



Surface characteristics of UV-irradiated chitin-based shape memory polyurethanes

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ABSTRACT

Shape memory polyurethanes (SMPUs) were prepared from polycaprolactone diol 4000 (PCL 4000), 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BDO), chitin, dimethylol propionic acid (DMPA), and triethylamine (TEA). The synthesized samples were irradiated for 50, 100, and 200 h in an UV exposure unit. The effects of chitin and DMPA contents in the polyurethane (PU) formulation on surface properties of the UV-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. Results of the aforementioned surface techniques revealed that the UV-irradiated PU samples were affected by varying the UV exposure period. The interactions of the PU films with solvents on the surface were clearly related to the contents of DMPA and chitin in the final polyurethane formulation and UV-irradiation time.

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1. Introduction

Chitin is considered the second most plentiful organic resource on the earth; occurring in plants, marine invertebrate, insects, cell walls of some fungi, and microorganisms (Gorovoj & Burdukova, 1996; Knorr, 1984; Muzzarelli, 1977). Shape memory polymers (SMPs) are polymer networks equipped with suitable molecular switches, which are sensitive to an external stimulus. Among various SMPs, shape memory polyurethanes (SMPUs) are receiving much attention for their easy control of glass transition temperature (T_g) around the room temperature and excellent shape memory properties at the room temperature. A series of SMPUs from polycaprolactone diol, 1,4-butanediol (BDO), dimethylol propionic acid (DMPA), and 4,4'-diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI) were synthesized (Han, Boung, & Byung, 2001; Hu, Yang, Yeung, Ji, & Liu, 2005; Jeong, Lee, Lee, & Kim, 2000; Kim, Lee, & Xu, 1996; Kim et al., 1998; Lee, Chun, Chung, Sul, & Cho, 2001; Li, Chen, Zhu, Zhang, & Xu, 1998; Li et al., 1996). Extensive work on detailed molecular characterization (Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008a), XRD studies (Zia, Bhatti, Barikani, Zuber, & Sheikh, 2008b), and thermal properties (Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008c) of chitin-based polyurethane elastomers (PUEs) have also been previously discussed and reported. In vitro biocompatibility and non-toxicity of chitin/1,4-butanediol blends based polyurethane elastomers has also been reported elsewhere (Zia, Zuber, Bhatti, Barikani, & Sheikh, 2009a, 2009b). Some reports

are also available on molecular characterization and shape memory properties of chitin-based shape memory polyurethane elastomers (Barikani, Zia, Bhatti, Zuber, & Bhatti, 2008; Zia, Zuber, Barikani, Bhatti, & Khan, 2009c).

For the application of 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. Attempts have been made to study the effect of UV-irradiation on surface properties of some common polymers (Kaczmarek & Chaberska, 2006; Kaczmarek & Podgorski, 2007; Zia, Bhatti, & Bhatti, 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, 2008d). Surface morphology of starch (Matsushita et al., 2008), cellulose (Yokota, Kitaoka, & Wariishi, 2008), and chitin–humic acid (Santosa, Siswanta, Sudiono, & Utarianingrum, 2008) have also been investigated and well documented. XRD studies and surface characteristics of UV-irradiated and non-irradiated chitin-based polyurethane elastomers have also been presented elsewhere (Zia, Barikani, Khalid, Honarkar, & Ehsan-ul-Haq, 2009g; Zia, Barikani, Zuber, Bhatti, & Barmar, 2009e, 2009f; Zia, Bhatti, Barikani, Zuber, & Bhatti, 2009d). No reference is still available on the study of the effect of different exposure time of UV radiation on surface characteristics of chitin/DMPA/BDO-based shape memory polyurethane elastomers. In this work, ultraviolet (UV) radiations were used to irradiate a series of polyurethane elastomers based on PCL, 4,4'-diphenylmethane diisocyanate (MDI), chitin, DMPA, BDO, and TEA. DMPA was used for preparing the SMPU, since DMPA can give higher recovery strain and lower

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residual strain (Kim et al., 1998). The effect of chitin and DMPA contents, and UV-irradiation time on the surface characteristics was 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), dimethylol propionic acid (DMPA), and 1,4-butanediol (BDO) were procured from Sigma–Aldrich Chemical Co., USA. Polycaprolactone polyol, CAPA 240, (molecular weight 4000 from Solvay Chemicals, Cashur England) and BDO were dried at 70 °C under vacuum for 24 h before use to ensure the removal of all air bubbles and water vapors. Molecular weight of CAPA 240 was confirmed by applying the procedure reported in ASTM D-4274C. 4,4'-Diphenylmethane diisocyanate (MDI) and all other materials were used as received. Dimethylformamide (DMF) and triethylamine were used after being dehydrated with a 4 Å molecular sieve for 2 days. Chitin ($M_v = 6.067 \times 10^5 \text{ g mol}^{-1}$) was kindly supplied by Iran Polymer and Petrochemical Institute, Iran. Chitin was purified according to already established methods in the literature (Wang, Qin, & Bo, 1991). Its molecular weight was deduced from the intrinsic viscosity, as described in the literature (Chen, Sun, Fan, & Zhang, 2002; Zia et al., 2008b). All the reagents used in this work were of analytical grade.

2.2. Synthesis of shape memory polyurethane (SMPU6) and UV exposure

For this investigation a prepolymer was synthesized as predicted in our previous studies by the step-growth polymerization of PCL and MDI (Barikani et al., 2008), and extended with different proportions of chitin, DMPA, and BDO (Table 1). The synthesized polymer (Fig. 1) was then placed in a hot air circulating oven at 100 °C and cured for 24 h. The cured sample sheets were then stored for 1 week at ambient temperature (25 °C) and 40% relative humidity before testing.

Irradiation of PUEs was carried out in an UV exposure chamber fitted with five 80 W medium pressure mercury vapor lamps (Latina Tendeng Co., 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 radiations. 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.

2.3. 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). 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 (γ_s^d) and polar (γ_s^p) components were calculated by Owens–Wendt method (Owens & Wendt, 1969) and Wu method (Abbasi, Ghaffarian, Mohammadi, & Falahi, 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, Barikani, Zuber, Bhatti, & Bhatti, 2008e). All the data presented were average of seven measurements.

3. Results and discussion

The main aim of this research work was to study the effect of UV exposure on the surface characteristics of chitin/DMPA/BDO-based shape memory polyurethanes. After synthesis the PU films of the same thickness (30 μm) were irradiated in UV exposure unit for 50, 100, 200 h and characterized.

3.1. Contact angle measurements

Structural changes on the surface of PU films and PU films containing chitin and DMPA were induced by UV-irradiation. The surface properties of the synthesized samples, as characterized by static water contact angle, are reported in Table 1 which represents the results of contact angle of two liquids (water and diiodomethane), with different polarity. Non-modified PU (0 irradiation time) is characterized by the θ values ranging from 51.7° to 95.2° and 39.6° to 55.4° for water and diiodomethane, respectively (Zia et al., 2009c). UV treatment significantly decreases the contact angle value for the samples: SMPU2 (51.7–25.9°); SMPU1 (66.5–32.6°), SMPU3 (56.9–23.8°), and it slightly decreases for the samples: SMPU5 (86.8–73.6°); SMPU6 (95.2–92.6°). There is a medium effect of UV radiation treatment on the SMPU4 (78.5–52.6°) irradiated samples. These variations in contact angles can be ascribed to modification of surface chemistry of PU samples varying chitin, DMPA, and BDO contents. 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 zero contents of chitin and higher contents of DMPA (SMPU2, SMPU3) in comparison of PU extended with vice versa contents of chitin (SMPU5, SMPU6) and DMPA (SMPU1). This means hydrophilicity of the final PU film increases by incorporating the DMPA into the PU formulations. Polyol and carboxylic acid are essential in polyurethane manufacturing system. Dimethylol propionic acid (DMPA; $\text{CH}_3\text{C}(\text{CH}_2\text{OH})_2\text{COOH}$), a crystalline solid contains two kinds of functional groups in one molecule. There are two primary hydroxyl groups and one tertiary carboxylic group which provide function of making hydrophilic polyurethanes. The main advantage of DMPA is that the carboxylic acid is sterically hindered and so preferentially reacts into the backbone through the hydroxyl groups. So the chemistry of DMPA makes the hydrophilic PU films and its hydrophilicity increase upon increasing irradiation time and DMPA contents. The values of contact angle using both the test liquids increases as the concentration of chitin into the PU backbone vary from 1.0 to 3.0 mol (SMPU4, SMPU5, and SMPU6). As it can be seen, there is a remarkable difference between precursor PU (SMPU4) and PU extended with 3.0 mol of chitin (SMPU6). It is clear from the results that hydrophilic character of the final PU film decreases by increasing the contents of chitin into the final PU formulations. This phenomenon is due to the fact that chitin itself is crystalline polysaccharide and its affinity with water is negligible and is thus very hydrophobic in nature. Therefore by increasing the molar ratio of chitin in the PU backbone, the hydrophobicity of the final PU increases. 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 increases the crystallinity of the synthesized polyurethane (Zia et al., 2009d). It is well known that increase in crystallinity ultimately increases the hydrophobic character of the polymers. Moreover, by increasing the percentage

Table 1

Sample code designation representing formulation of shape memory polyurethane and contact angle measurements varying chitin/DMPA/BDO composition and irradiation time with two different test liquids.

Sample code	MDI (mol) ^b	PCL4000 (mol) ^c	BDO (mol) ^d	DMPA (mol) ^e	Chitin (mol)	Irradiation time (h)	Contact angle θ with water and diiodomethane	
							Water ^g	Diiodomethane ^g
SMPU1 ^a	10	6	4	–	–	00 ^f	66.5 ± 0.4	39.6 ± 0.4
–	–	–	–	–	–	50	53.9 ± 0.5	38.9 ± 0.2
–	–	–	–	–	–	100	44.5 ± 0.4	38.4 ± 0.3
–	–	–	–	–	–	200	32.6 ± 0.6	38.1 ± 0.6
SMPU2	10	4	2	4	–	00 ^f	51.7 ± 0.5	42.9 ± 0.3
–	–	–	–	–	–	50	37.3 ± 0.4	42.2 ± 0.6
–	–	–	–	–	–	100	25.9 ± 0.5	41.4 ± 0.8
–	–	–	–	–	–	200	Nd ^h	Nd ^h
SMPU3	10	3	5	2	–	00 ^f	56.9 ± 0.2	45.1 ± 0.2
–	–	–	–	–	–	50	43.6 ± 0.6	44.7 ± 0.4
–	–	–	–	–	–	100	34.7 ± 0.5	44.3 ± 0.5
–	–	–	–	–	–	200	23.8 ± 0.7	43.6 ± 0.8
SMPU4	11	3	5	2	1	00 ^f	78.5 ± 0.5	48.7 ± 0.5
–	–	–	–	–	–	50	69.9 ± 0.5	48.5 ± 0.4
–	–	–	–	–	–	100	60.5 ± 0.4	48.1 ± 0.5
–	–	–	–	–	–	200	52.6 ± 0.6	47.7 ± 0.7
SMPU5	12	3	5	2	2	00 ^f	86.8 ± 0.5	51.3 ± 0.3
–	–	–	–	–	–	50	82.9 ± 0.5	52.9 ± 0.3
–	–	–	–	–	–	100	77.5 ± 0.4	52.4 ± 0.5
–	–	–	–	–	–	200	73.6 ± 0.6	51.9 ± 0.7
SMPU6	13	3	5	2	3	00 ^f	95.2 ± 0.3	55.4 ± 0.4
–	–	–	–	–	–	50	94.9 ± 0.6	55.1 ± 0.2
–	–	–	–	–	–	100	93.5 ± 0.5	54.8 ± 0.3
–	–	–	–	–	–	200	92.6 ± 0.7	54.1 ± 0.6

^a SMPU1, shape memory polyurethane.

^b MDI, 4,4'-diphenylmethane diisocyanate.

^c PCL4000, polycaprolactone polyol, CAPA 240.

^d BDO, 1,4-butanediol.

^e DMPA, dimethylol propionic acid.

^f Results from the previous study (Zia et al., 2009c).

^g Each value is expressed as mean ± standard error (SE) ($n = 7$).

^h Non-detectable surface.

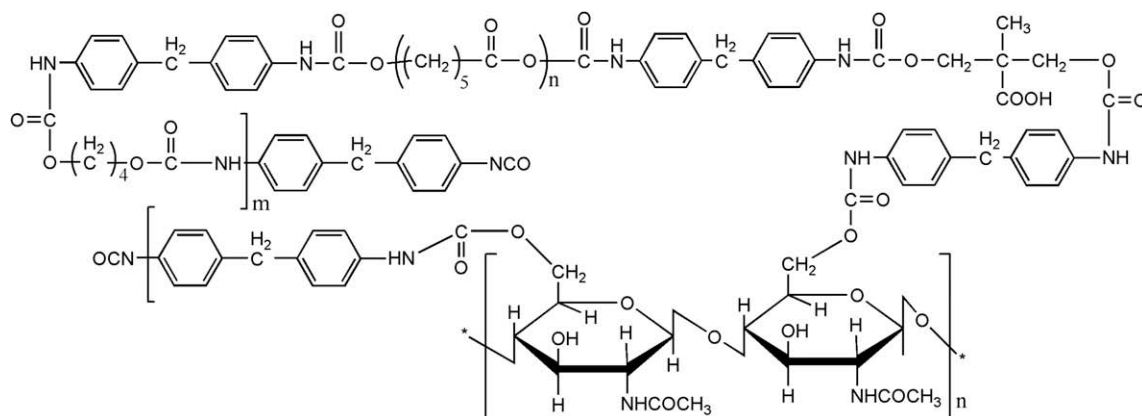


Fig. 1. General structure of the chitin/DMPA/BDO-based shape memory polyurethanes.

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., 2009e). The contact angle measurements have shown that the wettability of PU samples extended with lower contents of chitin and or higher contents of DMPA was changed by UV-irradiation at a higher rate than the wettability of PU extended with higher contents of chitin (SMPU5 and SMPU6). It means that photooxidation in samples SMPU5 and SMPU6 is somewhat retarded, probably because of strong interactions associated with the polyurethane and chitin.

3.2. Surface free energy

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. It is clear from the results that surface free energies calculated applying the both methods of the sample SMPU2 (the sample having higher contents of DMPA in PU backbone) is much higher than all the other

samples and this value decreases with lower (SMPU3) or zero contents (SMPU1) of DMPA (Table 2). Moreover upon increase in UV-irradiation time the surface free energy results to increase. It has been reported in the established literature that in an aqueous media, the surface tension of the polyurethane with different ionic or mixed ionic groups was increased with increase in concentration of ionic groups, because of the orientation of hydrophobic groups at the air–water interface. The ionic centre in DMPA provides function of making polyurethanes with more polar (γ_s^p) components.

The surface free energy of the PU extended with lower contents of chitin and higher contents of DMPA was 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 (SMPU5, SMPU6) extended with higher contents of chitin in comparison of PU extended with vice versa contents of chitin (SMPU5, SMPU6) and DMPA (SMPU1). Results revealed that in the samples SMPU2, the surface free energies were non-measurable after at 200 h UV exposure. 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 (Butt, Graf, & Kappl, 2003, chap. 7). 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.

3.3. Water adhesion to PU surface

The results of dispersive (W_A^d), polar (W_A^p), and total adhesion (W_A) are presented in Table 3. As can be seen, the work of the water adhesion to PU surface decreases with the decrease in DMPA contents. The sample with higher contents of DMPA (SMPU2) has maximum value of polar adhesion (W_A^p) while the sample with lower

Table 2

Total surface energy calculated data with Owens–Wendt and Wu Methods at different exposure time.

Sample code	Exposure time (h)	Owens–Wendt method total surface energy ^b (mN/m)	Wu method total surface energy ^b (mN/m)
SMPU1	00 ^a	41.33 ± 0.07	48.46 ± 0.07
–	50	42.56 ± 0.07	49.68 ± 0.11
–	100	43.85 ± 0.09	50.18 ± 0.15
–	200	44.12 ± 0.11	51.89 ± 0.20
SMPU2	00 ^a	48.60 ± 0.08	51.13 ± 0.06
–	50	49.65 ± 0.10	52.78 ± 0.14
–	100	50.45 ± 0.14	54.89 ± 0.23
–	200	Nd ^c	Nd ^c
SMPU3	00 ^a	45.62 ± 0.09	50.37 ± 0.08
–	50	46.23 ± 0.08	51.48 ± 0.18
–	100	47.58 ± 0.10	52.98 ± 0.26
–	200	48.98 ± 0.12	54.78 ± 0.33
SMPU4	00 ^a	40.95 ± 0.06	45.95 ± 0.10
–	50	41.45 ± 0.09	46.35 ± 0.16
–	100	41.98 ± 0.15	46.92 ± 0.26
–	200	42.36 ± 0.11	47.86 ± 0.30
SMPU5	00 ^a	40.87 ± 0.08	45.10 ± 0.09
–	50	41.05 ± 0.10	45.55 ± 0.11
–	100	41.76 ± 0.13	45.98 ± 0.16
–	200	42.48 ± 0.15	46.25 ± 0.20
SMPU6	00 ^a	40.60 ± 0.09	44.54 ± 0.06
–	50	40.82 ± 0.10	44.69 ± 0.09
–	100	40.91 ± 0.12	44.88 ± 0.14
–	200	41.01 ± 0.17	45.12 ± 0.19

^a Results from the previous study (Zia et al., 2009c).

^b Each value is expressed as mean standard error (SE) ($n = 7$).

^c Non-detectable surface.

(SMPU3) or zero (SMPU1) contents has least amount. Similarly the dispersive adhesion (W_A^d) decrease as the contents of DMPA decrease and the chitin increase. These changes in the polar and dispersive components attributed to the formation of different dispersive groups on PU film resulting of chitin incorporation, which increases surface hydrophobicity and decrease the share of polar interactions between polymer and water. It is clear from the results that the work of the water adhesion to PU surface increases with the increase 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_A^d was higher than W_A^p components in almost all PU films but after irradiation, the opposite situation was found: $W_A^p > W_A^d$. It is caused by the formation of different polar groups on PU film resulting from 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 much influenced with increase in DMPA contents and its value increased with increase in irradiation time. It is clear from the results (Table 3) that dispersive adhesion for the sample SMPU6 remained higher than polar adhesion even at 200 h exposure time whereas it was almost equal for the samples SMPU5. This phenomenon attributed to the incorporation of chitin contents into the PU backbone which results to increase in hydrophilicity of the said samples (SMPU5, SMPU6).

3.4. 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 irra-

Table 3

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

Sample code	Irradiation time (h)	Dispersive adhesion (W_A^d)	Polar adhesion (W_A^p)	Total work of adhesion ^b (W_A)
SMPU1	00 ^a	54.9	47.6	102.5 ± 1.0
–	50	50.0	68.2	118.2 ± 0.09
–	100	47.1	91.7	138.8 ± 0.17
–	200	45.3	103.9	149.2 ± 0.23
SMPU2	00 ^a	56.3	49.6	105.9 ± 1.1
–	50	45.0	77.8	122.8 ± 0.14
–	100	41.5	102.4	143.9 ± 0.21
–	200	–	–	Nd ^c
SMPU3	00 ^a	55.5	48.2	103.7 ± 1.2
–	50	51.6	70.8	122.4 ± 0.21
–	100	46.3	93.5	139.8 ± 0.26
–	200	41.6	105.2	146.8 ± 0.30
SMPU4	00 ^a	54.0	42.8	96.8 ± 1.1
–	50	52.1	50.6	102.7 ± 0.17
–	100	51.3	61.5	112.8 ± 0.23
–	200	49.5	68.9	118.4 ± 0.27
SMPU5	00 ^a	53.4	39.8	93.2 ± 1.3
–	50	52.2	43.2	95.4 ± 32
–	100	51.0	46.6	97.6 ± 0.37
–	200	49.7	50.8	100.5 ± 0.39
SMPU6	00 ^a	52.9	37.5	90.4 ± 1.3
–	50	51.4	40.4	91.8 ± 0.33
–	100	49.9	42.7	92.6 ± 0.37
–	200	49.1	44.3	93.4 ± 0.40

^a Results from the previous study (Zia et al., 2009c).

^b Each value is expressed as mean standard error (SE) ($n = 7$).

^c Non-detectable surface.

Table 4

Hydrophilicity and swelling data of irradiated and non-irradiated PU samples.

Sample code	Irradiation time (h)	Water absorption (%)						Equilibrium degree of swelling ^b
		1st day	2nd day	3rd day	4th day	5th day	7th day	
SMPU1	00 ^a	2.77	2.79	2.80	2.80	2.81	2.82	14.88 ± 0.17
–	50	4.74	5.00	5.19	5.41	5.65	5.78	16.35 ± 0.20
–	100	8.02	8.12	8.20	8.28	8.37	8.45	19.81 ± 0.22
–	200	10.97	11.16	11.38	11.59	11.85	12.02	22.15 ± 0.51
SMPU2	00 ^a	2.97	3.06	3.12	3.14	3.15	3.16	17.95 ± 0.19
–	50	4.81	5.45	6.07	6.55	6.89	7.45	19.82 ± 0.28
–	100	8.58	8.81	9.13	9.94	11.35	12.27	23.66 ± 0.44
–	200	Nd ^c	Nd ^c	Nd ^c	Nd ^c	Nd ^c	Nd ^c	Nd ^c
SMPU3	00 ^a	2.89	2.91	2.93	2.93	2.94	2.94	15.23 ± 0.17
–	50	4.78	5.16	5.28	5.40	5.53	5.69	17.82 ± 0.20
–	100	8.32	8.69	8.82	8.96	9.12	9.26	20.88 ± 0.30
–	200	11.40	11.98	12.16	12.30	12.44	12.59	22.96 ± 0.60
SMPU4	00 ^a	1.19	1.22	1.23	1.23	1.25	1.26	9.15 ± 0.17
–	50	3.01	3.66	3.82	3.98	4.11	4.25	9.45 ± 0.09
–	100	5.44	6.02	6.17	6.31	6.46	6.58	9.98 ± 0.90
–	200	8.12	8.47	8.57	8.66	8.77	8.88	10.68 ± 0.28
SMPU5	00 ^a	0.87	0.88	0.89	0.89	0.89	0.90	7.49 ± 0.09
–	50	2.22	2.66	2.79	2.91	3.05	3.18	7.92 ± 1.8
–	100	4.08	4.44	4.58	4.71	4.83	4.97	8.08 ± 1.8
–	200	5.89	6.28	6.42	6.55	6.69	6.90	8.22 ± 1.9
SMPU6	00 ^a	0.66	0.67	0.67	0.68	0.68	0.68	6.58 ± 0.14
–	50	1.34	1.45	1.59	1.70	1.81	1.92	7.92 ± 1.4
–	100	3.04	3.24	3.28	3.39	3.53	3.66	8.08 ± 1.6
–	200	4.11	4.19	4.33	4.41	4.57	4.87	8.22 ± 1.7

^a Results from the previous study (Zia et al., 2009c).^b Each value is expressed as mean standard error (SE) ($n = 5$).^c Non-detectable surface.

diation time, DMPA 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 DMPA contents, and decreasing chitin contents into the final PU samples. The results revealed that DMPA favours the formation of more hydrophilic polymers. This phenomenon may be due to the fact that the level of dimethylol propionic acid (DMPA) is critical as this controls the resulting particle size. As the amount of DMPA is increased, the particle size decreases, until eventually a water loving polymer is formed. Also, the increase in the concentration of hydrophilic centres results in a corresponding increase in water sensitivity of the dried polymer film. From the evaluation of the results of water absorption and contact angle measurement, we are able to state that DMPA enhance the hydrophilic character while the chitin favours the formation of hydrophobic character of the polymers due to modification of surface chemistry of PU samples.

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 and or DMPA contents increases, but it showed adverse effect by increasing the chitin contents i.e., it decreases with increase in chitin contents. It was found that SMPU6 has best solvent resistance as compared to SMPU2, and this resistance continuously decreasing as the chitin contents decreases and DMPA contents increases. This effect can be elucidated by the degree of physical crosslinking and hydrogen bonding in polyurethane. 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.

4. Conclusion

A series of shape memory polyurethanes (SMPUs) were prepared from polycaprolactone diol 4000 (PCL 4000), 4,4'-diph-

enylmethane diisocyanate (MDI), 1,4-butanediol (BDO), chitin, dimethylol propionic acid (DMPA), and triethylamine (TEA). 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/DMPA/BDO-based PU before and after irradiation were characterized using different surface technique. Results of the applied surface techniques revealed that the UV-irradiated PU samples were affected by varying the UV exposure period. The interactions of the PU films with solvents on the surface were clearly related to the contents of DMPA and chitin into the final polyurethane formulation and UV-irradiation time. 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, higher contents of DMPA and higher irradiation time.

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