

Properties of Crosslinked Polyurethanes Obtained by Acrylic Side-Group Polymerization and of Their Blends with Various Plant Oils

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ABSTRACT: Novel polyurethane elastomers have been developed to incorporate plant oil into their matrix. Bisphenol A glycerolate diacrylate was used as a chain extender for the polyurethane prepolymer obtained from poly(tetramethylene oxide) glycol and 1,6-hexane diisocyanate. The curing of the polyurethane acrylate matrix in the presence of the plant oil results in a network matrix which includes renewable resources in their structure. The effects of the inclusion of different vegetable oil (such as soybean oil, rapeseed oil, cotton oil, or sunflower oil) into the crosslinked polyurethane acrylates matrix were studied by evaluating various properties of the films such as the thermal behavior, the tensile properties, and the surface properties. The increases in chain extender content determine an increase of the thermal stability (the 10% weight loss decomposition temperatures increase from 325 to 375°C) and mechanical strength (from 3 to 9 MPa). Contact angle measurements have shown that the hydrophobic property of the films surface slightly increased with the incorporation of plant oil into the crosslinked polyurethane matrix. In addition, polyurethane/plant oil blends exhibit enhanced mechanical strength (from 3 to 9.8 MPa), as well as an increased roughness reaching a maximum average (113 nm) in the case of cotton oil. All polyurethane/plant oil blend present higher values for glass transition temperature and slightly enhanced values for thermal stability. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3640–3649, 2013

KEYWORDS: blends; crosslinking; mechanical properties; polyurethanes; thermal properties

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INTRODUCTION

Polyurethanes are important polymers in many application fields due to various useful properties such as high impact strength, good elasticity, high mechanical, and chemical resistance and good adhesion. The morphology and properties of these materials can be improved by the use of new chain extender structures which allow for new intermolecular associations and lead to an improved structural integrity of the hard segment domain. Additionally, the structural integrity of the polyurethane matrix can be improved by chemical crosslinks introduced by multifunctional chain extenders.^{1–12} Blending with new materials with low compatibility can open ways for obtaining new properties of the materials.¹³

Recently, environment-friendly materials from renewable raw materials such as cellulose, starch, polysaccharides, protein, plant oil, and so forth, have been used to obtain an easily degradable and low toxicity polymer matrix. This can be achieved by the synthesis of synthetic polymers from natural resources or by mixtures of synthetic polymers with natural

polymers.^{2,14,15} One of the most frequently used renewable raw materials for polymer applications are plant oils. The properties of the plant oils, when integrated in the polymer matrix, are different depending on the stereochemistry of the double bonds of the fatty acid chains, their degree of unsaturation as well as the length of the carbon chain of the fatty acids.^{16–19} But most of these materials have inferior mechanical and thermo-physical properties in comparison with conventional polymers.²⁰

To minimize these shortcomings we introduce the acrylate groups as side groups along the polyurethane main chain using Bisphenol A glycerolate diacrylate as chain extenders. Our goal is to develop novel flexible crosslinked polyurethane acrylates obtained by polymerization of multi-acrylates side-groups and inclusion into the resultant matrices of different amounts of plant oil. This ensures the preservation of the polymers networks properties and fixing of the plant oil into the enmeshing polymer matrix. The cured materials thus obtained were evaluated for their thermal-mechanical behavior and surface properties.

EXPERIMENTAL

Materials

The poly(ether)diol that was used was poly(tetramethylene oxide) glycol of a molecular weight of 1400 (Terathane 1400) (Aldrich, Switzerland) which was dried in high vacuum for 2 h at 120°C prior to use. All other chemicals were used as received. Rapeseed oil, cotton oil, and 1,6-hexamethylene diisocyanate (HDI) were obtained from Fluka (Switzerland). Soybean oil, sunflower oil and Bisphenol A glycerolate diacrylate (BPA-GDA, which contains two acrylates and two hydroxyl groups) were purchased from Sigma-Aldrich.

Preparation of the Polyurethane Prepolymer

The polyurethane acrylate prepolymer was synthesized using a two-step polymerization procedure. These polyurethanes were synthesized in the absence of any catalyst and with molar ratios of poly(ether)-diol/HDI/(BPA-GDA) of 1/2/1, 1/3/2, and 1/4/3. The composition of the samples is given in Table I while the chemical structures of the polyurethane acrylate and chain extender (BPA-GDA) are given in Figure 1.

First, the isocyanate end-capped urethane prepolymer was prepared by reaction of the required amounts of dried poly(ether)-diol and HDI, in a 250 mL glass reactor equipped with a mechanical stirrer, a drying tube connected to the vacuum pump and an oil bath, at 80°C for 2 h. Afterwards, the ending NCO groups of the obtained prepolymer were chain-extended using the stoichiometric amount of BPA-GDA and 15 mL DMF as solvent at 80°C until all the NCO groups were reacted, which was confirmed by the disappearance of the IR peak of NCO (2260 cm⁻¹). The samples of the polyurethane acrylate product were cast onto cleaned glass plates and kept at 80°C for 24 h to obtain the crosslinked pure polyurethane acrylate film. Polyurethane films thus prepared were used for the determination of thermal-mechanical and surface properties.

Preparation of the Polyurethane/Plant Oil Mixtures

For the preparation of polymers blends, 10 or 20% (by weight) of the plant oil was dispersed into the polyurethane acrylate prepolymer at the end of its synthesis. The polymers mixture

Table I. Formulations of the Obtained Polyurethane Acrylates and Polyurethane Acrylates/Plant Oil Mixtures

Samples	Polyether/HDI/BPA-GDA molar ratio	Type and amount of plant oil
P1	1 : 2 : 1	-
P2	1 : 3 : 2	-
P3	1 : 4 : 3	-
P4	1 : 2 : 1	Soybean oil (10 wt %)
P5	1 : 2 : 1	Soybean oil (20 wt %)
P6	1 : 2 : 1	Rapeseed oil (10 wt %)
P7	1 : 2 : 1	Rapeseed oil (20 wt %)
P8	1 : 2 : 1	Cotton oil (10 wt %)
P9	1 : 2 : 1	Cotton oil (20 wt %)
P10	1 : 2 : 1	Sunflower oil (10 wt %)
P11	1 : 2 : 1	Sunflower oil (20 wt %)

was stirred at 80°C, for a short amount of time (10 min) to avoid the thermal polymerization of vinyl groups in the reaction vessel, thus obtaining a homogeneous composition. These polymers mixtures were used to obtain polymers blends films by conventional solvent casting method from DMF solution onto glass plates. After casting, the polymer mixtures were left for 24 h at 80°C to cure completely by means of thermal crosslinking enabled by the acrylate side-groups and then the solvent was removed. Thus, the plant oil is dispersed into the mesh formed by the acrylate crosslinks. Finally, a series of plant oil/polyurethane acrylate crosslinked composite films were obtained. The films thus prepared were used for the determination of thermal-mechanical properties and for surface behavior evaluation.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 Instrument equipped with a Golden Gate single reflection ATR accessory. The spectra were recorded in the range of 600–4000 cm⁻¹ with a nominal resolution of 4 cm⁻¹.

Thermogravimetric experiments took place in an air atmosphere through thermogravimetric analysis (TGA) using a DERIVATOGRAF Q-1500 D apparatus (Hungary). The rate of the TGA scans was of 10°C/min. The initial weight of the samples was about 50 mg and the temperature range 30–700°C.

Dynamic mechanical properties measurement was performed with a dynamic mechanical analyzer (Perkin Elmer Diamond DMA) at a constant heating rate of 2°C/min and 1 Hz, within a temperature range of -100 to 150°C. The sample dimension was of 10 × 10 × 0.5 mm³ and the tests were performed in extension mode.

The mechanical properties were determined using a Shimadzu EZTest (Japan), equipped with a 5 kN load cell. Dumbbell-shaped specimens were prepared using dies (75 × 12.5 × 4 mm³; ISO 37 type 2). The test specimens that were cut from the samples were no more than 0.5-mm thick. The specimens were prepared so as to be free of surface roughness, fabric layers, and so forth. The tests were performed at room temperature (23°C), with a cross-head speed of 50 mm/min. All the tests were conducted on five samples of each product and the averaged values were reported.

The surface tension of the samples surfaces was measured by means of static contact angle using the sessile drop method on a Dataphysics Contact Angle System KSV Instruments, Finland. Contact angle measurements were performed at room temperature using deionized water and ethylene glycol. Each contact angle measurement was recorded within the first 10–20 s following the placement of the sessile drop over a fresh surface region and repeated for cross-verification. The contact angle was measured with an accuracy of ±2°.

Atomic force microscopy (AFM) measurements of the samples were performed at room temperature and ambient pressure, using a Scanning Probe Microscop SOLVER PRO-M, NT-MDT (Russia). The film surfaces morphology was investigated by AFM in the tapping mode with silicon cantilever NSG10.

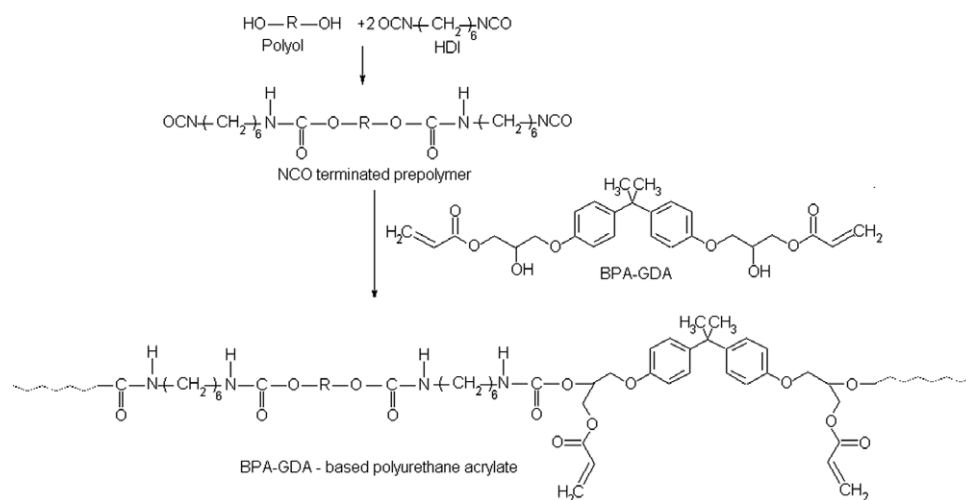


Figure 1. Schematic representation of BPA-GDA -based polyurethane acrylate synthesis.

RESULTS AND DISCUSSION

Polyurethanes with bisphenol A glycerolate moieties in the main chain and polymerized acrylates side-chain groups were synthesized in absence or by inclusion of the various plant oil content. Thus a designed crosslinked polyurethane architecture was obtained by polymerization of the unsaturated side-groups and by the inclusion of a relatively high content of unmodified plant oil into a specific morphological matrix, in order to preserve or improve chemical, physical and biological properties.

FTIR Spectroscopy

The effects of the chain extender content and plant oil nature on the polyurethane interchains bonds and polyurethane–plant oil interactions were studied by FTIR spectroscopic analysis. Urethane group formation is indicated by the absence of the peak around 2260 cm^{-1} for the free NCO group (Figure 2).

Also, the polyurethanes exhibit the typical signals of urethane absorption, with peaks for —NH at 3330 cm^{-1} , at $2856\text{–}2937\text{ cm}^{-1}$ (CH_2 and CH_3), as well as the ether stretching absorption at 1100 cm^{-1} (C—O—C). The carbonyl stretching vibration bands appears at 1721 cm^{-1} corresponding to urethane and acrylic ester groups.

The spectra of pure polyurethane acrylates (P1–P3) showed slight increases in the intensity of the absorption peaks at 1634 cm^{-1} (C=C), 1408 cm^{-1} (CH_2), and 831 cm^{-1} (CH) with the increase of the BPA-GDA—chain extender—content. This certifies that the acrylate C=C group had been incorporated into the polyurethane matrix.²¹

All the obtained polyurethane-plant oil blends showed a decrease in intensity for the peak at 1408 cm^{-1} and the peak from 981 cm^{-1} . The absorption peak at 981 cm^{-1} is assigned to the C—H out of the plane bending in acrylate group —CH=CH_2 .

Thermal Analysis

The TGA thermograms (Figure 3) show the thermal behavior of the polyurethane acrylates with different BPA-GDA content and of the polyurethane acrylate blended with different plant oils.

The increase of the BPA-GDA content enhances thermal stability [Figure 3(a)]. Thereby, the 10% weight loss decomposition temperatures of polyurethane acrylates rise from 325°C (P1) to 375°C (P3) both with increase in acrylate groups and in hard segment content. This is a result of the increased density of polymer crosslinks due to the presence of more acrylate groups which are crosslinked. The maximum weight loss decomposition temperature is around 400°C and is caused by the decomposition of the polymer backbone. The final loss at around $450\text{–}600^\circ\text{C}$ is attributed to the final decomposition of the crosslinked fragments and oxidation of the carbon residue.

Also, polyurethane acrylates blended with plant oil as soybean oil (P8) and cotton oil (P10) showed better thermal stability than pure polyurethane acrylates (P1). This can be explained by the strong interaction between the crosslinked polyurethane acrylate chains and the plant oil in the blends which delays thermal degradation. This slight increase in thermal stability can be attributed to the good thermal stability of the plant oil that prevents the easy migration of the volatile product resulted during thermal decomposition.

The influence of the chain extender content and plant oil nature on the thermal behavior was studied by the storage modulus (E') and $\tan D$ of the samples within the temperature range of $-100\text{–}150^\circ\text{C}$ through dynamic mechanical analysis (DMA). Figure 4 shows the storage modulus (E') and $\tan D$ curves as a function of temperature for different samples.

After rapid decreases of the storage modulus, corresponding to the glass transition temperature, a plateau appears in the storage modulus/temperature curves, as evidence for the existence of the crosslinked network in the polyurethane acrylates matrix. Only one peak was observed in the $\tan D$ versus T curves for all of the pure polyurethane acrylates as well as for the polyurethane/plant oil blends. This indicates that they are homogeneous samples. The glass transition temperature values—measured as the maximum in the $\tan D$ versus temperature curves—increased from -28°C (P1) to 1.5°C (P3) in the case of pure polyurethane acrylates [Figure 4(a)]. Also, a slight increase in intensity of the $\tan D$ peaks was observed as a result of the

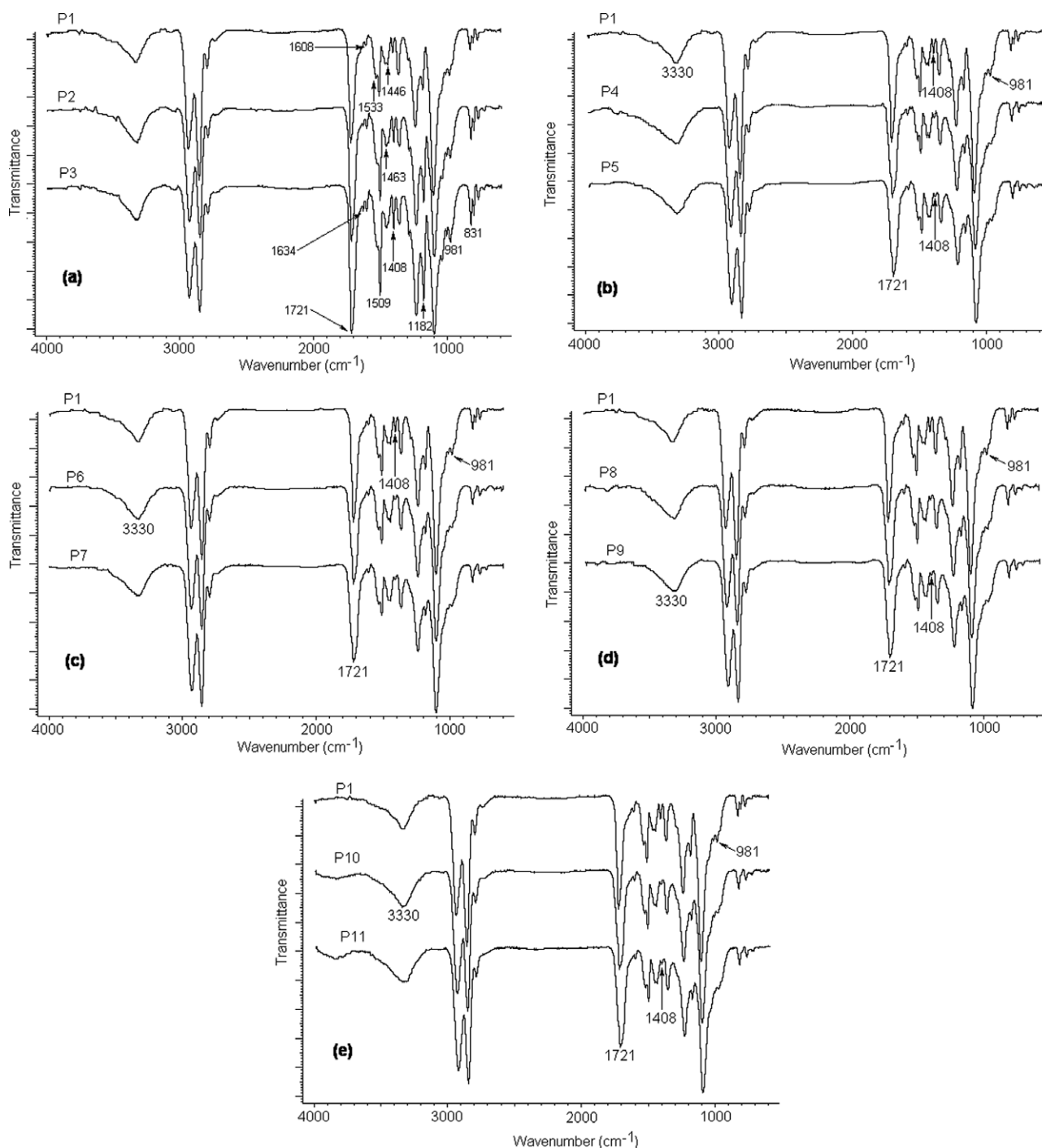


Figure 2. FTIR spectra of the pure polyurethane acrylates (P1–P3) and blends with plant oil (P4–P11).

increases of polymerized side-chain acrylate groups. In this case, the $\tan D$ intensity depends on the characteristics of the all major constituents and on the nature of their chains interactions. The sample with fewer acrylates side-chain groups and low hard segment content (P1) exhibit a strong hydrogen bond physical network within the urethane structure, which leads to a decrease in freedom of movement of the molecular segments. When increasing the amount of acrylates side-chain groups, the higher chemical crosslinks content hindered the formation of

the hydrogen bond physical network. This provides enhanced chain mobility between chemical crosslinks. This results in slight increases of the $\tan D$ intensity especially in the case of highly crosslinked networks (P3).

Mixtures of polyurethane acrylates–plant oil develop new interaction points that determine an increase in rigidity reflected in the decreases of $\tan D$ intensity. Also, higher glass transition temperatures were observed in polyurethane/plant oil blends

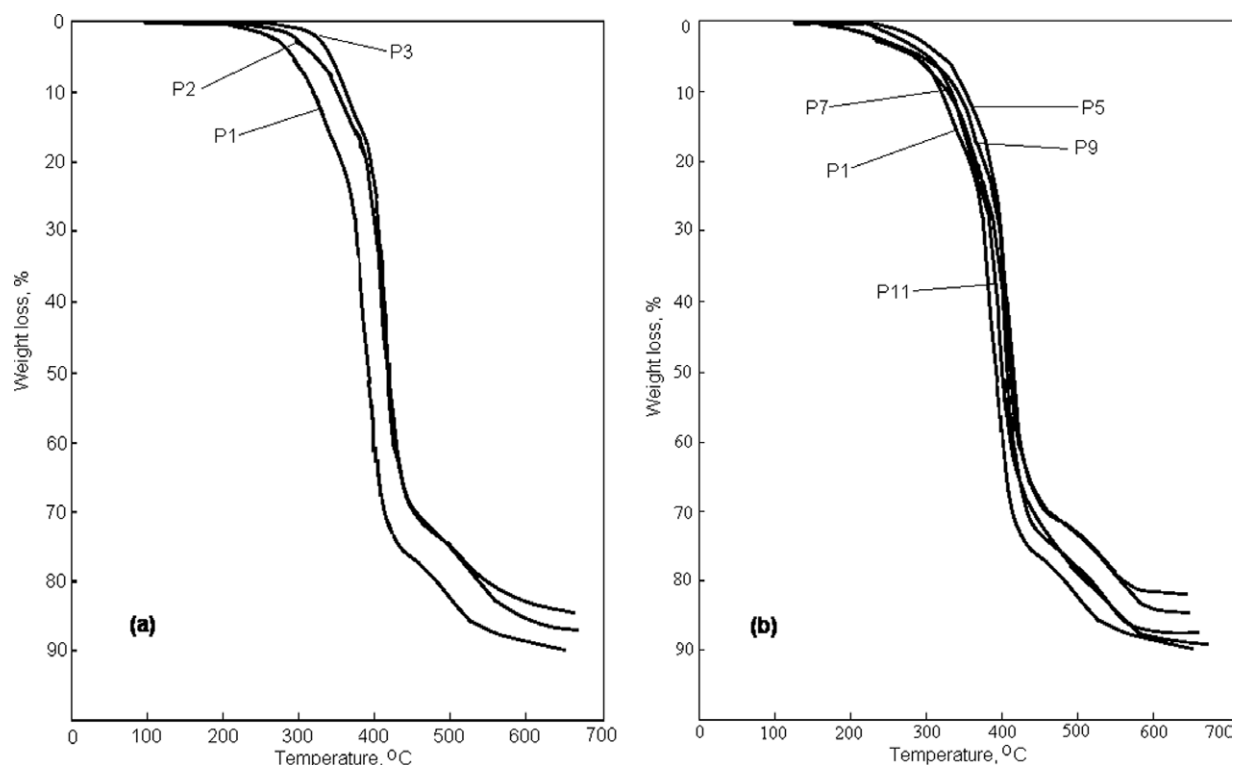


Figure 3. TGA thermograms of pure polyurethane acrylates (P1–P3) and high content plant oil blends (P5, P7, P9, and P11) under air atmosphere at a heating rate of 10°C/min.

compared with pure polyurethane acrylate resins. The introduction of plant oil into the polymerized polyurethane matrix increases glass transition temperature, concurred with a broadening and decrease in intensity of the $\tan \delta$ peaks of the polyurethane/plant oil blends. This may indicate that plant oil inclusion led to decreased interaction between polyurethane chains and increased the level of association between the polyurethane matrix and plant oil. In addition, the plant oil component introduces two contrary effects: on one hand, a hydrogen bonds intermolecular strengthening effect and, on the other hand, a plasticizing effect due to the dangling chain. The migration of plant oil inside polyurethane acrylates network can thus be prevented by exploiting these effects.

Mechanical Properties

Figure 5 shows the stress versus strain curves of the pure polyurethane films [Figure 5(a)] and polyurethane/plant oil blend films [Figure 5(b)].

The pure polyurethane acrylates films showed increased stress values with the increase of the BPA-GDA content, accompanied by a decrease in the strain values. This is a result of the higher hard-domain cohesion which determines changes in mechanical properties.

Samples containing plant oil into their matrices present enhanced stress values compared with the pure polyurethane acrylates from the polymer matrix. All the plant oil blend samples show decreased elongation at break values. This is consistent with other measurements results showing that plant oil

phase form an active interaction with the host polyurethane matrix. Each plant oil blend showed different thermal-mechanical behavior which are related to change in the structure and morphology of the unsaturated components.

Surface Properties

Contact Angle. If for modern applications as protective coatings and structural elastomers the polymers must have improved polarity, in the case of biomaterials the surface must be more hydrophobic.²² The surface properties are given by the mobility and flexibility of the molecular chain which in the case of polyurethanes are determined by the chemical and morphological structure of the hard segments. The hydrophobic or hydrophilic properties of the polymer surface can be measured by means of static contact angle. The contact angle is composed of interactions of the three interfaces as described by Young's equation:²³

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos(\theta) \quad (1)$$

The work of adhesion (W_a) of a liquid drop to a solid surface was calculated with the Young–Dupree equation²⁴

$$W_a = \gamma_{LV} (1 + \cos \theta) \quad (2)$$

where γ_{SV} , γ_{SL} , and γ_{LV} represent the interfacial tension of the solid/vapor, solid/liquid, and liquid/vapor interfaces. The equilibrium contact angle is represented by θ .

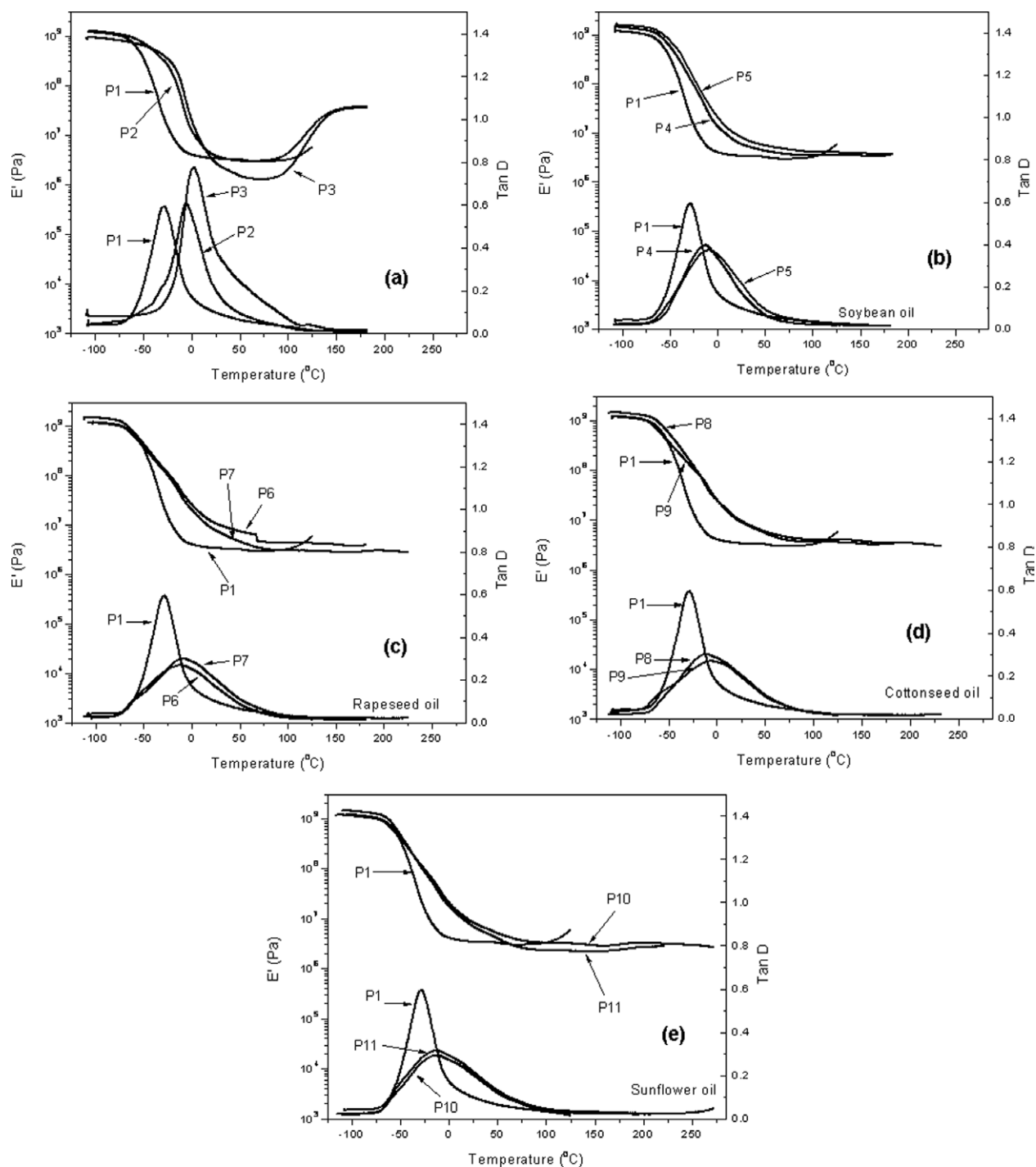


Figure 4. DMA spectra of pure polyurethane acrylates (P1–P3) and their blends with different plant oils (P4–P11).

The measured contact angles of pure polyurethane acrylates and mixtures with plant oils and the surface tension values are given in Tables II and III, respectively.

The pure polyurethane acrylates present a gradually decrease in contact angle values with the increase in BPA-GDA content. Thus the sample with the smallest content of chain extender (P1) has the highest contact angle (91°) and the sample with the highest content of chain extender (P3) has the smallest con-

tact angle (82°). This can be explained by the increased content of hard segment with polar acrylates groups which can be found at the surface of the polymer films.

In the case of plant oil blends the contact angle increase with the increase in plant oil content. This can be explained by the interaction of the plant oil with the polymer matrix and by the hydrophobic nature of the plant oil.

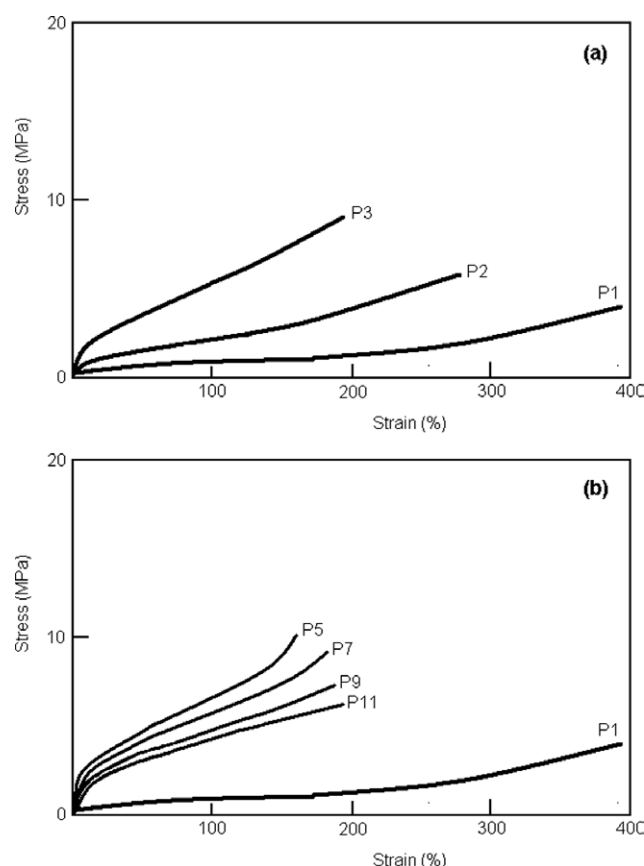


Figure 5. Stress versus strain curves for pure polyurethanes (P1–P3) and blends with different plant oils (P5, P7, P9, and P11) of the BPA-GDA-based polyurethane acrylates films.

The surface energy (γ_{SL}) for the solid phase (S), and wetting liquid (L) was found on the basis of the Owens–Wendt method and is a result of dispersion interactions and polar interactions.²⁵

$$\gamma_{SL} = \gamma_{SL}^d + \gamma_{SL}^p \quad (3)$$

Table II. Contact Angle (θ) and W_a Values of the Polyurethane Acrylate and Polyurethane Acrylate/Plant Oils Blend Film-Surfaces

Sample	Water		Ethylene glycol	
	θ (°)	W_a (mN/m)	θ (°)	W_a (mN/m)
P1	91	71	72	62
P2	85	79	72	62
P3	82	82	66	67
P4	89	73	73	61
P5	93	68	79	57
P6	87	76	66	67
P7	88	75	59	72
P8	93	69	71	63
P9	95	66	76	59
P10	93	68	72	62
P11	99	60	79	57

Table III. Interfacial Tension for a Solid-Liquid System (γ_{SL}) in Polyurethane Acrylate and Polyurethane Acrylate/Plant Oils Composite Films

Sample	γ_{SL}^p (mN/m)	γ_{SL}^d (mN/m)	γ_{SL} (mN/m)	
			Water	Ethylene glycol
P1	6	15	22.6	5.9
P2	13	8	15.3	7
P3	13	11	14.3	4.8
P4	9	10.6	18.9	6.3
P5	8	8.8	21.2	8
P6	7	16.8	20.3	4.5
P7	3	27.5	28.6	6.4
P8	4	18	26	6.5
P9	4	13.8	25.1	7.4
P10	4	17.2	25.8	6.7
P11	2	15.5	30.7	9.4

p—polar, d—disperse.

Polar interactions are given by permanent and induced dipoles interactions. Dispersive interactions are caused by the variation in time of the charge distribution within the molecules.²⁵ The surface energy for a liquid that interacts with a solid must also satisfy an Owens–Wendt equation:

$$\gamma_L \cdot \frac{1 + \cos\theta}{2} = \sqrt{\gamma_S^d \cdot \gamma_L^d} + \sqrt{\gamma_S^p \cdot \gamma_L^p} \quad (4)$$

where, θ is the experimentally found contact angle. The values calculated by eq. (4) are given in Table III. The values of the surface tension tend to decrease with the increase in chain extender content, following the same trend as contact angle values. The increase in surface energy for polyurethane acrylate/plant oil can be explained by the introduction of polar functional groups provided by the plant oil.

AFM. Surface morphology and roughness of the obtained films are determined by molecular surface-structures. The surface properties of the pure polyurethane acrylates and their blends with plant oil were also studied by AFM measurements (Figure 6 and Table IV).

Average roughness (S_a), root mean square roughness (S_q) and maximum height roughness (S_{max}) values slightly increase with the increase of the BPA-GDA content into polyurethane matrix. Average roughness has values up to 2 nm (P3) that result in highly uniform films. This indicates slight changes in the surface morphology of pure polymers accompanied by structural change of the hard domain, which is consistent with other made measurements (FTIR, stress–strain properties).

The roughness increased for polyurethane/plant oil blends, in that the lowest values (2.26 nm) were obtained for soybean oil (P5) and the highest values (113.3 nm) were obtained for

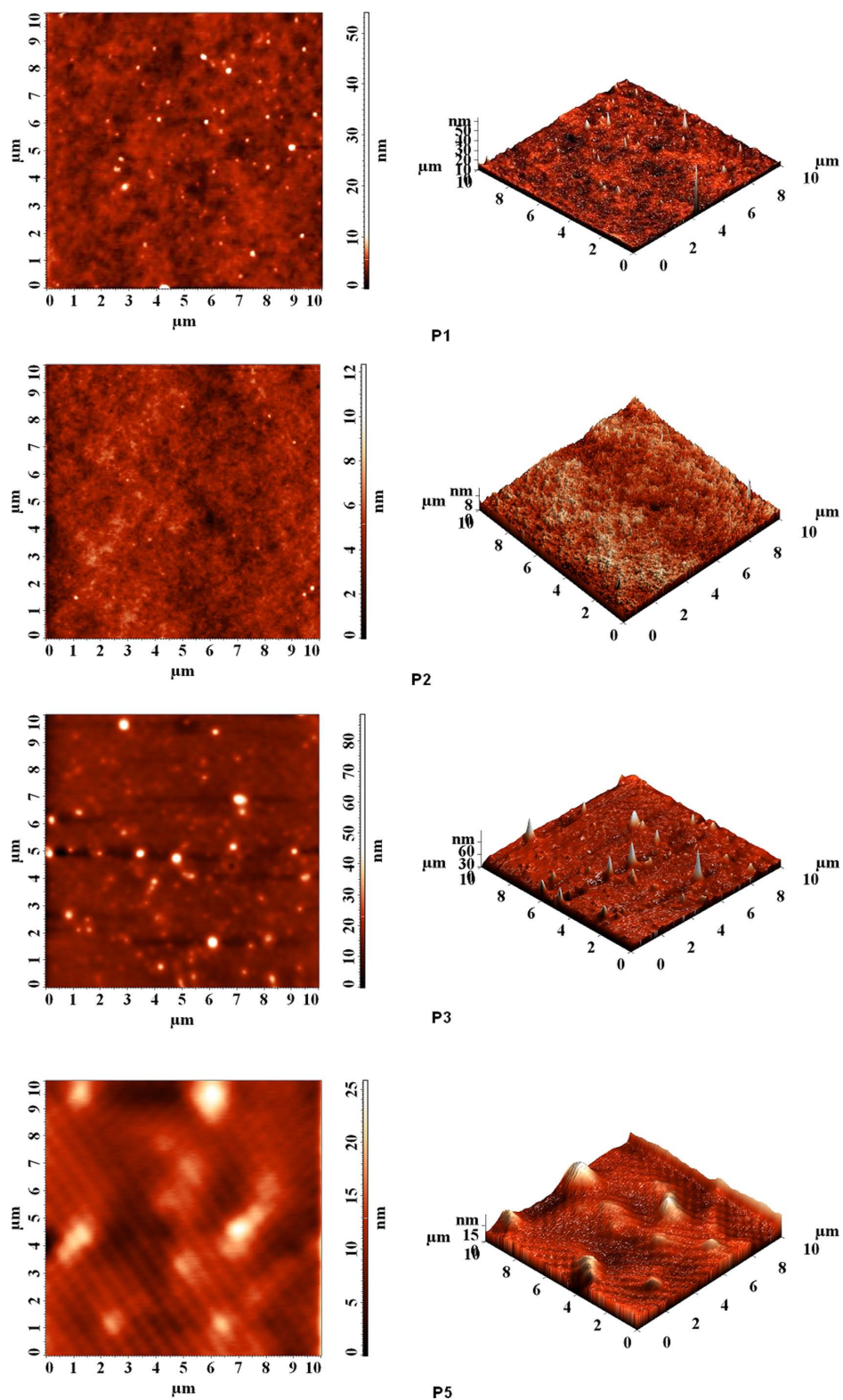


Figure 6. AFM tapping-mode images of the free surface for pure polyurethanes (P1-P3) and blends with different plant oils (P5, P7, P9, and P11) of the BPA-GDA-based polyurethane acrylates films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

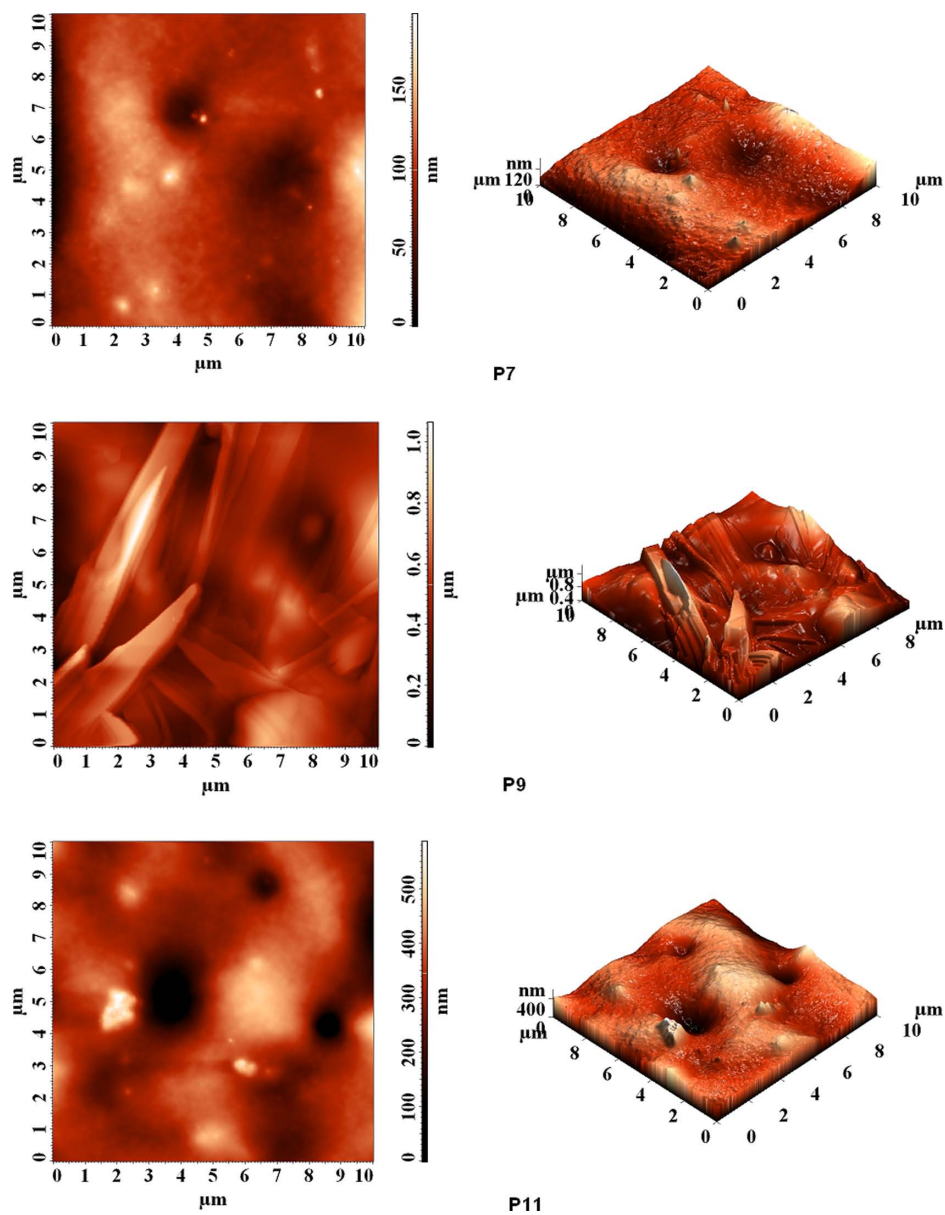


Figure 6. (Continued)

Table IV. Average Roughness (S_a), Root Mean Square Roughness (S_q), and Maximum Height Roughness (S_{max}) Values of Polyurethane Acrylates and Plant Oil/Polyurethane Acrylate Composites

Samples	Average roughness (S_a) (nm)	Root mean square roughness (S_q) (nm)	Maximum height roughness (S_{max}) (nm)
P1	0.63	0.86	12.31
P2	0.67	1	53.9
P3	2.12	3.78	88.3
P5	2.26	3.06	25.77
P7	21.86	27.98	198.03
P9	113.3	145.62	1061.79
P11	59.59	78.47	586.28

cottonseed oil blend sample (P9) which exhibited a more irregular surface morphology.

Figure 6, P5 shows an AFM image of the soybean oil blends, with the oil being well dispersed within the polyurethane matrix and presenting oval polymer aggregates similar to pure polyurethane acrylates with high hard domain content (P3). The blends with cottonseed oil (P9) present lamellar polymer aggregates accounting for the highest root mean square roughness (145 nm).

The blends with rapeseed oil (P7) and sunflower oil (P11) present small holes on surface as a result of poorer dispersion of the plant oil into the polymer matrix.

The interface structures between the polyurethane matrix and plant oil determine the miscibility and properties of polymer blends.²⁶ As the plant oil changes the roughness of the blend films, it can be deduced that the plant oil affects the morphology of crosslinked polyurethane molecules by mutual connections between the plant oil molecules and the polyurethane matrix. This is due to a good dispersion of the plant oil into the polyurethane network matrix.

CONCLUSIONS

Polyurethane networks were obtained by polymerization of the multiacrylic side-groups of the polyurethane chain-extended with Bisphenol A glycerolate diacrylate. A complementary series of mixture samples was also obtained by inclusion of different plant oils into polyurethane sites matrices.

Increasing the amount of chain extender leads to an improvement of the thermal and mechanical properties and of the surface behavior.

The presence of plant oil into the crosslinked polyurethane matrix changes some of the physical properties such as the surface, thermal and mechanical properties.

The inclusion of unchanged triglyceride oils into the crosslinked polyurethane matrix is expected to increase the biodegradability of these polymer blends, possibility which remains to be verified in future.

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