Physical and Surface Properties of Polyurethane Hydrogels in Relation With Their Chemical Structure

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Polyethylene glycol (PEG)/castor oil (CO)-based polyurethanes were prepared by one-shot bulk polymerization method with the potential for biomedical applications. Hexamethylene diisocyanate and 1,4-buthane diol were used as diisocyanate component and chain extender, respectively. Polyurethanes were prepared (1) with crosslinker and catalyst, (2) with crosslinker and without catalyst, and (3) without crosslinker and catalyst. The effects of the ratio of CO to PEG, and presence/absence of the crosslinker and catalyst on some physical and surface properties of the polyurethanes were investigated. The glass transition temperatures of prepared polyurethanes are below room temperature. The swelling ratio increased and the water contact angle decreased with increasing amount of PEG in polymer structure. The samples prepared with crosslinker and without catalyst showed the highest swelling ratio. Gas permeability of the samples was measured in a gas permeability system and surface roughness was determined by scanning electron microscope and atomic force microscope. Protein adsorption studies were performed for the samples synthesized without crosslinker and catalyst by using bovine serum albumin and bovine serum fibrinogen. Unexpected results were obtained for the samples which have low contact angles. They exhibited relatively high protein adsorption. POLYM. ENG. SCI., 00:000–000, 2013. © 2013 Society of Plastics Engineers

INTRODUCTION

Hydrogels are an important class of crosslinked polymeric networks that can absorb large amounts of water without dissolving. They serve a wide range of biomedical applications, including soft contact lenses, bioadhesive carriers, wound healing, implant coatings, and matrices for drug delivery. Synthetic hydrogels are excellent physicochemical mimetics of natural extracellular matrix and therefore, they are candidate for soft tissue scaffolds [1]. One of the most common hydrogels is poly(ethylene glycol) (PEG) for tissue engineering applications [2–7]. PEG-based hydrogels have been extensively investigated for regenerative medicine applications due to their excellent biocompatibility.

Swelling behavior of a polymeric hydrogel used for biomedical applications is very important. When the polymer swells too much, it may cause damage to the living tissues due to an increase in its volume. In order to control the swelling behavior of a material, several crosslinkers are used in its synthesis. In literature, castor oil (CO) was suggested as a polyol component for decreasing swelling degree of polymer due to its high content of ricinoleic acid, which has a hydroxyl functional group on the 12th carbon [8, 9]. The United States Food and Drug Administration has categorized CO as "generally recognized as safe and effective." For this reason, it has numerous applications in cosmetics and pharmaceutical, and in the field of material science [10–12].

The effect of CO content on some physical and chemical properties of the polymers was investigated by several researchers, and it was reported that polymer properties are strongly dependent on the amount of CO in the polymer structure. Two epoxy-terminated polyurethane prepolymers based on PEG and CO were synthesized by Yeganeh et al., and then elastomeric films were successfully prepared via these prepolymers [9]. The reactions were performed in solvent medium. The results showed that the degradation rate and mechanical properties of the final products could be controlled by adjusting the amount of CO in polymer structure. One of the most noteworthy results is that the amount of CO played a dominant role in swelling behavior of the polymers. PEG- and CO-based polyurethanes were synthesized for preparing transdermal drug-delivery films by Shelke et al. [13]. The catalytic reactions were performed in solvent medium. It was shown that the amount of drug release decreased with increasing amount of CO due to an increase in the hydrophobicity of the films. In other study, the effect of crosslink density on sorption behavior of CO-based polyurethanes was investigated by Somani et al., and it was found that the sorption coefficient degreased with an increase in crosslink density [14]. The effects of catalyst and crosslinker on physical and surface properties, and interaction between chemical structure of polymers and protein adsorption were not investigated in all those studies.

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This article describes the effect of chemical structure and synthesis procedure of the CO- and PEG-based polyurethane films on their physical and surface properties including protein adsorption. For this purpose, three different groups of polyurethane hydrogel were synthesized by bulk polymerization method for potential biomedical applications. First group of polyurethanes was prepared in the presence of both crosslinker and catalyst. For the second group of polyurethanes, only crosslinker was used in the synthesis. In third group neither crosslinker nor catalyst were used. The swelling behavior, gel content, crosslink density, thermal properties, and surface hydrophilicity were determined for each prepared sample. Protein adsorption, gas permeability, and surface topology studies were carried out only with the third group of polyurethanes. Since bovine serum albumin (BSA) and bovine serum fibrinogen (BSF) are the most abundant content of the blood, these proteins were chosen to study for adsorption studies.

EXPERIMENTAL

Castor oil (CO) with hydroxyl number 161.01 and acid number 0.99 is supplied by Sorel Chemicals. Polyethylene glycol (PEG) with a molecular weight of 3000 from Fluka and 1,6-hexamethylene diisocyanate (HDI) from Merck were used in polymer synthesis. Technical grade dibutyl-tin-dilaurate (DBTDL), 1,4-buthane diol (BDO), and triethanol amine (TEA) were used as catalyst, chain extender and crosslinking agent, respectively.

Synthesis

Hydrogels were prepared by one-step bulk polymerization technique. Prior to the synthesis, PEG was dried on a rotary evaporator for 6 h at 90–95°C and CO was dried at 80°C under vacuum for 24 h. BDO and TEA were dried overnight at 50°C in a vacuum oven.

PEG and/or CO were added into a flask and mixed. Depending on the synthesis procedure, 0.004% by weight of DBTDL and 1.25% by weight of TEA were used as catalyst and crosslinker, respectively. In all procedures 5.7% by weight of BDO was used as chain extender. The reaction mixture then transferred into a three-necked reaction flask equipped with a mechanical stirrer, dropping funnel, and N_2 inlet and outlet. Temperature was then increased to 50°C. HDI was added to the mixture at the stirring rate of 300 rpm. After 150 s, the reaction mixture was poured into the molds and kept in an oven at 80°C until the completion of the reaction, which was checked by Fourier transform infrared (FTIR) spectroscopy. The disappearance of the absorption peak at 2250 cm^{-1}, assigned to the N═C═O group, was sought to confirm that all the diisocyanate were consumed in the reaction. This was usually achieved in about 12 and 20 h for catalyzed and uncatalyzed reactions, respectively.

The hydrogels were prepared at different weight ratios of CO:PEG. They were designated using the abbreviation PU-*a*-*b*-*c*, where *a* indicates the CO percentage in mixture of CO and PEG, *b* and *c* indicates the polyurethane prepared with (WC) or without (NC) catalyst, and with (wc) or without (nc) crosslinker, respectively. For example, PU-0-NC-wc coded sample was prepared by the reaction between PEG and HDI in the absence of catalyst and in the presence of crosslinker, and PU-100-WC-nc coded sample was prepared from CO and HDI in the presence of catalyst and in the absence of crosslinker.

Characterization of the Polymers

FTIR spectra were obtained using a Perkin Elmer Spectrum One instrument. The crystallinity of polymer films was determined by using wide angle X-ray scattering. X-ray diffraction data were collected by X'PERT PRO X-ray diffractometer in the range of Bragg's angle $2\theta = 5 - 55°$. The thermal gravimetric analysis (TGA) was carried out using a Perkin Elmer Diomand TGA, by heating from room temperature to 550°C with a heating rate of 20°C/min under nitrogen atmosphere. The differential scanning calorimeter (DSC) measurements were carried out on a Perkin Elmer Diamond DSC between −60 and 150°C with a heating rate of 10°C/min. To observe the surface topography of polyurethane films, surfaces were examined by Nanomagnetics ezAFM atomic force microscope (AFM) operating in tapping mode. AFM images were taken 40×40 μm^2 areas. Scanning electron microscope (SEM, JOEL JSM 6390-LV) was employed to analyze the polymer surface. Static contact angle measurements were conducted using KSV CAM200 goniometer by placing 5 μL of distilled water on the polymer surface. Swelling ratio was determined by immersing polymer into distilled water at 37°C until equilibrium was reached, and determined gravimetrically by weighing the water saturated polymers after removing excess water on the polymer surfaces with a paper towel. Gel content of the polymer was determined by using Soxhlet extractor where acetone used as solvent. Density of the polymer was determined according to the method of gradient difference with Ray-Ran Density Gradient Column. The gas permeability of the hydrogels was measured in a gas permeability system based on constant volume/variable pressure technique [15]. All measurements were carried out at 35°C and the permeation rate of N_2 was determined. Each sample was tested three times and the average permeability value was reported. The reproducibility tests indicated a maximum measurement error of ± 5%.

Crosslink density (υ_c) and average molecular weight between two crosslinks (M_c) were determined by the equilibrium swelling method according to the Flory-Rehner equation (*Eq. 1*). Toluene was chosen as a solvent for the calculations.

$$M_C = \frac{v_S d_p (V_P^{1/3} - V_P/2)}{\ln(1-V_P) + V_P + \chi_{12} V_P^2} \quad (1)$$

where υ_S is the molar volume of the solvent, V_P is the volume fraction of the polymer in the swollen state, and

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χ_{12} is the polymer-solvent interaction parameter of the solvent, which can be calculated by *Eq. 2*.

$$\chi_{12} = 0.34 + \frac{v_S(\delta_P - \delta_S)^2}{RT} \quad (2)$$

where δ_P and δ_S are the solubility parameters of the polymer and solvent, respectively. Solubility parameters of the polymers were determined by swelling experiment. Polymers were swollen to equilibrium in several solvents such as toluene, acetone, 1,4-dioxane, N-methyl-2-pyrrolidone, and methanol at 25°C. The solubility parameters for the aforementioned solvents are 8.9, 9.9, 10, 11.3, and 14.5 $(cal/cm^3)^{1/2}$, respectively [16]. The equilibrium degree of swelling (Q) calculated according to *Eqs. 3 and 4* was plotted against the solubility parameters of the solvents.

$$V_P = \frac{W_P/d_P}{W_P/d_P + W_S/d_S} \quad (3)$$

$$Q = \frac{1}{V_P} \quad (4)$$

where W_P is dry weight of polymer, W_S is weight of the solvent, and d_S is density of solvent. The solubility parameters of the polymers were determined by observing the maximum equilibrium degree of swelling for each polymer. Crosslink density is calculated using *Eq. 5*.

$$v_C = \frac{d_P}{M_C} \quad (5)$$

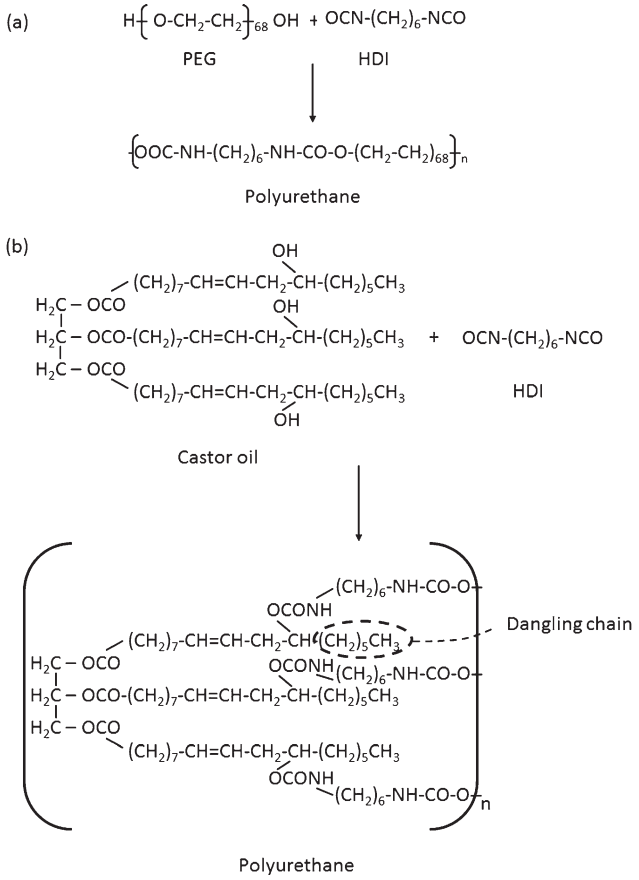

FIG. 1. Synthesis reaction of (a) PU-100- and (b) PU-0- based polyurethanes.

Protein Adsorption

BSA and BSF adsorption on the polyurethane membranes were studied batch-wise in phosphate (NaCl-KCl-Na_2HPO_4–KH_2PO_4) buffer media at about pH 7.4. The initial protein concentration was 1.0 mg/mL in each case. In a typical adsorption experiment, protein was dissolved in 60 mL of buffer solution, and polymer samples (1×1 cm^2) were added to that solution. These experiments were conducted at 28°C. At the end of the predetermined equilibrium period, the samples were removed from the solution. The amount of protein in the solution was determined by UV visible spectrophotometer at 280 nm, and the amount of adsorbed protein was calculated from the *Eq. 6*,

$$q = \frac{(C_0 - C)V}{A} \quad (6)$$

where q is the amount of protein adsorbed (mg/cm^2), C_0 and C are the initial and final protein concentrations (mg/mL), respectively, V is the volume of the aqueous phase (mL), and A is the total surface area (cm^2) of the polymer samples.

RESULTS AND DISCUSSION

Polymer Synthesis and Characterization

CO is a vegetable oil obtained from the castor bean. It consists of ~85–95% ricinoleic acid (12-hydroxy-9-*cis*-octadecenoic acid) which has one hydroxyl group per mole. Oleic and linoleic acids are the other significant components of CO. The average functionality (f) of CO was calculated to be 2.67, according to the *Eq. 7*,

$$\frac{MW}{f} = \frac{56,100}{HV} \quad (7)$$

where MW is molecular weight (= 932 g/mol) and HV is hydroxyl value of CO.

Polyurethane synthesis reactions with two different CO:PEG ratios (0:100 and 100:0 by weight) are shown in Fig. 1. The similar reactions can be written for the synthesis of polyurethane prepared from the mixture of PEG and CO as polyol component where PEG and CO molecules are randomly arranged in the polymer chain.

A typical FTIR spectrum of polyurethanes shows characteristic absorption band for N—H bending vibration in the amide II region at about 1530–1535 cm^{-1} and N—H stretching at about 3320 cm^{-1}. The FTIR spectra of PU-100-WC-wc and PU-0-WC-wc are presented in Fig. 2. In

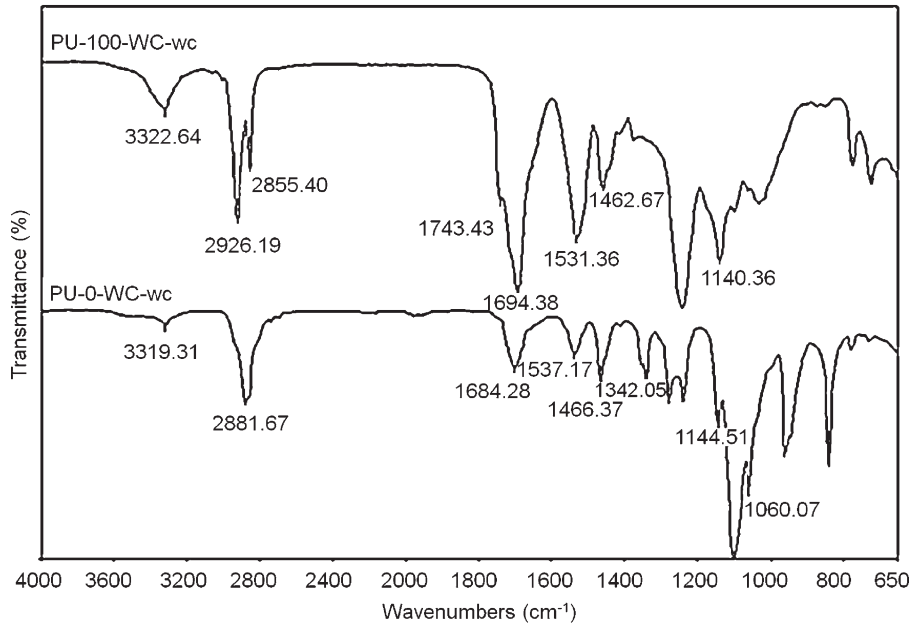

FIG. 2. FTIR spectra of polyurethanes.

the spectrum of PU-0-WC-wc, the bands for wagging at about 1342 cm^{-1} of methylene groups indicate that soft segments deriving from PEG are partially in amorphous conformation in polyurethane structure [6]. CO is an ester product of glycerol and ricinoleic acid, and hence the CO-based polyurethane chains include ester bonds besides urethane bonds. The peak about 1743 cm^{-1} is attributed to the carbonyl stretching of that ester group for the PU-100-WC-wc sample. There is no peak at 1740 cm^{-1} for the PU-0-WC-wc sample due to absence of CO in polymer structure.

It cannot be possible to prepare polyurethane films coded as PU-0-NC-nc, PU-30-NC-nc, and PU-40-NC-nc due to low mechanical properties of polymers. For this reason, the data related to these films were not available.

X-ray diffraction patterns of some polyurethane samples are given in Fig. 3. The PU-0-WC-wc and PU-0-NC-wc samples prepared without CO, exhibit some sharp peaks at around $2\theta = 20 - 25^\circ$, which are characteristic of PEG crystallinity [17]. From comparison of the x-ray diffraction patterns, one can observed that as the CO content increases the intensity of the peak at $2\theta = 20 - 25^\circ$ tends to decrease. Depending on the conditions of polymer preparation and the presence or absence of polymerization additives (catalyst and crosslinker), different x-ray diffraction patterns were obtained for PU-50-based polyurethanes. The polymerization reaction was finished in relatively short time when the catalyst was used, thus there was no enough time for polymer chains to get in order during the polymerization reaction. For this reason, the crystallinity of the PU-50-WC-wc was lower than the other PU-50 coded polymers, it was almost amorphous. PU-100-WC-wc, PU-100-NC-wc, and PU-100-NC-nc coded polymers showed a broad peak at around $2\theta = 20-22^\circ$, which can be attributed to the amorphous phase. The small but sharp peak at around $2\theta = 25^\circ$ in the x-ray diffraction pattern of PU-100-NC-nc was attributed to localized ordered-structure in polymer.

Density and Gel Content of Polymers

Density of the polymers is given in Fig. 4. Since the density of CO ($d = 0.96$ g/cm^3) is lower than the density of PEG ($d = 1.23$ g/cm^3), polyurethane density decreased with increasing CO content. There is no significant difference between the densities of the polymers prepared in the presence or absence of catalyst or crosslinker.

The gel contents for all polymers, except PU-50-NC-nc and PU-60-NC-nc were found to be 95–99% (by weight). This value was also found to be about 80% by weight for both polymers coded as PU-50-NC-nc and PU-60-NC-nc.

Crosslink Density and Average Molecular Weight Between Two Crosslinks

The crosslink density was calculated according to Flory-Rehner theory based on an affine network [18, 19]. The graph obtained from the plotted data of equilibrium degree of swelling and solubility parameter for the samples prepared in the absence of catalyst and crosslinker is given in Fig. 5. The similar graphs can be plotted for rest of the samples. Since N-methyl-2-pyrrolidone gave a maximum value for all samples, the solubility parameter of polymers was assumed to be 11.3 $(cal/cm^3)^{1/2}$. The calculated M_c and υ_c are given in Table 1. As expected, the crosslink density tended to increase with increasing CO:PEG ratio for all polymers. The average molecular

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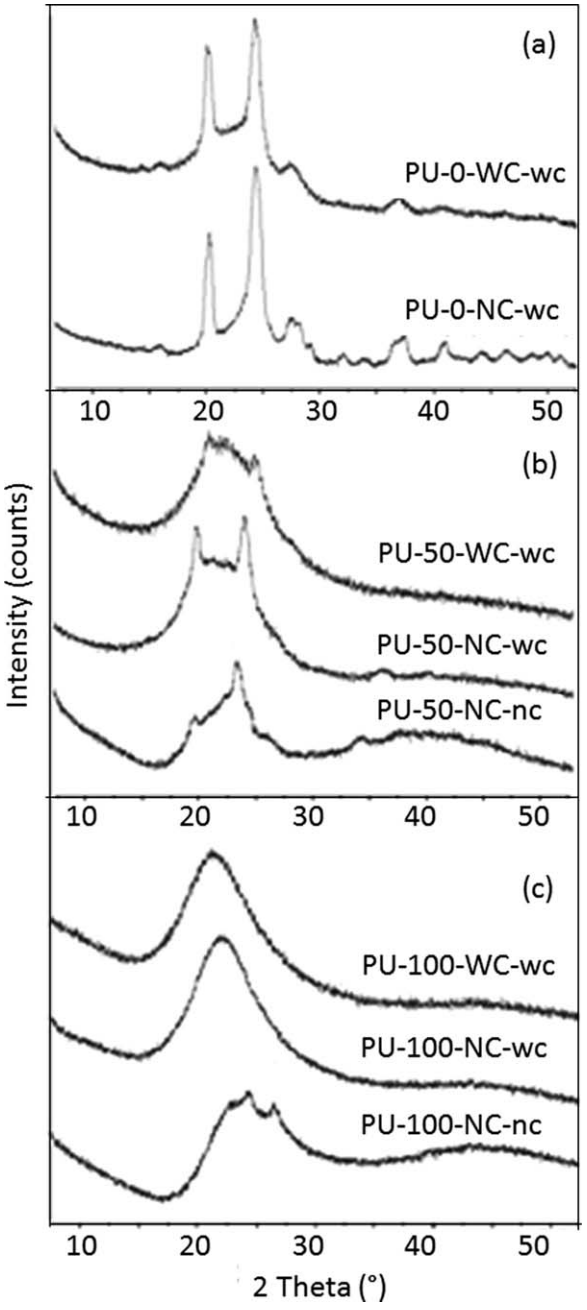

FIG. 3. X-ray diffraction patterns of polyurethanes prepared from; (a) PEG, (b) CO and PEG (CO/PEG = 50/50), and (c) CO.

weight between two crosslinks for all polymers tended to decrease with increasing CO:PEG ratio.

Thermal Properties

TGA thermograms of polyurethanes are presented in Fig. 6. As expected, the thermal decomposition of all samples was characterized with two distinctive steps, which correspond to the degradation of hard and soft segments in polyurethane structure. An intersection point was obtained for all TGA curves at 415 ± 10°C. The degradation pathway depends on the CO and PEG content of the synthesized polymer. There is no significant difference between the polymers prepared with and without catalyst or crosslinker.

The glass transition temperatures (T_g) of the polyurethanes determined by DSC measurements are below room temperature (Fig. 7), which indicate rubbery behavior at body temperature. This is an important parameter from the biomedical point of view.

Crystallinity and crosslink degree are two important parameters that affect T_g of the polymers. In general, increasing crystallinity and/or crosslinking in a polymer structure cause an increase in T_g. In this study, two types of polyol, CO and PEG, were used in polyurethane synthesis. PEG is semi-crystalline and has two functional groups in each molecule. Although CO has an amorphous structure, it also has more than two functional groups in its structure. Thus, the crosslink density (v_c) increased and the crystalline phase decreased with increasing amount of CO in polymer structure or vice versa the v_c decreased and the crystalline phase increased with increasing amount of PEG in polymer structure. At this point, the question is; how the ratio of monomers affects T_g of polymer, if both monomers are used in polymer synthesis. As shown in Fig. 7, T_g's of the polyurethane films prepared in various synthesis conditions tended to increase with increasing CO:PEG ratio. However, they decreased slightly for the polyurethane films containing 60–70% CO. The lack of crystalline melting temperature (T_m) for the samples, which contain more than 60–70% CO indicates that crystallinity has no effect on T_g for the samples containing more than 60–70% of CO.

Gas Permeability

The N_2 permeability coefficients of the PU-50-NC-nc and PU-100-NC-nc films were found to be 1.783 and 0.989 Barrer, respectively. This result is in agreement with the T_g and the crosslink density data. PU-50-NC-nc has lower T_g and has lower crosslink density than the PU-100-NC-nc, which may indicate relatively the high free volume of the PU-50-NC-nc, subsequently higher gas permeability.

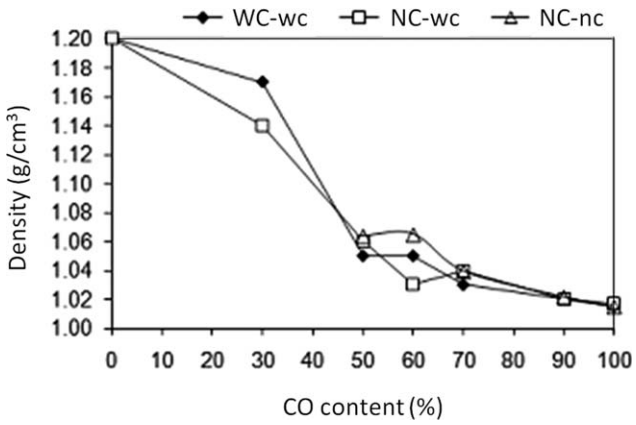

FIG. 4. Density of polyurethanes.

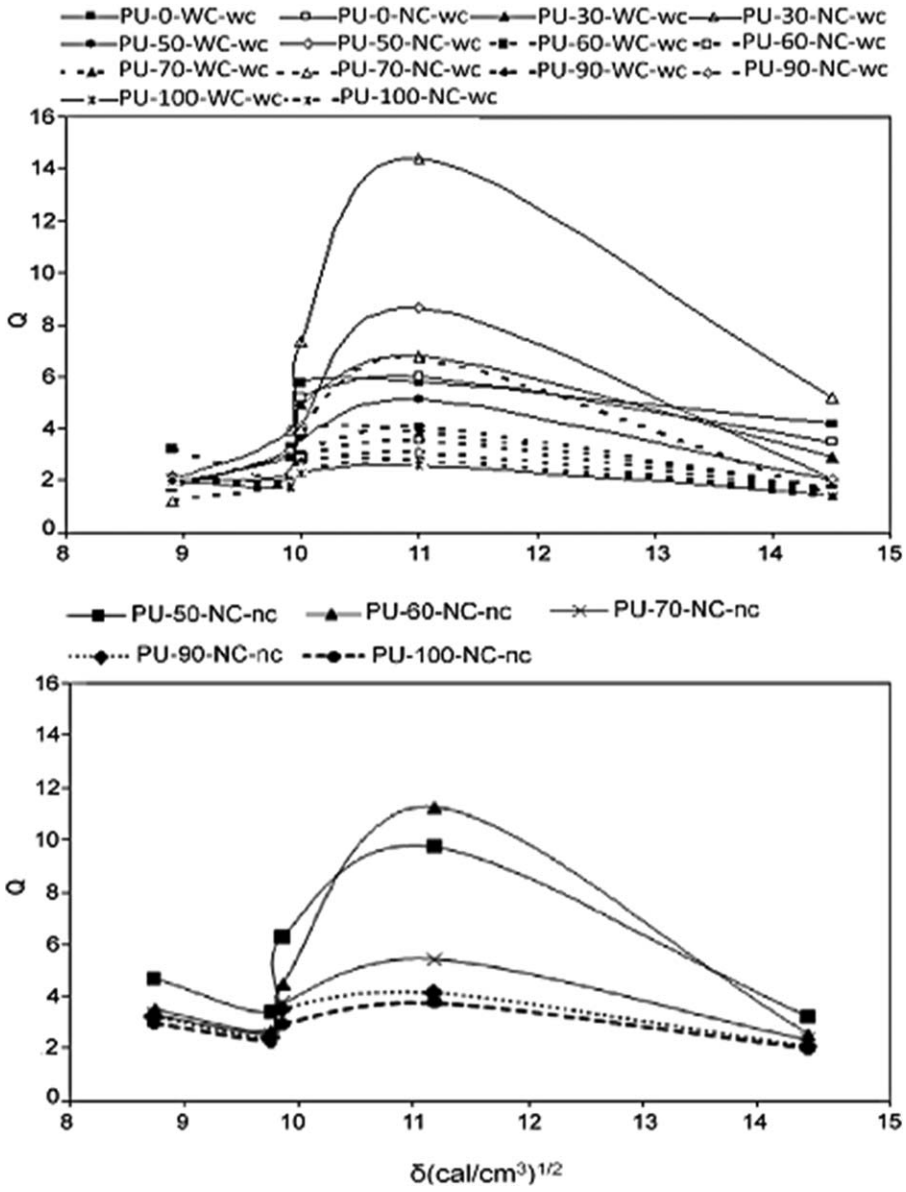

FIG. 5. Gaussian fit of the swelling coefficients versus solubility parameter.

Contact Angle and Swelling Ratio

Water contact angle itself is not an indicator of biocompatibility of a material, but some useful information may be obtained for blood- or tissue-compatibility. The static water contact angle for the polyurethanes is shown in Fig. 8. The contact angles of the polymers prepared with and without catalyst, and with and without crosslinking agent for the same CO content are close to each other. The contact angle of the polymers increased with increasing CO content due to hydrophobic properties of fatty acid groups of CO.

The swelling property is quantified by measuring the amount of absorbed water (Fig. 9). There is no significant difference between the polymers synthesized according to different procedures, which have the same amount of CO. The PEG content is the main factor that controls the amount of water absorbed. Decreasing PEG content caused to decrease the water absorption capacity of the polymer.

Surface Roughness

SEM images of the PU-50-NC-nc and PU-100-NC-nc samples are given in Fig. 10. The surface of the PU-50-NC-nc sample is rougher than that of PU-100-NC-nc sample. This observation is also in accordance with AFM results (Fig. 11). Roughness average is measured to be 37, 81, and 305 nm for PU-100-NC-nc, PU-70-NC-nc, and PU-50-NC-nc, respectively. The roughness of polymer surface increased with increasing PEG amount in polymer structure.

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TABLE 1. M_c and υ_c of polyurethanes.

Code	BDO	TEA	DBTDL	CO:PEG ratio	$\upsilon_c \times 10^3$ (mol/cm^3)	M_c (g/mol)
PU-0-WC-wc	+	+	+	0:100	1.59	621.0
PU-30-WC-wc	+	+	+	30:70	1.59	734.0
PU-50-WC-wc	+	+	+	50:50	2.46	426.3
PU-60-WC-wc	+	+	+	60:40	2.43	431.1
PU-70-WC-wc	+	+	+	70:30	2.21	466.1
PU-90-WC-wc	+	+	+	90:10	2.40	422.4
PU-100-WC-wc	+	+	+	100:0	1.60	585.0
PU-0-NC-wc	+	+	−	0:100	1.63	735.0
PU-30-NC-wc	+	+	−	30:70	1.57	725.0
PU-50-NC-wc	+	+	−	50:50	1.57	673.5
PU-60-NC-wc	+	+	−	60:40	2.36	444.0
PU-70-NC-wc	+	+	−	70:30	2.50	416.0
PU-90-NC-wc	+	+	−	90:10	2.30	443.2
PU-100-NC-wc	+	+	−	100:0	2.36	429.8
PU-50-NC-nc	+	−	−	50:50	1.23	979.4
PU-60-NC-nc	+	−	−	60:40	2.00	559.7
PU-70-NC-nc	+	−	−	70:30	2.15	517.2
PU-90-NC-nc	+	−	−	90:10	2.24	468.9
PU-100-NC-nc	+	−	−	100:0	2.52	413.0

Protein Adsorption

Protein adsorption experiments were carried out for the samples coded PU-50-NC-nc, PU-70-NC-nc, and PU-100-NC-nc and the results are given in Fig. 12. Among three polymer, PU-50-NC-nc adsorbed more protein than the others. However, PU-100-NC-nc, which has the more hydrophobic surface, adsorbed less protein than other two polymers. This observation was evaluated together with the surface hydrophilicity and surface roughness of the polymer films, since these two parameters have significant effect on protein adsorption [20].

The contact angles of the polymer films related with the surface hydrophilicity were determined to be 61, 69, and 90° for PU-50-NC-nc, PU-70-NC-nc, and PU-100-NC-nc, respectively. As mentioned above, contrary to the expectations, PU-50-NC-nc adsorbed more protein than the others. It is known that hydrophobic surfaces tend to adsorb more protein than hydrophilic surfaces, and PEG-based materials are known to be excellent protein repellents [21, 22]. However, there is also evidence that at certain conditions proteins even adsorbed on hydrophilic surface. It is reported that both BSA and BSF show high affinity for adsorption on both hydrophilic and hydrophobic surfaces. It is reported in literature [23–27] that BSF and BSA exhibited a step increase in adhesion force in cases the contact angle of the surface is >60°. The constant adhesion forces were observed across all of the wettable and nonwettable surfaces. Hydrophobic forces were not supported on surfaces when the contact angle was smaller than 62.4° [26]. The water contact angle of the PU-50-NC-nc surface is very close to this critical value. It is about 61°. Since there is no enough data to correlate the water contact angle (or water adhesion tension) and adhesion force for the polymer surfaces prepared, it is not possible to name the surface of PU-50-NC-nc as either "protein adherent" or "protein nonadherent." Similar to data reported by Xu and Siedlecki [23], it can be concluded that, excluding the effect of surfaces roughness, if

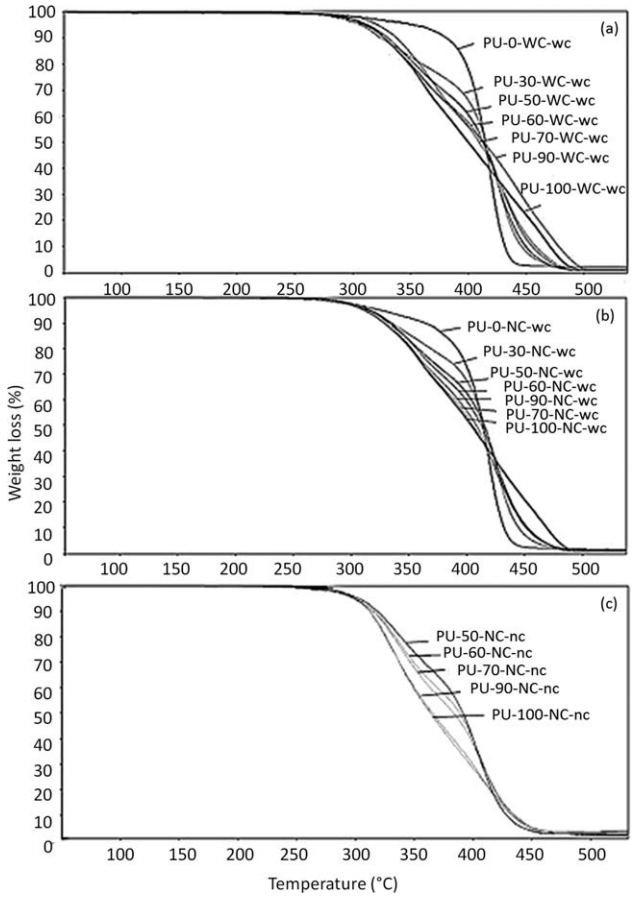

FIG. 6. TGA thermograms of polyurethanes prepared; (a) with crosslinker and catalyst, (b) with crosslinker and without catalyst, and (c) without crosslinker and catalyst.

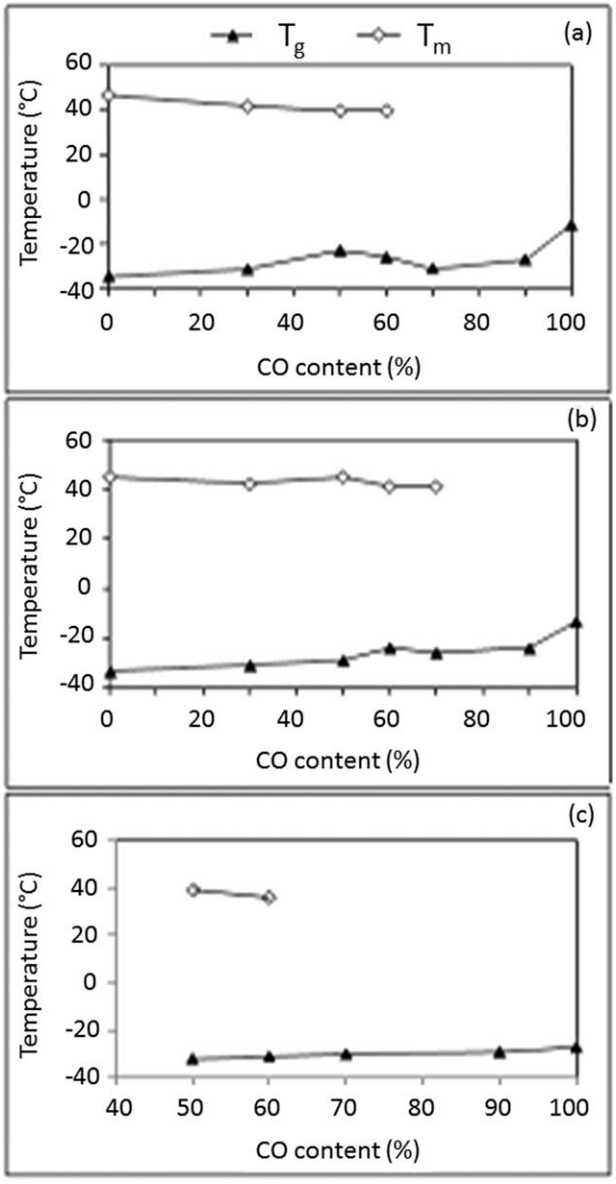

FIG. 7. T_g and T_m values of polyurethanes prepared; (a) with crosslinker and catalyst, (b) with crosslinker and without catalyst, and (c) without crosslinker and catalyst.

the PU-50-NC-nc surface had been protein adherent, the amount of the adsorbed protein would have been at the same level for both PU-50-NC-nc and PU-100-NC-nc.

However, above a critical protein concentration (0.5 mg/mL) fibrinogen adsorbed in higher amounts on hydrophilic surfaces than hydrophobic surfaces [28]. It might be one of the probable explanations of the result observed for the PU-50-NC-nc coded sample prepared in this study, where adsorption is conducted in solutions having protein concentration of 1 mg/mL.

The results for protein adsorption obtained in this study can be explained with the surface roughness of the polymers. According to the AFM results, the roughness of the PU-50-NC-nc surface, which adsorbed more protein than the others, was higher than that of PU-100-NC-nc. In literature, the effect of surface topology on protein-surface interactions has been extensively and systematically investigated by numerous researchers, and ongoing debate on this subject. For example, according to Xu and Siedlecki [23], surface roughness was not an important factor in case of fibrinogen adsorption to biomaterial surfaces. However, the nanometer-scale surface roughness was correlated with the adhesion strength of fibrinogen on both hydrophilic and hydrophobic membranes by Conti et al. [29]. The effect of surface roughness was also discussed in our previous study in detail [20], and similar results were obtained in accordance with Conti et al. In brief, greater the surface roughness, greater the surface area for protein-surface interactions. All these explanations and results obtained in this work lead that there are a significant correlation between the protein adsorption and the roughness of the polymer surface.

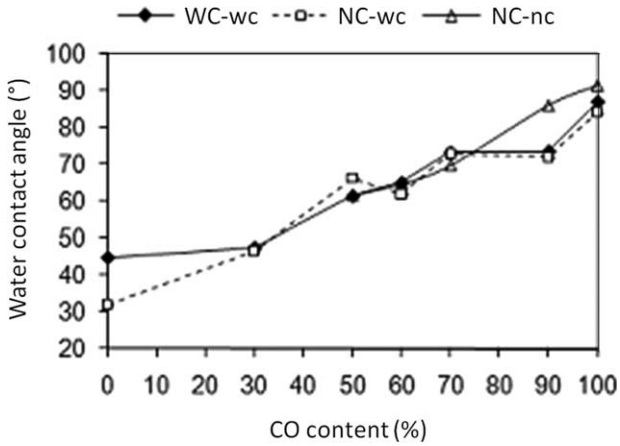

FIG. 8. Water contact angle of polyurethanes.

According to the experimental results, albumin adsorption was four times higher than fibrinogen adsorption for each polyurethane film. This is due to the molecular weight differences between albumin (molecular weight; 65 kDa) and fibrinogen (molecular weight; 340 kDa) and the determination method used for protein adsorption,

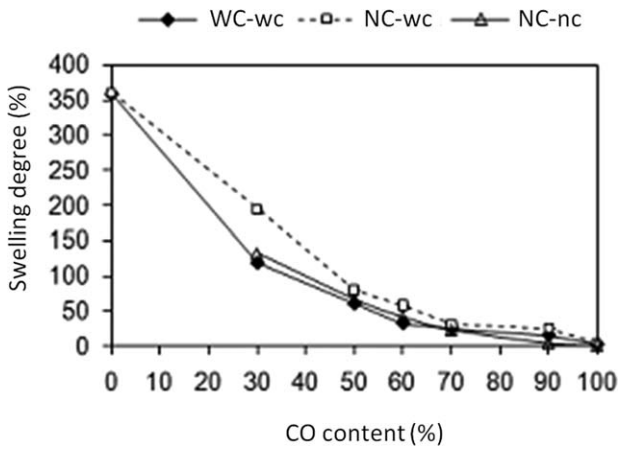

FIG. 9. Swelling degree of polyurethanes.

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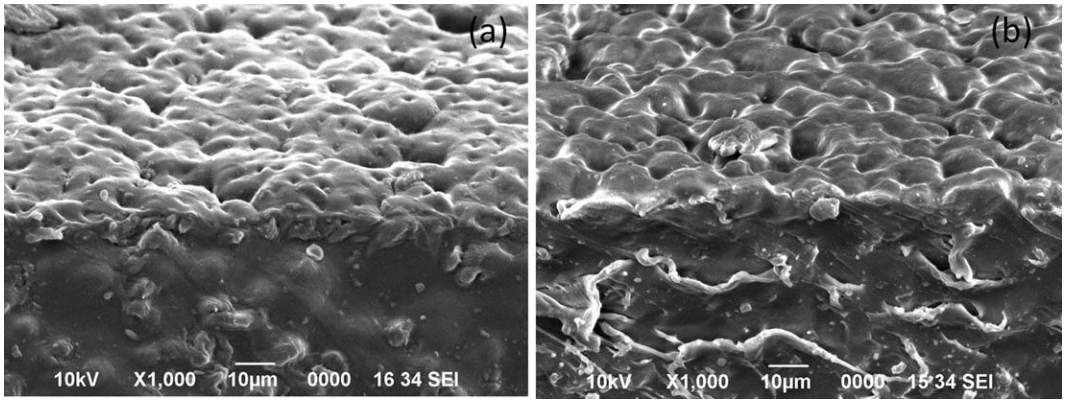

FIG. 10. SEM images of (a) PU-50-NC-nc and (b) PU-100-NC-nc.

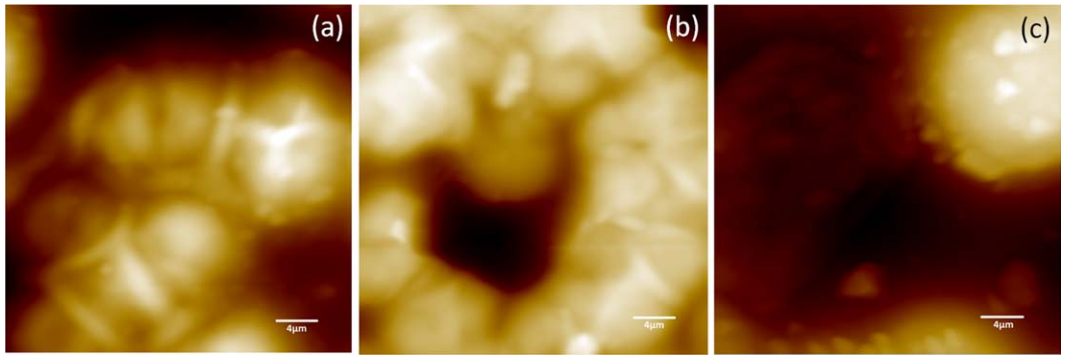

FIG. 11. AFM images of (a) PU-50-NC-nc, (b) PU-70-NC-nc, and (c) PU-100-NC-nc. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

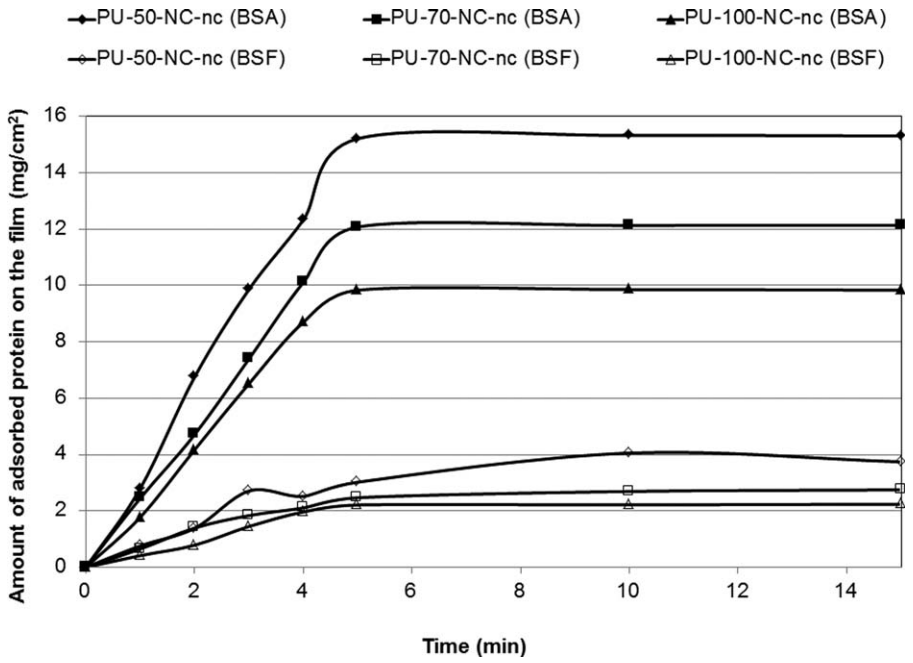

FIG. 12. BSA and BSF adsorption for the samples coded PU-50-NC-nc, PU-70-NC-nc, and PU-100-NC-nc.

which are based on measurement of the weight of the protein per unit area.

CONCLUSION

Polyurethane hydrogels are successfully synthesized from CO, which is natural polyol, and PEG in different monomer ratio. Any solvent can be used in polymer synthesis. The reactions are carried out as follows: (1) in the presence of catalyst and crosslinker, (2) in the presence of crosslinker and in the absence of catalyst, and (3) in the absence of both catalyst and crosslinker. Thus, polyurethanes having different density, hydrophilicity and swelling ratio can be obtained, and their physical and surface properties can be correlated to their chemical structure. The main results of the study can be resumed in the following items:

1. Since CO has more than two hydroxyl groups in each molecule, the increasing of CO content result in increase in the crosslink density of the polyurethane hydrogels, thus, decrease in swelling degree. Increase in CO content not only increase the crosslink density but also increase the water contact angle indicating the hydrophobic surfaces.
2. The crystallinity of the polymers decreases by increasing the CO:PEG ratio. Crystallinity also affected by the preparation method of the polymers. The polymers prepared in the presence of the catalyst have low crystallinity due to short polymerization time.
3. Hydrophilicity is not the only significant parameter in protein adsorption on polymers. Roughness plays a more important role than the hydrophilicity for protein adsorption on polyurethane prepared.

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