RESEARCH ARTICLE
Eurasian J Bio Chem Sci, 3(1):38-41, 2020
https://doi.org/10.46239/ejbcs.729216

Eurasian Journal of Biological and Chemical Sciences

Journal homepage: www.dergipark.org.tr/ejbcs

Synthesis of Bionanocomposite Films with PLA/Halloysite

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Received : 29/04/2020
Accepted : 05/06/2020

Abstract: Polylactic acid (PLA) is a kind of biodegradable and biocompatible polymer which can be replaced of other polymer groups based on petroleum. It is used in wider application areas such as packaging due to their unique properties. On the other hand, mechanical (brittleness) and thermal properties of PLA are inadequate so that it should be improved. Therefore, halloysite (HNTs) which is a kaolin group clay can be used to overcome from these obstacles due to their high mechanical strength and modulus. It is aimed to synthesize biocompatibility PLA/HNTs film and collaborate with plasticizer materials to improve mechanical properties of film. Moreover, it was examined effect of iron oxide proportion to features of film. PLA/natural HNTs films were prepared and plasticizer's material was mixed by solution casting method to investigate their tensile properties. In addition; HNTs sample which were taken from TURKEY contained iron impurities. Therefore, it was leached using by oxalic acid as a leaching agent. Fourier Transformed Infrared (FTIR), X-ray fluorescence (XRF) and X-ray diffraction (XRD) devices were used to characterization of HNTs clay. Additionally, the resultant films tensile properties were investigated. As a conclusion, it was observed that halloysite addition increased the tensile strength values of PLA/HNTs bionanocomposite films.

Keywords: Polylactic acid (PLA), halloysite (HNTs), solution casting method, leaching

1. Introduction

Using of non-biodegradable, petrochemical-based plastics materials have been led to environmental pollution. Therefore, it had been occured requirement of finding alternative solution instead of using petrochemical-based plastics materials (Rhim et al. 2006). Tendency of using biodegradable plastics which are produced from renewable resource has increased (De Silva et al. 2014). In result of that enviromentally harmful effects had been reduced due to utilization of biopolymer such as polylactic acid (Alakrach et al. 2019). Polylactic acid which is an aliphatic polyesters is synthesized from lactic acid deriving from renewable sources (Murariu and Dubois 2016). Synthesis and recycle of PLA are illustrated in Fig 1.

PLA is undoubtedly one of the important materials for future applications owing of its self-properties. PLA has unique physico-chemical properties; low carbon foot print, high strength, oil resistance, acces of commercial easily and the ability to recycle lactic acid (Alakrach et al. 2018). It can be used for different application including of medical devices (bone surgery, chemothrapy etc.), engineering application (automotive, electronic and electrical devices etc.), textile, composite materials and food packacing (Alakrach et al. 2019; Rhim et al. 2006). However, usage of PLA is limited owing to their properties which are thermal, low mechanical and barrier so that it should be improved. Halloysite clay (HNTs) can be attractive canditate for enhancing these properties (Risyon et al. 2020).

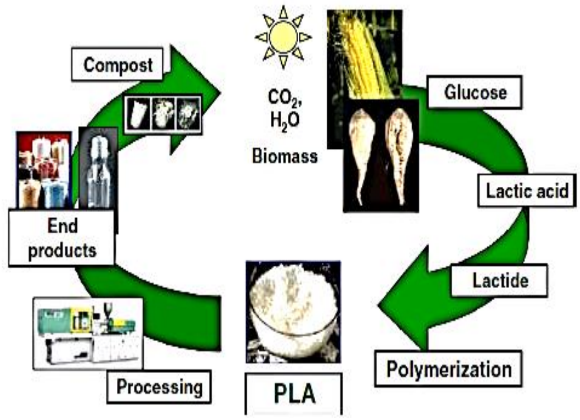

Fig 1. Synthesis and recycle life of PLA (Murariu and Dubois 2016).

HNTs which are aluminosilicate clay mineral is a sub-group of kaolin. HNTs empirical formula is $Al_2Si_2O_5(OH)_n$. Halloysite has distinctive properties such as nontoxic and biocompatible. Furthermore, HNTs have high cation capacity exchange so that it can exhibit good dispersion in PLA (Risyon et al. 2020). It has shown that quite important behavior for improving mechanical properties of PLA (De Silva et al. 2014; Risyon et al. 2020). HNTs incorporated into PLA biopolymer are shown in Fig 2.

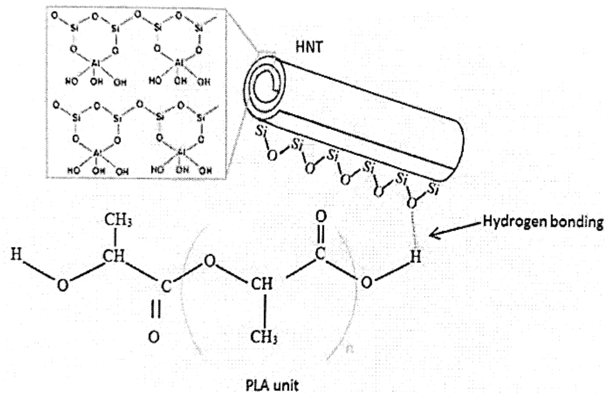

Fig 2. HNTs incorporation with PLA (De Silva et al. 2014)

Previous studies had shown that HNTs were affected for the improving mechanical properties of PLA. De Silva et al. (2014) synthesized PLA/HNTs bionanocomposite films including different concentrations of clay. Solution casting method was chosen to prepare the films. The films which were produced with 5 w/w % of HNTs had optimum results when compared with the other films results according to the tensile test (tensile modulus and strength) results. (De Silva et al. 2014).

In the present study, HNTs were leached for removing iron impurities and then were modified. In addition, HNTs were characterized using FT-IR, XRF and XRD. Furthermore, Solution casting method used to synthesis of PLA/HNTs bionanocomposite films and then their tensile properties were investigated.

2. Materials and Method

2.1. Materials

PLA was contributed by GEMApolimer. Density of PLA is 1.24g/cm^3, glass transition temperature (Tg) is in the 60 ^{o}C and melting temperature is 155 ^{o}C. Two HNTs types were supplied from different geological region, from Çanakkale, TURKEY. Chloroform, Hydrogen peroxide (H_2O_2, 34-37%), Oxalic acid and NaOH were purchased from Merck. Polyethylen glycol (liquid state) was provided from Sigma Aldrich.

2.2. Purification of Clay

Iron-containing halloysite clay (HNT-1) were purified using leaching method. HNTs were dissolved into 1 M oxalic acid solution. The solution with solid/liquid ratio 1:10 (g/mL) was stirred at 300 rpm and 80 °C, for 2.5 h After this slurry was filtered with distillated water until ph 3 and then dried 24 h at room temperature (Calderon et al. 2005; Akçıl and Tuncuk 2006). Consequently, HNT-2 was obtained.

2.3. Modification of Clay

30 gram of halloysite clays; HNT-2 and HNT-3 (untreated the other clay); was stirred in 30% hydrogen peroxide aqueous solution for 1 h. This aqueous solution was dispersed using by sonication probe for 10 min and then was centrifuged at 5000 rpm for 15 min. Solid phases were separated and were dried two steps gradually which are happened at 110 °C for 12 h in an oven and then at 60 °C in a vacuum oven for 10 h. The final products of HNTs were treated by sodium hydroxide. HNTs were dissolved in distillated water and then NaOH was added, and then obtained solution was magnetically stirred for 24 h at room temperature. The solution was centrifuged and rinsed with distillated water until the pH 7. In the last step, the HNTs treated by NaOH. Drying procedure which was mentioned above was repeated for the solution. Consequently, HNT-4 and HNT-5 were obtained (Zeng et al. 2014).

2.4.Synthesis of Bionanocomposite Films with PLA/Halloysite

Solution casting method was chosen to synthesis PLA/Halloysite films with some modification combining two methods used (De Silva et al. 2014; Risyon et al. 2020). Both PLA and halloysite were dried at 60 °C for 24 h before preparing films. Then, 4.25 gram PLA was dissolved in 85 ml of chloroform for 3h at 500 rpm. The blends of PLA/HNTs film were occurred by adding 2.5 w/w % of HNTs to PLA solution. In addition, 0.5 gram Polylethylene glycol was added and the solution was stirred for 1 h at 760 rpm. Thus, the blend was sonicated by ultrasonic probe for 20 min at 45 % amplitude.The solution was then cooled for 10 min at room temperature and was poured into petri dishes (diameter, 20 cm). The cast solution was dried at 30 °C for 72 h and then immersed in distillated water for 10 min before stripped from petri dishes. The previous steps were repeated with pure PLA (De Silva et al. 2014; Risyon et al. 2020).

2.5. Characterization

An infrared spectrum of halloysite which are untreated, leached and modified is characterized by using a Perkin Elmer Spectrum One Fourier transform infrared (FT-IR) spectrometer in the range of 4000-650 cm^{-1}.

The chemical analysis of halloysite which are untreated and leached was determined by X-ray Fluorescence (XRF) using a Panalytical MiniPAl4 spectrometer.

XRD patterns of the untreated halloysite was determined by Philips Panalytical X'pert-Pro X-Ray diffractometer, using Cu Kα radiation operated at 45 kV and 40 mA.

Tensile properties (tensile strength) of pure PLA and PLA/HNTs nanocomposite films were tested using universal testing machine (Zwick Z250Allround) based on

ASTM D882-18. 0.5 mm/s test speed was selected for entire tensile tests.

3. Results

3.1. FT-IR results

The obtained FT-IR absorption bands were given in Fig.3. The bands at 3695.61 and 3622.32 cm^{-1} corresponded to the characteristic O-H stretching of inner-surface and inner hydroxyl group. The band at 1645.28 cm^{-1} was attributed to H-O-H (adsorbed water) deformation. The O-H bending vibrations of the hydroxyl groups are observed at 908.47 cm^{-1} while the Si–O in plane stretching bands are observed at 1001.05 cm^{-1}. Also few functional peaks were observed at 1116.78 cm^{-1} as a perpendicular Si-O stretching. Al–OH vibrations of the surface hydroxyl groups are observed at 746.45 and 790.91 cm^{-1} (Saklar and Yorukoglu 2015; Saklar et al. 2012; Szczepanik et al. 2015).

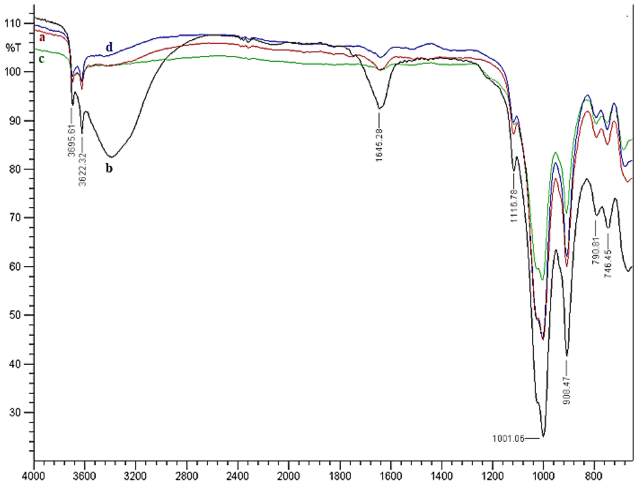

Figure 3. FT-IR spectrum of a) HNT-1, HNT-3 (untreated HNTs), b) HNT-2 (leached from HNT-1), c) HNT-4 (modified from HNT-2), d) HNT-5 (modified from HNT-3).

3.2. XRF results

The chemical analysis of halloysite was given in Table 1. The elemental composition was similar to the literature. Additionally, SiO_2 and Fe_2O_3 percentage has quite different between two untreated halloysite (HNT-1 and HNT-3) due to their region. Furthermore, XRF result of HNTs (HNT-2) showed that the leaching of HNTs (HNT-1) caused SiO_2, Al_2O_3 and Fe_2O_3 percentage decrease (Saklar and Yorukoglu 2015; Saklar et al. 2012).

3.3. XRD results

XRD pattern of halloysite which were untreated was illustrated in Fig.4. The XRD pattern of HNTs (HNT-1 and HNT-3) indicated the characteristic basal peaks of halloysite at 10 Å of halloysite. Furthermore, kaolinite also appeared at 12,43°. The peaks of minerals were quartz, hematite, kaolinite and meta halloysite as regard pattern (Tchakouté et al. 2020; Saklar et al. 2012; Szczepanik et al. 2015).

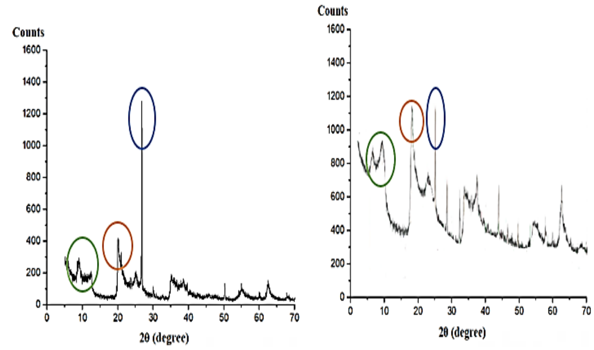

Figure 4. XRD patterns of untreated HNTs which were taken different region of TURKEY.

3.4. Tensile test results

Tensile strength test of pure PLA and PLA/ HNTs were given at Table 2. Tensile strength of all PLA/HNTs nanocomposites is higher than pure PLA. When compared two films which were prepared from halloysite, Tensile strength of PLA/HNT-5 (synthesis of HNT-5) is higher than PLA/HNT-4. This is because their iron oxide content is different. Moreover, HNT-5 has not been purified, just only modified from HNT-3 before starting to process of film so that it can be affected strength value.

Table 2. Tensile strength test result of neat PLA and 2.5 w/w % HNTs/PLA films

Materials	Tensile Strength MPa
Neat PLA Films	33.7
PLA/HNT-4	38.7
PLA/HNT-5	45.6

4. Discussion

In the present study, HNTs samples which were taken from TURKEY and contained iron impurities were leached using oxalic acid as a leaching agent. According to the XRF results, it was seen that, the iron oxide percentage: 61.62%, was reduced by leaching of HNT-1. Regarding to the FT-IR result, it can be said that HNTs had not been affected by the purification and modification procedures of clay. The tensile strength results of the films showed that halloysite addition increased successfully the strengths of film. The results are consistent with the literature.

Table 1. Chemical analysis of a) untreated HNTs (HNT-1), b) leached HNTs from HNT- 1 (HNT-2), c) untreated HNTs (HNT-3)

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	As_2O_3	SO_3	P_2O_5	Na_2O	Cl^-	LOI
a	60,23	32,81	4,169	0,621	0,534	0,485	0,362	0,227	0,186	0,16	0,12	0,057	0,044
b	53,07	21,87	1,6	0,58	0,58	-	0,28	0,3	0,6	-	0,25	0,0191	14,59
c	42,8	38,81	0,88	0,08	0,16	-	0,01	-	-	1,31	0,04	-	15,65

5. Conclusion

In this study, the effects of iron oxide content on the bond structure of clay were investigated. The entire treatment procedure did not affect the structure of HNTs and was confirmed by the literature. It was also aimed to investigate the effects of two different types of HNT on the tensile strength properties of PLA. According to the results of our studies; it was observed that the tensile strength values of films which were synthesis from clay were similar to each other and the films which produced from pure PLA without clay additive had the lowest value as expected.

Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for profit sectors.

Authors' contributions: S.B.K., N.T. and M.B.P. contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript

Conflict of interest disclosure:

The authors have no conflict of interest to study.

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