ISSN: 0067-2904
GIF: 0.851

Study of Mechanical, Thermal and Barrier Properties of Biodegradable Polylactic acid-Polyethylene Glycol- Alumina Nanocomposite

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Abstract

Tensile , thermal, and barrier properties of polylactide PLA-based nanocomposite films that were prepared by solvent casting method with polyethylene glycol (PEG), and alumina were studied. PLA/PEG blend showed decrease in tensile strength and Young modulus but increased in elongation in PLA/PEG and increased in crystalline of PLA but decrease in glass transition temperature with the increasing of PEG concentration . A nano blend composites of PLA/PEG/alumina (50/50/4) when compared to PLA/PEG blend indicated that tensile strength , Young modulus and glass transition temperature (Tg) increased with adding alumina nano particles, concentration and barrier properties improvement due to its nucleating and reinforcing function mineral when add nano alumina to PLA/PEG blend . These results indicated that the incorporation of Al_2O_3 enhanced the Oxygen barrier properties of the PLA.

Keywords: PLA, PLA/PEG blend , PLA/PEG /Al_2O_3 nanocomposites .

دراسة الخصائص الميكانيكية والحرارية والحجزية لمتراكب بولي لاكتك اسيد–بولي اثلين كلايكول – الومينا

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الخلاصة

تم دراسة كل من خصائص الشد والحرارية والحجزية للمتراكب بولي لاكتك اسيد التي تم تحضيرها بطريقة الاذابة مع البولي اثلين كلايكول ودقائق الالومينا النانوية . اظهرت خلائط بولي لاكتك اسد والبولي اثلين كلايكول نقصان في متانة الشد ومعامل يونك وزيادة في الاستطالة الحاصلة وكذلك زيادة في التبلور بينما قلت درجة الانتقال الزجاجي مع زيادة تركيز PEG (البولي اثلين كلايكول) في الخلطات . في المتراكب بولي لاكتك اسيد –بولي اثلين كلايكول –الومينا (50/50/4)عند مقارنتة مع خليط بولي لاكتك اسد والبولي اثلين كلايكول ازدادت متانة الشد ، معامل يونك ودرجة الانتقال الزجاجي عند اضافة دقائق الالومينا النانوية والخصائص الحجزية تحسنت نتيجة التنوي واضافة مواد نانوية الى الخليط . هذه النتيجة بينت ان اضافة الالومينا النانوية اثر على خصائص حجز الاوكسجين للبولي لاكتك اسيد .

1-Introduction

Over the last decades, there has been growing needs to find alternatives to petroleum-based plastics because of environmental concerns. Plastic waste becomes a serious problem because of its low weight-to-volume ratio and its inalterability over very long time duration. Today, incineration is a common method to get rid of polyolefin's, but this unfortunately leads to high emission of CO_2. One

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approach for solving this problems is to use biodegradable materials instead of non-renewable polymers, e.g. in packaging. These materials have the potential to reduce environmental pollution by lowering solid disposal waste and reducing the need for incineration [1]. PLA is a linear aliphatic thermoplastic polyester, produced from renewable resource and readily biodegradable. However, some disadvantageous properties retain PLA potential application in film manufacturing. In this way, PLA plasticization is required to improve PLA ductility. Poly ethylene glycol (PEG) has been used as PLA plasticizers. Nevertheless, the addition of plasticizers increases the PLA thermal stability and elongation, which is detrimental for food packaging use. Plasticizer lowers Tg and makes material more flexible because plasticizer interacts with the polymer chains on the molecular level as to speed up its visco-elastic response (or increase chain mobility [2,3].

The plasticizer should be miscible with PLA, thus creating a homogeneous blend and should not be too volatile because this would cause evaporation to occur at the elevated temperatures used at processing. Furthermore, the plasticizer should not be prone to migration because this would cause contamination of the materials in contact with the plasticized PLA and cause the blended material to reduce the brittleness of pure PLA. In addition, incorporation of plasticizers has many limitations including too low Tg may not be suitable for processing and molding; and migration to surface, which may be unsuitable for food packaging [4,5]. To improve barrier properties for shelf life of the foods it can be done by several approaches such as blending, or nanofillers addition, several nanoparticles are used such as nanoclays, aluminum oxide. However, to achieve the mentioned positive effects of nanoparticles on properties, adequate dispersion of nanofillers within the polymeric matrix is required. However, different parameters like polymer type and morphology, type and size of nano fillers, the interaction of nano fillers with the polymeric matrix and its volume content could influence the characteristics of nanocomposites[6,7].

The objective of this work is to study the crystallization behavior of PLA-PEG blends as well as the plasticization effectiveness of PEG for the development of films for food packaging. Poly lactic acid (PLA) and poly ethylene Glycol (PEG) are such biodegradable polymers which aim to replace commodity polymers in future applications and show effect of adding alumina to blend PLA/PEG .

2-Materials and Methods

Polymers studied in this work (PLA – 1001 was supplied by (Shenzhen Esun Industrial Co. Ltd. Chain) and PEG was supplied from Aldrich (USA).The weight average molecular weight (Mw) of PLA and PEG were approximately 60000 and 200 g/mol respectively. The nano alumina was supplied by Cristal Globa Phama Company with particle size (46.73 nm) as shown in (Figure-1) measured by Scanning Probe Microscope (SPM).

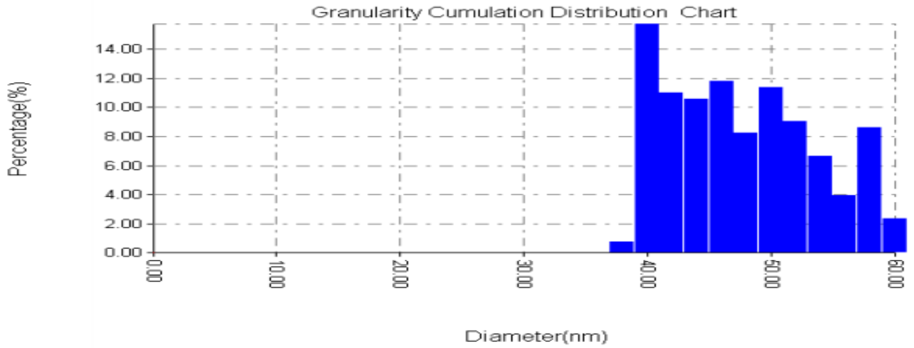

Figure 1- shows the percentage and particle diameter of Al_2O_3 nanoparticles.

2-1 Film preparation

Pure PLA blend and composites specimens (PLA/PEG, PLA/Alumina, and PLA/PEG/Alumina) were prepared by solvent casting with dichloromethane (DCM). The detailed compositions of films are presented in Table -1. Briefly, all ingredients were accurately weighted and thoroughly mixed by stirrer for 2 hour at 60 °C followed by addition of DCM. The resultant solution was poured into a glass Petri dish at room temperature under a chemical hood. Each dish was stored over a desiccater for overnight, and then films were peeled from the dishes and placed in a sealed container until time of use.

***Table 1**- Pure PLA, PLA/ blends and PLA/ nanocomposites Compositions*

Sample	PLA	PEG	Al_2O_3
Blend	100	-	-
	70	30	-
	50	50	-
	20	80	-
Nanocomposites	98 wt%	-	2%
	96 wt%	-	4%
	94 wt%	-	6%
Nanocomposites	50 wt%	50 wt%	4%

2-2 Thickness measurement

Thickness of films was determined using a digital micrometer (IDM) with ± 0.001 sensitivity it automatically cycles up and down at the push of a button, providing an accurate and repeatable thickness reading at the end of each cycle at 5 random locations around the film. Film specimens of 100 μm thickness were selected for all experiments.

2-3 Fourier Transform Infrared (FTIR) Analysis

The infrared spectra were recorded using spectrophotometer type SHIMADZU FTIR -7600 in range 400 to 4000 cm^{-1}. FTIR spectra gave information about the chemical structures of all films.

2-4 Tensile measurement:

The stress-strain properties of the tensile test were obtained at 25°C room temperature using Instron4467Universal testing machine equipped with a computerized data acquisition system. According to ASTMD-882 standard modulus of elasticity, tensile strength, elongation at break. Tested films were cut in 10 mm width and 80 mm in length and the initial gauge length and testing speed were fixed at 5 mm/min. Young Modulus calculated by Eq.1 of all films.

$E = F L_0 / A \Delta L$ ……………………1

Where: *F*: force exerted on an object under tension, L_0: original length, **A**: cross section area, Δ**L**: length of the object changes

2-5 Differential Scanning Calorimetric (DSC)

Thermal properties measure the difference in the heat required to increase the temperature of a sample and a reference as a function of temperature by Differential Scanning Calorimetric (Schimadzu DSC-60) from 20°C to 250°C. A heating rate of 5°C/min was used under nitrogen atmosphere and at a flow rate of 30 mL/min, the weight of the sample was 5 mg. DSC measure Tg, Tc and Xc from Eq.2

$Xc = \Delta Hm - \Delta Hc / \Delta Hm°$ ……………2

Where**:**

Xc degree of crystalline , Δ*Hm* enthalpies of fusion and Δ*Hc* enthalpies of crystallization, Δ*Hm* = 93 $J \cdot g^{-1}$ is the enthalpy of fusion of 100% crystalline poly(lactic acid).

2-6 Oxygen Transmission Rate (OTR)

Oxygen Transmission Rate (OTR) of the films was measured according to the ASTM D-3985 using gas permeation instrument Qualities (Canada). In the testing method, Firstly nitrogen gas is passed over both surfaces to remove oxygen in the sample. The nitrogen on one side is then replaced by oxygen, and the nitrogen flow on the other side then sweeps the surface to extract any oxygen that diffuses through the material. The diffusing oxygen is measured by a detector that is sensitive only to oxygen, after 12 to 16 hours test was completed .Before each measurement, the samples were kept dry in vacuum oven. The measured time interval is then transformed into the gas permeability rate expressed in cm^3/m^2.day. Gas permeability of the films were determined at constant temperature (23°C) and relative humidity (0% RH) conditions with speedy flow of gas between 5–10 cm^3/min and test Area $50cm^2$and thickness ≤ 3 mm .

Oxygen Permeability is based on the equal pressure method, and is professional applicable to the determination of oxygen transmission rate of film and package products, including plastic films, composite films.OTR is applicable in the measurement of gas permeability rate and permeability coefficient at various temperatures .The Oxygen permeability coefficient calculated in eq.(3) for all samples .

$P_{O2} = OTR\,.\,l\,/\,\Delta p$ …………………3

$OTR = V/A.t$ ………..4

Where

OTR oxygen transmission rate in cm^3/cm^2.day , *V* volume of oxygen , *A* area of samples , *t* time , P_{O2} Oxygen permeability coefficient , *l* thickness of sample , *Δp* partial pressure difference across the barrier.

3- Results and Discussion

3-1 FTIR of pure PLA, PLA/PEG blends, PLA/PEG/Al_2O_3 nanocomposites

FTIR spectra of reagents used in this work are presented in Figure -2 Polylactic acid spectrum contains characteristic absorption bands at 2800–3000, 1300–1500 and 756 cm^{-1} which can be assigned to methylene groups (stretching and deformation vibrations, respectively). Strong, sharp peaks at 1757 cm^{-1} due to carbonyls and 1186, 1094 cm–1 attributed to C–O–C groups appear Figure-2. Only very small, residual hydroxyl band at 3500 cm^{-1} that spectrum agree with Nikolic et al. [8].

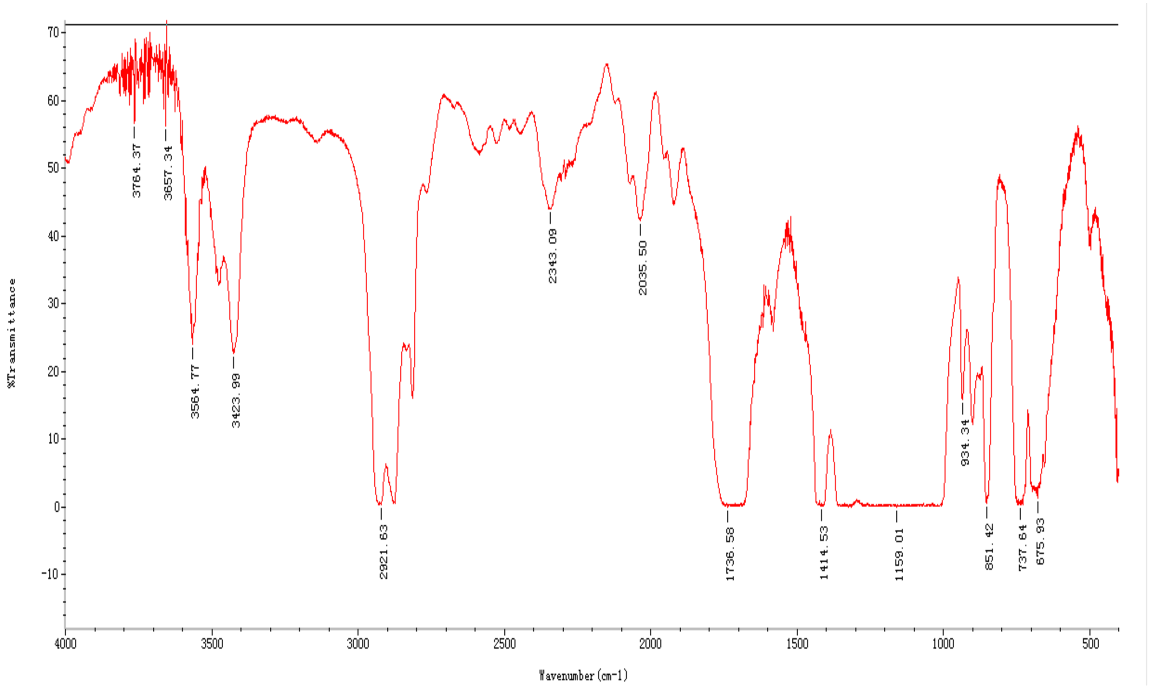

Figure 2- FTIR of pure PLA

Fig -3 shows that PLA/PEG at 50/50 Plasticizer (PEG) spectrum is relatively simple broad hydroxyl band is centered at about 3400 cm^{-1},methylene at 2874, 1458, 1351, 1250, 950 and 843 cm^{-1} (stretching and deformation) and ether(strong) at 1113 cm^{-1} . Additionally, two low intensity peaks appear at carbonyl region (1721, 1639 cm^{-1}) that mean bands of PEG appear when mixed with PLA.

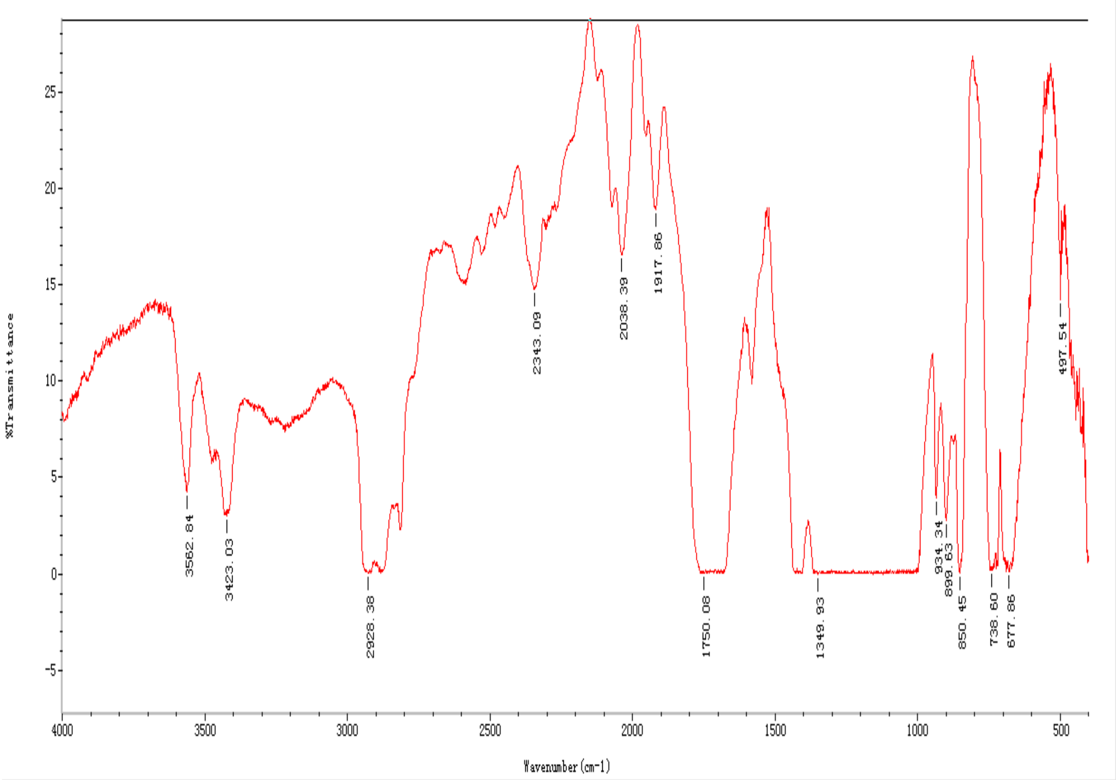

Figure 3- FTIR of PLA/PEG at 50/50 w/w

3-2 Tensile Measurement

The main goal of plasticizer (PEG) addition into PLA matrix was to decrease its rigidity and increase ductility of PLA. It is worth noting that pure PLA at room temperature was characterized by low elongation (nominal strain at break = 5.7%) together with tensile strength (28 MPa) appear in Figure-4 and is quite brittle. PLA have been fails as soon as it passes the yield stress. Apparently, pure PLA has a strong strain softening which, however, is not stabilized by a strain hardening. Upon drawing, strain softening stimulates strain localization which causes the build-up of local tri-axial stresses. If the local strain could not be delocalized, this local tri-axial stresses will induce void nucleation and crazes in the matrix leading to brittle failure behavior for this reason PLA is brittle [9]. Adding plasticizer to PLA enhanced plastic elongation and reduced brittleness, significant decrease of the tensile strength (TS) and an increase of the elongation at break (%). The stress–strain curve after the yield point shows a combination of strain softening and cold drawing. In this region, there is competition between the orientation of PLA chains and crack formation. Hence, there is a drop in stress with increasing strain. The elongation at break of PLA blends was improved dramatically with the increase of plasticizer content. While the plasticized compositions were found to have reduced tensile strength, and generally, this decrease (from 18 MPa to 6.9 MPa) is quite well correlated with the percentage of plasticizer (30, 50 and 80%).

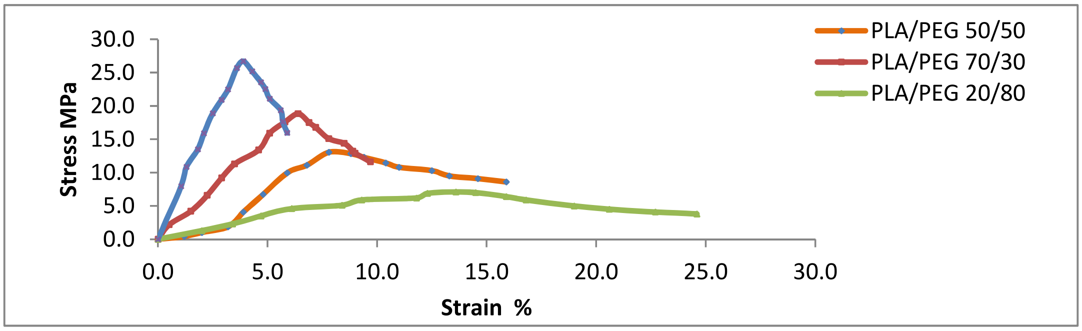

Figure 4- Stress – Strain curve of Pure PLA and PLA/PEG blends

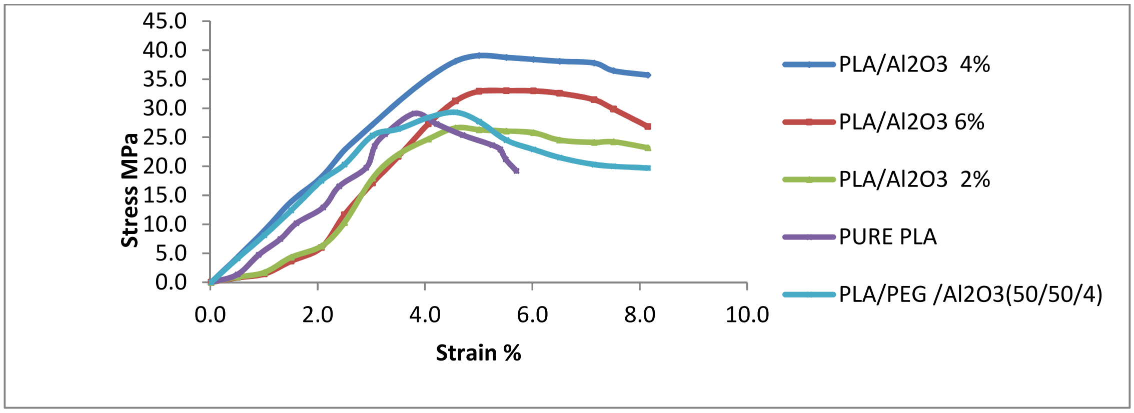

Figure 5-Stress – Strain curve of Pure PLA , PLA/Al_2O_3 nanocomposites and blend nanocomposites

Figure -5 shows typical Stress-Strain curves for pure PLA, PLA/Al_2O_3 (2, 4 and 6%) and Table -1 shows that values of tensile strength and Young modulus for nanocomposites is increased with nano alumina it is well known that the modulus of a filled system depends on the properties of the filler and the matrix of the film components. The nanofillers were effective to increase tensile strength and (especially) Young's modulus. The elongation was slightly impaired, but only at nanofiller concentrations above 10%.

Table 2- Tensile measurements of pure PLA, PLA/PEG blends, PLA/ Al_2O_3 nanocomposites determined by Stress-Strain curve

Samples	Tensile Strength MPa	Young Modulus GPa	Elongation %
PLA	28	2.3	5.1
PLA/PEG 70/30	18	1.9	10.2
PLA/PEG 50/50	13	1.1	15.3
PLA/PEG 20/80	6.9	0.8	25
PLA/ Al_2O_3 2%	38	3.6	8
PLA/ Al_2O_3 4%	32	3.1	8.1
PLA/ Al_2O_3 6%	29	2.7	7.5
PLA/PEG/Al2O3 (50/50/4%)	29.3	2.4	8.1

3- 3 Thermal Properties

Since the glass transition temperature (Tg) is an excellent indicator of chain mobility, plasticizing efficiency has therefore been evaluated by measuring the decrease of Tg as a function of plasticizer concentration. All the blends realized in this work show only one Tg in the DSC diagrams indicating a good miscibility between polymer and plasticizer [9, 10]. The decrease of Tg highlights the effect of the plasticizer in PLA compositions with increasing molecular mobility. The plasticizing effect is confirmed by the modification of Tg which is significantly decreased by comparison with the pure PLA matrix. The plasticizer decreased Tg from about 51.47ºC (for pure) PLA to 40 ºC for the blends with different proposition of plasticizers. The use of plasticizers reduced the crystallization temperature by 95-90ºC from the value of 99ºC found for pure PLA film.

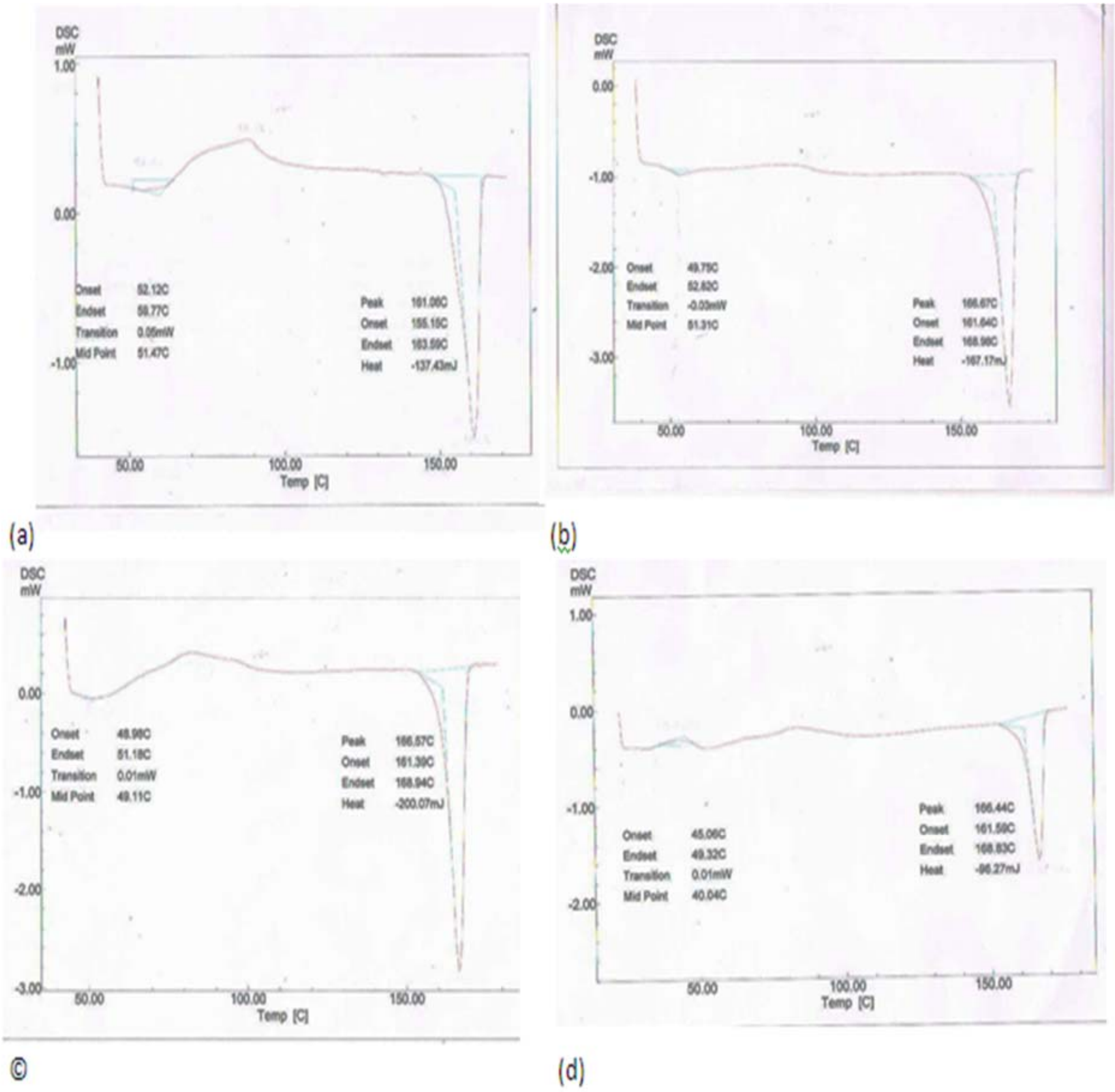

Figure 6-DSC diagrams of (a)pure PLA , (b) PLA/PEG(70/30) , (c) PLA/PEG 50/50, and (d) PLA/PEG20/80

The addition of PEG plasticizer lowered the glass transition temperature (Tg) and increased the crystalline rates appear in Table - 3 of the blends. This was attributed to the enhanced segmental motion of the PLA molecular chains [10]. The types, the loading contents and efficiency of plasticizers such as PEG related to the miscibility in molecular level as well as the thermal behaviors of those blends and yielding polymers with 15–18.3% crystalline. PLA plasticizer is a material incorporated in a plastic to increase its workability and its flexibility or elongation.

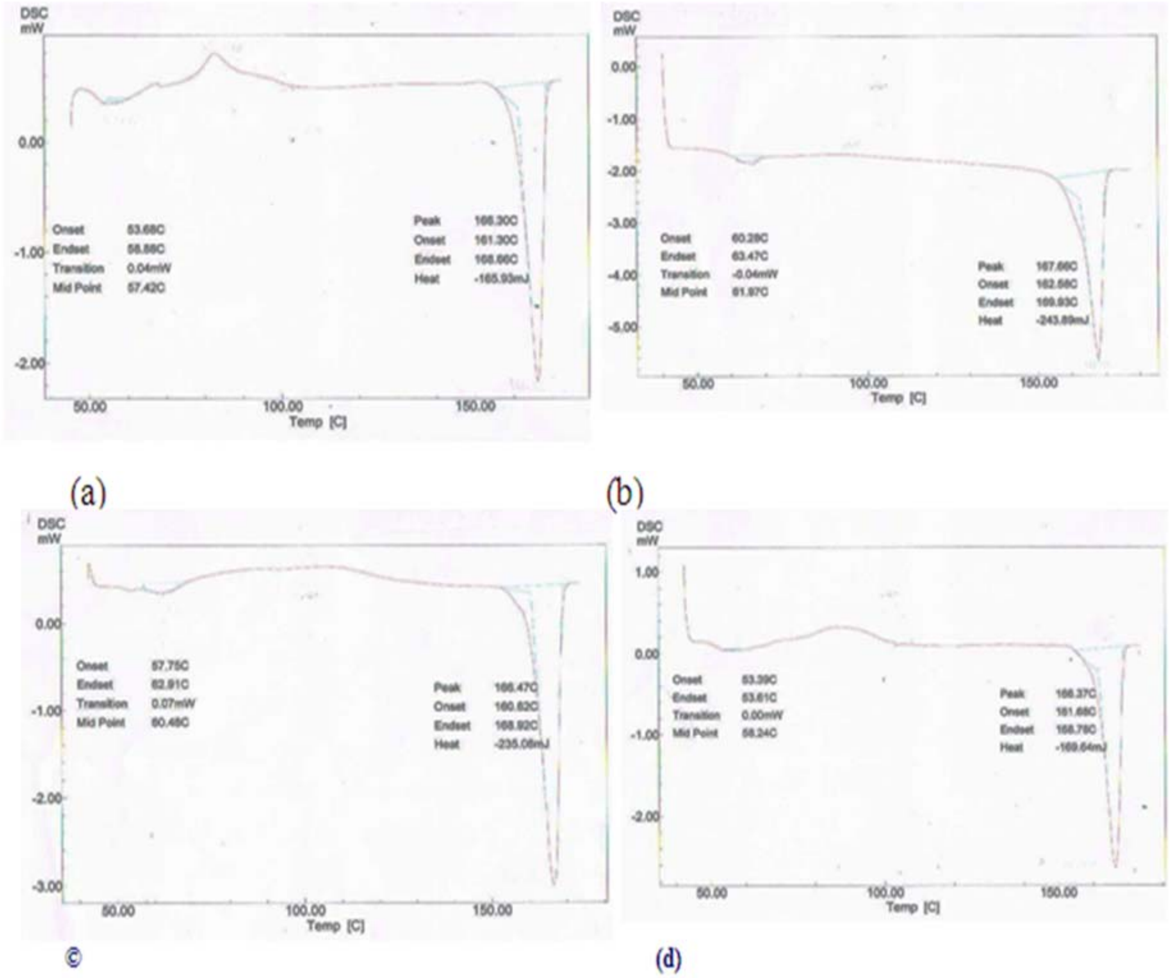

Figure 7-DSC diagrams s of (a) PLA/Al_2O_3 2%, (b) PLA/Al_2O_3 4%, (c) PLA/Al_2O_3 6%(h) PLA/PEG/ (50/50/4%) Al_2O_3.

PLA/Al_2O_3 nanocomposites (2, 4, 6%) that the addition of alumina increased T_g appear in Figure -7 and Xc of PLA nanocomposites due to the crystallization process and crystal formation of PLA and accelerates the crystallization of PLA [6] which subsequently increased the degree of crystallinity of PLA/ Al_2O_3 nanocomposites appear in Table -3

Table 3- Thermal properties of pure PLA , PLA/PEG blends and PLA/ Al_2O_3 nanocomposites

Samples	Tg °C	Tc °C	Xc%
PLA	51.47	96	13
PLA/PEG 70/30	51.30	95	15.0
PLA/PEG 50/50	49.11	91	16.1
PLA/PEG 20/80	40.04	90	18.3
PLA/ Al_2O_3 2%	57.42	97	16.3
PLA/ Al_2O_3 4%	61.31	90	17.4
PLA/ Al_2O_3 6%	60.48	91	19.7
PLA/PEG/Al_2O_3 (50/50/4%)	58.24	98	18.5

3-4 Oxygen Transmission Rate (OTR)

Table -4 shows that pure PLA with oxygen permeability coefficients value 22cm^3.mm/m^2.day.atm .The main limitations of PLA as a packaging material are high gas permeability (O_2)and increased in PLA/PEG blends between (24.3-29.8) cm^3.mm/m^2.day.bar because that addition of a plasticizer caused reduce intermolecular forces and increases free volume between polymer chains, which is not only increases flexibility, but also oxygen permeability coefficient[10] .Some disadvantageous properties retain PLA potential application in film manufacturing PLA the addition of plasticizers increases the PLA gas permeability, which is detrimental for food packaging use. Therefore Polymer nanocomposites usually have much better polymer/filler interactions than blends. A uniform dispersion of nanofillers into a polymer matrix results in a very large matrix/filler interfacial area, which restricts the mechanical mobility of the matrix, and improves its barrier properties. The ratio of the largest to the smallest dimension of filler is an important property known as aspect ratio. Fillers with higher aspect ratios have higher specific surface area, providing better reinforcing effects. In addition to the effects of the nanoreinforcements themselves, an interphone region of decreased mobility surrounding each nanofiller results in a percolating interphone network in the composite which plays an important role in improving the nanocomposite properties that appear to reduce OTR when add Al_2O_3 in Table-4 because of tortuous path for a permeate through a polymer- nanocomposite for gas diffusion and the filler materials are essentially impermeable inorganic crystals, gas molecules must diffuse around them rather than taking a (mean) straight line path that lies perpendicular to the film surface.

Table 4- Oxygen gas permeability of PLA, PLA/PEG blends and PLA/Al_2O_3 nanocomposites

Samples	Oxygen Permeability Coefficient ($cm^3 \cdot mm/m^2$.day.atm.)
PLA	22
PLA/PEG 70/30	24.3
PLA/PEG 50/50	26.7
PLA/PEG 20/80	29.8
PLA/ Al_2O_3 2%	19
PLA/ Al_2O_3 4%	17.5
PLA/ Al_2O_3 6%	18.7
PLA/PEG/Al_2O_3 (50/50/4%)	16.5

4-Conclusion

1- Tensile measurement shows that high elongation (25%) in PLA/PEG (20/80) and high Young Modulus (3.6)GPa in PLA/Al_2O_3 at 2% .

2-Thermal stability corresponding in Tg shows that high value (61.31°C) in PLA/Al_2O_3 at 4% .

3-Barrier properties show that low OTR (16.5cm.^{3}mm/cm^2.day.atm) in PLA/PEG/Al_2O_3 blend – composites.

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