

DNA adsorption and dynamic mechanical analysis of polymeric oil/oil acid copolymers

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Abstract A variety of new polymeric materials [Polylinseed oil-g-PMMA (PLO-g-PMMA), Polylinseed oil-g-PS (PLO-g-PS), Polysoybean oil-g-PMMA (PSB-g-PMMA), Polylinoleic acid-g-PMMA (PLina-g-PMMA), Polylinoleic acid-g-PS (PLina-g-PS), Polylinoleic acid-g-PnBMA (PLina-g-PnBMA), Polyhydroxy alkanoate-sy-g-Polysoybean oil-g-PMMA (PHA-PSB-PMMA) and Polyhydroxy alkanoate-sy-g-Polylinoleic acid-g-PMMA (PHA-PLina-PMMA)] were prepared from soluble polymeric oil/oily acid peroxides initiating the co-polymerization of Poly(methyl methacrylate) (PMMA), Polystyrene (PS) and Poly(n-butyl methacrylate) (PnBMA). Pure PMMA, PS, PnBMA and these copolymers contain different polymeric oil/oil acid initiators were investigated as to the relationship between their dynamic mechanical properties. The DMA results show that the transition from glassy to rubbery behavior is broad for these polymers due to the presence of the triglyceride/oil acid molecules acting like plasticizers in the system. Furthermore, they were compared with dynamic mechanical analysis (DMA) and differential scanning calorimeter (DSC) analysis results. The mechanical properties

of these homopolymer and copolymers were also assessed by tensile tests of the polymers in terms of the stress and strain values at the break point. When these results were compared with those for PMMA and PnBMA, it is worth noting that copolymer samples containing PLO, PSB, or PLina in its structure showed changed stress at their break point or in the strain value at its break point. The contact angle testing and DNA adsorption of oil/oil acid copolymers were also studied. Compared with homopolymers, the hydrophilicity and DNA adsorption of the copolymer samples improved because of the presence of PLO, PSB, or PLina blocks. Considering all these results, it is recommended that the copolymers used as candidate biomaterials.

Keywords Polymeric oil/oily acids copolymers · Poly(3-hydroxyalkanoate)s · Acrylic polymers · Dynamic mechanical properties · Stress–strain behavior · DNA adsorption

Introduction

Today, natural oils and fats are considered to be the most important class of renewable resources for the production of biodegradable polymers in two ways. The first is the production of poly(3-hydroxyalkanoates) (PHAs) as an energy reserve material by some microorganisms using plant and fish oils [1–3]. The second is direct polymerization of the oils; examples include a copolymerization with divinyl benzene and styrene leading to thermoset copolymers [4], or by polymerization of vinyl [5], maleic anhydride [6], glycidyl ether [7], and norbornyl [8] derivatives of the oil.

The auto-oxidation of polyunsaturated oil is a versatile tool to obtain bio-based materials for medical applications. Auto-oxidized polymers contain peroxide moieties that initiate the free radical polymerization of vinyl monomers. We have recently reported the auto-oxidation of unsaturated

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edible aliphatic oils, such as linseed oil (LO), soybean oil (SB), and linoleic acid (Lina), to prepare polymeric peroxy initiators coded as PLO, PSB, and PLina, respectively, for free radical polymerization [9–11]. This polymerization system does not require any metal catalyst or solvent that may be harmful to the environment. Therefore, this polymerization system can also be considered suitable for green chemistry. Our latest research involved the synthesis of some new types of biodegradable polymer materials-graft copolymers containing PHA-soya (Polyhydroxy alkanooate-sy), polymeric oil/oily acid, and PMMA [12]. Similarly, unsaturated (PHA)s can be auto-oxidized [13–15] and grafted with poly(ethylene glycol) (PEG) [3, 16, 17] and PMMA [18, 19] to obtain bio-based materials for medical applications [20].

The presence of oil/fatty acid chains in the polymer structure improves some physical properties of polymers in terms of flexibility, adhesion, and resistance to water and chemicals. In biological applications, their biocompatibility and/or biodegradability play an important role [5]. Fatty acids are suitable candidates for the preparation of biodegradable polymers because they are natural body components, and they are considered safe and are hydrophobic; thus, they may retain an encapsulated drug for longer time periods when used as drug carriers [21–25].

PMMA is an acrylic hydrophobic biostable polymer that is widely used in the biomedical field, especially in intraocular lenses, as bone cement in orthopedics and traumatology, and as an implant carrier for sustained local delivery of anti-inflammatory or antibiotic drugs [26]. PMMA is an amorphous glass below 110 °C and exhibits brittle fracture under normal conditions below 80 °C. PMMA has a wide range of applications, which are principally concerned with transparency and light transfer, with good weathering resistance and high surface hardness and durability. Applications include glazing in aircraft and other transportation, transparent guards and covers, lenses, baths, washbasins and sanitary ware, and rear-light assemblies for road transportation [26]. Acrylate-based polymers on magnetic particles are chosen as coating materials due to their biocompatibility and radiation stability in several areas of applications [27–34].

The selection of the materials used in the construction of prostheses and implants is basically focused on their ability to maintain mechanical, chemical, and structural integrity and on various characteristics that allow this function to substitute for any organ or tissue properly and exhibit safe, effective performance within the body. Biocompatibility has been defined as the ability of a material to perform with an appropriate host response in a specific application. Contact angle itself is not an indicator of biocompatibility of a material, but some useful information may be obtained for blood or tissue-compatibility [35]. Any material used satisfactorily in orthopedic surgery may be inappropriate for cardiovascular applications because of its thrombogenic

properties. Deleterious effects may be encountered if used under stress-strain conditions [35].

Surface properties play an important role in biological applications of polymeric materials. The immobilization of DNA on various solid materials has become an important issue in various fields ranging from medicine to analytical chemistry and, more recently, molecular electronics. Adsorption is among the different immobilization procedures [36, 37]. Therefore, in this study, DNA adsorption on the PMMA, PS, PnBMA, and their polymeric oil/oil acid copolymers were also studied.

In previous papers, we reported our progress in understanding the relationships of the synthesis, characterization of Polymeric Oil/Oil Acid Copolymers and some biological test as biocompatibility, bacterial adherence and protein adsorption [9–12]. Moreover, we investigated to using drug delivery system of these copolymers [25]. In this paper, the work described is the other part of a long-range research program that deals with these Polymeric Oil/Oil Acid Copolymers. The present paper reports our results on the mechanical properties, tensile test, deals with the effect of the chemical structure on surface properties (contact angle measurements) and DNA adsorption of these copolymers. Furthermore, the glass-transition temperatures of these copolymers and homopolymer were compared with the new results of DMA and previous results of DCS methods. In this study, stress and strain behaviors at the break point are given as the results of tensile test mechanical properties.

Experimental

Materials

Denatured DNA solution from the thymus of a calf for hybridization was supplied from Sigma. All other chemicals were reagent grade and used as received.

Synthesis of the copolymers

The used copolymers in this work were produced and characterized in our research laboratories. For the synthesis of these copolymers, the auto-oxidation of the unsaturated edible aliphatic oils—such as LO, SB, and Lina—gave polymeric oil/oily acid peroxy initiators coded as PLO, PSB, and PLina, respectively, afterward the free radical polymerization of S, MMA *n*BMA and a series of their copolymers derived from polymeric oil/oily acids (PLO-g-PS [9], PLO-g-PMMA [9], PSB-g-PMMA [10], PLina-g-PS [11], PLina-g-PMMA [11], PLina-g-PnBMA [11], PHA-PSB-PMMA [12], and PHA-PLina-PMMA [12]) (see Scheme 2). We explained their results and conditions of these copolymers in previous papers However, to be able

to make a comparison, these results are listed again in Table 1 [9–12].

Polymer characterization

Dynamic mechanical analysis

The dynamic mechanical properties of the copolymers were obtained with a Netzsch DMA 242 dynamic mechanical analyzer in a tension mode. The tension mode is preferable for the measurement of films and fibers or thin rubber samples. The lower end of the sample was held in place, whereas the upper end was clamped to the oscillating push rod. Each specimen was first cooled to about $-50\text{ }^{\circ}\text{C}$ and then heated at $3\text{ }^{\circ}\text{C}/\text{min}$ and a frequency of 1 Hz under nitrogen. The viscoelastic properties that is the storage modulus E' and the mechanical loss factor (damping) $\tan \delta$, were recorded as a function of temperature. The glass-transition temperatures of polymers were obtained from the peaks of $\tan \delta$ curves from DMA. Figure 1 shows dynamic mechanical experiments as a function of temperature for the study samples, for example storage modulus, loss modulus and $\tan \delta$. Table 2 describes glass temperature for PMMA and the polymeric oil/oil acid-g-PMMA copolymers as a function of $\tan \delta$ from DMA.

Tensile test

For the polymer samples, the tensile tests were performed using an AG-I 5 kN Shimadzu Autograph test machine with

a constant tensile speed of $0.5\text{ mm}/\text{min}$. The dimensions of the test specimens are given in Table 3. In Table 3, the stress and strain values at the break point of the three polymer specimens are presented. Figure 2 shows the stress–strain behavior of the specimens that were subjected to the tensile test described above.

Contact angle measurement

The contact angle of the oily/oily acid copolymer samples was determined using a KRUSS DSA100 (Hamburg, Germany) instrument. The contact angle of the polymer surface was measured using the Sessile Drop method with 1 water drop. 40 separate photos were taken from the different parts of the polymer surfaces. Figure 3 shows photographs of the water drops on the copolymer films. The contact angle values were measured for each drop. The measured contact angle values were obtained as the left contact angle, the angles from the left contact point of the droplet with solid, and the right contact angle from the right contact point. In addition, The contact angle values for the oil/oil acid copolymer surfaces were the average of the 40 measurements (see Fig. 4).

DNA adsorption

A DNA solution derived from a calf thymus for hybridization was used for adsorption assays. The concentration of DNA solution was adjusted to $0.2\text{ mg}/\text{ml}$ TE (10 mM Tris; 1 mM EDTA buffer). Polymer disks (thickness $\sim 1\text{ mm}$, $\phi =$

Table 1 Results and conditions for the polymerization of polymeric oil/oily acid copolymers at $80\text{ }^{\circ}\text{C}$

Run no	PLO (g)	PSB (g)	PLina _s (g)	PHA (g)	S (g)	MMA (g)	n-BMA (g)	Molecular weight		PLO, PSB, PLina in copolymer mol%
								Mw $\times 10^4$	MWD	
PLO-g-PS (39-5) ^a	0.50	–	–	–	4.55	–	–	12	2.82	19
PLO-g-PMMA (39-6) ^a	0.50	–	–	–	–	4.7	–	47	1.97	12
PLO-g-PMMA (55-3) ^a	1.00	–	–	–	–	1.03	–	3.7	1.32	–
PSB-g-PMMA (56-3) ^b	–	1.00	–	–	–	1.03	–	31	1.6	–
PSB-g-PMMA (56-5) ^b	–	1.50	–	–	–	3.01	–	–	–	8
PLina-g-PS (68-1) ^c	–	–	0.75	–	3.0	–	–	17.5	2.2	–
PLina-g-PMMA (67-1) ^c	–	–	0.75	–	–	3.09	–	23.5	2.1	–
PLina-g-PMMA (67-2) ^c	–	–	1.502	–	–	3.09	–	15.7	2.0	9.7
PLina-g-PnBMA (62-2) ^c	–	1.03	–	–	–	–	2.42	44	1.5	–
PLina-g-PnBMA (69-2) ^c	–	1.50	–	–	–	–	3.00	18.8	1.9	10.7
PHA-PSB-PMMA (58-1) ^d	–	1.00	–	0.50	–	3.00	–	57.8	5.30	PSB=80 PHA=15
PHA-PLina-PMMA (59-1) ^d	–	–	1.00	0.50	–	3.00	–	57.2	3.30	PLina=75 PHA=5

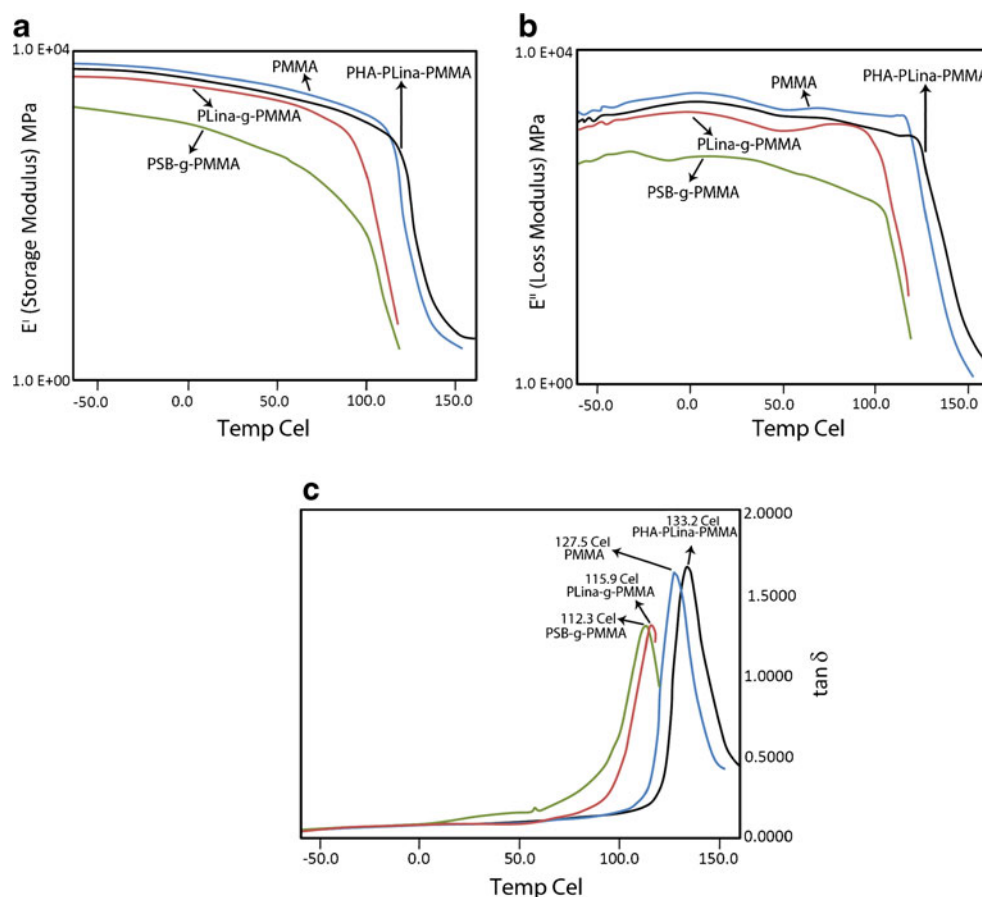
^a Ref. [9]

^b Ref. [10]

^c Ref. [11]

^d Ref. [12]

Fig. 1 Dynamic mechanical experiments as a function of temperature for the studied samples **a)** Storage modulus **b)** Loss modulus **c)** Tan δ



6 mm) were treated with 1.5 ml of the DNA solution for 2 h in a shaker incubator; adsorption conditions were 37 °C and pH 7.4. The DNA adsorption of homopolymers and copolymers was detected by monitoring the decrease in UV absorbance at 260 nm. All experiments and the samples were performed in replicates of three. Figure 5 shows DNA adsorption of PS, PMMA and polymeric oil/oil acid graft copolymers.

Results and discussion

Oils contain saturated and unsaturated acids, which the carboxyl group hydrophilic and ionized when solubilized in water, whereas the carbon chain and terminal methyl group were hydrophobic, making the entire molecule amphipathic. Most of the triglyceride oils consist of various types of fatty

acids (seen in Scheme 1). Depending on the fatty acid distribution, each type of oil has specific physical and chemical properties affecting the final properties of the prepared polymer. The linseed oil and soybean oil compositions were largely oleic, linoleic, and linolenic acids. The amounts of linoleic acid in linseed oil and soybean oil were found to be 15 wt.% and 53 wt.%, respectively [9–11]. In medicinal front, it is claimed that linseed oil is useful in treating anxiety, prostate problems, vaginitis, weight loss and certain types of cancer, but appropriate research is lacking [38]. The vegetable oils and their derivatives are copolymerized with different olefinic monomers such as S, MMA and nBMA for improve their film properties. These copolymers have excellent chemical and physical properties, including enhanced hydrolytic and thermal stability [38]. In this point of view, It is very important to know performans properties of polymer (thermal, mechanic and surface) for industrial application properties. Therefore In this work are evaluated, stres-strain, transition temperature, hydrophibility and dna adsorbition. Polymeric oil peroxy initiators [9–11] were prepared the auto-oxidation of unsaturated edible aliphatic oils such as linseed oil, soybean oil, and linoleic acid for free radical polymerization. These polymeric peroxy initiators produce polymeric oil/oily acid radicals, which can initiate the polymerization of S, MMA, nBMA, and also attack the double bonds of both MMA and PHA as

Table 2 The glass temperature (T_g) for PMMA and the polymeric oil/oil acid-g-PMMA copolymers from DMA

Batch no	T_g (°C)
PMMA	127.5
PSB-g-PMMA (56-3)	112.3
PLina-g-PMMA (67-2)	115.9
PHA-PLina-PMMA (59-1)	133.2

Table 3 Dimensions of the tensile test specimens and test data of the polymeric oil/oil acid graft copolymers

	Thickness (mm)	Width (mm)	Gauge length (mm)	Stress at break (N/mm ²)	Strain at break (%)
PMMA ^a	0.2150	5	15	12.5	34
PLO-g-PMMA (39-6)	1.0	5	15	0.6	7.6
PSB-g-PMMA (56-3)	0.05	5	15	7.5	12.1
PLina-g-PMMA ^a (67-2)	0.05	5	15	55	30
PHA-PLina-PMMA ^a (59-1)	0.05	5	15	48	9
PnBMA	0.4	5	15	7.5	370
PLina-g-PnBMA (62-2)	0.3	5	15	3.4	500

^aRef. [12]

seen in Scheme 2. After the free radical polymerization reactions, many graft copolymers were obtained different properties and compositions with used to different amounts of polymeric oil/oily acid and monomers. The graft copolymers used in this study were PLO-g-PMMA, PLO-g-PS, PSB-g-PMMA, PLina-g-PS, PLina-g-PMMA, PLina-g-PnBMA, PHA-PSB-PMMA and PHA-PLina-PMMA. The results and conditions of them are listed in Table 1 [9–12] for comparison.

Dynamic mechanical analysis

A number of methods have been developed to measure the glass transition temperatures of polymer thin films using optical probes, including X-ray reflectivity, ellipsometry, positron lifetime spectroscopy, Brillouin light scattering, optical waveguide spectroscopy, and FT-IR spectroscopy [39]. To measure the glass transition temperatures, other methods include differential scanning calorimeter and dynamic mechanic analysis.

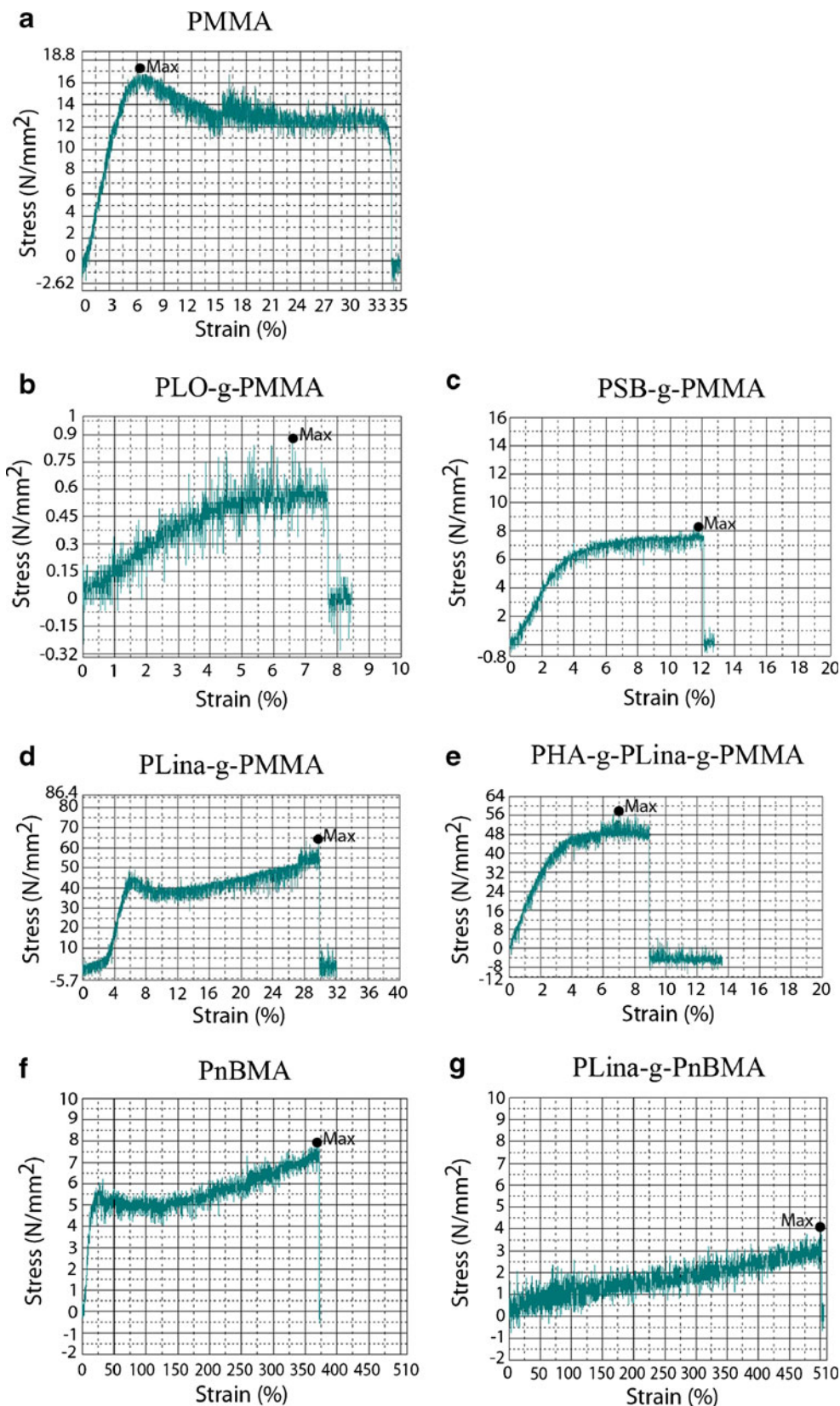
DMA is a sensitive technique used to study and characterize the macroscopic responses of the materials as well local internal motions. By monitoring property changes with respect to the temperature and/or frequency of oscillation, the mechanical dynamic response of the material comprises two distinct parts: an elastic part (E' , storage modulus) and a viscous component (E'' , loss modulus). The storage modulus is a measure of the stiffness of the material, and the loss modulus is the determined energy loss in internal motion [35]. The damping is called the tan delta, loss factor, or loss tangent; the T_g were determined as $\tan \delta = E''/E'$. With increasing temperature, various physical states were revealed: glassy, leathery, rubbery and elastic with rubbery flow, and viscous flow. The glass transition is easily identified from dynamical mechanical data because of the sharp drop in storage modulus and peaks of loss dispersion modulus, or $\tan \delta$. The $\tan \delta$ peak may occur at higher temperatures than those given by E' drop or E'' peak because it responds to the volume fraction of the relaxing phase; its shape and height depends on the amorphous phase, being a good measure of the “leather-like” midpoint between the glassy and rubbery states. The glass transition temperature is often measured by DSC,

but the DMA technique is more sensitive and yields more easily interpreted data. This is common, as the degree of dependence is specific to the transition type. DMA can also resolve sub- T_g transitions, such as beta, gamma, and delta transitions, in many materials that the DSC technique is not sensitive enough to pick up. The magnitude of the low-temperature relaxations is much smaller than that of a-relaxation, considered to be the glass transition. These relaxations are due to local mode (main chain) relaxations of polymer chains and rotations of terminal groups or side chains, or the crankshaft motion of a few segments of the main chain [35, 40]. The values obtained from these methods can differ up to 25 °C from each other on the same run. In addition, a 10–20 °C difference from the DSC is also seen in many materials [41, 42].

Considering this literature information, for our polymer samples, as seen in Table 2 and Fig. 1, Figs. 1a, b, and c show the elastic modulus, loss modulus and $\tan \delta$ as a function of the temperature, respectively. In all of the storage modulus curves, it was observed that the modulus showed a decrease with increasing temperature. In the glassy region, the components were in a frozen state and highly immobile. Thus, the storage modulus value did not show much variation. When temperature increased, the substance became more mobile and lost its close packing arrangement, and as a result, the modulus decreased. The significant fall was observed in the region between 110 and 130 °C for PMMA. However, for the various copolymers, the significant falls were observed in the region between 90 and 120 °C for PSB-g-PMMA, 95 and 120 °C for PLina-g-PMMA, and 120 and 140 °C for PHA-PLina-PMMA. The sudden and sharp fall in modulus in comparison to PSB-g-PMMA led to a lower modulus. Clearly, the modulus drop corresponds to the onset of segmental mobility in the polymer chains.

E'' was seen shoulder peak as seen in Fig. 1b. PMMA exhibits a very broad E'' transition that is notably high over a broad temperature range (−34.4 °C to 54.5 °C) and small peak (62.1 °C to 92.4 °C). The similar to, (−50 °C to 41.26 °C) and (59.5 °C to 100 °C) for PLina-g-PMMA and (−50 °C to 54.5 °C) and (72.7 °C to 115 °C) for PHA-PLina-PMMA. On the contrary, PSB-g-PMMA was observed small peak (−50 °C

Fig. 2 Stress–strain curves **a)** PMMA ref. [12] **b)** PLO-g-PMMA (batch no 39-6) **c)** PSB-g-PMMA (batch no 56-3) **d)** PLina-g-PMMA (batch no 67-2) ref. [12] **e)** PHA-PLina-PMMA (batch no 59-1) ref. [12] **f)** PnBMA **g)** PLina-g-PnBMA (batch no 62-2)



to -13.3°C) and very broad E'' peak (-1.7°C to 61.7°C). These small and broad E'' transitions may involve local motion of polymer constituents about the chain backbone of a relatively

small number of monomer units or with motion of side groups. For example, these peaks may be associated with side-chain motion of CH_3 -, ester groups attached to the main chain

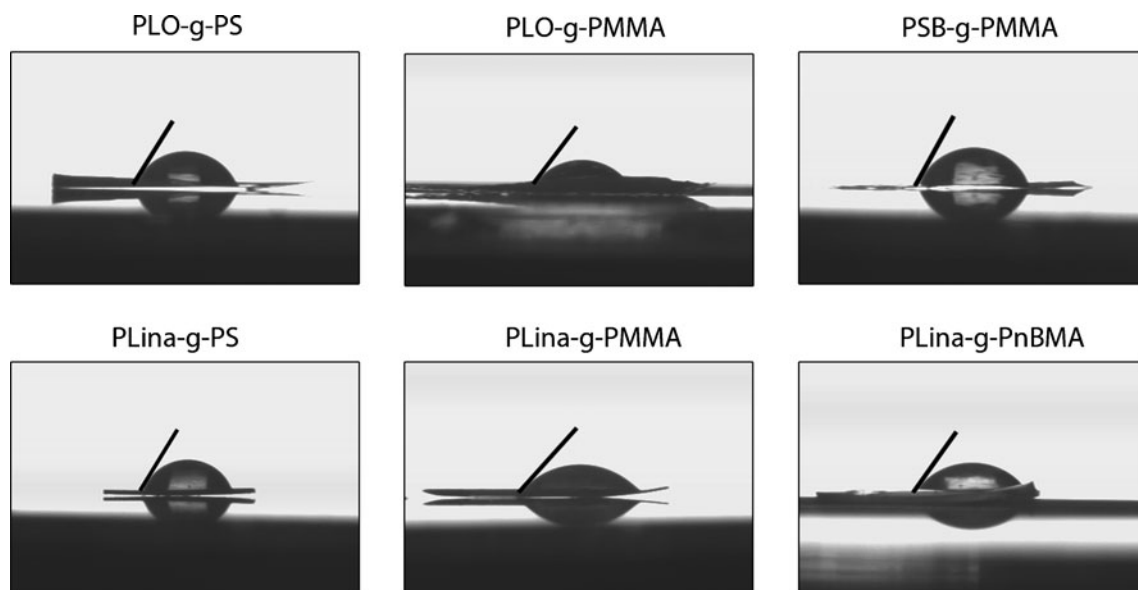


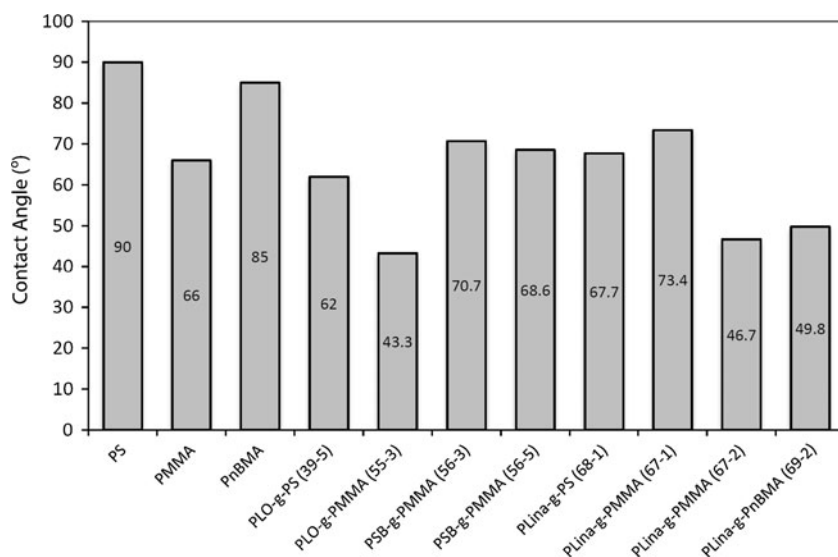
Fig. 3 Photographs of the water drop on the Polymeric oil/oil acid copolymers film surfaces

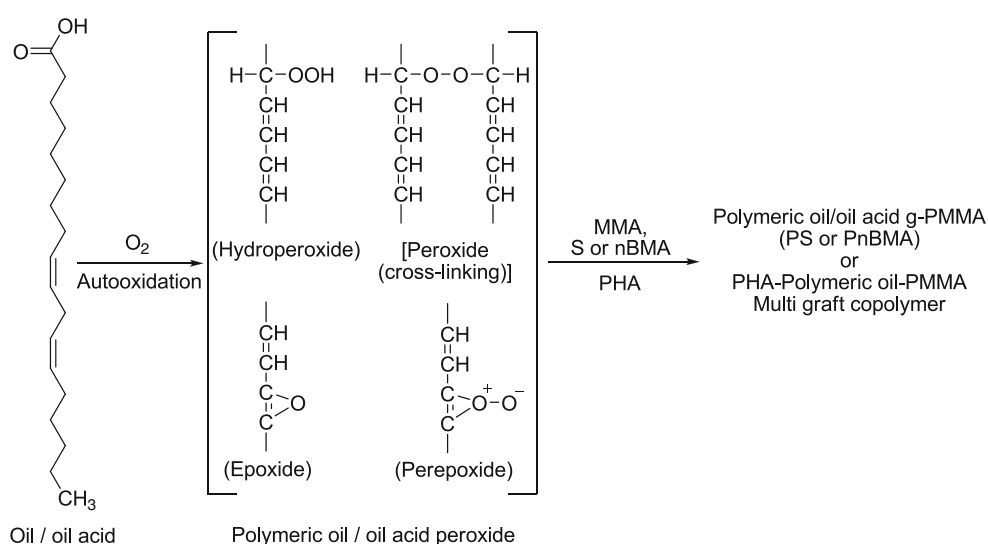
for PMMA and motions of the large number of CH_2 present in the aliphatic chains of the triglyceride should be observed. However, sudden and sharp fall in loss modulus are observed 121.2°C for PMMA, 108°C for PSB-g-PMMA, 100°C for PLina-g-PMMA, 121.7°C for PHA-PLina-PMMA. These values of E'' may suggest greater mobility of the polymer chains associated with dissipation of energy when the polymer is subjected to deformation.

$\tan \delta$ is a damping term that can be related to the impact resistance of a material. As the damping peak occurs in the region of the glass transition where the material changes from a rigid to a more elastic state, it is associated with the movement of small groups and chains of molecules within the polymer structure, all of which are initially frozen [43]. The height of the damping peak is a measure of mobility of

the molecular chains, and relates to the degree and strength of chemical bonds in the polymer structure [43, 44]. Therefore, the higher the $\tan \delta$ peak value is, the greater its degree of molecular mobility will be [43]. Glass transition temperatures were found to be very well differentiated from both DSC and DMA techniques in this work (See Table 2 and Fig. 1). The mechanical, dielectric, and thermal properties of PMMA in the bulk strongly depended on the tacticity, i.e. the molecular configuration of the polymer chain as literature. The glass transition temperatures were reported to be 75°C for iPMMA, 103°C for aPMMA, and 122°C for sPMMA [39, 45]. As literature; two peaks were observed for pure PMMA. The first peak located at 31°C is associated with side-chain motion of CH_3 - and ester groups attached to the main chain. The second peak at 134°C is assigned to the α -

Fig. 4 Contact angles of PMMA, PS PnBMA and polymeric oil/oil acid graft copolymers



Scheme 2 Formation of the polymeric oil/oil acid copolymers

the graphs, PMMA has approximately 12.5 MPa stress at the break point and 34 % strain [12]. It is worth noting that the data for PMMA may show discrepancies with the data given in the literature because these properties are highly dependent on the tacticity of PMMA. Containing PLina in its structure, PLina-g-PMMA copolymer has increased values for stress at its break point (55 MPa), more or less preserving the strain value at its break point (30 %) when compared to PMMA [12]. However, for the PHA-PLina-PMMA copolymer containing both PLina and PHA, the strain at the break point is reduced up to approximately 9 %, more or less preserving the high stress values at its break point (48 %) when compared to PLina-g-PMMA [12]. Similarly, when PLO or PSB is contained in its structure, PLO-g-PMMA or PSB-g-PMMA copolymers display decreased values for the stress at its break point (0.6 MPa and 7.5 MPa). The strain value at its break point (7.6 % and 12.1 %, respectively) when compared to PMMA. PnBMA has approximately 7.5 MPa stress at the break point and 370 % strain at the break point. Likewise, when PLina is contained in its structure, the PLina-g-PnBMA copolymer is reduced values for the stress at its break point (3.4 MPa), further increasing the strain value at its break point (500 %) when compared with PnBMA. The copolymer films prepared due to the presence of the triglyceride molecules acting as plasticizers in the system increased the tensile strength while decreasing elongation at break.

Contact-angle techniques are used routinely in the characterization of biomaterials to describe surface hydrophilicity (wettability). According to the literature, the optimal water contact angle of a material for protein adsorption and cell adhesion was suggested to be in the range of 40–65 [38, 48]. The contact angles were measured through the water phase, so relatively small contact-angle values indicate a relatively more hydrophilic surface. Figure 3 shows the photographs of the water drops on the polymeric oil/oil acid polymer films. The surface hydrophilicity of polymeric

oil/oil acid graft copolymers, as characterized by contact angle, is shown in Fig. 4. In the literature, the contact angle measurements were 66° for PMMA, 90° for PS, and 85° for PnBMA. PMMA is less hydrophobic than PS, with PMMA having a hydrophilic ester group in its repeat unit. Water is a poor solvent for PMMA and even poorer for PS; the former had a lower water contact angle ($\theta_{\text{PMMA}} \sim 66^\circ$) than the latter ($\theta_{\text{PS}} \sim 90^\circ$). Thus, the kinetics of the collapse for the two polymers may be different. PS forms a single compact globule, whereas PMMA undergoes a “pearling” transition before completely collapsing [49–53]. As described in earlier publications, the advancing water contact angle of tethered PS-*b*-PMMA brushes increased from 74° (characteristic value for PMMA) to 99° (characteristic value for PS) [54]. Furthermore, contact angle measurements polystyrene-poly(β -hydroxynanoate graft copolymer films cast from different solvents (chloroform, toluene, cyclohexanone, and butyl acetate) were used [55].

In our results, the contact angle measurements of polymeric oil/oil acid graft copolymers were compared with those of pure PMMA, PS, and PnBMA. While 90° for PS, the contact angle measurements of the PLO-g-PS (62°) and PLina-g-PS (67.7°) decreased with the inclusion of polymeric linseed oil and linoleic acid in the copolymer structure. Similarly, whereas it has been 66° for PMMA, the contact angle measurements of polymeric oil/oil acid copolymers were found to 43.3° for PLO-g-PMMA, 70.7° and 68.6° for PSB-g-PMMA, and 73.3° and 46.7° for PLina-g-PMMA. The reason for the decreasing values was the inclusion of polymeric linseed oil, soybean oil, or linoleic acid in the copolymer structures. Similarly, other values were found 85° for PnBMA and 49.8° for PLina-g-PnBMA. Thus, polymeric oil/oil acid including these copolymers were indicated the surface hydrophilicity.

For specific applications, it is often necessary to optimize the surface properties of polymeric biomaterials through various surface modification methods [36]. However in this work, DNA adsorption experiments on untreated polymer

surfaces were conducted at pH7.4 and were detected by monitoring the decrease in UV absorbance at 260 nm. The results obtained are shown in Fig. 3. The amount of DNA adsorption on hydrophobic PMMA, PS, PnBMA and surfaces was 3.3 μg and 3.6 μg , respectively. However, the DNA adsorption of Polymeric Oil/Oil Acid-g-PMMA (PS or PnBMA) was lower than that of PMMA and PS. For example, the DNA adsorption amounts were found to be 0.83 μg for PLin-g-PMMA, 1.95 μg for PSB-g-PMMA, 1.13 μg for PHA-PSB-PMMA, 2.14 μg for PLina-g-PMMA, 1.87 μg for PLina-g-PnBMA, and 1.95 μg for PLina-g-PS. The reason for the reduction is the polymeric linseed oil, polymeric soybean oil, or polymeric linoleic acid found in the structure of polymeric oil/oil acid graft copolymers.

Conclusion

Considering the results in this work, it is clear that PLO, PSB, and PLina blocks acting like plasticizers in the copolymer affect the mechanical strength and ductility of polymers. For Tg of PHA-PLina-PMMA multigraft copolymer is higher than PMMA, PLina blocks may not acting like plasticizers But Plina and PHA blocks affect the mechanical strength and ductility of multigraft copolymers. Tg of a polymeric oil/oil acid-g PMMA were compared with pure PMMA. They were found to be different from those of both the DSC and DMA analysis results. The glass transition temperature determined from the peak of the $\tan \delta$ curve is higher than the one determined by DSC, which can be related to the heat-transporting hysteresis for large-scale samples in DMA. Hydrophilicity describes a surface characteristic of promoting water absorption in the polymer. The presence of the triglyceride/oil acid molecules plays an important role in decreasing hydrophobicity and adsorption of DNA. As a result, the biocompatible polymeric oil/oil acid copolymers may be a promising biomaterial for medical and industrial applications with low bacterial adherence and protein adsorption, as previous papers have implied [9–12].

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