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Preparation of poly(lactic acid) based biocomposites with poly(ethylene glycol) and montmorillonite clay by solvent casting method

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ABSTRACT

Poly(lactic acid) is one of the most widely used bioplastics. PLA is derived from lactic acid monomer which is produced by fermentation using microorganisms. It is renewable, biodegradable, biocompatible, and low-cost aliphatic thermoplastic bioplastic. However, it displays low barrier properties to use packaging applications compared with conventional polymers. PLA has brittle, low toughness, and low thermal resistance properties. To improve the weak properties of PLA, copolymers of lactic acid are synthesized or blends of PLA with other synthetic and biodegradable polymers are prepared. PLA has been used as mulching films, biomedical devices, packaging, and membrane materials. In this study, PLA films were prepared by solution casting method using a high shear mixer for 90 sec. PLA films were blended with different concentrations of poly(ethylene glycol) (PEG) and Montmorillonite (MMT). Properties of mechanical, thermal, and optic of biodegradable films were determined using mechanical testing machine Zwick Z 1.0 kN, thermogravimetric analysis, differential scanning calorimetry (DSC), and optical microscopy, respectively.

I. INTRODUCTION

Biodegradable polymers can be produced by microorganisms, animals, and plants naturally besides petrochemical resources [1, 2]. They are important because of environmental and economic interests [3, 4]. Poly(lactic acid) (PLA) is a renewable and biodegradable polymer that is used in different areas as packaging, automotive, and disposal parts [5]. It has been used in the medical industry and tissue engineering for drug releasing immobilization material and implants, biodegradable mulch, and coating, and releasing fertilizer and pesticides for agricultural application [4, 6–9]. Blend and composites of PLA are employed to enhance mechanical and thermal properties. [10, 11]. Polymer composite and blends have been used to enhance mechanical, thermal, and rheological properties [12]. Zeolites also have been used for active packaging applications because of their oxygen consumption abilities [13, 14]. Erpek et. al. studied with halloysite (HNT), carbon nanotubes (CNT), thermoplastic polyurethane (TPU) with PLA. The tensile strength of the PLA increased with CNT, however, decreased with HNT. PLA was toughened by TPU [15]. Wu et. al. prepared biodegradable PLA/MMT nanocomposites using the solution casting method. Chitosan was used to increase the chemical connection between the PLA and MMT [16]. PLA and chitosan composite films were studied by Sebastien et. al., to enhance bio-based and antifungal packaging film [17]. Varying chemicals have been investigated to plasticize PLA such as citrate esters to prevent the fragility of PLA [18]. The plasticization of PLA with triacetin [19], glycerol [20–23], sorbitol [23, 24], acetyl triethyl citrate [24–27], acetyl(tributyl citrate) [28–30] were reported in the literature. In this study, PLA was plasticized with

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PEG400 to enhance flexibility. In addition, Montmorillonite was used to increase the mechanical properties of PLA.

II. EXPERIMENTAL METHOD

2.1 Materials and Preparation Techniques

4032 D grade Ingeo PLA was obtained from Resinex from Turkey. Montmorillonite was obtained from Sigma-Aldrich. Dioxane and Poly(ethylene glycol) (PEG400, Mw=400 g/mol) were bought from Merck and ZAG respectively. All chemicals were used without further purification.

PLA was dissolved in dioxane and mixed different concentrations of Montmorillonite (MMT) using by high shear mixing apparatus (Mazerustar KK-2503). MMT-based biodegradable films were prepared with solution casting method with MMT and PEG in PLA matrix. PLA was prepared at 10% (w/v) concentration in dioxane. PEG400 was added to polymer solution at different concentrations such as 5%, 7.5%, and 10% (w/v) with respect to the contents of the polymer matrix. PLA/PEG400 was blended by a magnetic stirrer at room temperature. PLA/PEG blend was cast on the glass flat surface by a manual film applicator.. This film was then immediately immersed in an ethanol/water coagulation bath for phase inversion separation. Films were incubated in a coagulation bath for 2 hours and dried at room temperature for 24 hours.

III. RESULTS AND DISCUSSIONS

Biodegradable and miscible blends are consisting of PLA and PEG. The tensile strength value of PLA/PEG blends decreases with increasing PEG content. PEG increases with interfacial adhesion and reduces the Tg of the polymer [31]. PLA displays brittle and low thoughness material properties [32]. PLA was blended with PEG400 to increase flexibility in this study. PLA exhibits low strain properties in Table 1. PLA/PEG blend films have higher elongation values than PLA. As shown in Table 1, the brittleness of PLA in PEG/PLA blend films was reduced by PEG 400. In this study, improving poor properties of PLA, PLA blends and composites were prepared with PEG400 and MMT, respectively by using high shear mixing apparatus.

Table 1. Mechanical properties of PLA/PEG blend films

Sample	Tensile Strenght (MPa)	Elongation at Break (%)	Young Modulus (GPa)
Neat PLA	30.72	10.28	2.98
PLA 95%/PEG 5%	28.20	60.27	0.47
PLA 92.5%/PEG 7.5%	24.99	106.37	0.3
PLA 90%/PEG 10%	20.41	39.82	0.51

The mixing of hydrophobic polymers with hydrophilic polymers has been used to grow the hydrophilicity of the polymer matrixs, and enhance their anti-fouling properties [33]. The PLA/PEG blends were studied using a twin-screw extruder by melt blending method with different concentration and molecular weight PEG. Li et al. reported that the tensile stress at break of the PLA/PEG 10,000 blend significantly increased when the PEG 10,000 content was 5-15% by weight, and then decreased when the PEG 10,000 content exceeded 15% by weight [34].

The addition of plasticizer to modify PLA is a method that is used widely in the plastics industry with respect to thermoplastic materials such as PLA. The addition of plasticizers to the matrix should meet several necessary requirements. In addition to improving the deficiencies mentioned previously, it is essential to retain the main properties. The compatibility of the plasticizers with polymers should be evaluated. In addition, they should hardly migrate toward the surface of the polymer matrix to amplify the plastic effects and increase the longevity

PLA/PEG blend films have higher elongation values than PLA. Brittleness of PLA was gradually disappeared with PEG400 at PEG/PLA blend films and was obtained tough structures. PEG decreased young modulus of the blends films due to lowering stress values and low strain properties as shown in Table 1. Effects of some plasticizer were summarized and compared our results in Table 2. Plasticizers enhanced the elongation at break and elasticity of PLA blend films.. PLA is a brittle material with low toughness PLA shows low strain properties. PLA/PEG blend films have higher strain and elongation than PLA in Fig. 1. In addition, 92.5-7.5% wt PLA-PEG films displayed a higher elongation value than PLA/PEG-5%, and PLA/PEG-10% films. Up to a certain extent, the additive of PEG improved the mechanical properties of PLA. However, the addition of 10% by weight PEG exhibited the lowest mechanical properties. The best mechanical properties were achieved in 7.5% PEG added PLA film. Chieng et. al. studied with 10% wt PEG200 content to plasticize PLA by the melt blending process. They reported 29.76, 413.1, and 424 values for tensile strength (MPa), elongation (%), and tensile modulus (MPa) [35].

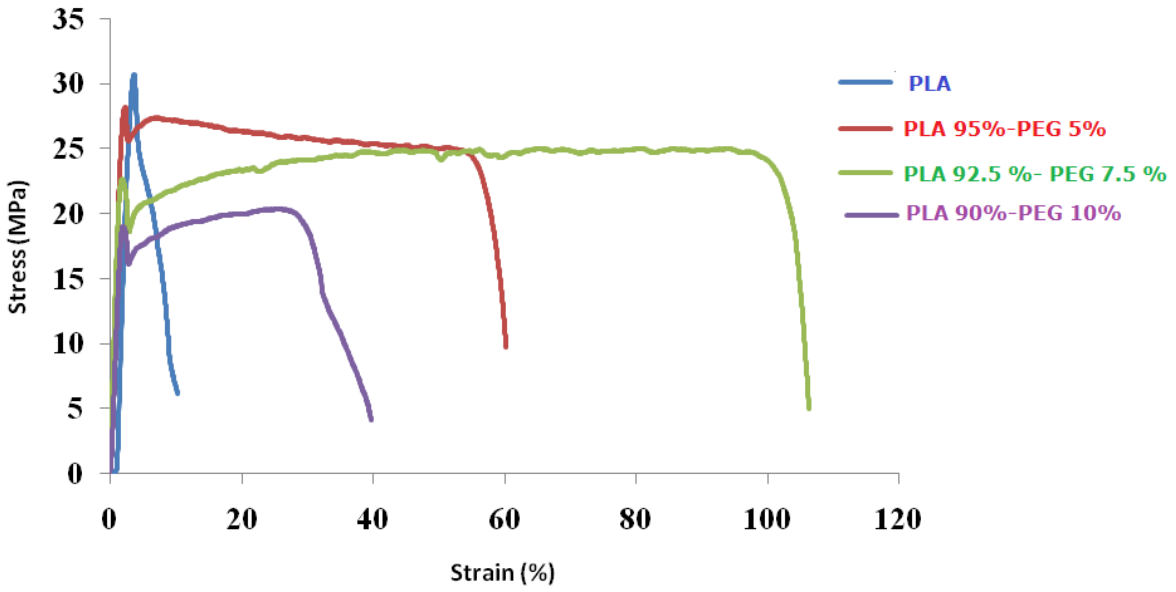

Figure 1. Strain-stress curves of PLA and PLA/PEG blends

PLA films have higher stress values but does not show high elongation values in Fig. 1. This brittleness of PLA disappeared with PEG200 at PEG/PLA blend films and obtained a tough structure. PEG decreased the young modulus of blend films with lowering stress values as shown in Table 1.

Table 2. Comparison obtained results with the literature

Sample	T_g (°C)	Modulus (GPa)	Elongation at break (%)	Ref.
PLA	58	2.050	9	[36]
Neat PLA	64.4	2.98	10	This study
PLA90%/10% OLA	37	1.256	32	[36]
PLA 95%/PEG 5%	n.d	0.47	60	This study
PLA 92.5%/PEG 7.5%	n.d	0.3	106	This study
2PLA 90%/PEG 10%	n.d	0.51	40	This study
PLA90%/10% PEG400	30	1.488	26	[36]
PLA80%/20% PEG400	19	0.5	71	[37]
PLA80%/20% PEG10 KDa	34	0.7	130	[37]
PLA80%/20% ATBC	24	0.1	298	[37]
PLLA 80%/Starch 20%	59	2.8	2.5	[38]
PLLA 80%/ Starch 20% + 5% PEG400	49.4	1.1	3.0	[38]
PLLA 80%/ Starch 20% + 5% Gycerol	49.9	0.7	4.7	[38]
PLLA 80%/Starch 20% + 5% Laurly alcohol	47	1.5	1.5	[38]

PEG400: Polyethylene glycol. ATBC: Acetyl tributyl citrate. OLA: oligomeric lactic acid n.d: not defined

As the concentration of PLA in the solution increased from 5% to 10%, the melting point increased from 168.9 to 169.1. With the increase in the concentration of the polymer in the solution, there was no significant change in the increase in the melting point. Adding MMT to PLA increased the melting point of PLA (5%wt)-MMT (0.01%) PLA (5%wt)-MMT (1%) PLA from 167.9 to 168.9 °C.

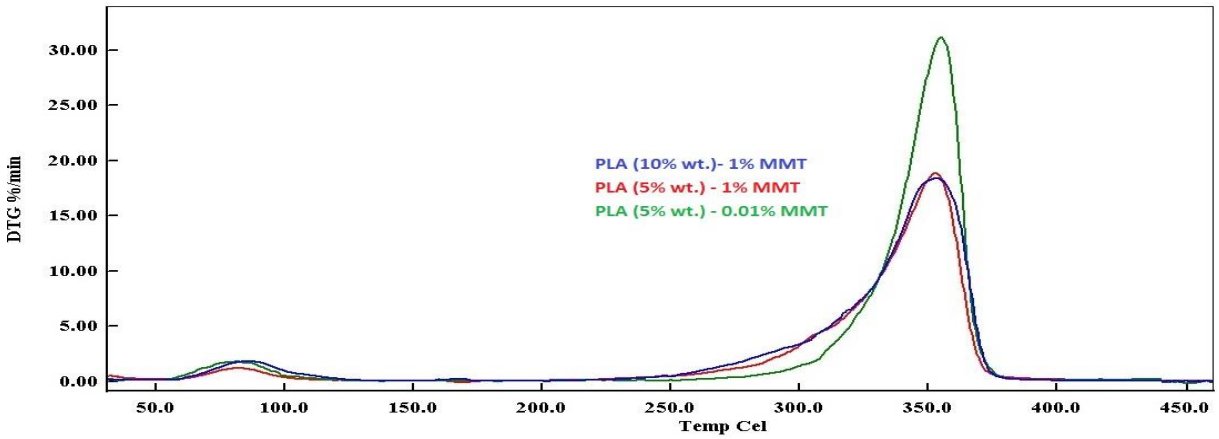

Figure 2. TGA results of PLA (10% wt.)- MMT (1% wt.), PLA (5% wt.)-MMT (1%), PLA (5%)-MMT 0.01%)

As seen in Fig. 3, the PLA concentration of 5% or 10% in the PLA solution did not affect the degradation rate of PLA. Increasing the concentration of MMT in solution from 0.01% percent to 1% decreased the degradation rate of PLA and provided thermal stability.

Table 3. Mechanical properties of PLA-MMT composites

Sample	σ_{low} MPa	σ_{high} MPa	E_t MPa	σ_M MPa	ε_M %	σ_B MPa	ε_B %	ε_{tB} %
PLA (5% wt.)-1% MMT	0.44	1.23	386.45	6,22	1.35	6.22	1.35	1.35
PLA (5% wt.)-0.01%MMT	0.45	1.50	480.15	65,63	3.15	65.63	3.15	3.15
PLA (10% wt.)- 1% MMT	0.48	1.58	546.49	16,65	2.71	15.95	2.61	3.07

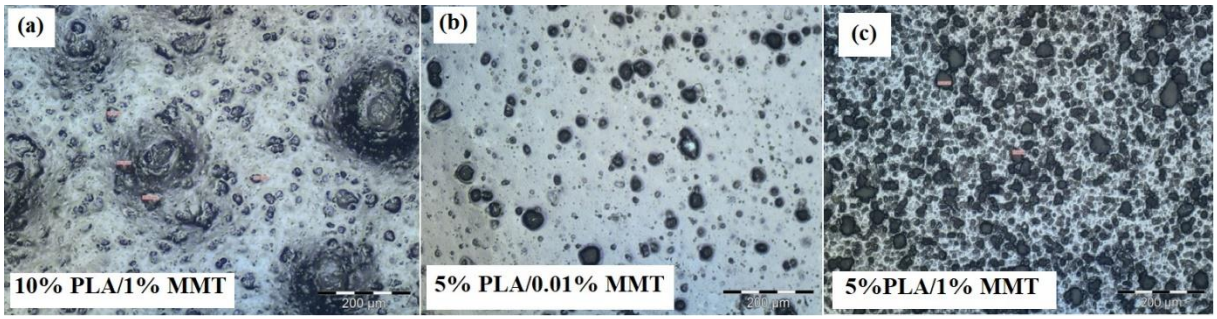

Figure 3. Optical Microscopy images of PLA composites with different amounts of PLA and MMT; a) PLA (10%wt.) and MMT (1%), b) PLA (5%wt.) and MMT (0.01%), c) PLA (wt5%) and MMT (%1)

As seen in Figure 3, it is seen that as the concentration of PLA in the solution increases, the agglomeration is higher (10% by weight of PLA), agglomeration decreases as the polymer concentration decreases to 5% and the blends are mixed more homogeneously. In addition, As seen in Fig 3, more homogeneous distribution was obtained with the addition of 1% of MMT to PLA.

In Fig. 3, 10% PLA (w/w) was prepared high content 1% MMT concentration. The high content of MMT caused to agglomeration of particles. Homogeneous distribution is more difficult espacially at high concentrations of the MMT particles than low concentration such as 5% (w/w) PLA and 0.01% MMT. PLA has studied with higher molecular weight PEGs [34] and low molecular weight PEG200 [35] in the literature. But the blend of PEG 400 did not studied in our knowledge. The high molecular weight of PEG will reduce the diffusion of PEG plasticizer from the amorphous phase into the polymer solution [35]. Therefore, low molecular weight PEG was preferred.

IV. CONCLUSIONS

Blend and composites of PLA are employed to enhance mechanical and thermal properties. PLA blends and composites were prepared with PEG400 and MMT respectively in this study to improve mechanical properties of PLA. xOnce developing new methods for PLA synthesis and decrease the cost, biodegradable and synthetic PLA blends will be commonly used in agriculture and packaging industry. In addition to this PLA, composites are suitable for other areas such as medical, tissue engineering and automobile industries. Finally, PLA will gain wide acceptance for different applications instead of polyolefins and polyethylene terephthalate. Biodegradable blends and composites of PLA are predicted to be used more and more today than petroleum-derived polymers for potential applications in the future.

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