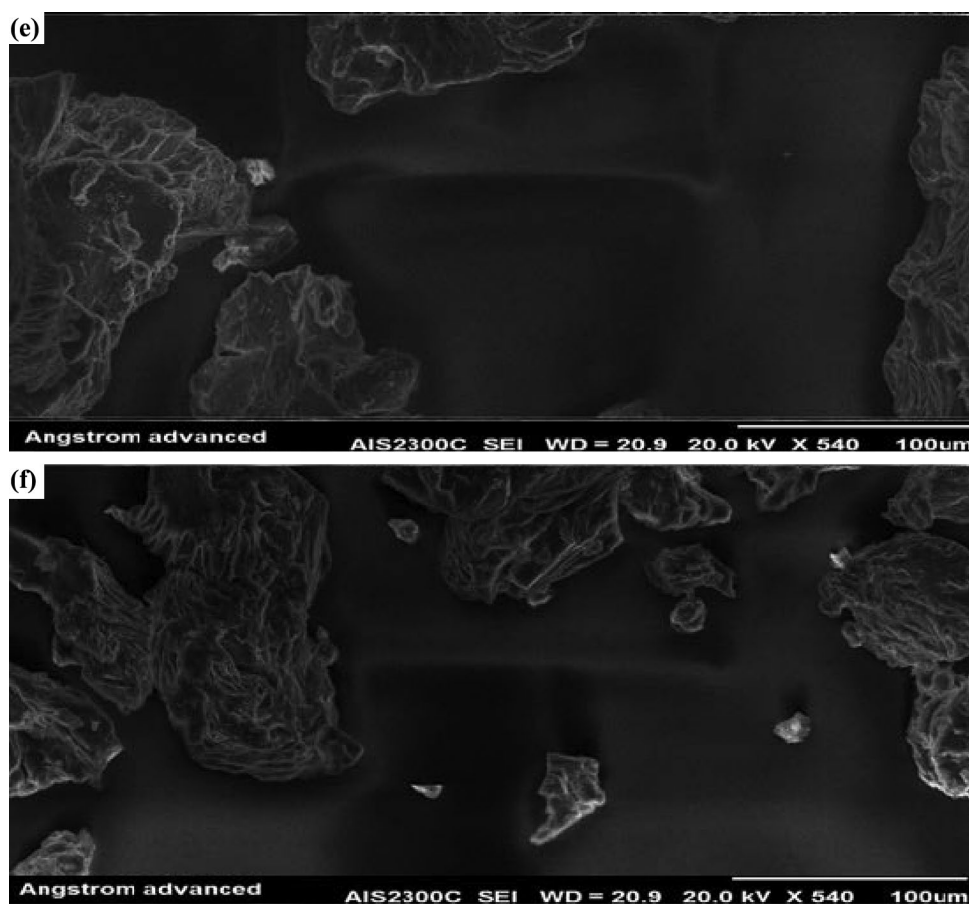
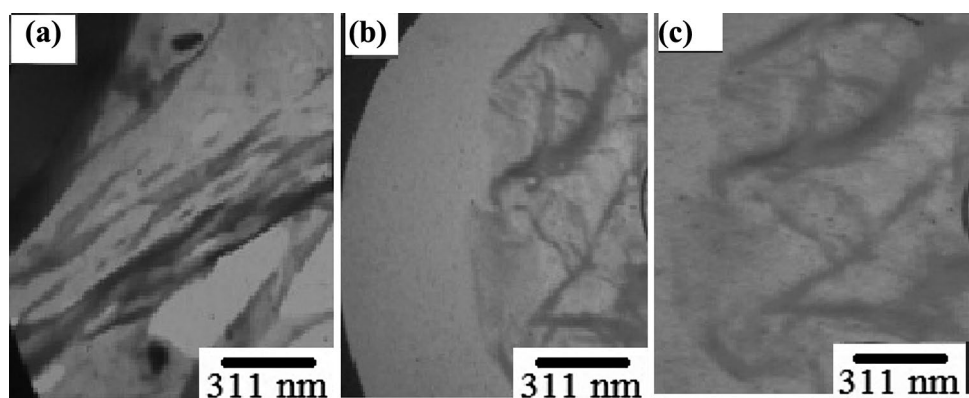


Fig. 9 TEM **a** PBS/EPO/HDA-MMT, **b** PBS/EPO/TDA-MMT and **c** PBS/EPO/CH-MMT



properties. The results of TGA are shown in Fig. 7 The onset of the degradation of the nanocomposites is higher, that is 259, 263, and 269 °C, for PBS/EPO containing HDA-MMT, TDA-MMT, and CH-MMT, respectively, compared to the PBS/EPO blend (245 °C).

The results show that the thermal stability increases with addition of the HDA-MMT, TDA-MMT, and CH-MMT. The presence of silicate layers dispersed homogeneously in the polymer sheet hinders the permeability of volatile

degradation products out from the material and helps delay the degradation of the nanocomposites.

3.5 SEM

The aggregated clay morphology was characterized with SEM. Because of the differences in the scattering densities between the clay and the matrix PBS, EPO/HDA-MMT, large clay aggregates could easily be imaged with SEM. SEM micrographs of fractured surface of the

nanocomposites are presented in Fig. 8. These images did not exhibit inorganic domains at the maximum possible magnification, which means that nanolayers are distributed well in the PBS, EPO/HDA-MMT matrix. The absence of MMT particles indicates that the agglomerate is broken down to a size (submicron) that cannot be seen at this magnification.

3.6 TEM

TEM micrographs of the PBS/EPO composites promote it can be watched that the original Na-MMT stack morphology was fully preserved with PBS/EPO due to the incompatible nature of both constituents (Fig. 9) (Al-Mulla et al. 2011). The dark lines represent the thickness of the individual clay layers or agglomerates (tactoids, stacks). The organoclay does not show its original layered structure. The related structure can be referred to as intercalated lamellae, tactoids composed of a variable number of lamellae and aggregates of tactoids. The TEM micrograph of shows a higher degree of intercalation and some exfoliated zones presence of the PBS/EPO/HDA-MMT, PBS/EPO/TDA and PBS/EPO/CH-MMT.

4 Conclusion

In this study, new biopolymer nanocomposites were prepared by treatment of EPO-plasticized PBS-modified MMT with CH, HDA, and TDA. PBS/EPO–clay nanocomposites have been prepared by incorporating 2% of CH-MMT, HDA-MMT and TDA-MMT. TEM analysis shows that the prepared nanocomposites were intercalated with partially exfoliated types (CH-MMT, HDA-MMT and TDA-MMT). These nanocomposites represent a good candidate to produce disposable packaging because they have good thermal properties and processability, and produced from renewable, biodegradable, environmental friendly and easily available raw materials. In addition to their applications in textile industry and medical fields, biopolymer nanocomposites prepared in this study are a promising candidate to produce disposable packaging.

References

- Agag T, Takeichi T (2000) Polybenzoxazine–montmorillonite hybrid nanocomposites: synthesis and characterization. *Polymer* 41:7083–7089
- Al-Mulla EAJ (2011a) Preparation of polylactic acid/epoxidized palm oil/fatty nitrogen compounds modified clay nanocomposites by melt blending. *Polym Sci Ser A* 53(2):149–157. doi:10.1134/S0965545X11020015
- Al-Mulla EAJ (2011b) Preparation of new polymer nanocomposites based on poly(lactic acid)/fatty nitrogen compounds modified clay by a solution casting process. *Fibers Polym* 12(4):444–450. doi:10.1007/s12221-011-0444-2
- Al-Mulla EAJ (2011c) Polylactic acid/epoxidized palm oil/fatty nitrogen compounds modified clay nanocomposites: preparation and characterization. *Korean J Chem Eng* 28(2):620–626. doi:10.1007/s11814-010-0373-6
- Al-Mulla EAJ (2011d) Lipase-catalyzed synthesis of fattythioic acids from palm oil. *J Oleo Sci* 60:41–45. doi:10.5650/jos.60.41
- Al-Mulla EAJ, Yunus WMZ, Ibrahim NA, Rahman MZ (2009) Synthesis and characterization of *N,N'*-carbonyl di fatty amide from palm oil. *J Oleo Sci* 58:467–471
- Al-Mulla EAJ, Yunus WMZW, Ibrahim NAB, Rahman ZAM (2010a) Epoxidized palm oil plasticized polylactic acid/fatty nitrogen compound modified clay nanocomposites: preparation and characterization. *Polym Polym Composites* 18:451–459
- Al-Mulla EAJ, Yunus WMZW, Ibrahim NAB, Rahman ZAM (2010b) Properties of epoxidized palm oil plasticized polylactic acid. *J Mater Sci* 45:1942–1946. doi:10.1007/s10853-009-4185-1
- Al-Mulla EAJ, Yunus WMZW, Ibrahim NAB, Rahman ZAM (2010c) Di fatty acyl urea from corn oil: synthesis and characterization. *J Oleo Sci* 59:157
- Al-Mulla EAJ, Suhail AH, Saadon AA (2011) *Indust Crops Prod* 33:23–29
- Arroyo M, Lopez-Manchado M, Herrero B (2003) Organo-montmorillonite as substitute of carbon black in natural rubber compounds. *Polymer* 44:2447–2453
- Cho HS, Moon HS, Kim M, Nam K, Kim JY (2010) Biodegradability and biodegradation rate of poly(caprolactone)-starch blend and poly(butylene succinate) biodegradable polymer under aerobic and anaerobic environment. *Waste Manag* 31:475–480. doi:10.1016/j.wasman.2010.10.029
- Dean K, Yu L, Bateman S, Wu DY (2007) Gelatinized starch/biodegradable polyester blends: processing, morphology, and properties. *J Appl Polym Sci* 103(2):802–811. doi:10.1002/app.25149
- Giannelis EP (1998) Polymer-layered silicate nanocomposites: synthesis, properties and applications. *Appl Organomet Chem* 12:675–680
- Giannelis EP, Krishnamoorti R, Manias E (1999) Polymer–silicate nanocomposites model systems for confined polymers and polymer brushes. *Adv Polym Sci* 138:107–143
- Hoidy WH, Ahmad MB, Al-Mulla EAJ, Yunus WMZ, Ibrahim NA (2010) Synthesis and characterization of fatty hydroxamic acids from triacylglycerides. *J Oleo Sci* 59:15–19
- Kim DJ, Kim WS, Lee DH (2001) Modification of poly(butylene succinate) with peroxide: crosslinking, physical and thermal properties, and biodegradation. *J Appl Polym Sci* 81(5):1115–1124. doi:10.1002/app.1534
- Kulinski Z, Piorkowska E (2005) Crystallization, structure and properties of plasticized poly(L-lactide). *Polymer* 46:10290–10300
- Liu L, Yu J, Cheng L, Qu W (2009) Mechanical properties of poly(butylene succinate) (PBS) biocomposites reinforced with surface modified jute fibre. *Composites Part A Appl Sci Manuf* 40:669–674. doi:10.1016/j.compositesa.2009.03.002
- Oishi A, Zhang M, Nakayama K, Masuda T, Taguchi Y (2006) Synthesis of poly(butylene succinate) and poly(ethylene succinate) including diglycollate moiety. *Polym J* 38(7):710–715. doi:10.1295/polymj.PJ2005206
- Park JW, Im SS (2002) Phase behavior and morphology in blends of poly(L-lactic acid) and poly(butylene succinate). *J Appl Polym Sci* 86:647–655. doi:10.1002/app.10923
- Paul MA, Alexandre M, Degée P, Henrist C, Rulmont A, Dubois P (2003) Nanocomposite materials based on plasticized poly(L-lactide) and organomodified montmorillonite: thermal and morphological study. *Polymer* 44:443–450
- Pospisil M, Kalcndova A, Capkova P, Simonik J, Valaskova M (2004) Structure analysis of intercalated layer silicate: combination of

- molecular simulations and experiment. *J Colloid Interface Sci* 227:154–161
- Radhi MM, Al-Mulla EAJ (2015) Use of a grafted polymer electrode to study mercury ions by cyclic voltammetry. *Res Chem Intermed* 41:1413–1420. doi:[10.1007/s11164-013-1282-1](https://doi.org/10.1007/s11164-013-1282-1)
- Reddy MM, Mohanty AK, Misra M (2012) Biodegradable blends from plasticized soy meal, polycaprolactone, and poly(butylene succinate). *Macromol Mater Eng* 297:455–463. doi:[10.1002/mame.201100203](https://doi.org/10.1002/mame.201100203)
- Ren Z, Dong L, Yang Y (2006a) Dynamic mechanical and thermal properties of plasticized poly(lactic acid). *J Appl Polym Sci* 101:1583–1590
- Ren Z, Dong L, Yang Y (2006b) Dynamic mechanical and thermal properties of plasticized poly(lactic acid). *J Appl Polym Sci* 101:1583–1590
- Sadiq SA, Atiyah EM, Numan AT, Sanak KA (2015) Synthesis and characterization of new bidentate chalcone ligand type (NO) and its Mn^{II} , Co^{II} , Ni^{II} and Cu^{II} complexes with study of their antibacterial activity. *Diyala J Pure Sci* 11(3):2222–8373
- Shemmari FA, Rabah AAA (2014) Comparative study of different surfactants for natural rubber clay nanocomposite preparation. *Rend Fis Acc Lincei* 25:409–413. doi:[10.1007/s12210-014-0307-z](https://doi.org/10.1007/s12210-014-0307-z)
- Sugihara S, Toshima K, Matsumura S (2006) New strategy for enzymatic synthesis of high-molecular-weight poly(butylene succinate) via cyclic oligomers. *Macromol Rapid Commun* 27:203–207. doi:[10.1002/marc.200500723](https://doi.org/10.1002/marc.200500723)
- Xi Y, Martens W, He H, Frost RLJ (2005) Thermogravimetric analysis of organ clays intercalated with the surfactant octadecyltrimethylammonium bromide. *J Therm Anal Calorim* 81:91–97
- Yokohara T, Yamaguchi M (2008) Structure and properties for biomass based polyester blends of PLA and PBS. *Eur Polym J* 44:677–685. doi:[10.1016/j.eurpolymj.2008.01.008](https://doi.org/10.1016/j.eurpolymj.2008.01.008)
- Zidelkheir B, Abdelgoad M (2008) Effect of surfactant agent upon the structure of montmorillonite. *J Therm Anal Calorim* 94:181–187