

MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Synthesis, Characterization and Physicomechanical Properties of Novel Water-based Biodegradable Polyurethane Dispersion¹

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Abstract—Novel water-based biodegradable polyurethane dispersions with an aim to develop environmental-friendly materials, including medicine, various industries, have been prepared in this study. Biodegradable ionic polyurethanes (IPU) were synthesized based on polyols from renewable resources, such as castor oil (CO), in the presence of a polyester polyol and polyethylene glycol (PEG) with hydrophilic property and 1,6-hexamethylene diisocyanate. 1,4-Butanediol and dibutyltin dilaurate, were used as a chain extender and catalyst, respectively. The comprehensive investigations of the structure and properties of five types of synthesized polyurethanes demonstrated biodegradability relationship of these polyurethanes with their structure and composition. In this research effects of different types and content of polyols on biodegradability and physico mechanical properties of prepared PUDs were investigated. The structure, properties and physico mechanical and application behavior of mentioned materials were characterized by ¹H NMR, FTIR spectroscopy, thermogravimetric analysis (TG/DTG) and dynamic mechanical thermal analysis (DMTA). The adhesion properties were measured by pull off test as well. Particle size was measured by dynamic light scattering (DLS) methods. The biodegradability of prepared polyurethane dispersions was confirmed by water uptake, hydrolytic and enzymatic degradation in phosphate buffer saline (PBS) with lipase enzyme in PBS. Results showed that by the incorporation of natural components into the polymer chain, adjusting of hydrophilic and hydrolytic liability properties of soft segments and especial relevant designs, useful polyurethane can be synthesized with desirable property of biodegradability and dispersion stability. Except for one sample, other samples were decomposed totally in enzymatic media.

Keywords: polyurethane, water-based, dispersion, biodegradable, renewable

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INTRODUCTION

Water-based biodegradable polyurethane dispersions have many useful properties which related to structure and composition of their components. These useful products have advantages of water-based polyurethane dispersions (PUDs), on the other hand, have also beneficial properties of biodegradable polyurethanes.

Damages and difficulties of volatile organic solvents have forced the scientists, experts, and producers of solvent-based polymers to develop solvent-free or little

content solvent products. In the recent decade, solvent-based polyurethane in many industries, especially in the coating industry are replaced successfully with water-based polyurethane dispersions [1, 2]. PUDs have an important role in a wide range of applications: In the first by environmental considerations of eliminating or solvent vapors reduction into the atmosphere [3–5]. Typical commercial solvent-based polyurethanes coatings have high solvent content and do not qualify for low volatile organic content (VOC) applications. For these reasons, there is currently the real need for low or near zero VOC coating systems due to current environmental regulations. These useful polymers are obtained

¹ The text was submitted by the authors in English.

Table 1. Chemical composition of PUDs samples in term of equivalent weight^a

Code	HDI(eq)	CO(eq)	PEG(eq)	1233(eq)	DMPA(eq)	BDO ^b (eq)	TEA
CO	0.025	0.008	–	–	0.008	0.004	0.004
CO PEG	0.025	0.006	0.002	–	0.008	0.004	0.004
PEG	0.025	–	0.008	–	0.008	0.004	0.004
CO PEG1233	0.025	0.006	0.001	0.001	0.008	0.004	0.004
CO 1233	0.025	0.006	–	0.002	0.008	0.004	0.004

^a For polyols equivalent weight was calculated by the following equation: Equivalent weight = $56\ 100/\text{OH}_{\text{NO}}$, and for other components were calculated by equation: Equivalent weight = M_w/n (n is number of equivalents).

^b BDO = 1,4-butanediol.

from different kind and content of various raw materials and synthetic methods [6–8].

The polyurethane dispersions have a good resistance to chemical and mechanical stress [9, 10]. These polymers can be formulated for adhesives and coatings without volatile and expensive organic solvents [11, 12]. Water-based polyurethane dispersions (PUDs) are usually prepared by the incorporation of ionic (polar) groups onto the polymer backbone that causes polymer to be well dispersed in the water phase in the final step. In this report, in the first step, a medium molecular weight isocyanate-terminated polymer as prepolymer was synthesized. Then an internal emulsifier was added to allow the dispersion of the polymer in water. After that chain extender was added. Finally, prepolymers with ionic groups were neutralized with a bulky organic base, typically triethylamine, to form a hydrophilic group ($-\text{COO}-\text{N}^+\text{R}_3$) which is a polar group and capable of interaction via hydrogen bonds.

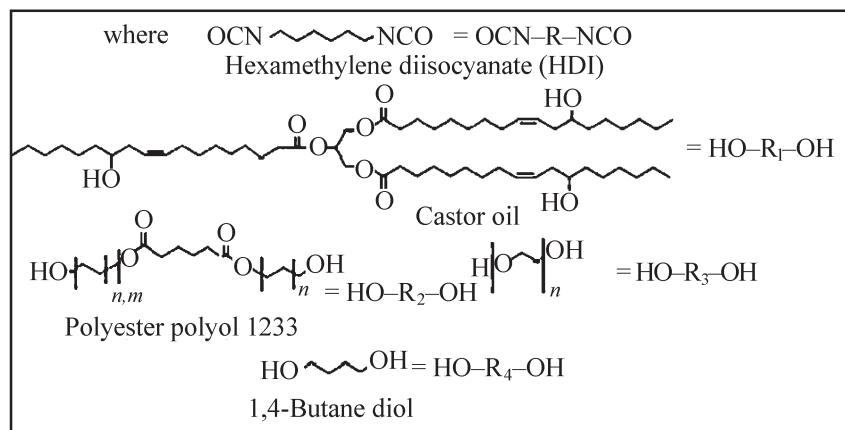
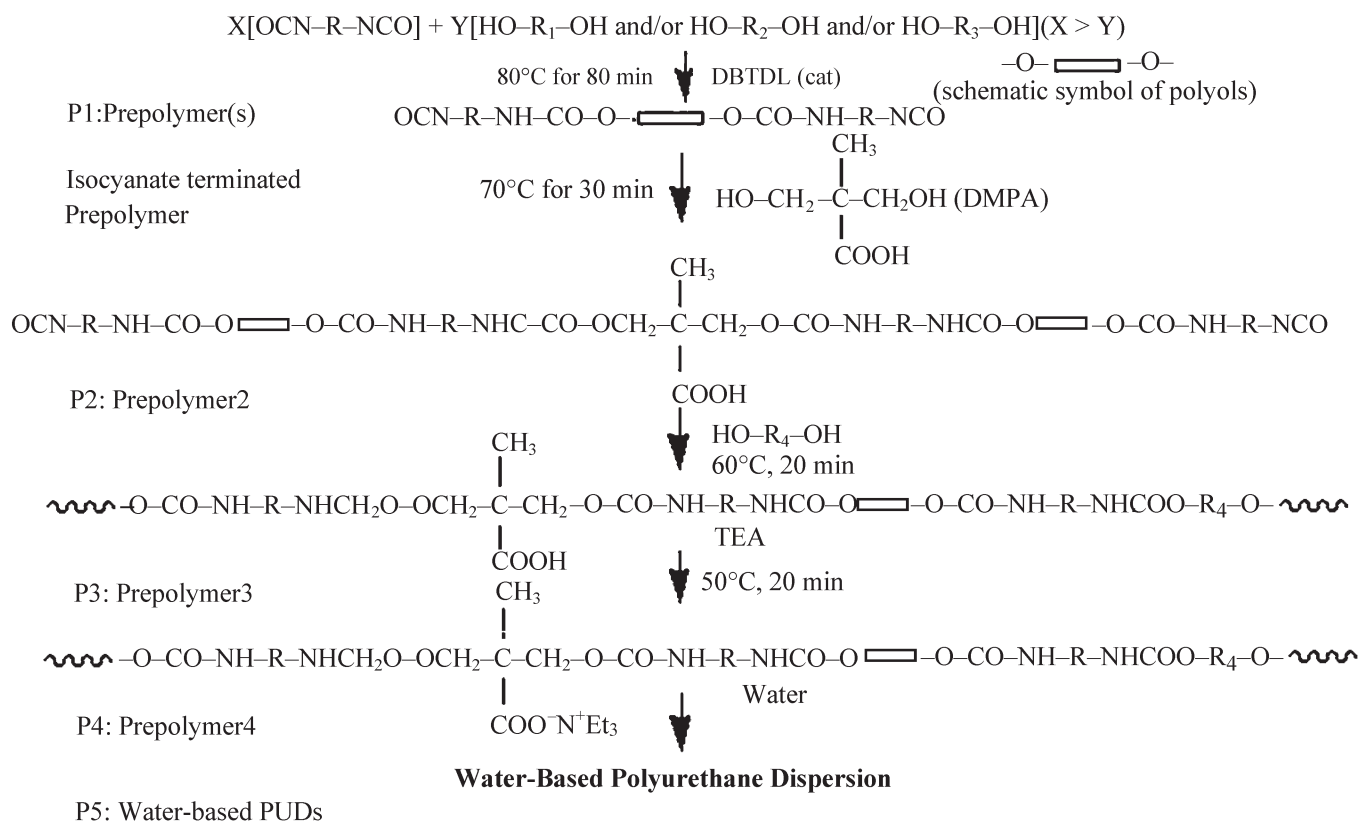
Properties of this polyurethanes dispersion with ionic groups that called PU ionomers related to phase behavior of soft and hard segments and their ionic character [13–15]. The final step was the dispersion of the prepolymer in distilled water. One prominent perspective of this work is the use of castor oil as vegetable oil-based polyols which are attractive in view of environmental concerns and finite petroleum resources [16–18]. These bio-based polyurethanes have also shown satisfactory adhesion to other surfaces [19–21]. We also used polyethylene glycol with the hydrophilic property that increases the degradation rate and Domopol 1233 a trademark of polyester polyol to add hydrolytic liability [22–24]. This research focused on the effects of different types and content of soft segments in reaction with linear aliphatic Isocyanate HDI (hexamethylene diisocya-

nate) and had close attention simultaneously to all details which required for water-based polyurethane dispersion synthesis. With adjusting of hydrophilic properties and hydrolytic liability of polyols, useful PUDs with desirable property of biodegradability and dispersion stability were prepared. These novel polyurethanes have advantages of water-based polyurethane dispersions (PUDs) and biodegradability polyurethanes together. Except for one sample, other samples were decomposed totally in enzymatic media. This study provides new results on properties of special formulation for the synthesis of novel water-based biodegradable polyurethane dispersions.

EXPERIMENTAL

Materials. Castor oil (Sigma-Aldrich, Germany), Polyethylene glycol 600 (Merck, Germany), Domopol 1233 (trademark of a linear polyester based on adipic acid and glycols (OH_{NO} :53-59), phosphate-buffered saline (Sigma-Aldrich), dimethylformamide (Merck, Germany), hexamethylene diisocyanate (Merck, Germany), lipase enzyme (Sigma-Aldrich, Germany), triethylamine (Merck, Germany), dimethylolpropionic acid (DMPA, Sigma-Aldrich, Germany), dibutyltin dilaurate (DBTDL, Aldrich), 1,4-Butanediol (Merck, Germany).

Polyurethanes synthesis. The synthesis was carried out in a 200 mL round-bottomed four-neck flask equipped with a mechanical Teflon stirrer, a thermometer, and a condenser. The round bottom flask was put in an oil bath with a controllable temperature. All applied polyols in this reaction which included castor oil (CO), polyethylene (molecular weight 600), Domopol 1233 (trademark of a polyester polyol), were dehydrated at 100–105°C under vacuum for 2 h. Monomers were mixed together according to the formulations in Table 1 and allowed to

Scheme 1. Elementary steps for synthesis of PUDs samples.

react. The reaction scheme for all stages (from P1 to P5) and the relevant processes is outlined in Scheme 1.

In the first step, relevant NCO terminated prepolymers was made. This reaction was carried out in the presence of the catalyst DBTDL (0.01 wt % respect to HDI content) at 80°C for 80 min under a dry nitrogen atmosphere. In the second step, the solution of DMPA in the dimethylformamide (at least content) was added to the mixture and mixed at 70°C for 30 min. At the end of this stage, isocyanate-terminated

polyurethane with carboxyl groups in its backbone was prepared. In the third step, the temperature was reduced to 60°C and 1,4-butanediol was added to the mixture. Mixing process was continued for 20 min. In fourth step, the temperature was reduced to 50°C again, trimethylamine (TEA) was charged into the mixture dropwise to neutralize the carboxyl group for 20 min. In the final step, the relative viscose polyurethane was emulsified by a high agitation rate (1200 rpm), with 50°C distilled water slowly charged for nearly 20 min.

All emulsion samples were stable over 6 months after synthesis at ambient temperature.

After stirring, the reactor was connected to vacuum to remove air bubbles from the bulk of the mixture. Then, organic solvent free aqueous dispersions were obtained by transferring the resultant mixture to a rotary evaporator with a partial vacuum of 70 mmHg at 50°C. Finally, this solution was poured slowly on leveled Teflon plate and cured at 60°C for 12 h. The films were stored in a desiccator at room temperature for subsequent studies.

Instrumentation and Procedures

Fourier-transform infrared (FTIR) spectra of polymer films were obtained at room temperature using thermos Nicolet 8700. The spectra were recorded in the range of 400–4000 cm^{-1} . ^1H NMR spectra were recorded on Bruker AV-300 with tetramethylsilane (TMS) as an internal reference with deuterium dimethyl sulfoxide (DMSO) as a solvent.

Dynamic mechanical thermal analysis of polyurethane films was performed by using a Triton DMTA machine. The specimen films with a determined dimension were examined at a frequency of 1 Hz at a constant cyclic strain of 0.05%. Data were collected from –100 to 150°C at a heating rate of 5°C/min. Results were reported in the form of $\tan \delta$ and storage modulus with respect to the temperature.

The thermal stability of polyurethane samples was studied by thermogravimetry analysis on a Perkin-Elmer Paris diamond instrument under a nitrogen purge gas. Samples were scanned from 30–800°C at a heating rate of 7.5°C/min. TG data was prepared and analyzed in the form of mass loss and derivative of TG (DTG) as the rate of change for the degree of conversion.

Dispersion particle sizes were determined by dynamic light scattering (DLS) method which performed on zetasizer Nano zsp (ZEN 5600 Malvern Co) particle analyzer. All PUDs samples for acquiring to required concentration were diluted with distilled water and the resultant dispersions were homogenized. The analysis was done with estimated solution parameters: duration used 50 s, the refractive index 1.31, viscosity 0.8872 cp.

Water uptake, hydrolytic and enzymatic degradation studies. For water uptake experiment the film of samples was placed in a vial, containing distilled water and kept for 1, 3, and 7 days in an incubator maintained at 37°C. The samples were removed from the water at deter-

mined time intervals, wiped gently with filter paper, and weighed with an analytical balance (0.1 mg). The sample mass change resulting from the water uptake (expressed as a percentage) was calculated according to Eq. (1):

$$\text{Water uptake\%} = [(m_{\text{fin}} - m_i)/m_i] \times 100, \quad (1)$$

where m_{fin} is the final mass of sample (in each experiment) and m_i is the dry mass of samples. Weight loss (%) in hydrolytic and enzymatic was also calculated by replacing water uptake variable with these parameters. The hydrolytic degradation of PUDs films was evaluated by immersing an exact weight of the dried sample in phosphate buffer saline (PBS, pH 7.4) at 37°C constant temperature. In every week interval, the degradation media of samples have been refreshed. The samples were taken out at the determinate time and at each time point, the samples were rinsed several times with distilled water. The surfaces of samples were dried under vacuum at 35°C before weight loss measurements. The degradation percentage was calculated with the Eq. (1).

The solution of 0.1 wt % lipase in phosphate buffer saline was prepared as an enzymatic degradation solution. Samples were cut and weighed to an accuracy of 0.1 mg. The samples were immersed in this solution. Each sample was placed into an individual vial containing specific content of an enzyme in solution at 37°C. Samples of each formulation were removed from this solution after determinate time and prepared as was mentioned above. The degradation medium was refreshed every 1 week, and the samples were reweighed in a specific period to measure the enzymatic degradation (%) with Eq. (1).

Pull off Test for adhesion strength by means of portable adhesion tester was carried out with adhesive coating of each sample on stone according to ASTM D4541.

RESULTS AND DISCUSSION

FTIR analysis. The PUDs samples were characterized by usual spectroscopic methods. In FTIR spectroscopy characterization, two categories were noted. In the first, the process stages were investigated and the changes which occurred in the polymer structure were traced. These changes included the signals of functional groups which disappeared in reactant components, on the other hand, the signals which created in the resultant polymer structure. In another part, the final polyurethane structure

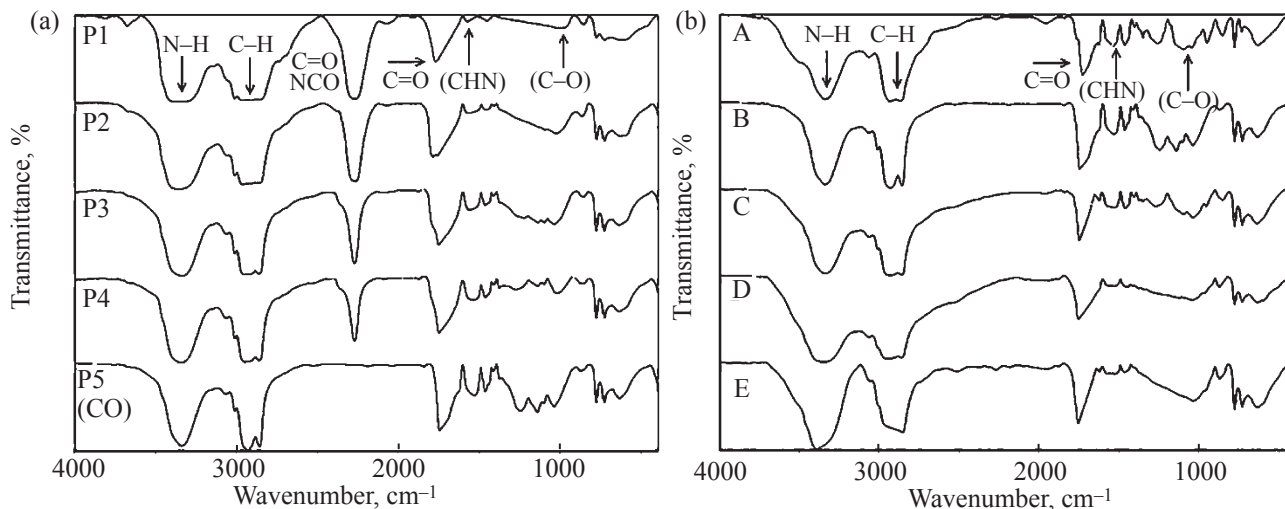


Fig. 1. FTIR spectrum of (a) prepolymers of process stages, P1–P5 (CO sample) and (b) final PUDs samples, where A, B, C, D, and E are PEG, CO, PEG-CO, CO-1233, CO-PEG-1233 sample, respectively.

of each formulation was studied separately. Figure 1a depicts the FTIR spectrum of synthesized prepolymers in each step of the process. In the first step P1 and relevant formed prepolymer, broad and strong band, at 3357 cm^{-1} was attributed to N–H stretching frequency, and peaks at 2967 cm^{-1} was assigned to $-\text{CH}_2-$ and $-\text{CH}_3$ stretching frequencies. Intense bond at 1768 cm^{-1} assigned to a carbonyl group (C=O) stretching. While signals of C=O and $-\text{OH}$ group of castor oil appears in 1744 and 3405 cm^{-1} , respectively. The signals at 1573 and 1028 cm^{-1} were attributed to CHN vibration and C–O stretching, respectively. The peak at about 2260 cm^{-1} ($-\text{NCO}$ group) confirmed the excess HDI in reaction as a reactive functional group for the next stages and proved the prepolymer

was $-\text{NCO}$ terminated. In other stages from the second stage until the fourth stage, the signal of the isocyanate group was observed. In the second stage, dimethylolpropionic acid was incorporated into the polymer backbone through reaction of its hydroxyl group with remaining unreacted isocyanate groups.

In third stage 1,4-butanediol (BDO) as chain extender reacted with a remaining isocyanate group. In the fourth stage, trimethylamine (TEA) as a bulk base reacted with the carboxyl group to neutralize it and an ionic hydrophilic group $-\text{COO}^-\text{N}^+\text{R}_3$ in polymer backbone was formed. Related isocyanate signals were seen in 2261 , 2271 , 2271 cm^{-1} , respectively. Finally, water reacted with free NCO groups and consequently aminated molecules

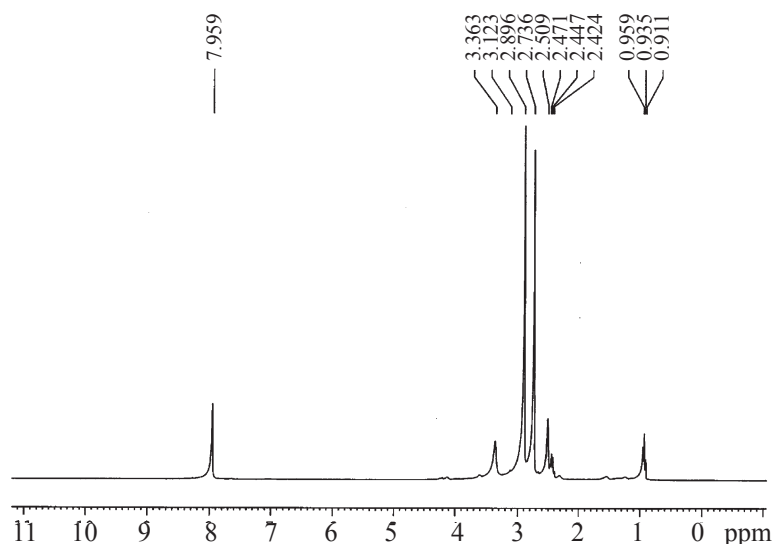


Fig. 2. ^1H NMR of the first stage prepolymer related to CO sample with castor oil as a polyol.

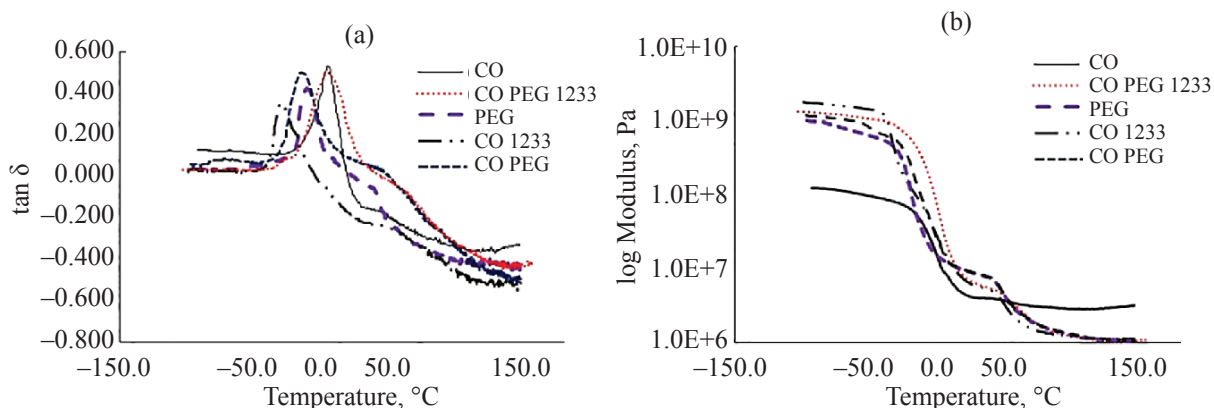


Fig. 3. DMTA results of PUDs samples. (a) $\tan \delta$ and (b) storage modulus of PUDs (Pa) vs. temperature ($^{\circ}\text{C}$).

formed and released CO_2 appeared as a bubble in the dispersion solution.

In the final step and end of the polymerization reaction, the signal of the isocyanate group was disappeared. In the resultant polyurethane dispersion (CO sample in Fig. 1), NH stretching bond of urethane group combined with OH group stretching and appeared at 3339 cm^{-1} .

Therefore, the existence of corresponded signals with C–O stretching vibrations, C=O stretching vibrations, combined NH stretching vibrations, and free OH bond and absent of isocyanate group signal in the end product which existed in penultimate stages, confirmed related polyurethane structure. Because of similarity in reactant materials and functional groups, the overall shape of their spectra in process stages was close together and a relevant signal of each mentioned group with a small change in shape and frequency appeared.

FTIR spectra of five final products (PUDs) are shown in Fig. 1b. As it can be seen, important functional groups which foregoing were discussed and explained in the final product in CO sample (P5 in Fig. 1), with trivial differences in frequency were observed in all final products.

$^1\text{H NMR}$ study. Figure 2 shows the $^1\text{H NMR}$ spectrum of the first prepolymer which was synthesized by reaction of castor oil with HDI in the first stage of polymer reaction (according to the composition in row 1 of Table 1).

$^1\text{H NMR}$ spectrum of this prepolymer was also in accordance with the molecular FTIR spectrum. The peak at $0.92\text{--}0.98\text{ ppm}$ was assigned to methyl groups of polyol. The methylene groups attached to the carbonyl carbon of esteric groups (CH_2COO) were observed at about 2.4 ppm . The methylene groups attached to the urethane nitrogen atom were detected at 2.8 ppm . The signal at

3.36 ppm can be attributed to $-\text{CH}_2$ groups attached to the urethane oxygen atom, and finally proton of urethane group ($-\text{N}-\text{H}-\text{CO}-\text{OR}$) was observed at 7.9 ppm .

Dynamic mechanical thermal analysis. Effects of polymer structure on mechanical properties on dynamic mechanical thermal analysis (DMTA) are obviously pictured in Fig. 3. Figure 3a shows the $\tan \delta$ results of PUDs samples as a function of temperature.

Related results of $\tan \delta$ and glass transition temperature T_g were tabulated in Table 2. Investigation of these data shows that the highest and lowest content of $\tan \delta$ is related to samples of CO and CO 1233 (with the composition of castor oil and a trademark polyester polyol Domopol 1233), respectively.

Obtained data also showed that with increasing of PEG content ratio in related PUDs formulation, the $\tan \delta$ peak associated with T_g gradually shifted to lower temperature and amplitude of $\tan \delta$ peaks was diminished. This phenomenon can be attributed to the decrease in the degree of freedom for segmental mobility in polymer chain which arises from an increase in physically crosslink content. These results nearly corresponded with previous related studies [25].

As will be explained later, these properties are attributed to their polymeric structures which can affect other properties such as physico-mechanical, morphological, and thermal behaviors, water uptake and resultant biodegradability of polyurethane samples. Curves in Fig. 4 show that the highest and lowest storage modulus is related to CO 1233 and CO samples, respectively. The CO sample is considered as a reference. Therefore, it can be studied the influence of other adducted polyol on this parameter. As a hard

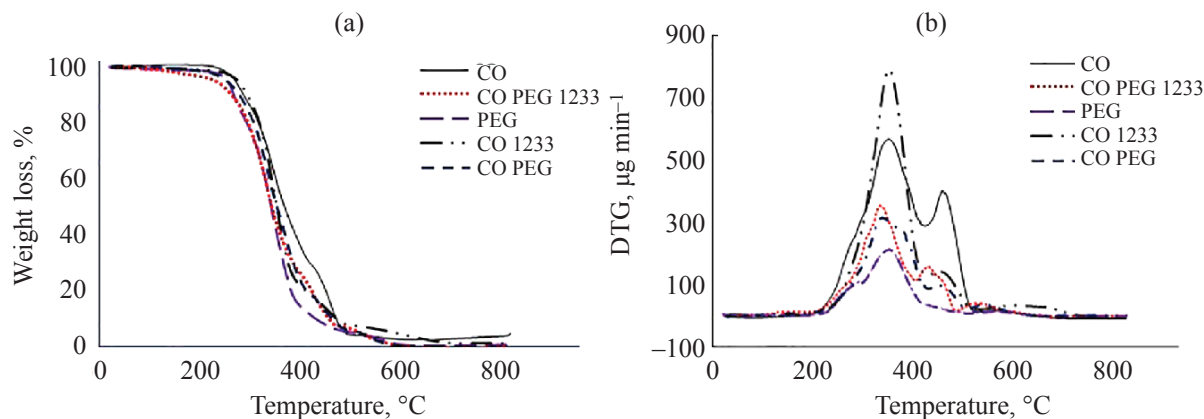


Fig. 4. Thermogravimetry analysis for PUDs samples. (a) TG curves and (b) DTG curves vs. temperature (°C).

segment and other factors were constant, it is logical, these changes of storage modulus and other properties are attributed to the effect of the soft segment on polyurethane characteristic.

A strong inter-chain interaction of the ester groups is likely responsible for the higher modulus for CO 1233 sample. It can be also related to strong ester groups interaction which lowers the mobility of polymer chains that improves the modulus [26]. In the other samples which had an ester group in their structure such as castor oil or polyester polyol, with increasing the mass ratio of polyethylene glycol (PEG) as a soft segment, storage modulus was increased. This improvement in modulus behavior is due to increased domain cohesion that is arisen from extra dipole–dipole interactions of polar ether bonds of PEG and $\text{O}=\text{C}=\text{O}$ (ester groups) bond of castor oil or polyester polyol, and the presence of crystalline domains that acts as a physical crosslink (crosslink density is enhanced) [27].

The thermal stability. The thermal stability of the prepared polyurethanes was evaluated by thermogravimetry analysis (TG/DTG). The results were presented in Fig. 4. The results of the DTG curve were also tabulated in Table 3.

Table 2. Obtained data on DMTA

Code	$\tan \delta^a$	$T_g^b, ^\circ\text{C}$
CO	0.54	5.8
CO PEG1233	0.50	4.6
CO PEG	0.49	-15
PEG	0.40	-11.8
CO 1233	0.34	-30.8

^a The altitude of $\tan \delta$ peak.

^b T_g was determined based on maxima of $\tan \delta$ peak.

The thermal decomposition of these polymers, as was revealed in DTG curves, involved three stages. Decomposition of these polymers, based on data of Table 3, and DTG curves, started at about 183–248°C which was related to the first degradation of weak urethane bonds. The maximum temperatures of this stage were between 337 and 355°C, obtained from DTG curves. The first degradation takes place through the cleavage to relevant alcohol and isocyanate, or the formation of primary amines and a terminal olefinic groups on the polyether or polyester chains and the formation of CO_2 and secondary amines.

As it is shown in TG and DTG curves, due to the similarity in the basic chemical structure of backbone, soft segment, NCO/OH ratio, and other process parameters in all samples are identical, nearly all PUDs samples showed similar patterns of thermal degradation [27, 28]. Second stage degradation which relates to soft segment scission took place at the temperature range of 431–462°C. The third stage was observed at temperature range 540–620°C.

This degradation, which occurred at higher temperatures, was related to the most stable structures that had a polar group such as an ester group or had

Table 3. Values of decomposition temperature obtained from DTG curves

Code	Decomposition onset, °C	$T_{10\%}, ^\circ\text{C}$	$T_{50\%}, ^\circ\text{C}$	$T_{90\%}, ^\circ\text{C}$
CO	246	287	369	473
CO PEG	214	279	355	466
PEG	218	269	343	432
CO PEG1233	183	256	345	459
CO 1233	248	295	354	473

strong internal interaction. These phenomena generally are observed due to C–C bond cleavage. As is observed in Table 3 and DTG curves, the maximum temperatures of $T_{10\%}$, $T_{50\%}$, $T_{90\%}$, decomposition onset, the first, second, and third degradation stage, were related to CO 1233 and CO samples (CO 1233 nearly in more cases).

It pertains to very strong force or internal interaction such as highly pure or physical crosslink that exists in their polymer chains. The thermal stability of PUDs mainly relates to the heat resistance of the functional groups or polar section which is there in the polymeric structure [29, 30].

Dynamic light scattering. The particle size of five PUDs samples was determined by dynamic light scattering. For acquiring the required concentration, all samples were diluted before measurement with distilled water. The results were tabulated in Table 4.

Water uptake, hydrolytic and enzymatic degradation experiment. The water uptake results in different types of polyurethane in a determinate time period were given in Table 5. The relative water uptake of the samples was calculated based on Eq. (1). Since the main mechanism for hydrolytic degradation of these polyurethane samples, takes place through hydrolysis of urethane and ester groups, therefore, the measurement of water absorption rate in these polymers is important.

As it is shown in Table 5, CO 1233 sample with a polyester polyol and castor oil in its structure and PEG sample with polyethylene glycol polyol, showed the lowest and highest content of water uptake, respectively. CO sample also showed little water uptake. The results, clearly demonstrated that with increasing of polyethylene glycol (PEG) content (based on of Table 1), the water uptake characteristic was increased. This behavior is mostly due to the new hydrogen bonding interaction between water molecules and PEG segments of polyurethane samples which have PEG in their polymer structure. As formerly mentioned, CO 1233 sample because of its molecular structure, improved crystallinity property of polymer and this increase confirmed that the crystalline fraction of the polymer largely remained un-degraded due to the poor penetration of water molecules [26, 27].

Contrary to PEG content role in water absorption improvement and better resultant degradation, increasing amount of castor oil within polymer composition, lowered the water uptake in linear polyurethane. Castor oil unlike to PEG decreased the hydrophilicity of polymers. It comes back to its hydrophobic property. When crosslink

Table 4. Particle size of PUD's sample

Code	Particle size, nm
CO	122
CO PEG	128
PEG	134
CO PEG1233	115
CO 1233	168

Table 5. Water uptake of PUD's sample

Code	1st day	3rd day	7th day
CO	1.2	1.5	1.7
CO PEG	1.3	1.8	2.4
PEG	1.8	2.5	3
CO PEG1233	0.9	1.4	2.1
CO 1233	0.8	1.3	1.4

content increases, polymer structure becomes dense and rigid and the probability of water molecules for penetration to the polyurethane films decreases. Data on water uptake (%) show that PEG as hydrophilic polyol is the determinative factor on the amount of absorbed water.

Figure 5a shows the degradation (%) of polyurethane samples as a function of time in phosphate buffer saline. Owing to the little susceptibility of water for penetration to polymeric bulk, CO and CO 1233 samples showed the lowest degradation and other samples with increasing in PEG content showed accumulative degradation rate. The degradation rate of these PUDs samples corresponded to the water absorption ability, with more degradation found in phosphate buffer saline.

The high water absorption amount which results in an absorbed polymer matrix, as mentioned in other studies, facilitates the degradation rate by creating more free volume for mass transfer and easy migration of the degradation components. Polyethylene glycol with increasing these free spaces or porosity of the materials provides a greater surface region for accessibility of water molecules to the ester groups of castor oil with a hydrophobic property. It also provides more water molecules in the vicinity of ester groups which accelerates the degradation rate. This degradation takes place through increasing number of effective collisions

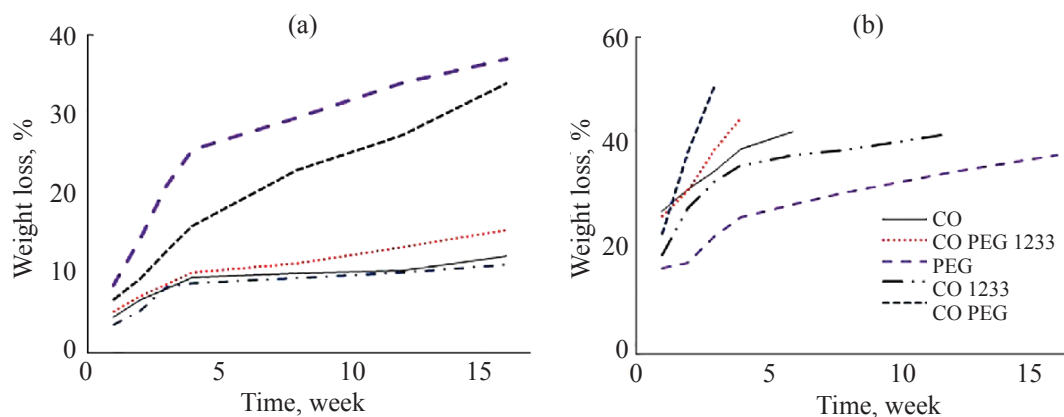


Fig. 5. Degradation profile of PUD's sample vs. time. (a) In PBS, (b) enzymatic degradation.

of water molecules and ester groups which enhances reaction rate kinetically. The curves in Fig. 5a show the rate of hydrolysis increase over time. This relates to hydrophilicity increase of a polymer owing to the creation of amine, hydroxyl, and other polar groups during the process of degradation. These functional groups can have dipole–dipole interaction with water molecule [31, 25].

Hydrolytic degradation is the well-known mechanism for degradation of polyurethane products. Small amount addition of polyethylene glycol (PEG) to castor oil increased degradability which was obviously seen in the degradation experiment. The excess addition or perfect replacing decrease this property and may harm to another parameter such as adhesion strength.

Figure 5b shows the Enzymatic degradation of polyurethane samples as a function of time. CO PEG and PEG samples showed the highest and lowest enzymatic degradation, respectively. PEG sample which had only PEG polyol in its composition and showed the highest rate of water uptake and hydrolytic degradation experiment, in enzymatic degradation, located in the lowest position. This event

obviously proved that other parameter(s) should be effective. CO sample with castor oil and CO 1233 sample, which contained polyester polyol and castor oil in its structure, showed better degradation in lipase environment than in phosphate buffer solution (PBS). Lipase catalyzes the hydrolysis of ester bonds in triacylglycerol effectively and did not show any effect on hydrolysis of PEG sample with the relatively stable etheric functional group in polyethylene glycol.

The biodegradability of polyurethanes was generally due to the incorporation of the labile and hydrolyzable section into the polymer backbone [26]. In the case of CO sample should be noted that, although natural oils are commonly biodegradable substances, the biodegradability of these oil-based polyurethanes was found to be limited because of their crosslinked systems [32, 33]. Sensitive and reactive sites for potential hydrolysis and resultant biodegradation were ester bonds and urethane linkages.

Biodegradability was also affected by the hydrophobicity of the system as well as the morphology of a polymer [34, 35]. Figure 6 shows an image of samples after the determinate interval in enzymatic degradation solution. CO PEG, CO PEG 1233, CO, CO 1233 decomposed totally after 3, 4, 6, 12 weeks, respectively. PEG sample showed weight loss as presented in relevant profile but did not destroy in enzymatic media as others. These results in attention to its structure as polyether polyol were predictable.

Pull off test. The adhesion strength measurement of polyurethane samples was carried out according to ASTM-D4541. Related results are tabulated in Table 6.

Table 6. Adhesion strength of PUD's sample

Code	Adhesion strength, MPa
CO	8.05
CO PEG	7.6
PEG	6.86
CO PEG1233	4.46
CO 1233	6.68

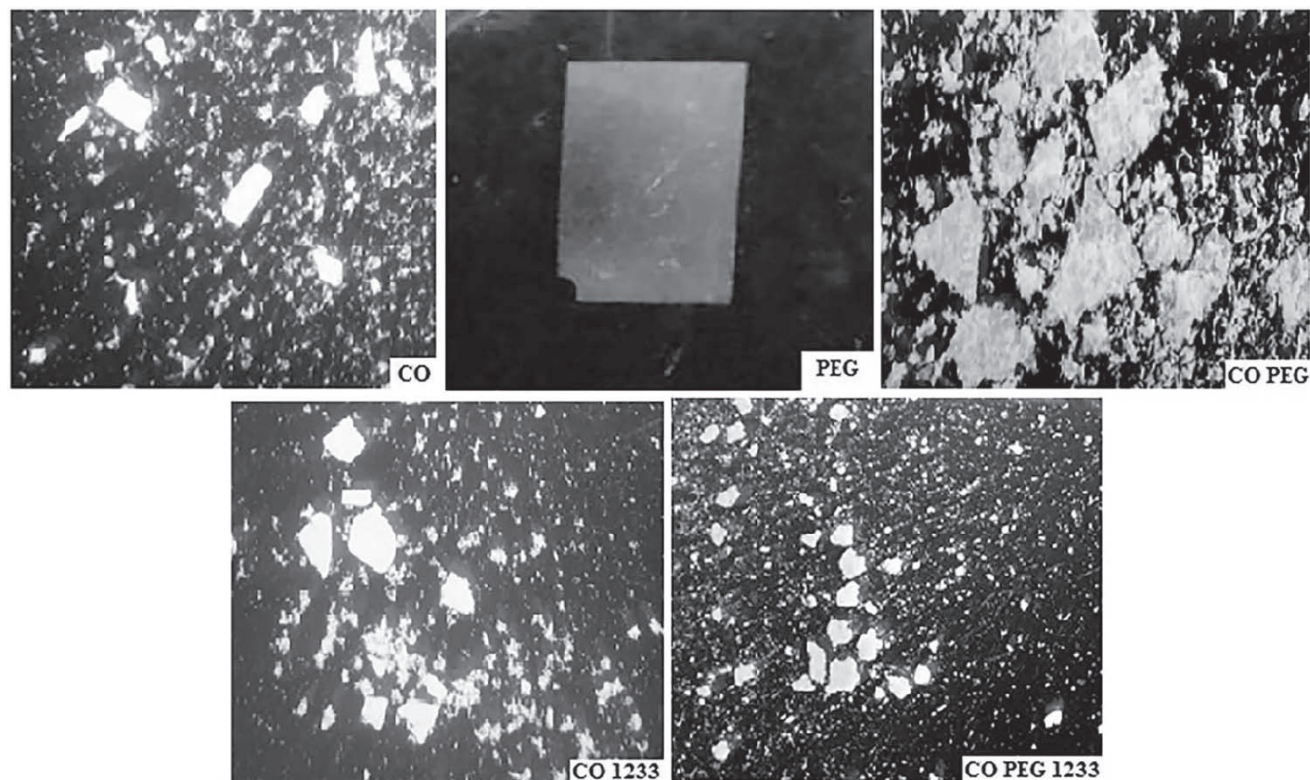


Fig. 6. Photographs of biodegraded PUDs samples taken out of the lipase environment at 37°C after the given interval.

As it is presented, the CO sample showed the highest adhesion property among other samples. Related data indicate that increasing of PEG content to castor oil-based polyurethane composition decreases adhesion strength of castor oil-based polyurethane.

CONCLUSIONS

In this study, novel water-based biodegradable polyurethane dispersions with a goal to develop biodegradable materials were prepared. Physicomechanical and biodegradability of polyurethane dispersions with different composition of soft segments were investigated. Novel polyurethanes with at least solvent content were prepared which have both benefits of water-based polyurethane dispersions (PUDs) and biodegradability polyurethanes together. With this method, movement toward synthesis route of low or near zero volatile organic content (VOC) composition with satisfactory biodegradability was possible.

A general conclusion which could be drawn based on the results and discussion consists in the fact that in identical NCO/OH ratio the hard segment, and other

relevant process parameters, the changes in type and content of soft segment have a determinative role. The mechanical properties and hydrolytic degradation, thermal stability behavior of polyurethane dispersion could be adjusted by incorporation of suitable polyol into the polymer backbone.

Our experimental study revealed that different polyols as soft segments in these polyurethanes can change crystalline domains which have an important effect on mechanical, thermal stability, hydrolytic and enzymatic degradation of this novel water-based biodegradable polyurethane dispersion.

The degradation rate was increased when labile and hydrolyzable moieties were incorporated into the polymer structure. The water uptake and resultant biodegradability of these PUD's samples were affected by differences in type and content of polyol in their polymer composition. The enzymatic degradation based on the type and content of the incorporated group in polymer backbone showed the different results in comparison with hydrolytic degradation. Finally, synthesized PUDs, except for PEG sample, were decomposed totally with the different rate in enzymatic media.

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