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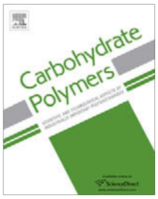

Surface characteristics of UV-irradiated chitin-based polyurethane elastomers

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ABSTRACT

Chitin-based polyurethane elastomers (PUEs) constituted on 4,4′-diphenylmethane diisocyanate (MDI), poly(ε-caprolactone) (PCL) and extended with blends of chitin/1,4-butane diol were first synthesized via two step polymerization technique and then irradiated for 50, 100 and 200 h in an UV exposure chamber as such the spectral distribution of the light is good match for terrestrial solar radiation. The surface properties of the irradiated PU samples were investigated by contact angle measurements, surface free energy and water absorption (%), total work of water adhesion to polymer and equilibrium degree of swelling. The effects of UV-irradiation time and chitin contents in chain extenders (CE) proportion on surface properties were investigated. Results of the aforementioned surface techniques revealed that the UV-irradiated polyurethane samples were affected by varying the UV exposure period.

1. Introduction

Surface properties which are different from bulk properties of polymers play an important role in many applications. For the application of polyurethane (PU), their stability against terrestrial weathering is important. One of the greatest factors in the terrestrial weathering of PUEs is ultraviolet (UV) radiation in the wavelength range 330–410 nm. This energy, from incident energy solar radiation, initiates an auto oxidative degradation process in PUEs that can chemically crosslink the chain extensively, embrittling and insolubilizing the PUEs (Bhowmick & Stephens, 1998, chap. 11). Polymer pyrolysis is the chemical process of thermolytic degradation by chain scission, randomly along the chain backbone. These fragments can recombine to give different pyrolytic products. Pyrolysis is necessary for gasification and combustion of natural and synthetic macromolecules and is thus a common and important chemical reaction (Zia, Bhatti, & Bhatti, 2007). The thermal degradation of polymers especially polyurethane has been the centers of thermal analysis studies for many years (Gao, Kaneko, Amasaki, & Nakada, 2003). Segmented polyurethanes, consisting of hard and soft segments are known to have microphase separated structure, which make them useful in various ways such as adhesives, coatings, biomedical materials and elastomers (Barikani & Hepburn, 1986, 1987). Molecular characterization and morphological studies of polyurethane elastomers (PUEs) have been reported by many researchers. The effect of the diisocyanate structure and chain extender (CE) length using α,ω-alkane diols on the crystallinity, surface morphology and thermo-mechanical properties of PUEs have been investigated and reported (Rogulska, Podkoscielny, Kultys, Pikus, & Pozdzik, 2006; Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008b; Zia, Barikani, Zuber, Bhatti, & Bhatti, 2008a). Detailed molecular characterization, thermal and shape memory properties of chitin-based polyurethane elastomers have been previously discussed and reported (Barikani, Zia, Bhatti, Zuber, & Bhatti, 2008; Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008d; Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008c). Surface characteristics and XRD studies of polyurethane elastomers based on chitin/BDO blends and varying diisocyanates structure have also been documented elsewhere (Zia, Bhatti, Barikani, Zuber, & Sheikh, 2008e, 2008f, 2009b).

Chitin is structurally similar to cellulose, but it is an amino polysaccharide having acetamide group at the C-2 positions in place of hydroxyl group. Chitin itself is a crystalline polymer of *N*-acetyl-D-glucosamine (GlcNAc) monomer, its crystalline structure has been previously reported and well documented (Cardenas, Cabrera, Taboada, & Miranda, 2004; Zia et al. 2008f, 2009b). Attempts have been made to study the effect of UV-irradiation on surface properties of some common polymers (Gu et al., 2006; Kaczmarek & Chaberska, 2006; Kaczmarek & Podgorski, 2007). Photooxidative behavior and effect of chain extender length in polyurethane on photooxidative stability have also been reported (Zia, Barikani, Zuber, Bhatti, & Islam-ud-Din, 2008g). Investigations on the surface properties of chitin and carbon aerogels from chitin alcogels have been reported elsewhere (Tsioptsias, Michailof, Stauropoulos, &

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Panayiotou, 2008). Surface morphology of starch (Matsushita et al., 2008), cellulose (Cerne, Simoncic, & Zeljko, 2008; Yokota, Kitaoka, & Wariishi, 2008) and chitin–humic acid (Santosa, Siswanta, Sudiono, & Utarianingrum, 2008) have also been investigated and well documented. XRD studies of UV-irradiated chitin-based polyurethane elastomers have also been presented elsewhere (Zia, Barikani, Zuber, Bhatti, & Barmar, 2009a). No reference is still available on the study of the effect of different exposure time of UV radiation on surface characteristics of polyurethane elastomers extended with blends of chitin/BDO. It is known that PUEs undergo significant structural changes on exposure to UV-irradiation which causes deterioration in their surface properties. In this work, we have irradiated a series of polyurethane elastomers based on PCL and 4,4′-diphenylmethane diisocyanate (MDI), extended with different proportion of chitin and BDO by ultraviolet (UV) radiations. The effect of chitin contents and UV-irradiation time on the surface characteristics is currently being investigated and reported using contact angle measurements, surface free energy, and water absorption calculations, total work of water adhesion to polymer and equilibrium degree of swelling.

2. Experimental

2.1. Chemicals

4,4′-Diphenylmethane diisocyanate (MDI) and 1,4-Butane diol (BDO) were procured from Sigma–Aldrich Chemical Co. (Saint Louis, MO, USA). Polycaprolactone polyol, CAPA 225, molecular weight 2000 from Solvay Chemicals Co. (Cashur, England) and BDO were dried at 80 °C under vacuum for 24 h before use to ensure the removal of air and water tracers that may otherwise interfere with the isocyanate reactions. Molecular weight of CAPA 225 was confirmed by applying the procedure reported in ASTM D-4274C. All the other materials were used as received. All the reagents used in this work were of analytical grade.

Chitin was provided by Department of Polymeric Biomaterials, Iran Polymer and Petrochemical Institute Tehran, Iran. Chitin was purified according to already established methods in the literature (Wang, Qin, & Bo, 1991). Its molecular weight was deduced following the established methods reported in the literature (Chen, Sun, Fan, & Zhang, 2002; Zia et al., 2008f).

2.2. Synthesis of PU

For this investigation a prepolymer was synthesized as predicted in our previous studies (Barikani & Hepburn, 1986, 1987) by the step-growth polymerization of PCL and MDI, and extended with different proportions of chitin and BDO (Table 1). The polymerization was completed to get the final product according to the method reported elsewhere (Zia et al., 2008c).

2.3. UV exposure

Irradiation of PUEs was carried out in an UV exposure chamber fitted with five 80 W medium pressure mercury vapor lamps (Latina Tendeng Corp., China) constructed with borosilicate glass envelopes which filter all wavelength below 300 nm. These conditions provided the spectral distribution of the light that is good match for terrestrial solar radiation. Irradiation was performed with sample to lamp distance of 20 cm at ambient relative humidity. Samples were irradiated for the time of 50, 100 and 200 h.

2.4. Measurements

The static contact angle (θ) was measured by a sessile drop method at constant room temperature (20 °C) using the drop shape analysis (DSA) G10 goniometer of Kruss GmbH (Germany), equipped with software for a drop shape analysis. Diiodomethane (analytically pure, UCB, Belgium) and deionized water were applied as the test liquids. The image of liquid drop (volume of 2–3 μl) was recorded by video camera and fitted by means of mathematical functions. Each given θ value was the average of at least seven measurements and the precision was 1°. Surface free energies (γ_s) and their dispersive ($\gamma^d{}_s$) and polar ($\gamma^p{}_s$) components were

Table 1
Contact angle measurements varying chitin/BDO composition and irradiation time with two different test liquids.

S. no.	Sample code	Composition (chitin/BDO[a]) % by mass	Molar ratio (whole number) of CAPA225[b]/MDI[c]/chitin/BDO[a]	Irradiation time (h)	Contact angle θ with water and diiodomethane	
					Water[e]	Diiodomethane[e]
1	SPU1	0/100	1:3:0:2	00[d]	73.1 ± 0.2	43.8 ± 0.2
2	–	–	–	50[f]	59.4 ± 0.3	43.7 ± 0.3
3	–	–	–	100[f]	47.6 ± 0.3	43.4 ± 0.4
4	–	–	–	200[f]	36.8 ± 0.7	43.1 ± 0.8
5	SPU2	25/75	1:3:0.5:1.5	00[d]	77.4 ± 1.0	45.6 ± 1.0
6	–	–	–	50	70.8 ± 0.6	45.5 ± 0.3
7	–	–	–	100	61.4 ± 0.9	45.4 ± 0.3
8	–	–	–	200	57.4 ± 0.8	45.1 ± 0.5
9	SPU3	50/50	1:3:1:1	00[d]	82.6 ± 0.5	46.0 ± 1.0
10	–	–	–	50	77.4 ± 0.3	46.0 ± 0.3
11	–	–	–	100	72.3 ± 0.3	45.9 ± 0.4
12	–	–	–	200	67.4 ± 0.7	45.8 ± 0.8
13	SPU4	75/25	1:3:1.5:0.5	00[d]	90.5 ± 0.5	51.6 ± 0.5
14	–	–	–	50	87.1 ± 0.4	51.6 ± 0.4
15	–	–	–	100	84.4 ± 0.6	51.5 ± 0.8
16	–	–	–	200	80.1 ± 0.8	51.5 ± 0.8
17	SPU5	100/0	1:3:2:0	00[d]	93.4 ± 1.0	52.0 ± 0.5
18	–	–	–	50	91.9 ± 0.9	52.0 ± 1.0
19	–	–	–	100	90.7 ± 0.6	52.0 ± 0.9
20	–	–	–	200	88.2 ± 0.8	51.9 ± 0.6

[a] 1,4-Butane diol.
[b] Polycaprolactone polyol (molecular weight; 2000 g mol^{-1}).
[c] 4,4′-Diphenylmethane diisocyanate.
[d] Results from the previous study (Zia et al., 2008e).
[e] Each value is expressed as mean ± standard error (SE) ($n = 7$).
[f] Results from the previous study (Zia et al., 2008g).

calculated by Owens–Wendt method (Owens & Wendt, 1969) and Wu method (Abbasian, Ghaffarian, Mohammadi, & Fallahi, 2004). From θ measurement, the work of water adhesion to PU surface was also obtained. Water absorption (%) and equilibrium degree of swelling were determined following the method as reported in our previous studies (Zia et al., 2008a). All the data presented were average of seven measurements.

3. Results and discussion

3.1. Molecular characterization

Isocyanate (NCO) terminated polyurethane prepolymer was first synthesized by the reaction of one equivalent of polyol with three equivalents of MDI, which was subsequently extended with two equivalents of chain extender with different proportions of chitin/BDO (Zia et al., 2008c). The final polyurethanes were characterized by conventional spectroscopic methods. Fourier transforms infra-red (FTIR), ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (400 MHz, DMSO-d_6) spectra of final synthesized polyurethane samples were in accordance with proposed polyurethane structures (Zia et al., 2008c).

The main aim of this research work was to study the effect of UV exposure on the surface characteristics of polyurethane elastomers extended with blends of chitin/1,4-butane diol. After synthesis the PU films of the same thickness (30 μm) were irradiated in UV exposure unit for 50, 100 and 200 h and characterized. Surface properties of the samples were studied using contact angle measurement, surface free energies and water absorption (%) calculations and equilibrium degree of swelling.

3.2. Surface morphological studies

3.2.1. Contact angle measurement

Contact angle measurement is very sensitive method to surface changes although does not give information about types of group present. It is a measure of non-covalent forces between liquid and the first monolayer of the tested material. Thus, in case of strong interactions between the studied phases, the liquid drop spreads on the solid and wets it. The results of contact angle of two liquids (water and diiodomethane), with different polarity are listed in Table 1. Non-modified PU (0 irradiation time) is characterized by the θ values ranging from 73.1° to 93.4° and 43.8° to 52.0° for water and diiodomethane, respectively (Zia et al., 2008e). UV treatment significantly decreases the contact angle value for the samples: SPU1 (73.1–36.38°); SPU2 (77.4–57.4°), and it slightly decreases for the samples: SPU4 (95.0–80.1°); SPU5 (93.4–88.2°). There is a medium effect of UV treatment on the SPU3 (82.6–67.4°) irradiated samples. These variations in contact angles can be ascribed to modification of surface chemistry and the surface roughness of the PU samples. UV-irradiation significantly changes θ values for polar liquid (water) but only slightly influences the θ value for non-polar diiodomethane in PU samples extended with lower or zero contents of chitin (SPU1, SPU2) in comparison of PU extended with higher contents of chitin (SPU4, SPU5). This phenomenon is due to the fact that chitin itself is crystalline polysaccharide and its affinity with water is negligible, it means the synthesized material is very hydrophobic in nature. Therefore, by increasing the percentage of chitin in the PU backbone, the hydrophobicity of the final PU increases which ultimately resist the attack of UV radiations. It has been previously reported that the wettability increase is faster in the PU samples extended with lower contents of chitin than PU samples extended with higher contents (Zia et al., 2008e). The contact angle measurements have shown that the wettability of PU samples extended with lower contents of chitin was changed by UV-irradiation at a higher rate than the wettability of PU extended with higher contents of chitin (SPU4 and SPU5). It means that photooxidation in samples SPU4 and SPU5 is some what retarded, probably because of strong interactions associated with the polyurethane and chitin. Chitin should be fairly hydrophilic in nature as it contains many polar groups (OH, CH_2OH and $NHCOCH_3$) in the structure. On the other hand, it has also been previously reported that involvement of chitin results in increasing the crystallinity of the synthesized polyurethane (Zia et al., 2008f). It is well known that any increase in crystallinity of polymer ultimately results in increasing the hydrophobic character of the polymers. XRD pattern of the studied samples has shown that increase in chitin favour the formation of more ordered structure (Zia et al., 2008f), which ultimately results to increase in the hydrophobic character of polyurethane. Moreover, the decrease in water wettability of solid surfaces is attributed to the thermodynamic driving force to minimize the surface free energy. It is believed that chemical functional groups responsible for the enhanced wettability gradually migrate away from the surface exposed to dry air to the interior of polymeric material. The migration of the functional groups to minimize the solid surface energy is facilitated by the local segmental motion of polymers.

3.2.2. Surface free energy

There is no direct method for the estimation of the surface free energy of the solid polymers (γ_s). It can be obtained from the contact angle measurements. Thus Young equation describing the three phase equilibrium is usually used:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \tag{1}$$

where γ_{sv}, γ_{sl} and γ_{lv} are the polymer–vapour, polymer–liquid and liquid–vapour interfacial energies, respectively, and θ is the contact angle. However, the assumption that the spreading pressure, which represents the decrease in solid surface tension due to vapour adsorption may be neglected ($\pi_e \cong o$), have to be done. In such case $\gamma_s = \gamma_{sv}$ and Eq. (1) can be expressed as

$$\gamma_s = \gamma_{sl} + \gamma_l\cos\theta \tag{2}$$

where γ_l is a surface tension of liquid. The contact angle can be measured by a sessile drop method. It is known that, the hydrophilic surface with a high surface energy spreads the drop of polar liquid and gives a low contact angle, while the hydrophobic surface with a low free energy gives a high contact angle (Garbassi, Mora, & Occhiello, 1998; Zenkiewicz 2000). According to Owens–Wendt method (Owens & Wendt, 1969), γ_s is a sum of dispersive ($\gamma^{d}{}_{s}$) and polar ($\gamma^{P}{}_{s}$) components of surface free energy:

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{3}$$

and γ_{sl} can be expressed as the geometric mean:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left(\sqrt{\gamma_s^d\gamma_l^d} + \sqrt{\gamma_s^p\gamma_l^p}\right) \tag{4}$$

where subscripts 's' and 'l' indicate the value for solid and liquid, respectively. By combining the above relationship (4) with Young equation (1) and measurement of contact angle for at least two liquids, we can resolve the system of two equations with two unknown (γ^d and γ^p for polymer). Only the values of γ for test liquids (including polar and dispersive components) have to be known. Where as Wu method (Abbasian et al., 2004) utilizes a similar approach but uses a harmonic mean equation to sum the dispersive and polar contributions. Contact angles against two liquids with known values of γ^d and γ^p are measured. The values for each experiment are put into the following equation;

$$(1 + \cos\theta)\gamma_l = 4(\gamma_l^d\gamma_s^d/\gamma_l^d + \gamma_s^d + \gamma_l^p\gamma_s^p/\gamma_l^p + \gamma_s^p) \tag{5}$$

Table 2
Total surface energy calculated data with Owens–Wendt and Wu methods.

Sample code	Exposure time (h)	Owens–Wendt method			Wu Method		
		Disperse part (mN/m)	Polar part (mN/m)	Total surface energy[b] (mN/m)	Disperse part (mN/m)	Polar part (mN/m)	Total surface energy[b] (mN/m)
SPU1	00[a]	36.67	11.19	47.86 ± 0.09	38.40	11.78	50.19 ± 0.09
–	50[c]	35.52	13.07	48.59 ± 0.92	37.24	14.62	51.86 ± 0.99
–	100[c]	33.44	17.59	51.03 ± 1.08	35.06	18.23	53.29 ± 1.01
–	200[c]	–	–	Nd[d]	–	–	Nd[d]
SPU2	00[a]	37.66	6.57	44.23 ± 0.7	39.88	9.46	49.34 ± 0.06
–	50	37.24	7.73	44.97 ± 1.0	39.37	10.57	49.94 ± 0.06
–	100	36.87	8.81	45.68 ± 0.7	38.79	11.77	50.56 ± 0.06
–	200	36.56	9.78	46.34 ± 0.7	37.12	14.37	51.49 ± 0.06
SPU3	00[a]	38.30	5.34	43.64 ± 0.10	41.42	4.81	46.23 ± 0.08
–	50	38.06	5.93	43.99 ± 0.92	41.12	5.54	46.66 ± 0.99
–	100	37.86	6.37	44.23 ± 1.08	40.96	6.22	47.18 ± 1.01
–	200	37.64	7.14	44.78 ± 1.92	40.23	7.36	47.59 ± 1.92
SPU4	00[a]	39.16	3.22	42.38 ± 1.05	42.48	2.86	45.34 ± 1.10
–	50	39.00	3.66	42.66 ± 1.11	42.17	3.51	45.68 ± 1.28
–	100	38.79	4.19	42.98 ± 1.86	41.98	3.96	45.94 ± 1.92
–	200	38.04	5.25	43.29 ± 1.86	41.56	4.73	46.29 ± 1.98
SPU5	00[a]	40.14	1.04	41.18 ± 1.08	43.27	0.81	44.08 ± 1.15
–	50	39.98	1.41	41.39 ± 1.16	43.08	1.18	44.26 ± 1.08
–	100	39.57	2.11	41.68 ± 1.25	42.87	1.48	44.35 ± 1.19
–	200	39.22	2.69	41.91 ± 1.19	42.43	2.55	44.98 ± 1.26

[a] Results from the previous study (Zia et al., 2008e).
[b] Each value is expressed as mean ± standard error (SE) ($n = 7$).
[c] Results from the previous study (Zia et al., 2008g).
[d] Non-detectable surface.

where γ refers to surface tension (surface free energy), the subscripts ‘l’ and ‘s’ refer to liquid and solid, and the superscripts ‘d’ and ‘p’ refer to dispersive and polar components.

The surface free energy of the PU extended with lower contents of chitin much increased with increase in UV exposure time, whereas very small change of energy was found in case of PU extended with higher contents of chitin (Table 2). Such results may suggest some surface photo-resistance of the PU samples (SPU5) extended with higher contents of chitin (100% chitin) in comparison to the PU samples (SPU1) extended with lower or zero contents of chitin (100% BDO). The calculations of dispersive ($\gamma^{d}{}_{s}$) and polar ($\gamma^{p}{}_{s}$) components of surface free energy have given more detailed information on the surface properties of the samples studied (Table 2). It is clear from the results that the dispersive components decreased and simultaneously the polar components of surface energy increased with the irradiation time of all the studied samples. The increase in polar components ($\gamma^{p}{}_{s}$) is considerable in PU extended with lower or zero proportion of chitin (SPU1) in the chain extender but negligible in PU extended with higher proportion of chitin (SPU5). Results revealed that in the samples SPU1, the surface free energies were non-measurable after at 200 h UV exposure (Zia et al., 2008g). It is connected with the significant increase in the surface free energy and its polar components, which increases after this time (200 h). This phenomenon is due to that fact that decrease in contact angle values leads to increase in surface energy. The contact angle of a liquid with a solid surface is related to the solid surface energy γ_S, liquid surface tension γ_L, and solid–liquid interfacial tension γ_{SL} by the well known Young’s equation (Butt, Graf, & Kappl, 2003, chap. 7).

$$\cos\theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \tag{6}$$

Young’s equation shows that higher the solid surface energy γ_S, or the lower the liquid surface tension γ_L, the lower the contact angle becomes. In other words, one can make a solid surface more wettable either by lowering the surface tension of the liquid or by increasing the surface energy of the solid (Noda & Rubingh, 1992). The increase in polarity of samples indicates that efficient photooxidation takes place on their surfaces. Free radicals formed during UV-irradiation may react with atmospheric oxygen leading to the formation of different oxygen containing group, namely of carbonyl, hydroxyl and hydroperoxide type, strongly altering $\gamma^{p}{}_{s}$. The low change of this parameter observed for the PU samples extended with higher proportion of chitin used as chain extender prove that photooxidation is some what inhibited.

3.2.3. Water adhesion to PU surface

The data of contact angle measurements allow calculating the work of liquid adhesion (W_A) to polymer surface, which is defined as the work done on the system, when two condensed phases, forming an interface of unit area, are separated reversibly to form of both unit areas (Garbassi et al., 1998; Zenkiewicz, 2000). From practical point of view, it is interesting to know the adhesion of water to PU, which can be expressed as following:

$$W_A = \gamma_s + \gamma_w + \gamma_{sw} \tag{7}$$

or

$$W_A = \gamma_w(\cos\theta_w + 1) \tag{8}$$

where γ_s is the surface free energy of solid (polymer), γ_w the surface tension of water and γ_{sw} is the interphase (polymer–water) free energy.

In case of polymers, the important components of surface free energy are: dispersive adhesion ($W^{d}{}_{A}$), for which mainly the van der Waals forces are responsible, and non-dispersive/polar ($W^{p}{}_{A}$) adhesion, due to different interactions such as dipole–dipole, acceptor–donor and hydrogen bonds. Both components are the sum of total adhesion (W_A):

$$W_A = W_A^d + W_A^p = 2\sqrt{\gamma_s^d\gamma_w^d} + 2\sqrt{\gamma_s^p\gamma_w^p} \tag{9}$$

Knowing the γ values for water from literature ($\gamma_w = 72.8$ mJ/m^2, $\gamma^{d}{}_{w} = 21.8$ mJ/m^2), the components ($W^{d}{}_{A}$ and $W^{p}{}_{A}$) water adhesion and total water adhesion (W_A) to PU surface were calculated from Eq. (9). The results are presented in Table 3. As can be seen, the work of the water adhesion to PU surface increases with the in-

Table 3
The work of water adhesion to PU films obtained before and after UV-irradiation.

Sample code	Irradiation time (h)	Dispersive adhesion ($W^{\mathrm{d}}_{\mathrm{A}}$)	Polar adhesion ($W^{\mathrm{p}}_{\mathrm{A}}$)	Total work of adhesion[b] (W_{A})
SPU1	00[a]	53.1	47.1	100.2 ± 1.0
–	50[c]	50.9	68.9	119.8 ± 1.8
–	100[c]	47.1	91.4	138.5 ± 3.0
–	200[c]	44.8	104.1	148.9 ± 4.1
SPU2	00[a]	53.5	45.0	98.5 ± 1.1
–	50	51.6	62.2	113.8 ± 1.7
–	100	49.4	75.5	124.9 ± 2.4
–	200	46.2	89.5	135.7 ± 3.8
SPU3	00[a]	54.1	43.6	97.7 ± 1.2
–	50	52.4	56.4	108.8 ± 1.8
–	100	50.8	65.6	116.4 ± 3.0
–	200	48.2	72.9	121.1 ± 4.1
SPU4	00[a]	54.7	41.2	95.9 ± 1.1
–	50	53.1	52.8	105.9 ± 2.6
–	100	51.3	56.4	107.7 ± 5.1
–	200	49.4	60.3	109.7 ± 5.1
SPU5	00[a]	55.2	38.8	94.0 ± 1.3
–	50	54.4	40.8	95.2 ± 1.8
–	100	53.6	43.0	96.6 ± 1.9
–	200	52.7	45.1	97.8 ± 2.1

[a] Results from the previous study (Zia et al., 2008e).
[b] Each value is expressed as mean ± standard error (SE) ($n = 7$).
[c] Results from the previous study (Zia et al., 2008g).

crease in irradiation time. These changes are caused mainly by the increase in polar components, contrary to dispersive one, which somewhat decreases during exposure. Before irradiation, $W^{\mathrm{d}}_{\mathrm{A}}$ was higher than $W^{\mathrm{p}}_{\mathrm{A}}$ components in all films expect SPU5 but after irradiation, the opposite situation was found: $W^{\mathrm{p}}_{\mathrm{A}} > W^{\mathrm{d}}_{\mathrm{A}}$. It is caused by the formation of different polar groups on PU film resulting of photooxidation, which increases surface hydrophilicity and increase the share of polar interactions between polymer and water. As can be seen, the work of the water adhesion to PU surface decreases with the increasing chitin contents. These changes are caused mainly by the decrease in polar components, contrary to dispersive one, which somewhat increases by increasing chitin proportion into the final polyurethane. It is clear from the results that water adhesion decreased with increase in chitin contents and its value increased with increase in irradiation time. The $W^{\mathrm{p}}_{\mathrm{A}}$ component was not much lower than $W^{\mathrm{d}}_{\mathrm{A}}$ components in the PU sample extended with zero contents of chitin and 100% BDO (SPU1), but after the addition of chitin contents in the mixture of chain extender, there was appreciable difference between the polar ($W^{\mathrm{p}}_{\mathrm{A}}$) and dispersive ($W^{\mathrm{d}}_{\mathrm{A}}$) components. These changes in the polar and dispersive components attributed to the formation of different dispersive groups on PU film resulting of chitin incorporation, which increased surface hydrophobicity and decreased the share of polar interactions between polymer and water. It is clear from the results (Table 3) that dispersive adhesion for the sample SPU5 remained higher than polar adhesion even at 200 h exposure time. This phenomenon attributed to the incorporation of chitin contents in to the PU backbone which results to increase in hydrophobicity of the said sample (SPU5). The mechanism of photooxidative degradation of PU is known (Allen & Edge, 1992), the degraded chains become shorter and more mobile, which facilitate their rearrangements and local conformational changes. Creation of oxidized groups in PU during UV-irradiation can lead to change in deeper layers. It is well known that photooxidative degradation is free radical chain process and after initiation on surface, the propagation occurs even without light. The efficiency of degradation inside the film depends on the diffusion and migration of radicals, oxygen and other reactive species. These processes are facilitated by the surface defects which ultimately lead to enhance the water adhesion to PU surface. The rate of surface defects is much lower in the PU samples extended with higher contents of chitin used as chain extender.

3.2.4. Evaluation of water absorption (%) and swelling behavior

Water absorption as a function of time and type of samples are collected in Table 4. There was a considerable difference in the amount of absorbed water as a function of soaking time. The irradiation time and chitin contents were the main factor that can control the amount of absorbed water. The results presented clearly showed that water absorption of samples increased with increasing irradiation time and decreasing chitin contents in to the final PU samples. The wettability increase is faster in the PU

Table 4
Hydrophilicity and swelling data of samples before and after UV-irradiation.

Sample code	Irradiation time (h)	Water absorption (%)						Equilibrium degree of swelling[b]
		1st day	2nd day	3rd day	4th day	5th day	7th day	
SPU1	00[a]	2.59	2.62	2.63	2.65	2.67	2.69	14.39 ± 0.08
–	50[c]	4.58	4.67	4.82	4.95	5.12	5.28	16.35 ± 0.21
–	100[c]	7.46	7.63	7.75	7.89	8.0	8.15	19.81 ± 0.42
–	200[c]	10.82	10.97	11.11	11.31	11.59	11.81	22.15 ± 0.75
SPU2	00[a]	2.37	2.39	2.39	2.40	2.40	2.42	9.18 ± 0.22
–	50	4.12	4.23	4.35	4.51	4.68	4.83	11.84 ± 0.26
–	100	5.32	5.44	5.52	5.60	5.64	5.68	13.44 ± 0.46
–	200	6.07	6.19	6.28	6.36	6.42	6.51	15.05 ± 0.59
SPU3	00[a]	1.80	1.81	1.83	1.83	1.84	1.85	8.28 ± 0.22
–	50	2.59	2.64	2.65	2.66	2.67	2.68	9.35 ± 0.21
–	100	3.12	3.16	3.17	3.17	3.19	3.19	10.71 ± 0.32
–	200	4.23	4.28	4.30	4.31	4.31	4.32	11.66 ± 0.64
SPU4	00[a]	1.08	1.11	1.13	1.14	1.15	1.15	8.00 ± 0.22
–	50	1.23	1.26	1.26	1.27	1.27	1.28	8.45 ± 0.09
–	100	1.53	1.56	1.56	1.57	1.57	1.58	8.89 ± 0.99
–	200	2.29	2.33	2.33	2.34	2.35	2.35	9.24 ± 0.22
SPU5	00[a]	0.80	0.80	0.84	0.85	0.87	0.87	7.82 ± 0.8
–	50	0.93	0.95	0.97	0.98	1.0	1.0	7.92 ± 1.0
–	100	1.05	1.07	1.09	1.10	1.11	1.12	8.08 ± 1.0
–	200	1.17	1.20	1.22	1.23	1.24	1.24	8.22 ± 1.0

[a] Results from the previous study (Zia et al., 2008c).
[b] Each value is expressed as mean ± standard error (SE) ($n = 5$).
[c] Results from the previous study (Zia et al., 2008g).

samples extended with zero or lower contents of chitin than PU samples extended with higher one. In addition to this swelling behavior was also in accord with water absorption (Table 4). The swelling ability of final PU steadily increases as the irradiation time increases, but it showed adverse effect by increasing the chitin contents i.e. it decreases with increase in chitin contents. It was found that SPU5 has better solvent resistance as compared to SPU1, and this resistance continuously decreasing as the chitin contents decreases. This effect can be elucidated by the degree of physical crosslinking and hydrogen bonding in polyurethane. This behavior has been confirmed in detailed by FTIR and NMR studies of these polymeric materials (Zia et al., 2008c). It is known that chitin is a crystalline polymer of *N*-acetyl-D-glucosamine monomers. The linked glucosamine rings on chitin can play a role in establishing and increasing H-bonding between soft segment and NH group in the hard segment. Therefore, the samples extended with higher contents of chitin have shown much resistant against solvent as compared to the samples having lower contents. Photooxidation of PU surface leads to fast increase in surface free energy and its polar component. Simultaneously, the water absorption and swelling behavior increases significantly during UV-irradiation. The observed changes during modification by UV can also be caused by influence of deeper polymer layers on surface macromolecules. PU contain electronegative oxygen atoms, thus bond C–O is polarized, resulting of which, the specific interactions at the interphase occur. Chain orientation and functional group rotation, which occurs during the film formation (i.e. in solution, where macromolecules are still mobile), can change polymer susceptibility to photooxidative degradation. Adsorbed chains have restricted mobility but entangled internal particles, loops; free ends are more mobile and can interact with neighboring macromolecules. Moreover, low molecular weight degradation products, which usually accumulate at the surface, act as plasticizer and increase the molecular mobility and, hence cause the water absorption and swelling behavior more rapidly in the PU samples extended with zero contents of chitin.

4. Conclusion

A series of polyurethanes (PU) elastomers were prepared by the reaction of poly(ε-caprolactone) (PCL) and 4,4′-diphenylmethane diisocyanate (MDI). The prepolymer was extended with different proportion of chitin/BDO used as chain extenders. The synthesized samples were irradiated for 50, 100 and 200 h in an UV exposure unit as such the spectral distribution of the light is good match for terrestrial solar radiation. The modifications in the chemical structures of the chitin-based PU before and after irradiation were characterized using different surface technique. The interactions of polyurethane with water and diiodomethane on the surface were clearly related to the mass ratio of chitin content and irradiation time. The equilibrium degree of swelling and water absorption were affected accordingly. Incorporation of chitin contents into the final PU result to decrease in surface free energy and its polar components. Simultaneously, the work of water adhesion to polymer decrease significantly by increasing the chitin contents in the synthesized polymer. The higher changes of surface properties, observed by water absorption (%), equilibrium degree of swelling, as well as monitored by contact angle measurement and surface free energies, were found for the PU samples extended with lower contents of chitin and higher irradiation time. Results suggest that macromolecular rearrangement during film formation (i.e. during solvent evaporation) and upon UV-irradiation (where main chain scission leads to higher mobility of degraded molecules) is process dependent on chitin contents and irradiation time.

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