

Structural Characteristics of UV-Irradiated Polyurethane Elastomers Extended with α,ω -Alkane Diols

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ABSTRACT: A series of polyurethane (PU) elastomers were prepared by the reaction of poly (ϵ -caprolactone) (PCL) and 4, 4'-diphenylmethane diisocyanate (MDI), extended with a series of chain extenders (CEs) having 2–10 methylene units in their structure. The synthesized samples were irradiated for 50, 100, and 200 h as such the spectral distribution of the light is good match for terrestrial solar radiation. Fourier transform infrared (FTIR) spectroscopy was used to study the chemistry of monomers and final PU samples. The structural changes in the PU samples upon ultraviolet (UV) irradiation were characterized using FTIR spectroscopic technique. In comparison with non irradiated samples, there was a continuous decrease of the bands upon long-term UV irradiation. The

results revealed that final PU sample extended with 1,6-hexane diol (1,6-HDO) to 1, 10 decane diol (1,10-DDO) have been fully degraded at 200 h irradiation. Comparing PU sample extended with 1, 6-HDO and 1, 10-DDO, it was found that the degradation rate of later is higher than former. It was concluded that CEs length has considerable effect on thermal degradation of PU and by increasing CEs length thermal degradation upon UV irradiation shifted to lower temperature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2843–2850, 2009

Key words: polyurethane; chain extender; α ; ω -alkane diols; structural characteristics; UV-irradiation

INTRODUCTION

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.^{1,2} Polyurethanes have potential array of commercial applications as they can be molded, injected, extruded, and recycled.³ Molecular characterization and morphological studies of polyurethane elastomers (PUEs) have been reported by many researchers. The effects of the diisocyanate structure⁴ and chain extender (CE) length on the crystallinity, surface morphology,⁵ and thermo-mechanical properties⁶ of PUEs have also been investigated and well documented.

PUEs are possibly the most versatile class of polymers. For their application, 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 as a part of incident solar radia-

tion on exposure to direct sunlight initiates an auto-oxidative degradation process in PUEs that can chemically crosslink the chain extensively.⁷

Although the materials with urethane structure exhibit good mechanical properties, their use as surface coatings in outdoor applications is limited by the sensibility to the photo-oxidative degradation, which can lead to the discoloration and even the total destruction. Several studies have been developed on the UV degradation of polyurethane. Such photo-degradation has already exhibited formation of free radicals, recombination, scission of bonds, oxidation, and cross-linking reactions.^{8–10} However, comparatively few articles have appeared on PU degradation, which also occurs under other radiation such as gamma rays^{11,12} or electrons beams.¹³ Structural modification using Fourier transform infrared (FTIR) and UV spectroscopy upon electron beam irradiation of polyester urethane have been studied and documented.¹³ Photooxidative behavior of segmented aliphatic polyurethane¹⁴ and effect of different molecular weight of soft segment in polyurethane on photooxidative stability have also been reported.¹⁵ No reference is still available on the study of the effect of different exposure time of UV radiation on polyurethane elastomers extended with series of chain extender (α , ω -alkane diols). It is known that PUEs undergo significant

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structural changes on exposure to UV irradiation which causes deterioration in their physical and mechanical properties. In the present project, a series of PUEs were prepared by the reaction of poly (ϵ -caprolactone) (PCL) and 4, 4'-diphenylmethane diisocyanate (MDI). The prepolymer was extended with a series of chain extenders having 2-10 methylene units in their structure. A systematical explanation to study of the effect of UV exposure on the structural characterization of polyurethanes elastomers has been provided.

EXPERIMENTAL

Materials

MDI, a mixture of 97% w/w of the 4,4' isomer and 3% w/w of 2,4 isomer was purchased from Sigma-Aldrich Chemical Co (St. Louis, MO). Chain extenders 1,2-ethane diol (1,2-EDO) 99% purity; 1,3-propane diol (1,3-PDO) 99% purity; 1,5-pentane diol (1,5-P'DO) 98% purity and 1,8-octane diol (1,8-ODO) 99% purity were obtained from Merck Chemicals (Darmstadt, Germany). 1,4-Butane diol (1,4-BDO) 99% purity; 1,6-hexane diol (1,6-HDO) 97% purity and 1,10-decane diol (1,10-DDO) 99% purity, were supplied by Sigma-Aldrich Chemical Co (St. Louis, MO). Polycaprolactone diol (PCL) CAPA 225, (molecular weight 2000) was supplied by Solvay Introx (Cashire, England). PCL and all the chain extenders used in this study were dried at 80°C under vacuum for 24 h before use to ensure the removal of all air bubbles and water vapors that may otherwise interfere with the isocyanate reactions. Molecular weight of CAPA 225 was confirmed by applying the procedure reported in ASTM D-4274C. The NCO content in the prepolymer was obtained by titration with *n*-butylamine (ASTM D 2572-80). All the reagents used in this work were of analytical grade.

Synthesis of polyurethane elastomers (PUEs)

The synthesis of PUEs was performed by two steps procedure as presented in our previous studies^{5,6} by the polymerization of PCL (31.25 g; 0.0156 mole) and MDI (11.95g; 0.047 mole), and extended with series of chain extenders (Table I) i.e., 1,2-EDO (1.94 g; 0.0313 mole); 1,3-PDO (2.38 g; 0.0313 mole); 1,4-BDO (2.82 g; 0.0313 mole); 1,5-P'DO (3.25 g; 0.0313 mole); 1,6-HDO(3.69 g; 0.0313 mole); 1,8-ODO(4.56 g; 0.0313 mole) and 1,10-DDO (5.44 g; 0.0313 mole).

UV exposure

Irradiation of PUEs was carried out in an UV exposure unit which irradiation chamber uses five 80 W medium pressure mercury vapor lamps (Latina Tendeng Cor., China) constructed with borosilicate glass envelopes which filter all wavelength below 300 nm. As such, the spectral distribution of the light is good

TABLE I
Sample Code Designation and Different Formulation of PU Samples (Molar Ratio of CAPA225 (0.0156 moles): MDI (0.047 moles): CE^a (0.0313 moles)

Sr #	Sample code	Irradiation time (h)	Prepolymer extended with	Mass in g of CE ^a
01	Et0	00	1,2-EDO	1.94
02	Et50	50	–	–
03	Et100	100	–	–
04	Et200	200	–	–
05	Pr0	00	1,3-PDO	2.38
06	Pr50	50	–	–
07	Pr100	100	–	–
08	Pr200	200	–	–
09	Bt0	00	1,4-BDO	2.82
10	Bt50	50	–	–
11	Bt100	100	–	–
12	Bt200	200	–	–
13	Pn0	00	1,5-P'DO	3.25
14	Pn50	50	–	–
15	Pn100	100	–	–
16	Pn200	200	–	–
17	Hx0	00	1,6-HDO	3.69
18	Hx50	50	–	–
19	Hx100	100	–	–
20	Hx200	200	–	–
21	Dc0	00	1,10-DDO	5.44
22	Dc50	50	–	–
23	Dc100	100	–	–
24	Dc200	200	–	–

^a Chain extender.

1,2-EDO (1,2-ethane diol), 1,3-PDO (1,3-propane diol), 1,4-BDO (1,4-butane diol), 1,5-P'DO (1,5-pentane diol), 1,6-HDO (1,6-hexane diol), 1,10-DDO (1,10-decane diol).

match for terrestrial solar radiation. Irradiation was performed with sample to lamp distance of 20 cm at ambient relative humidity. Samples were irradiated for 50, 100, and 200 h.

Measurements

FT-IR spectra of thin films were obtained in the transmission mode using a Bruker-IFS 48 FT-IR spectrometer (Ettlingen, Germany). FTIR scans were collected on completely dried thin films prepared on KBr discs from *N,N'*-dimethylformamide (DMF) solution. The spectra covered the infrared region 4000–500 cm⁻¹, the number of scans per experiment was 100 and resolution was 6 cm⁻¹. A blank sample was made before irradiation to eliminate possible errors due to non-homogeneity or thickness variation between films.

RESULTS AND DISCUSSION

The main aim of this research work was to study the effect of UV exposure on the structural characteristics of polyurethane elastomers extended with α , ω -alkane diols. So synthesis of PUEs was carried out following the synthetic route as outlined in our previous study.⁶ After synthesis the samples were

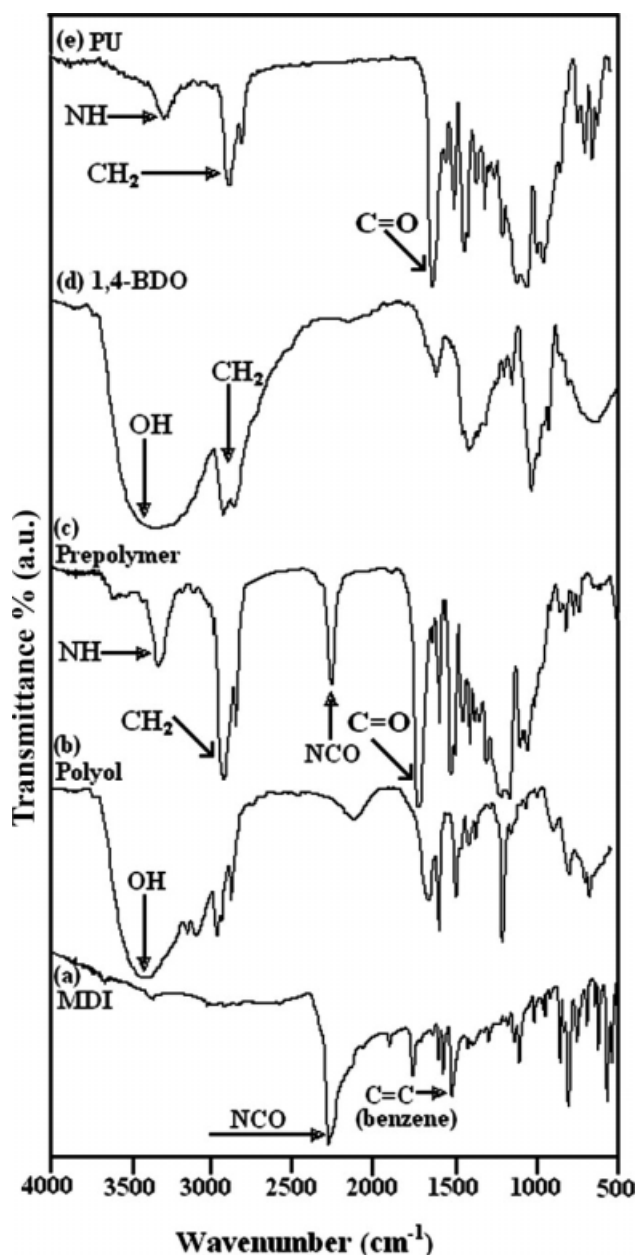


Figure 1 FT-IR spectra (a) 4,4'-diphenylmethane diisocyanate (MDI); (b) poly(ϵ -caprolactone) (PCL); (c) polyurethane (PU) prepolymer; (d) 1,4-Butane diol (1,4-BDO); (e) Final PU prepolymer extended with 1,4-butane diol.

irradiated in UV exposure unit and characterized using different spectroscopic techniques.

Structural characterization

Structural characterization was done using FT-IR spectroscopic technique. The structural characterizations of the designed samples using ^1H NMR and ^{13}C NMR spectroscopic techniques have already been explained and reported.⁶ FT-IR spectroscopy obtained from the monomers and films of polymer samples before and after irradiation is shown in Figures 1 and 2, respectively.

Polymer synthesis studies

FTIR spectra of MDI, PCL, NCO terminated polyurethane prepolymer, 1,4-BDO and polyurethane extended with 1,4-BDO is shown in Figure 1(a–e). FTIR spectrum of MDI [Fig. 1(a)] showed very strong peak at 2255 cm^{-1} attributed to the isocyanate ($-\text{NCO}$) group attached to 4,4'-diphenylmethane diisocyanate. The FTIR spectra show sharp peaks at 1527 cm^{-1} , which is due to the $\text{C}=\text{C}$ stretching of benzene ring. The observed peaks in the FTIR spectrum of PCL [Fig. 1(b)] were assigned as: 3447 cm^{-1} (OH stretching vibration); 2865 cm^{-1} (asymmetric CH_2 stretching); 2949 cm^{-1} (symmetric CH_2 stretching); 1727 cm^{-1} ($\text{C}=\text{O}$ stretching); 1293 cm^{-1} ($\text{C}-\text{O}$ and $\text{C}-\text{C}$ stretching in the crystalline phase); 1240 cm^{-1} (asymmetric COC stretching); 1190 cm^{-1} ($\text{OC}-\text{O}$ stretching); 1170 cm^{-1} (symmetric COC stretching); 1157 cm^{-1} ($\text{C}-\text{C}$ stretching in the amorphous phase). FTIR spectrum of NCO terminated PU prepolymer has also been presented in Figure 1(c). It can be clearly observed that the peak for the OH groups disappeared and that of the intensity of NCO groups has reduced to some extent resulting that all the isocyanate group has been reacted (except those present at chain ends), and a signal for NH units appeared at 3298 cm^{-1} suggesting that PU prepolymer had been formed [Fig. 1(c)]. The other observed peaks in the FTIR spectrum of PU prepolymer [Fig. 1(c)] were assigned as: 2942 cm^{-1} (CH symmetric stretching of CH_2); 2872 cm^{-1} (CH asymmetric stretching of CH_2 groups); 2255 cm^{-1} (isocyanate ($-\text{NCO}$) group); 1727 cm^{-1} ($\text{C}=\text{O}$ stretching of soft segment of PCL). The changes in the intensity of the signal of the carbonyl groups ($\text{C}=\text{O}$) of the PCL at 1728 cm^{-1} indicates the chemical reaction of the diisocyanate with PCL. The chain extender (1,4-BDO) was added in the final step to complete the polymerization reaction. FT-IR spectra of 1,4-BDO [Fig. 1(d)] showed that broad OH stretching vibration band appeared at 3443 cm^{-1} . The CH symmetric and asymmetric stretching vibrations of CH_2 groups were observed at 2943 , and 2874 cm^{-1} , respectively. To provide clear information about the vibrational mode changes due to involvement of 1,4-BDO in to the polyurethane backbone during the polymerization reaction, FT-IR spectrum obtained from the cast film of PU based on 1,4-BDO is shown in Figure 1(e). In the FT-IR analysis obtained for the PU sample, the disappearance of the NCO peak at 2255 cm^{-1} and the appearance of N–H peak at 3330 cm^{-1} confirmed the completion of polymerization reaction. The observed peaks in the spectrum imply that the reaction was completed and the pre-designed PU was formed. FTIR spectra obtained support the proposed structure of the final polymer. FTIR spectra showed characteristic bands of urethane groups at 3330 cm^{-1} (N–H stretching). The other

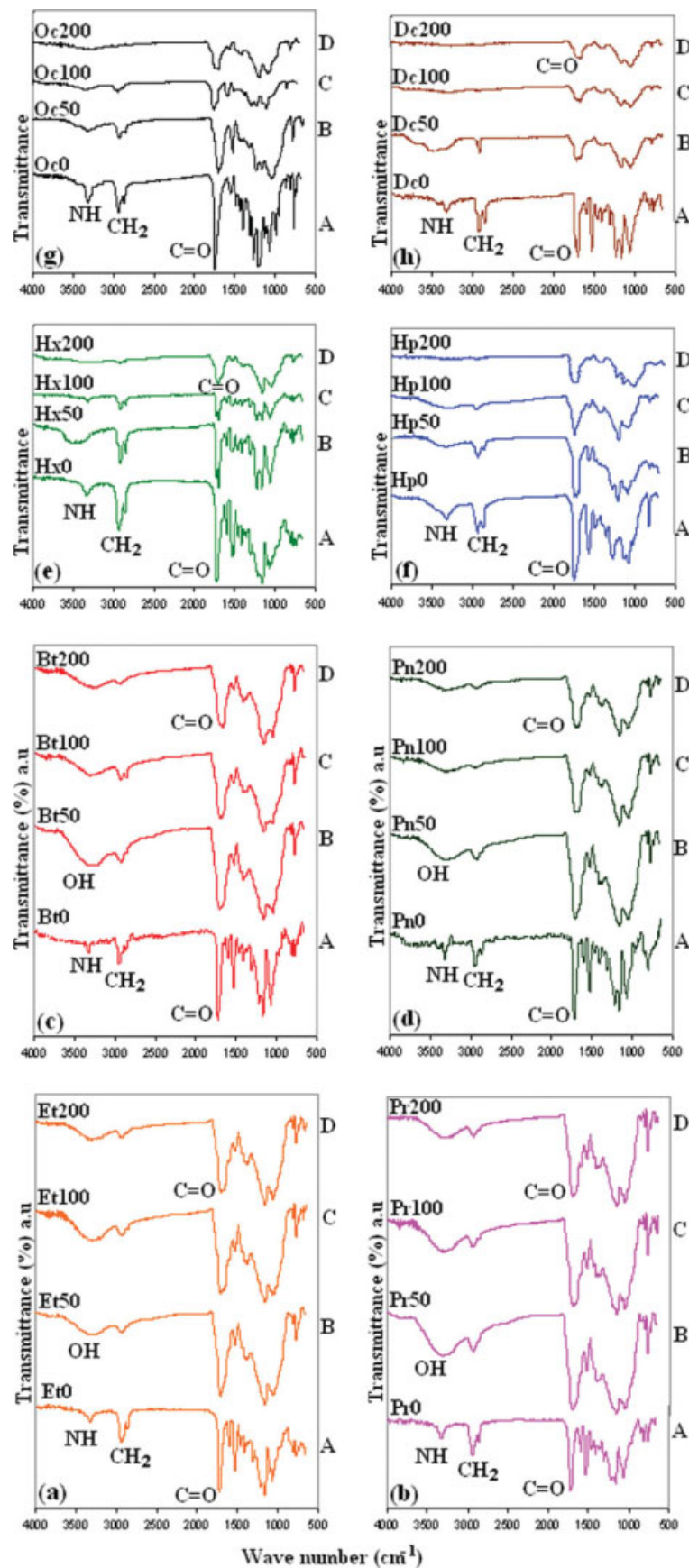


Figure 2 FT-IR spectra of polyurethane (PU) samples at 0, 50, 100 and 200 h UV-irradiation; PU samples extended with (a) 1,2-ethane; (b) 1,3-propane diol; (c) 1,4-butane diol; (d) 1,5-pentane diol; (e) 1,6-hexane diol; (f) 1,7-heptane diol; (g)

TABLE II
Infrared Characteristic Frequencies of Polyurethane for the Blank and Irradiated Samples

Wave number (cm ⁻¹)	Main assignments	Morphological region
3500	ν (O—H) stretching associated with N—H	Soft segment
3330	ν (N—H) stretching with H bond	Hard segment
2947	ν (CH) associated stretching of CH ₂	Soft segment
2867	ν (C—H) stretching of CH ₂	Soft segment
1728	ν (C=O) stretching of ester	Soft segment
1701	ν (C=O) stretching of ester associated with urethane	Hard segment
1531	ν (C—N) stretching with (N—H) bending	Hard segment
1180	ν (C—O—C) stretching of ester	Soft segment
1077	ν (C—O—C) stretching of ester of urethane	Hard segment

peaks observed were assigned as: 2947 cm⁻¹ (CH symmetric stretching vibrations of CH₂); 2810 cm⁻¹ (CH asymmetric stretching vibrations of CH₂ groups); 1728 cm⁻¹, 1642 cm⁻¹ (C=O bond); 1599 cm⁻¹, 1529 cm⁻¹ (NH deformations); 1407 cm⁻¹ (CH bending vibration); 1311 cm⁻¹ (CH₂ wagging). By extending prepolymer with 1,4-BDO, the FT-IR spectra showed a very strong, new peak at about 1728 cm⁻¹ which was assigned to C=O stretching of soft segment of PCL. Another new peak was also observed at about 1464 cm⁻¹ which was assignable to urethane —NH group. Peaks correspond to the absorption of —NH, —CO, —CHN were observed at 3330 cm⁻¹, 1728 cm⁻¹ and 1464 cm⁻¹, respectively, which indicate the new synthesized product having —NHCOO group. The observed N—H bending vibrations at 1529 cm⁻¹, C—O—C stretching absorption band corresponding to the ether oxygen of soft-segment at 1000–1150 cm⁻¹ also provide strong evidence for the formation of PU.

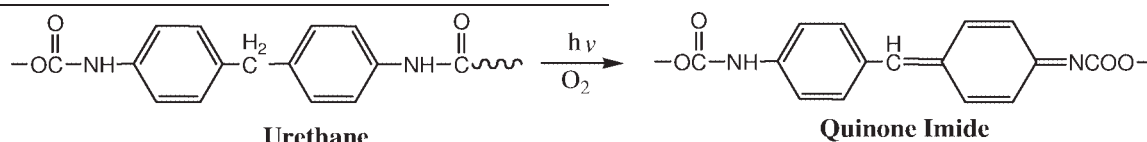
Structural modification studies after UV irradiation

FT-IR study was also used to check the chemical modification of the final PUEs structure before and after UV irradiation. During irradiation the systematic changes in the IR spectra of the tested samples were noticed. The change of transmittance in the IR spectra recorded for PUEs before and after irradiation are given in Figure 2 (a–d), where the IR spectra of non irradiated sample (A), irradiated sample for 50 h (B), irradiated sample for 100 h (C) and irradiated sample for 200 h (D) are presented. The corresponding frequencies and morphological region are given in Table II.

Long-term UV irradiation of PU led to a continuous decrease of the bands which were recorded for the non irradiated samples. After irradiation the resolution of the peak from carbonyl groups decreased. A new broad band appeared at 3500 cm⁻¹ which could be because of the formation of hydroxyl groups. The spectra show the

oxidation occurs in the PUEs during irradiation due to dissolved oxygen present in the original polymer.¹⁶ It was responsible for alkoxy group creation, which led to the OH-bond formation. This new bond (OH-bond) is highlighted in the Figure 2(a–d) at 3500 cm⁻¹. The alkyl function, present in the soft segment of the polymer, can be dehydrogenated directly by a radical, generated by the irradiation.¹⁶ The presence of oxygen causes the peroxide radical formation. Then the molecular reorganization controls a carbonyl and alcohol function with a scission in the polymer. The new carbonyl functions can be observed by the C=O broad peak in the range of 1705 to 1625 cm⁻¹. This is attributed to the formation of new oxidized carbonyls in the chains after decomposition and oxidation of carbonyl groups resulting decrease in intensity of carbonyl band. The decrease in intensity of carbonyl band is an evidence of side group elimination from PU chains upon UV exposure. Simultaneously, the broadening of the whole carbonyl band indicates that new oxidized groups are formed resulting of photochemical reactions. This type of chemical reaction has already been described for polyethylene oxidation under gamma rays.¹⁶

The absorption peaks due to the urethane groups appear at 1702–1728 cm⁻¹, 1529 cm⁻¹, and 3330 cm⁻¹. Absorption at lower frequency of 1702 cm⁻¹ can be assigned to the hydrogen bonded urethane carbonyl groups and absorption at 1728 cm⁻¹ to the non bonded urethane carbonyl groups. The intensities due to urethane bands (C=O, C—N) decreased as result of irradiation. A significant decrease in NH (3330 cm⁻¹) peak intensity was observed when the polymer was irradiated. The degradation process because of UV exposure is believed to generate quinone-imide structures^{10,17} in aromatic PUEs having proquinoid structure (eq. 1) that can follow by active hydrogen moiety in addition to the quinone-imide that would crosslink PUEs chains (eq. 1).

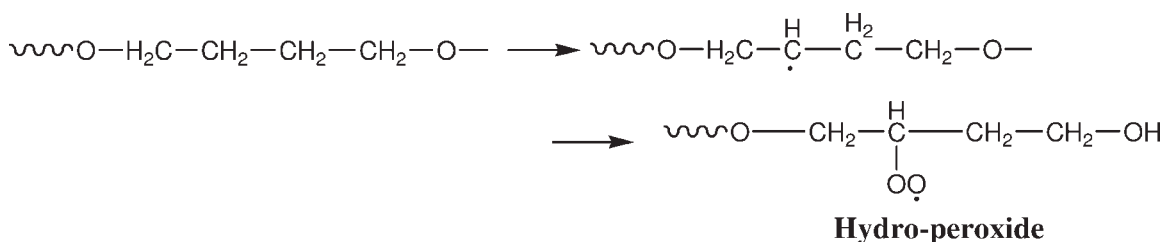


This decrease in NH peak intensity attributed to the quinoid group formation, which leads to a disaromatization of the hard segment and a un-saturation of the polymer. Concerning the C—H bond, a decrease in peak intensity of the CH₂ function was observed when the polymer was irradiated.

The intensities of the peaks in the range of 1085–1115 cm⁻¹ also decreased after irradiation. This indicates the degradation of the ester segment and their oxidation to hydroxyl groups. These changes in FTIR spectra with UV irradiation may be an indication of degradative processes in PUEs. This observation has been confirmed for their mechanical behavior discussed else where.¹⁸ The degradation processes of the ester group are more prominent in PUEs. Structural changes associated with the degradative process influence the flexibility of the amorphous soft segment and their interaction with hard segment. As for the C=O bond, no peak intensity variation occurred. A large decrease in the band at

1180 cm⁻¹ attributed to the decarboxylation of the polyester segment. The decrease in the band at 1077 cm⁻¹ indicates a possible break in the C—O bond of the urethane group. For the C—N bond (1531, 1310, 1230 cm⁻¹) its generation is not characterized because the C—N bond signal is always associated with the NH signal.

The decrease of the intensity of the bands with the duration of irradiation could be due to the presence of some radical induced photooxidative processes,¹⁷ which are responsible for the gradual yellowing and even the total destruction of the initial structures. The main decrease of the band intensities can be associated with the loss of the urethane structure during UV irradiation. It is well known that in the PU structures oxygen attacks at CH₂ groups in the aliphatic diol part, with hydro-peroxides formation.¹⁹ The hydro-peroxides decompose relatively fast and form carbonyl groups, as was evidenced by IR spectra of the compound (Fig. 2a–d).



It is said that the early stage degradation occurred mainly in the hard segments where urethane groups first undergo depolymerization, resulting individual monomers (Fig. 3), and then their further reaction produce carbon dioxide.²⁰ Consequently, it may be proposed that the first step of the degradation consists of the reverse of the reaction of polyaddition which lead to the formation of alcohol and isocyanate groups in agreement with the literature.^{21–23} However, a band around 1536 cm⁻¹ assigned to N—H bond still exists. As a consequence, it may be suggested that the isocyanate from the depolymerization which is very reactive dimerizes to form carbon-diimide (which is not observed while it is very reactive) and CO₂ molecule. Carbon-diimide should further react with alcohol to give substituted urea. In the last step of degradation, when the material degrade slowly, the urea bonds decompose (the band around 1680 cm⁻¹ disappears) leading to the formation of a charred carbonaceous structure.²⁴ All these reactions are summarized in Figure 3.

Effect of chain extender length

The comparison of the segmented formulations clearly indicated that the higher the chain extender

length in the PU backbone, the more likely they are prone to be degraded. It means that the number of methylene units in the aliphatic diols used as chain extender has considerable effect on the structure of irradiated PU samples. This decrease in NH peak intensity is probably due to the significantly lower MDI mass fraction and, therefore, a lower inter-urethane H-bond concentration. It is considered that increase in chain extender leads to dilute the urethane linkages which results in lowering the inter-urethane H-bond concentration. During polymerization reaction, the MDI ratio used to establish a prepolymer remains the same for the whole study whether the prepolymer have been extended with 1,2-EDO, 1,3-PDO, or 1,10-DDO. As the chain extender length is increased the MDI mass fraction leads to decrease, resulting lowering in inter-urethane H-bond concentration. It is known that better phase separation resulted from H-bonding, and if H-bonding is within hard segment then final PU has better thermal stability than PU having H-bonding between the hard segment and the soft segment. It can be clearly observed from Figure 2(d–h) that final PU sample extended with 1,6-HDO (Hx200) and 1,10-DDO (Dc200) have been fully degraded at 200 h irradiation. Comparing PU sample extended with

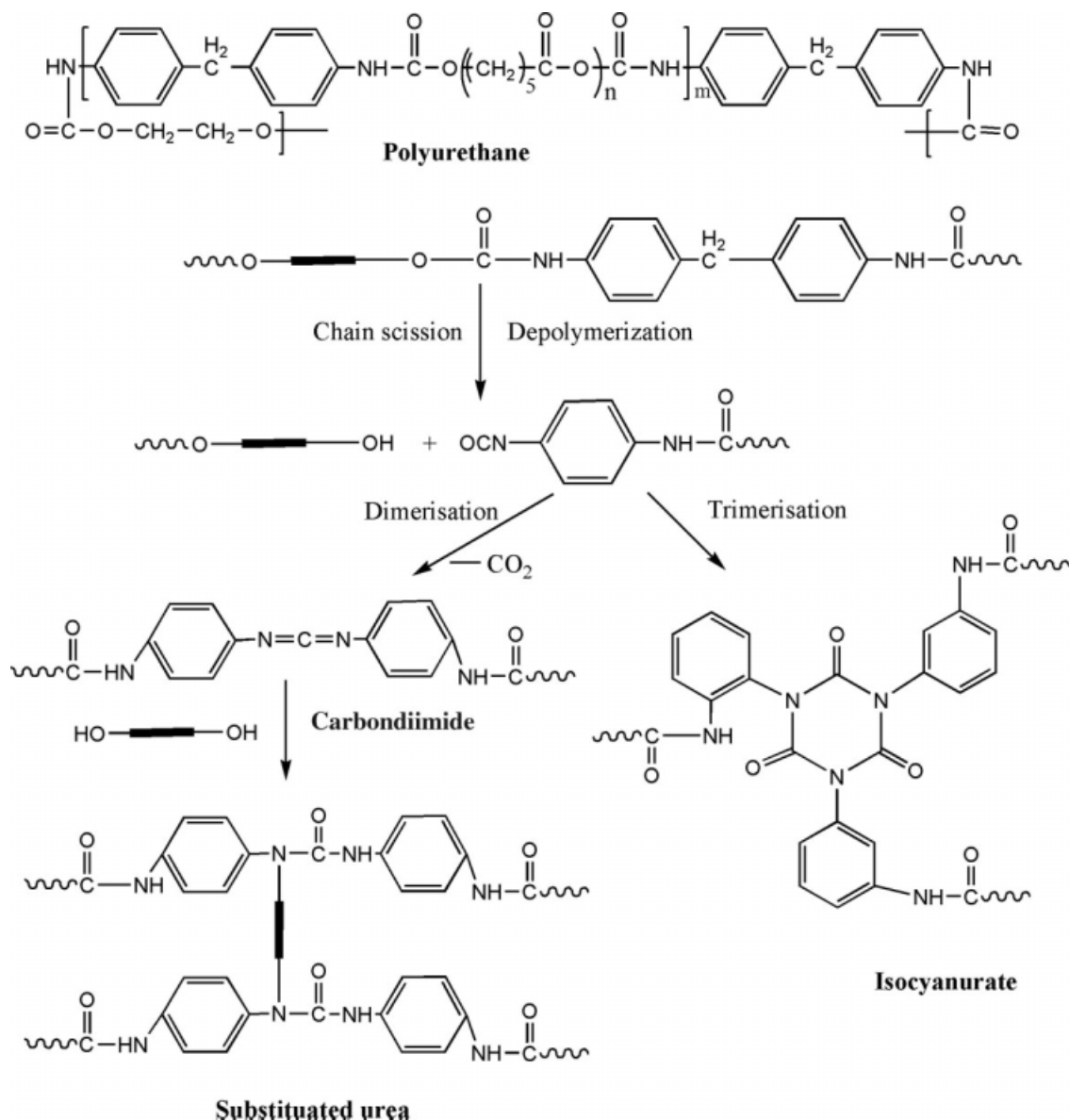


Figure 3 Thermal degradation mechanism of polyurethane.

1,6-HDO and 1,10-DDO, it can be noticed that the degradation rate of Dc sample is higher than Hx. It is obvious from the IR spectra of the sample (Fig. 2h) that Dc sample has been degraded more likely even at after 100 h irradiation. It can be concluded that CE length has considerable effect on the thermal degradation of PU and by increasing CE length; the complete degradation is started even after 100 h irradiation, as it is obvious from the Figure 2(d-h).

CONCLUSION

Polyurethane elastomers based on MDI, PCL and extended with series of chain extender (having 2-10 methylene units) were synthesized via two steps polymerization technique. The synthesized samples were irradiated for 50, 100, and 200 h as such the

spectral distribution of the light is good match for terrestrial solar radiation. The chemical structures of the monomers and prepared PU before and after UV irradiation were characterized by FTIR spectroscopic technique. The effects of irradiation time on thermal degradation of the final polyurethane having different chain extender length were studied.

It was found that long-term UV irradiation of PU led to a continuous decrease of the bands which were recorded for the non irradiated samples. The results revealed that final PU sample extended with 1,6-hexane diol (1,6-HDO) to 1,10 decane diol (1,10-DDO) have been fully degraded at 200 h irradiation. Comparing PU sample extended with 1,6-HDO and 1,10-DDO, it was found that the degradation rate of later is higher than former. It can be concluded that CEs length has considerable effect on rate of thermal

degradation of PU and by increasing CEs length thermal degradation upon UV irradiation shifted to lower temperature.

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