

Synthesis and Characterization of Linseed Oil Polyurethanes

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Abstract

Polyurethane (PUR) plastic sheets (PLOH/PEG/HMDI and PLOH/PPG/HMDI) were prepared by reacting hydroxylated polymeric linseed oil (PLOH) synthesized from autoxidized linseed oil with diamine terminated polyethylene glycol (PEG) or diamine terminated polypropylene glycol (PPG) in the presence of hexamethylene diisocyanate (HMDI). The polyurethane and PLOH was used to identify chemical reactions by the fourier transform infrared (FTIR), nuclear magnetic resonance technique (¹H-NMR) techniques. These polyurethanes have different valuable properties that are determined by their chemical composition. The effect of stoichiometric balance (i.e., the PLOH/PEG/HMD and PLOH/PPG/HMDI weight ratio) on the final properties was evaluated. The properties of the materials were measured by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA).

Key words: Polyurethane, Linseed oil, Autoxidation, Hydroxylated Linseed oil.

1. Introduction

Polyurethanes, which are among the most important polymeric materials, exhibit versatile properties that are suitable for use in many fields, such as the footwear, machinery, automotive and furniture industries, as well as in the production of paints, adhesives, construction materials and coatings, flexible and rigid foams, rigid insulation materials, elastic fibers, and medical devices [1, 2]. Recently, due to their excellent biocompatibility and biostability, polyurethanes have found application as biomedical materials [3]. In recent decades, most of the starting materials for the production of PUs have been derived from petroleum-based resources, which are widely regarded as unsustainable [4]. With the depletion of petrochemical resources, the replacement of classical petrochemical reactants with bio-based molecules is of increasing importance [5]. The design of polyurethanes derived from renewable sources has increased demand because of the depletion of the global crude oil stock and economical, environmental, and social concerns. [6] Plant oils, as well as fatty acids, have been used in polyurethane technology for a long period of time. [1]. Polyurethane is defined as a polymer, which contains urethane groups (–NH–COO–) in the main polymeric chain, and may also contain other functional groups, such as ester, ether, urea and amide [7, 8]. The polymeric chains consist of alternating short sequences of soft (flexible) polyol and hard (rigid) isocyanate segments. The physical, mechanical, and adhesive properties of polyurethane strongly depend on the composition and chemical structure of the hard and soft segments. PU possesses excellent abrasion resistance, low temperature flexibility, high strength, aging, and chemical resistance [7, 8]. Therefore, the synthesis of bio-based polyurethanes has been widely studied with respect to the use of macrodiols derived from vegetable oils, such as castor, rapeseed, and linseed oil, in the past several decades [6]. In our continuing research, polymeric oil peroxides

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derived from polyunsaturated vegetable oils by autoxidation have been used in the polymerization of vinyl monomers to obtain graft copolymers [9–12]. Hazer and colleagues have synthesized water soluble hydroxylated soya oil polymer from autoxidized soya oil polymeric peroxide and diethanol amine [13]. Their other work prepared segmented PUR from polymeric soybean oil polyols (PSb-OH) and polyethylene glycol (PEG) in the presence of a diisocyanate, isophorone diisocyanate (IPDI) [8]. In other work, triglyceride oil-modified polyurethane films for wound dressing applications were prepared from linseed oil-based hydroxyl containing material and hexamethylene diisocyanate and/or diphenylmethane diisocyanate (MDI) [14].

Our efforts in this work to prepare PLOH/PEG/HMDI and PLOH/PPG/HMDI from PLO and diamine terminated polyethylene glycol or polypropylene glycol in the presence of a diisocyanate, hexamethylene diisocyanate. The thermal properties of obtained polyurethanes were evaluated.

2. Materials and Method

2.1. Materials

Linseed oil (LO) was a gift from Arifoğlu Baharat Gıda San. Ltd. (Şti, Turkey). The LO composition included 46.8 wt% linolenic acid, 16.03 wt% linoleic acid, 25.73 wt% oleic acids, 3.4 wt% stearic acid, and 6.8 wt% palmitic acid.

Polymeric Linseed Oil (PLO) was obtained by the auto-oxidation of linseed oil in air at room temperature as previously described [9]. The yield of the soluble polymeric linseed oil was 60 wt%. Mw: 5100 and Mn: 3100 g/mol.

Antioxidant adduct inside this commercial linseed oil was removed by leaching with ethanol three times. Diamine ended polypropylene glycol (Polyoxypropylenediamine) with the trade name Jeffamine D-2000 (PPG) is a difunctional primary amine with an average molecular weight of approximately 2000. Diamine ended polyetheramine based on a predominantly PEG backbone. [i.e., another name for polyethylene glycol (PEG) under the trade name Jeffamine ED-2003 (polypropylene glycol–block polyethylene glycol–block polypropylene glycol)] is a water-soluble aliphatic diamine with MW~2000 g/mol. The PPG-2000 and PEG-2000 were a gift from Huntsman Co. (Istanbul). Hexamethylene diisocyanate (HMDI) and diethanol amine were supplied from Merck. Tin(II) 2-ethylhexanoate (tin(II) octoate or stannous octoate) (Sn(Oct)₂) were supplied by Sigma-Aldrich. The solvents were supplied by Aldrich and were used after conventional purification processes.

2.2. Synthesis of Hydroxylated Linseed Oil (PLOH)

Synthesis of hydroxylated linseed oil was carried out by using the procedure as reported before [13]. The hydroxylation reaction of PLO and diethanol amine was performed in a round-bottom flask at 90°C for 24 h. For example, a round-bottom flask (250 mL) containing 5.0 g of PLO and 5.0 mL of diethanol amine were kept in an oil bath at 90°C for a day. The crude product was dissolved in 20 mL of acetone. It was filtered, then PLOH was precipitated into 100 mL of petroleum ether. Next the product was dried under vacuum at room temperature for 24 h.

2.3. Synthesis of PURs

In this work, two different methods were applied to obtain PURs as a film

Method A:

PURs were synthesized from polymeric linseed oil polyol and PEG or PPG with a molecular weight of -2000 by using HMDI as a coupling reagent in a solution. Typically, 1 g of PLOH ($M_n = 3100$), 1 g of HDMI, and 1 g of PEG ($M_n = 2000$) were dissolved in 10 mL of anhydrous 1,2 dichloroethane containing two drops of stannous octanoate. The reaction mixture was stirred at 115 °C under dried nitrogen for 12 hours. The resultant PLOH/PEG/HMDI segmented polyurethane was precipitated from methanol and dried under vacuum. PLOH/PPG/HMDI was produced according to the same method. The PUR samples were prepared as a film.

Method B:

In the amounts indicated in table 2, PLOH, PEG with molecular weight -2000 D, and two drops of stannous octanoate and dry xylene were placed in a reaction flask and stirred on the atmosphere conditions for 30 min. The reaction mixture was heated to 45°C and different amounts of HMDI were added slowly over a 30-min period under the nitrogen atmosphere. The solution was spread and molded into a steel ring on a teflon-coated glass. This PU formation was carried out with this teflon-coated glass mould by placing it into an oven preheated to 90 °C at 24 h. Xylene solution was evaporated at room temperature for 24 h. The results of the grafting procedure are listed in Table 2. The resultant PLOH/PEG/HMDI segmented polyurethane was precipitated from methanol and dried under vacuum. PLOH/PPG/HMDI was produced according to the same method.

Characterization

FT-IR spectra of the samples were recorded using a Perkin Elmer 400 FT-IR Spectrometer Spotlight 400 Imaging System model FT-ATR Fourier Transform Infrared Spectrometer.

The molecular weight of the polymeric samples were determined by Malvern Viscotek model gel permeation chromatography (GPC) in THF solution at 35 °C, at a low rate of 1 mL/min using OmniSEC 4.7 Software. This GPC system contained an OmniSEC column furnace (35 °C), three separation columns (OmniSEC TGuard, LT4000L, T2500), an RI Detector OmniSEC 3580, and an OmniSEC 2500 UV detector.

A CHNS-932 model LECO elemental analyzer was used for the elemental analysis of C and H in the PLOH.

Differential scanning calorimetry thermograms were obtained on a Perkin Elmer DSC 400 with a CC 200 liquid nitrogen cooling system to determine the glass transition temperatures (T_g) and melting transitions (T_m). For DSC analysis, samples were heated from -50 to 300 °C at a rate of 10 °C/min (first heating) and held at the final temperature for 1 min to eliminate the thermal history applied to the samples. After being cooled to -50 °C, they were then reheated to 300 °C at a rate of 10 °C/min (second heating). Thermogravimetric analysis was performed with a Seiko SII TG/DTA 7200 instrument to determine thermal degradation (T_g). The samples were heated 25 to 900 °C for TGA in a nitrogen atmosphere at a heating rate of 10 °C/min.

Hydroxyl Number

The hydroxyl values of the polyols were determined as 250 mg KOH/g polyol, using acetylation by acetic anhydride method [15]. For example, the solution of 0.1 g of PLOH and 1.5 mL of acetic anhydride was refluxed under N_2 atmosphere for one hour. Then, 1 mL of distilled water was added to this solution. After 5 mL of 95% ethanol was added, the hydrolyzed acetic anhydride residue

was titrated with 0.5 M ethanolic KOH solution in the presence of phenolphthalein indicator. The same process was repeated for the blank experiment without PLOH. The hydroxyl number was calculated by the equation below:

$$\text{Hydroxyl number (mg KOH=g polyol)} = \frac{(V_o - V) \times 0.5 \times 56}{0.1}$$

here V and V_o are the volume of the 0.5 M KOH used for the sample and blank titration, respectively.

Sol-Gel Analysis

For determining the degree of cross-linking, typically 0.01 g of PUR film was placed in 25 mL of chloroform for 24 h at room temperature. The swollen gel was taken from the solvent and the remaining solution was evaporated. The polymer residue and swollen gel were dried in a vacuum oven at 20 °C. A cross-linked fraction in the cross-linked crude sample was calculated as shown below and dried in a vacuum oven at 20 °C.

$$\text{Cross linked fraction wt \%} = \frac{(m_c - m_s)}{m_s} \times 100$$

It was weighed and the soluble part (sol fraction) was marked as m_s and the dry swollen gel (gel fraction-cross-linked fraction) was marked as m_c.

3. Results

This work consists of two steps, which include a cold water soluble PLOH and polyurethanes synthesis by using this PLOH.

3.1. The Synthesis of Hydroxylated Polymeric Linseed Oil

For the first time in this work, a cold-water-soluble PLOH was synthesized by autoxidation of the linseed. During the linseed oil autoxidation, linseed oil reacts with molecular oxygen of the air [9]. After the oxidized linseed oil polymer was reacted with diethanol amine to obtain hydroxylated linseed oil (scheme 1). The conditions and results of the hydroxylation reactions were listed in Table 1.

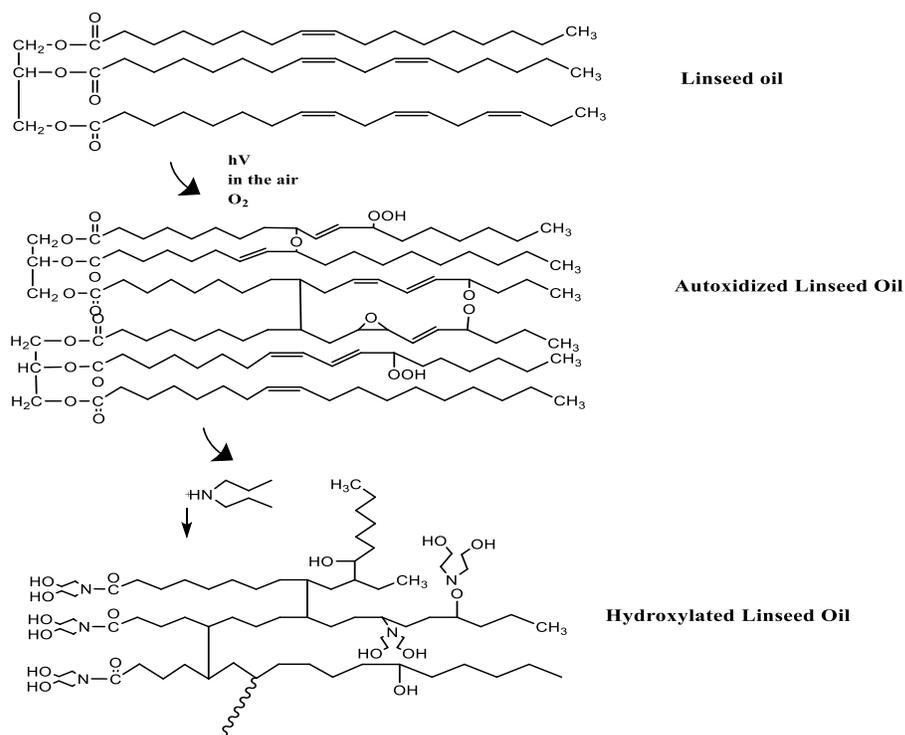
Table 1. Hydroxylation of the oxidized linseed oil polymers by using diethanol amine.

Code	Linseed Oil (g)	DEA (mL)	Yield (g)	Hydroxyl number	Elementel Analysis			
					C	H	N	O
PLOH	30	30	56.45	560	46.77	10.69	6.54	36

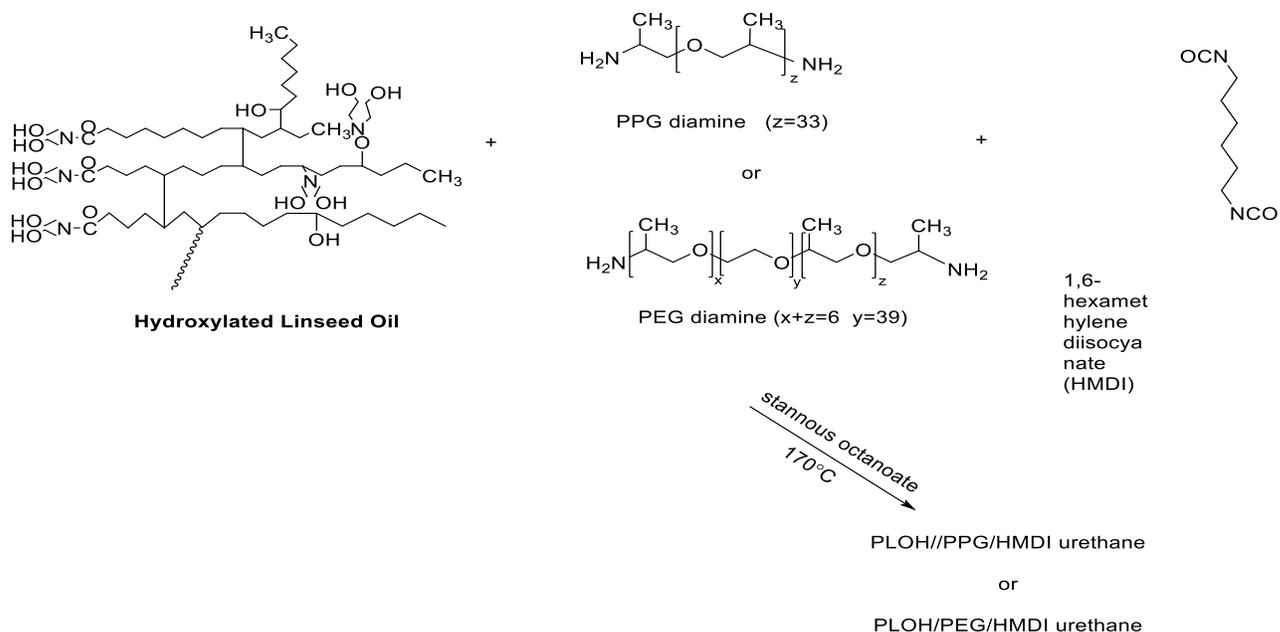
3.2. The Synthesis of Polyurethanes

For this research, a series of PURs containing linseed oil were synthesized from PLOH, PEG, or PPG diamine at different input molar ratios by using stoichiometric amounts of HDMI and stannous

octanoate as catalysts at two different temperatures (115 °C and 90 °C). The polymerization processes are shown in scheme 2, and the results and conditions of the obtained polyurethanes are shown in table 2.



Scheme 1. Representative chemical structure of the linseed oil polymer obtained by autoxidation of linseed oil



Scheme 2. Synthesis of segmented polyurethanes. Chain extension reactions of PLOH and PEG or PPG using HMDI.

Table 2. Reaction conditions and results of polyurethanes

Code	Hydroxylated Linseed oil (g)	PEG (g)	PPG (g)	HMDI (g)	Yield		Physical Apparance
					Soluble polymer (g)	Jel (g)	
PLOH/ PEG/HMDI (BC-301)	1.04	2.01	-	0.75	1.79	1.53	Soft elastic Light yellow
PLOH/ PEG/HMDI (BC-303)	2.04	2.00	-	1.2	-	5.68	Soft elastic dark yellow
PLOH/PEG/HMDI (BC-305)	1.00	2.03	-	0.9	-	4.45	Hard elastic dark yellow
PLOH/PEG/HMDI (BC-307)	1.05	1.03	-	0.6	2.33	-	waxy
PLOH/PPG/HMDI (BC-302)	1.1	-	2.2	0.75	3.63	-	waxy
PLOH/PPG/HMDI (BC-304)	2.04	-	2.03	1.5	2.53	2.70	Hard elastic dark yellow
PLOH/PPG/HMDI (BC-306)	1.00	-	2.04	0.9	-	2.85	Elastic film yellow
PLOH/PPG/HMDI (BC-308)	1.03	-	1.04	0.6	-	2.15	Very soft elastic film Light yellow

After drying, FTIR was used to analyze the characteristic groups of the bio-based polyurethanes (Figure 1). All of the compositions show a similar behavior. The isocyanate groups were completely converted into urethane moieties in the dispersion, as shown by the absence of the isocyanate band at 2270 cm^{-1} for PU, according to the type of polyols being studied (Figure 2). The synthesized bio-based polyurethanes show that the new bands specific to urethane moieties are attributed to: NH stretching vibration at a range from approximately 3307 to 3322 cm^{-1} . The shoulder of both symmetrical and asymmetrical stretching bands indicate that most of the NH functions make hydrogen bonding with carbonyl functions from urethane or ionic chain extender carboxylate [14]. NH bending and NHCO stretching bands of urethane group 1532 and 1546 cm^{-1} . The higher the hard segment content, the higher the peak absorbance. COC(O) stretching bands from urethane moieties at 1250 cm^{-1} . NH out-of-plane wagging of the urethane moieties at 784 cm^{-1} . Moreover, the zoom in the area around $1707\text{--}1621\text{ cm}^{-1}$ highlights the distinction of many C=O stretching bands: Linseed oil carboxylate and urethane carbonyl functions at approximately 1620 cm^{-1} , partially overlapping the polyol ester band at 1700 cm^{-1} . In this way, linseed oil polyurethanes are less able to associate properly because of their cross-linked structure, and that is why a shoulder appears between 1624 and 1700 cm^{-1} . In addition, the typical polyether band that is attributed to a PEG or PPG segment in the PUR samples occurred at 1095 cm^{-1} .

Figure 2 shows the ^1H NMR spectra of the oxidized linseed oil polymer, hydroxylated linseed oil polymer by DEA and linseed oil-based polyurethanes (PLOH/PEG/HMDI (BC-301s) and PLOH/PPG/HMDI (BC-302s)). The ^1H -NMR spectrum of oxidized linseed oil polymer in Figure 2 has the characteristic signals that are the same as those of the oxidized linseed oil [9]: δ (ppm): 5.4 (-CH=CH-), 4.1–4.2 (doublet, $\text{CH}_2\text{O}(\text{OC}-)\text{CHO}(\text{OC}-)\text{CH}_2\text{O}(\text{OC}-)$), 2.7 (-CH=CH-CH₂-CH=CH-), 2.3 (-CH₂-COO-), 2.0 (-CH₂-CH₂-CH=CH-), 1.6 (-CH₂-CH₂-COO-), 1.3 (CH₂)-n,,

0.9 [CH₃-(CH₂)-n]. In the ¹H-NMR spectra of the hydrolyzed linseed oil polymer obtained by using diethanol amine (Figure 2), new bands [13] appeared at 4.1 (-N-CH₂-CH₂-OH), 3.5–3.8 (-C-O, -C-OH induced) and 2.7 (-N-CH₂-CH₂-OH) while the band 4.1–4.2 (doublet, CH₂O(OC)-CHO(OC)-CH₂O(OC)-) disappeared. All these results confirmed that the transamidation reactions occur during the hydroxylation reactions induced by the diethanol amine. Additional signals are as follows: (ppm), 7.99–7.82 (hydrogen bonded -HNCOO-), 7.1–6.9 (non-hydrogen bonded -HNCOO-), 4.1–3.9 (-HNCOOCH₂-), and 2.25 (CH₂ of HMDI). These spectral studies support the formation of PLOH through the reaction of free -OH groups of PLOH with -NCO groups of HMDI. PEG diamine and PPG diamine samples also gave the characteristic signals of the N-CH₂-group at ppm 3.2 and 3.4, respectively, in the ¹H NMR spectrum (see Figure 2).

Figure 3 shows the DSC profiles that were obtained during the second heating cycle of the linseed oil polyurethanes. The first glass transition point (Tg1) at a low temperature was attributed to the soft segments Another glass transition point (Tg2) at a high temperature was attributed to the hard segments [14]. The thermal characteristics were provided in Table 3 for the studied samples. Two glass transition temperatures (Tg1 and Tg2) were observed in the thermograms.

A typical TGA curve and values of PLO, diamine-terminated PEG, diamine-terminated PPG and PUR samples were indicated Figure 4 and Table 3. Thermal degradation of soluble PLOs showed between 150–543 °C with 90 wt% weight loss. Diamine-ended PPG observed one degradation stage at between 180–345 °C, while diamine-ended PEG 150–543 were observed in two decomposition steps at a range between 180–272 °C and 272–360 °C with 30- 25 wt% weight loss, respectively. All PU samples were attributed to the 8 wt% weight loss of trapped solvent or moisture up to about 200 °C. Two decomposition steps were observed to be cross-linked and soluble PUr samples (Table 3).The first stage of degradation may be due to the breaking of the urethane moieties and a breakdown of the soft ester segments through chain scission, while the second step of degradation may be attributed to probable C-C bond cleavage [17].

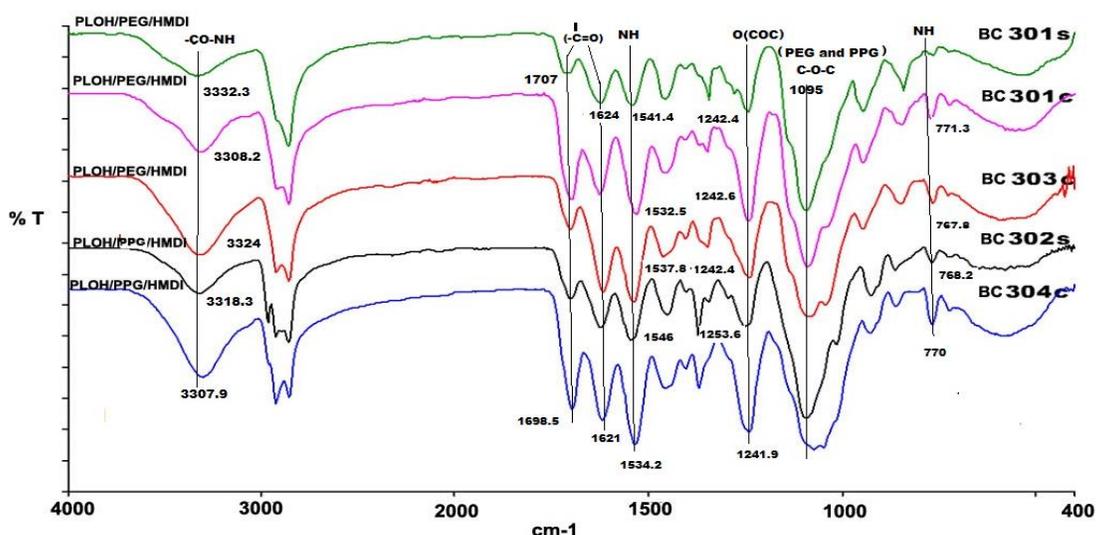


Figure1 FTIR spectrum of Linseed Oil PURs.

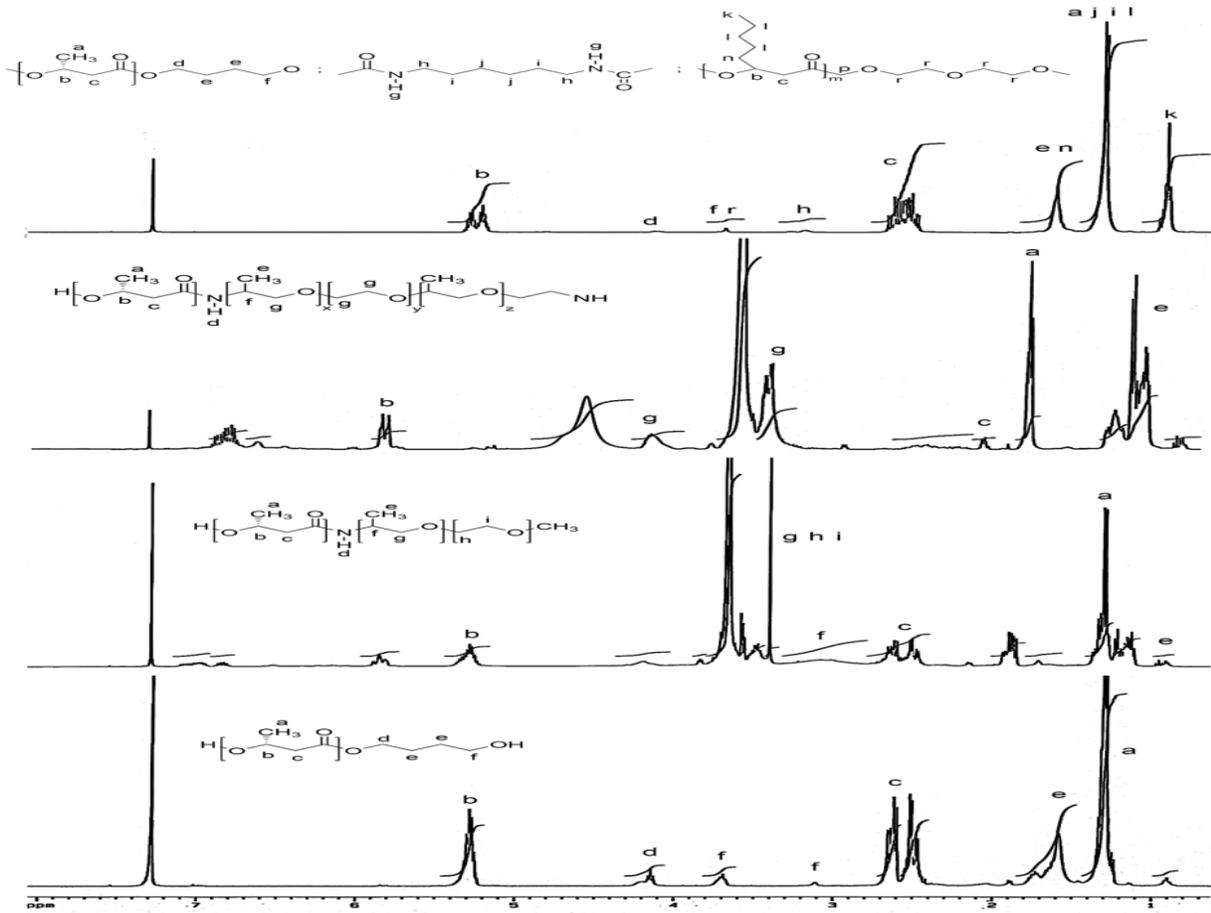


Figure 2. ¹H NMR spectrum PURs containing Linseed oil.

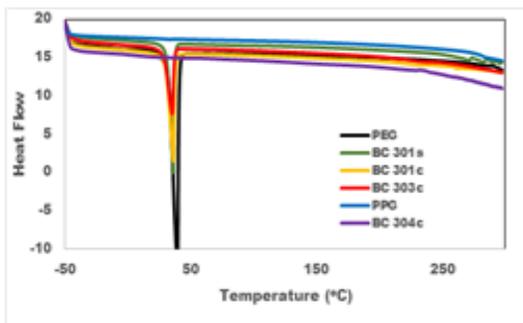


Figure 3. DSC Thermograms of PEG, PPG and Linseed Oil Polyurethane.

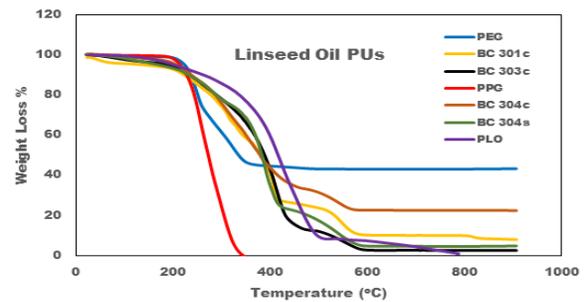


Figure 4. TGA Thermograms of PEG, PPG and Linseed Oil Polyurethane.

Table 3. Thermal Analysis Results of the PURs containing linseed Oil and the Related Homopolymers.

Code	DSC				TGA			
	T _{g1} °C	T _{g2} °C	T _m °C	ΔH J/g	T _{d1} °C	Weight Loss %	T _{d2} °C	Weight Loss %
PLOH	8	180	-	-	-	-	-	-
PEG	-10	21	39	100.8	180-272	30	272-360	25
PPG	281	-	32.8	0.1	180-345	89	-	-
PLOH/PEG/HMDI BC-301s	-	-	36	52.1	-	-	-	-
PLOH/PEG/HMDI BC-301c	-10	11	8.8	48.4	198-420	65	420-581	20
PLOH/PEG/HMDI BC-303c	-5.3	212	35	35.3	208-455	80	412-584	10
PLOH/PPG/HMDI BC-302s	-	-	341.7	32.19	-	-	-	-
PLOH/PPG/HMDI BC-304c	4.4	220	-	-	200-448	60	448-577	13

4. Discussion

The polyurethanes prepared from vegetable oils exhibit a number of excellent properties that are attributable to hydrophobicity. Natural plant oils, such as soybean oil, sunflower oil, palm oil, rapeseed oil, cottonseed oil, and linseed oil, are predominantly comprised of triglyceride molecules (triesters of glycerol with long-chain fatty acids) with varying compositions of fatty acids, depending on the plant, the crop, the season, and the growing conditions. The linseed oil used in this work contains 46.8 wt% linolenic acid, 16.03 wt % linoleic acid, and 25.73 wt% oleic acids. Our study consists of two steps. First, the PLOH was obtained from reacted diethanol amine with polymeric linseed oil peroxide obtained by the autoxidation with air oxygen (scheme 1, Table 1). After the autoxidation process, linseed oil consists of soluble and cross-linked parts. The whole mass of linseed oil transformed to a sticky, waxy linseed oil polymer, which was used for the hydroxylation reaction. The linseed oil polymer was hydroxylated in this manner, but it was not soluble in water. In this study, we have used diethanol amine to prepare wholly cold water soluble linseed oil polymer. Diethanol amine also produces hydroxyl groups by the reaction of peroxide groups (Sch.1 (b)). In this case, an alkoxy amine is induced during the reaction and then it has a tendency to decompose into an alcohol and a Schiff base. In the third reaction of an amine with oxidized triglyceride, the amidation reaction of a diethanol amine with ester groups was carried out. As the results of the elemental analysis of the PLOH also confirmed, diethanol amine was introduced into the linseed oil polymer since the structure of the hydroxylated linseed oil was confirmed by FTIR and H-NMR. The percentage of the C, H, N, and O in the hydroxylated linseed oil polymers are shown in Table 1. After diethanol amine was reacted with a autoxidation linseed oil, oxygen was observed at 6.54 wt%.

In the second part of this work, PURs containing linseed oil were synthesized from polymeric linseed oil polyol, PEG (or PPG) by using an aliphatic diisocyanate HMDI as a coupling reagent in a solution and stannous octanoate as a catalyst (scheme 2). The properties of linseed oil PURs change depending on soft segment amount (PLOH, PEG (PPG)) or the hard segment amount (HMDI) in the structure. The harder polyurethanes with an increasing HMDI amount or softer polyurethanes with an increasing PEG amount is obtained (Table 2).

Conclusions

There is synthesis of polyurethanes containing linseed oil in the literature (ref.14). However, in a continuation of this work, for the first time a polymeric hydroxylated linseed oil was obtained from the auto-oxidation of linseed oil with diethanol amine and its polyurethanes. In fact, the precursor PLOH is already a hydrophilic polymer that is highly soluble in methanol and, therefore, the PUR samples obtained from this precursor have some amphiphilic characteristics. As expected, PEG units have increased the hydrophilic character of the PUR samples. This amphiphilic character of the PUR samples that were obtained can be crucial for medical applications.

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