Preparation and Physical, Thermal Properties of Polycaprolactone/ m-Halloysite Nanocomposite

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Abstract- The modified halloysite (HNT) with 3aminopropyl-trimethoxysilane (APS) and 3glycidoxypropyl-trimethoxysilane (GPS) and nonmodified HNT were added to the polycaprolactone (PCL) matrices to prepare HNT PCL and m-HNT PCL nanocomposites via solvent casting method. The nanocomposite films with high transparency, similar to neat PCL films, were obtained without depending on the amount of added HNT. In this paper physical and thermal properties of PCL nanocomposites were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron microscope (SEM), fourier transform infrared spectroscopy (FT-IR), atomic force microscope (AFM) and drop shape analyzer (DSA). The results showed that the thermal stability of nanocomposite films could be improved due to a good interfacial interaction between the modified HNT and PCL matrix.

Keywords— Polycaprolactone, halloysite nanotube, nanocomposite, surface modification

I. INTRODUCTION

The scientists research to investigate biobased of product concerning related because to environmental issues in recent years. Particularly, plastic wastes attract attention due to rise directly proportional with global population [1]. Because of this reason, biodegradable polymers gain importance in last few decades [2]. Biopolymer nanocomposites can rapidly degrade and they can be produced from natural sources [1]. The main disadvantage of biodegradable polymers is their unsatisfied mechanical properties. Polymer/clay nanocomposites represent a new class of materials, which are synthesized to enhance the physical, thermal and mechanical properties of polymers [3-5]. Among the numerous biopolymers, polylactic acid (PLA), poly Llactide (PLLA) and poly(ɛ-caprolactone) (PCL) have been widely investigated.

PCL is commonly chosen as biopolymer matrix, because it can be easily processed and industrially available in the market. PCL is an excellent biodegradability and biocompatibility linear aliphatic

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polyester, which can be chemically synthesized by ring-opening polymerization of ε-caprolactone [4, 6]. It has also a low melting point (59-64°C), low glass transition temperature (-60°C) and has good solubility been widely PCL has considered [7]. for environmentally friendly packaging. medical applications, and pharmaceutical controlled release systems [8]. However, there are several factors holding back the progressive development and applications of PCL. The main reason of limited usage of PCL is insufficient physical, thermal and mechanical properties [9]. To reduce the restrictions of PCL, one of the cheapest environmentally and efficient alternative is to integrate nanofillers to produce nanocomposites [10]. Recently, different types of PCL nanocomposites have been researched. In study of Ahmed et al., PCL was combined with bentonite solvent bv casting method and nanocomposites were prepared. As a result, Tg temperature of the material by adding more clay was not observed but there was an increase in temperature Tm and Tc [11]. In study of Fukushima et al.; montmorillonite and sepiolite were dispersed with PLA and PCL by using melt mixing method. Because of the montmorillonite and sepiolite good distribution in the PLA and PCL matrix, improvement in thermomechanical properties was observed [12]. Taghizadeh et al. investigated physical properties of carbon nanotube (CNT) PCL and thermoplastic starch nanocomposites by melt blending method. The results underlined the importance of the process conditions of adding nanotubes [13]. Clay minerals have played a remarkable role in the recent developments of improved hybrid systems [14]. Halloysite (HNT) is a type of naturally occurring clay mineral with a chemical composition similar to kaolin having chemical formula Al₂Si₂O₅(OH)₄.2H₂O. The HNT dispersion in the polymer matrix is easier. Thanks to this feature, it is used to reinforce

mechanical and thermal properties of polymers [8, 15]. In recent years, various types of modified HNT polymer nanocomposites have been reported. *Moslehyani et al.* were investigated to gain antibacterial properties to HNT/PVDF nanocomposite membranes. HNTs were modified by silver lactate and N- β -(aminoethyl)- γ -aminopropyltrimethoxy silane. Produced nanocomposite membrane showed a great

potential for antibacterial applications [16]. *Deng et al.* were studied surface treatments with potassium acetate, Z-6020 silane and cetyltrimethyl ammonium chloride were conducted to obtain halloysite–epoxy nanocomposites with improved homogeneity of HNTs in the epoxy matrix and enhanced mechanical performance-of the nanocomposites [17]. *Zhong et al.* studied that HNTs was modified by N-cyclohexyl-2benzothiazole sulfanamide (CZ) (HNTs-s-CZ) and the vulcanization degree and mechanical properties of styrene-butadiene rubber (SBR) nanocomposites were improved [18].

Unlike the literature on montmorillonite-based nanocomposites, halloysite-based nanocomposites have been relatively less studied. Therefore, the aim of this study was to characterize the physical and thermal properties of PCL nanocomposites containing modified/non-modified HNT. Two different surface modifiers were used. The HNT PCL nanocomposites were prepared by solvent casting technique. The prepared m-HNT/HNT PCL nanocomposites may provide wide range of various structural and functional applications such as packaging, biomedical, and many more fields.

II. EXPERIMENTAL

A. Materials

Polycaprolactone, halloysite nanotubes and chloroform were supplied by Sigma-Aldrich. 3-Aminopropyl-trimethoxysilane (APS) and 3-Glycidoxypropyl-trimethoxysilane (GPS) were purchased from Sigma-Aldrich. PCL and HNT were dried for 2 h under vacuum at 70 °C.

B. Surface modification of halloysite nanotube

The surface of halloysite nanotube (HNT) was modified by 3-Aminopropyl-trimethoxy silane (APS) and 3-Glycidoxypropyl-trimethoxy silane (GPS) by using chloroform as a solvent. Firstly, 2 ml of APS dissolved in 30 ml chloroform. 2 g HNT was added into the solution and stirred in an ultrasonic bath at room temperature for 1 hour. Stirring this mixture by using magnetic stirrer for 6 hours at 120°C is provided to evaporate chloroform. ASP-HNT was filtered and washed 3 times with chloroform and dried in a vacuum oven at 120°C for 24 hours. The same procedure was repeated by using GPS.

C. Preparation of HNT PCL, APS-HNT PCL and GPS-HNT PCL nanocomposite films

Solvent casting technique was used to prepare HNT PCL, APS-HNT PCL and GPS-HNT PCL nanocomposite films. PCL was dissolved in chloroform to produce an initial polymer weight to solvent ratio of 5% (w/v). The polymer solution was stirred until dissolve completely. Simultaneously, clay solution was prepared by dissolving HNT, APS-HNT and GPS-HNT in chloroform. Desired amount of clay solution was added to polymer solution to prepare nanocomposite mixtures with various amounts (1 and 5 wt.%). Afterwards, each mixture was sonicated for 1

h in ultrasonic bath at room temperature to improve the dispersion of HNT in the polymer solution. Finally, the solutions stirred by using magnetic stirrer for 1 h. Every mixture was casted onto the petri dishes and put in vacuum oven at room temperature for more than three days to remove solvent.

D. Characterization of nanocomposite films

Modified and non-modified HNT nanocomposite films were studied by FTIR spectroscopy. FTIR spectra were collected with a Perkin Elmer FT/IR-480 instrument. The spectra were recorded from 4000 to 600 cm⁻¹.

Thermal properties of PCL and various PCL/HNT nanocomposite films were studied by DSC and TGA. Differential scanning calorimeter (DSC) measurements were carried out a Perkin Elmer DSC 8000 in the heating process from -90 °C to 200 °C at a heating rate of 10°C/min. The glass transition temperature (T_g), melting temperature (T_m) and melting enthalpy (ΔH_m) were measured. Crystallinity of the PCL was calculated using the following equation [19]:

Crystallinity of PCL (%) =
$$\left[\frac{\Delta H_m}{139.6}\right] \times 100$$
 (1)

where ΔH_m is the melting enthalpy (J/g) that was calculated from the fusion peak in DSC curve. The theoretical enthalpy of completely crystalline PCL is 139.6 J/g [19]. TGA (Perkin Elmer Diamond) was used to determine the thermal stability of nanocomposite films. The measurements were performed at heating rate of 10°C/min from 25°C to 600 °C.

Surface wetting properties of the nanocomposites were assessed by measuring water contact angles using a drop shape analyzer (Krüss DSA 100). The contact angle measurement was carried out via the sessile drop method. The values of water contact angle and the image were acquired in 5 s after dropping of a distilled water drop about 10 μ L at room temperature. Three readings were averaged to obtain the most representative contact angle value for each sample.

The surface topography of the nanocomposites was measured by atomic force microscopy (AFM; XE-100E instrument).

The cross-section morphologies of all the samples were observed using a scanning electron microscopy (SEM). The surfaces of nanocomposites were plated with a thin layer of gold palladium before inspection under SEM. The SEM observations were conducted with JEOL JSM-7001FTTLS LV SEM machine.

III. RESULTS AND DISCUSSION

A. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra of HNT, APS-HNT and GPS HNT are shown in Figure 1. According to the FT-IR spectrum of HNTs, the peaks at 3692 cm⁻¹ and 3620 cm⁻¹ are correlated with the stretching vibrations of inner surface hydroxyl groups. Interlayer water is indicated by the bend in vibration at 1652 cm⁻¹. The 1115 cm⁻¹ peak is attributed to the Si-O bonding. The peak at 909 cm⁻¹ is assigned to the bending vibration of AI-OH. The peak detected at 539 cm⁻¹ and 466 cm⁻¹ ¹ is the bending vibrations of Al-O-Si and Si-O-Si, respectively [20, 21]. Compared with neat HNT and APS-HNT reveals some new FT-IR peaks. The peak at 1557 cm⁻¹ is attributed to the N-H bending vibration. The 2927 cm⁻¹ peak is assigned to the vibration of CH₂ Also, APS-HNT shows a decrease in the intensity of the OH vibration (3621 cm⁻¹). All of these observations point out that APS-HNT is prepared successfully. Compared the neat HNT and GPS-HNT exhibits some new peaks also. The peaks discovered at 2942 cm⁻¹ is CH₂ vibration. Epoxide ring deformation was observed at 907 cm⁻¹. The appearance of this peak revealed that GPS has been attached onto the surface of HNT.





Figure 2, Figure 3 and Figure 4 show that the FT-IR spectra of PCL nanocomposites. In the case of neat PCL, the peak 1720 cm⁻¹ shows that carbonyl stretching vibration (C=O). The others important peaks are given as follows: C-H vibration at 2919 cm⁻¹, C-O vibration at 1241 cm⁻¹ and C-C vibration at 1473 cm⁻¹ [22]. A comparison between neat PCL and HNT/PCL nanocomposites showed that a peak at 961 cm⁻¹ and it is vibration of AI-OH. While HNT ratio increases in nanocomposites, the area of the peak increases. Thus, it is shown that HNT is participated in PCL.



Fig 2. FT-IR spectra of (a) neat PCL, (b) 5%APS-HNT PCL and (c) 5% GPS- HNT PCL



Fig 3. FT-IR spectra of (a) neat PCL, (b) 1%APS-HNT PCL and (c) 5% APS- HNT PCL



Fig 4. FT-IR spectra of (a) neat PCL, (b) 1%GPS-HNT PCL and (c) 5% GPS- HNT PCL

B. Thermal Analysis

1) Differential Scanning Calorimetry (DSC) DSC curves are given in Figure 5. Polycaprolactone (PCL) is a semi crystalline polymer with a crystallinity of around 45%. The crystallinity of neat PCL is 44.9%, this ratio increased HNT to 57.5% with the addition of HNT. It means the addition of HNT increased the regularity. Thermal structural and crystalline properties of neat PCL and nanocomposites are given in Table 1. As shown in Table 1, the melting points (T_m) of PCL/HNT nanocomposites were higher than neat PCL. This increase is due to removal of the polymer chain by introducing HNT nanoparticles into the structure. The increase of the melting enthalpy values confirms the increase in melting temperature.



Fig 5. DSC curves of PCL and PCL/HNT nanocomposites

TABLE I.	THERMAL AND CRYSTALLINE PROPERTIES OF NEAT PCL
AND THE NANOG	COMPOSITES

TABLE II. THE DEGRADATION TEMPERATURES OF NEAT $\ensuremath{\mathsf{PCL}}$ and nanocomposite films

Sample	T _m (°C)	ΔH (J/g)	Xc (%)
PCL	65.5	62.7	44.9
%1 HNT PCL	65.7	79.0	56.6
%5 HNT PCL	66.1	80.2	57.4
%1 APS-HNT PCL	66.8	68.8	49.3
%5 APS-HNT PCL	66.0	74.8	53.6
%1 GPS-HNT PCL	67.2	32.7	23.4
%5 GPS-HNT PCL	68.4	34.2	24.5

2) Thermal Gravimetric Analysis (TGA)

Figure 6 illustrates TGA curves of neat PCL and nanocomposites films. TGA curve of neat PCL and nanocomposite films showed a single and continuous weight loss.



Fig 6. TGA curves of neat PCL and PCL nanocomposites

The first weight loss is at about 370°C. The neat PCL has first degradation temperature 375°C. When the clay has been added to the polymer, the last degradation temperature decreased from 428 °C for the neat PCL to 410 °C for 5% HNT PCL. The most decreased occurred about 18 °C by the 5% HNT added. The first and last degradation temperatures of the 5% HNT PCL were found 365 °C and 410 °C, respectively. The last degradation temperature was not observed a regular change with the addition of clay. Table 2 shows that the first and last degradation temperatures of neat PCL and nanocomposite films. The addition of non-modified and modified HNT nanoparticles into PCL increased the residual weight of nanocomposites at high temperature (600 °C) as listed in Table 2.

	First		Last	
Sample	Degradation	T50%	Degradation	Residue
	Temperature	(°C)	Temperature	(%) (at
	(°C)		(°C)	600°C)
Neat	375.06	415.02	428.13	1.029
PCL				
%1 HNT	371.16	409.12	413.82	2.240
PCL				
%5 HNT	365.20	407.62	410.06	2.215
PCL				
%1 APS-	373.78	412.30	429.35	N/A
HNTPCL				
%5 ASP-				
HNT	370.0	400.28	425.53	5.485
PCL				
%1 GSP-				
HNT	372.15	410.20	425.78	N/A
PCL				
%5 GSP-				
HNT	367.80	398.34	426.04	3.321
PCL				

C. Morphology of Nanocomposites

1) Scanning Electron Microscope (SEM)

To understand the changes PCL mechanical and physical performance by adding HNT, the surface structure of the HNT-PCL nanocomposites were observed by SEM. All of images of neat PCL and nanocomposites were given in Figure 7.



(c) (d) Fig 7. SEM images of (a) neat PCL, (b) %5 HNT–PCL, (c) %5 APS– HNT–PCL, (d) %5 GPS– HNT–PCL nanocomposite films

The neat PCL showed a smooth and ordered morphology of surface. SEM results exhibits that dispersed in uniformly of HNTs in the PCL matrix. The well dispersion of HNT in polymer could be attributed to the tubular morphological character of HNT and the relatively weak tube-tube interactions made them easy to be dispersed in polymers by shear forces [23]. They show a greater amount of bead formation [24]. No aggregates could be observed in the sample.

2) Atomic Forced Microscope (AFM)

Figure 8 shows the AFM images of the surface topography of neat PCL and nanocomposites. As seen from the Figure 8-b, the addition of 1% HNT to PCL has not very influenced to structure. Homogeneous or sequential plate could not be observed. In Figure 8-d, addition of 5% HNT to PCL plates are intertwined and surface modification with APS enter the space between this plate and has provided better binding between molecules of HNT and polymer bond. Consequently, it has been improved has good mechanical properties and homogeneous polymer composite.



Fig 8. AFM 3D images 5x5 of (a) neat PCL, (b) %1 HNT–PCL, (c) %1 APS–HNT–PCL, (d) %5 HNT–PCL, (e) %5 APS–HNT–PCL, (f) %1 GPS–HNT–PCL and (g) %5 GPS–HNT–PCL

Theoretically, adding clay changes the morphology of polymer matrix and increased the surface homogeneity. Table 3 summarizes the surface roughness values of neat PCL and nanocomposites. According to these data, neat PCL is the smoother surface structure than nanocomposites. The roughness of surface increases by increasing percentage of HNT in nanocomposites. These results which obtained by atomic force microscopy confirmed theoretical expectations.

TABLE III. SURFACE ROUGHNESS OF NEAT PCL AND NANOCOMPOSITES $% \left({\left| {{{\rm{CL}}} \right.} \right|_{{\rm{CL}}}} \right)$

Sample	R _z * (nm)	Ra** (nm)
	10.0	
Neat PCL	49.9	7.6
%1 HNT PCL	286.6	48.4
%5 HNT PCL	216.1	44.9
%1 APS HNT PCL	63	13.0
%5 APS HNT PCL	51.9	12.6
%1 GPS HNT PCL	291	96
%5 GPS HNT PCL	381	250

D. Surface Wettability Properties of Nanocomposites (DSA)

All the water contact angles of the neat PCL and its nanocomposites are given in Table 4. Results of contact angle measured with water shows that adding of HNT in PCL increased the hydrophilicity of nanocomposites (decrease in contact angle). With increase in HNT ratio in nanocomposites, the surface of nanocomposite films became more hydrophilic. The change in the ratio of C=O or C-O bonds is an important factor affecting the hydrophilicity of PCL [25]. Also, it has hydrophilic property gained by -OH groups in the HNT structure. As the contact angle increases, the level of C=O bonds tends to decline.

TABLE IV.	CONTACT	ANGLES	OF	WATER	ON	THE	SURFACES	OF
NEAT PCL AND	NANOCOM	POSITES						

Sample	Contact angle, Θ, (deg.)
Neat PCL	87.6±0.44
%1 HNT PCL	82.8±0.32
%5 HNT PCL	77.0±0.08
%1 APS HNT PCL	88.2±5.04
%5 APS HNT PCL	73.9±0.28
%1 GPS HNT PCL	63.5±2.29
%5 GPS HNT PCL	63.7±0.78

Figure 9 and Figure 10 shows that contact angle values of nanocomposite films decreased when compared with neat PCL. The contact angle value of 5% APS HNT PCL (73.9°) nanocomposite shifted to lowest value according to neat PCL (87.6°). The reason of decline is amino groups in the structure of APS. Also, the contact angle value decrease from 87.6° to 63.5° by adding GPS HNT in PCL matrix.

These results indicated that adding modified HNT can improve the hydrophilicity of PCL significantly.



Fig 9. Contact angle images of water on (a) neat PCL, (b) %5 HNT–PCL, (c) %5 APS–HNT–PCL and (d) %5 GPS–HNT–PCL



Fig 10. Contact angles of water on the surface of neat PCL and nanocomposites

IV. CONCLUSIONS

This investigation focused on the physical, thermal and morphological properties of PCL nanocomposites by preparing solvent casting method. The PCL matrices were implanted with two different concentrations of HNT (1 and 5%). HNT was successfully modified with 3-Aminopropyl-trimethoxy silane and 3-Glycidoxypropyl-trimethoxy silane. As seen SEM results, HNTs were uniformly dispersed into the PCL matrices due to effective surface modification of HNT. Adding HNT, APS-HNT and GPS-HNT into the polymer matrices improve the hydrophilicity of PCL significantly. Especially, the contact angle of 5% APS HNT PCL (73.9°) nanocomposite has lower value according to neat PCL (87.6°). On the other hand, adding GPS-HNT decrease the contact angle from 87.6° (neat PCL) to 63.5° (1% GPS HNT PCL). According to the DSC results, the crystallinity value increased from 44.9% (neat PCL) to 57.7% (5% HNT PCL). Also, the melting point of nanocomposite increased by adding HNT from 65.5°C (neat PCL) to 68.4°C (5% GSP HNT PCL). Based on TGA results, the first degradation temperature of neat PCL is 375 °C. Adding HNT decreased this temperature to 365°C (5% HNT PCL). According to AFM results, the roughness of surface increases by increasing percentage of HNT in nanocomposites. For neat PCL this data is 49.9 nm, for 5% GPS HNT PCL is 381 nm. As a result, thermal and physical properties of HNT/m-HNT PCL nanocomposites were improved compared to neat PCL. The prepared HNT/m-HNT PCL nanocomposites may provide wide range of various structural and functional applications such as packaging, biomedical, and many more fields.

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