QUV Accelerated Aging Effects on the Structure and Properties of Polyether Polyurethane Fibers

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Abstract. This paper presents an experimental study about the effects of UV irradiation on polyether polyurethane (PU) fibers investigated by FTIR, SAXS and AFM, and the multiple mechanism is finally proposed. The results show that, at low UV irradiation (0.6W/m², 0.9W/m²), the mechanism responsible for UV degradation of polyether PU fibers could be described as a primary reaction causing the break up of chemical bonds and forming the new quinone structure, along with a secondary reaction to explain hydrogen peroxide formed in the presence of UV irradiation, water and oxygen environment which promotes QUV aging by providing loose structure of polyether PU fibers. Moreover, the micro phase separation is promoted for a parallel reaction occurred to produce new polyether PUs and more compact micro domains by the residual isocyanate in pre-polymerization stage and alcohols formed under QUV aging. Under higher UV irradiation (1.2W/m², 1.5W/m²), in addition to the primary reaction, a tertiary reaction showing the re-polymerization occurred under accumulation of aging products (carboxylic acids and alcohols) is also considered as the mechanism, while the secondary reaction would be inhibited for the peak assigned to H₂O₂ is not observed. Also, this decreases micro phase separation of polyether PU fibers for the primary reaction is dominant.

1. Introduction
Polyurethanes are a segmented block co-polymer with alternating hard and soft parts. Soft segments are composed of polyether or polyester which are in a high elastic state at normal temperature to make polyurethanes flexible, while hard segments are formed by isocyanate which are in a glass state at normal temperature and play a role of physical crosslinking points to impart strength to polyurethanes [1], [2], [3]. Similar to PU foams and PU coatings, one of the especial disadvantages of PU fibers is their extreme sensitivity to UV radiation. As reported, polyether PUs undergo significant changes in structure when exposure to QUV light, which causes the degradation in their chemical and mechanical characteristics [4], [5], [6], [7], [8]. Many papers [9], [10], [11], [12] on this subject focus on the photo-Fries type rearrangement resulting in yellowing of polyurethanes made with an aromatic isocyanate on exposure to UV radiation. The yellowing is caused by oxidation reaction in methylene groups in the α position to N-H groups. Compared to the UV aging studies on polyether PU coatings and polyether PU foams [13],[14], few studies have been published concerning the UV radiation effects on polyether PU fibers. Thus, it is a general requirement to figure out the mechanism of UV degradation of polyether PU fibers to have improvement in efficiency and lifetime. Hence, the purpose of this study is to obtain the influence of different UV radiation on the structural and mechanical properties of polyether PU fibers, especially, the specific mechanism of every irradiated environment is analyzed in detail. In this work, experiments were carried out through accelerated QUV aging test.
which provided elevated UV radiation without altering temperature and humidity. ATR-FTIR was used to evaluate the changes in chemical structure while micro-domain structure including microphase separation and chain changes was examined by SAXS and AFM.

2. Experimental

2.1. Materials
Polytetramethylene ether glycol (PTMG), diphenylmethane-4,4’-diisocyanate (MDI), ethylene-diamine (EDA) and N,N-dimethylacetamide (DMAc) were supplied by Sichuan Tianhua Fubang Chemical Industry Co., Ltd., Yantai Wanhua Chemical Group Co., Ltd., Japan Tosoh Corporation and Zhejiang Jiangshan Chemical Industry Co., Ltd., respectively.

2.2. Synthesis of Polyether PU Fibers
The synthesis of polyether PU fibers was conducted by prepolymer method. Firstly, MDI and PTMG were taken for the reaction with a molar ratio of 1.6, and then they dissolved in DMAc to obtain prepolymer solution. In the next step, the chain extender (EDA) solution was added to prepolymer solution to obtain spinning solution. To this end, fibers (105D) were formed after the spinning solution was solidified in the tunnel at appropriate drafting ratio, tunnel temperature and wind speed.

2.3. QUV Aging
UV aging was performed using the QUV Accelerated Weathering Tester machine manufactured by Dongguan Aigu Testing Instrument Co., Ltd. In the tester, the panel temperature was set at 25°C while the humidity and duration were 30% and 150h, respectively. The samples were subjected to aging with irradiance of 0.6, 0.9, 1.2 and 1.5W/m².

2.4. ATR-FTIR
FTIR analysis of polyether PU fibers was performed using a Vector-33 Spectrometer manufactured by Bruker company, Germany. The frequency range covered was from 4000cm⁻¹ to 50cm⁻¹ by averaging 32 scans at a resolution of 0.5 cm⁻¹. Samples were dried before the test.

2.5. SAXS
SAXS experiments of polyether PU fibers were carried out using a SAXSess small-angle X-ray system purchased from Anton Paar, Austria, emitting X-rays with a wavelength of 0.1542nm. The distance from the sample to the detector was 261.2mm. Samples were cut up and then filled into the sample well.

2.6. AFM
Tapping-mode atomic force microscopy (AFM) observations were performed by MFP-3D-SA (Asylum Research company, America). The sample was prepared by cutting a strip with a width of 2 mm from a single fiber and then the surface of the strip was observed.

3. Results and Discussion

3.1. The Effect of UV Irradiation on the Chemical Structure of Polyether PU Fibers
Fig.1a shows the results of the FTIR analysis of the QUV aged samples from 875cm⁻¹ to 1625cm⁻¹. It can be seen that the intensity of some urethane and ether related peaks first increased with 0.6 and 0.9W/m² irradiation followed by a decreasing trend with further irradiation, which is attributed to the reaction producing new segments occurred during the low UV irradiation enhancing the intensity, but higher irradiation would break chemical bonds that leads to lower intensity of the corresponding peaks. Besides, new species might generate during the irradiation, because new peaks emerge at 1574cm⁻¹(N-H), 1260cm⁻¹(OH), 1016cm⁻¹(C-O-C)cm⁻¹, 979cm⁻¹(OH)and 960cm⁻¹(C-O)in IR spectrum of four aged samples [15], [16], [17].
The new peak emerges at 1260 cm\(^{-1}\) (OH) in IR spectrum of the irradiated sample under 0.9 W/m\(^2\) is due to the hydrogen peroxide. It has been reported that, in the presence of UV irradiation (<400 nm), moisture, and air, hydrogen peroxide will be created on the surface of PUs during the complicated aging process [18], [19]. The new peak emerges at 1574 cm\(^{-1}\) (NH) in IR spectrum of four irradiated samples, is attributed to the break up of amide II -CO-NH-(1535 cm\(^{-1}\))[17].

What’s more, the new peaks emerge at 1016 cm\(^{-1}\) (C-O-C), 979 cm\(^{-1}\) (OH) and 960 cm\(^{-1}\) (C-O) in IR spectrum of four aged samples are associated to the break up of C-O-C and new species [20]. To define the new species generated during the break up of C-O-C, Fig. 1b show the deconvolution of overlapping bands in the regions from 1175 cm\(^{-1}\) to 875 cm\(^{-1}\) for the irradiated fibers under 1.5 W/m\(^2\). After deconvolution, there are two additional bonds appear at 1085 cm\(^{-1}\) and 1034 cm\(^{-1}\), which are attributed to the formation of new C-O and O-H bonds in carboxylic groups and alcohols [21], [22], combining C-O (979 cm\(^{-1}\)), OH (1016 cm\(^{-1}\)) and O-H (960 cm\(^{-1}\)) emerged after aging. And the proposed reactions to form carboxylic acids and alcohols are described in Fig. 1c.

![FTIR plots of polyether PU fibers with various UV irradiation from 875 cm\(^{-1}\) to 1625 cm\(^{-1}\) (a), Deconvolution result of 1.5 W/m\(^2\) irradiated polyether PU fiber from 875 cm\(^{-1}\) to 1175 cm\(^{-1}\) (b), Reactions to form carboxylic acids and alcohols (c).](image)

Fig. 2a shows the results of the FTIR analysis of the QUV aged samples from 3450 cm\(^{-1}\) to 2650 cm\(^{-1}\). The hydrogen bonding NH with C=O (NH\(_{carbonyl}\)) is observed in 3320 cm\(^{-1}\) of QUV aged samples with higher intensity and the aged sample with low intensity. The free NH (NH\(_{free}\)) and hydrogen bonding NH with C-O-C (NH\(_{ether}\)) are only appeared in IR spectrum of the aged sample at 356 cm\(^{-1}\) and 3283 cm\(^{-1}\) [16], which indicates more NH groups are combined with C=O to form hydrogen bonding instead of C-O-C after exposure to QUV light. Both peaks at 2937 cm\(^{-1}\) and 2918 cm\(^{-1}\) are assigned to CH\(_2\) [16], and the peak at 2918 cm\(^{-1}\) almost disappears while another peak intensity at 2937 cm\(^{-1}\) becomes higher under the highest irradiation (1.5 W/m\(^2\)). It is most likely associated to the oxidation of the central methylene group in the aromatic urethane, as shown in Fig. 2b (b), resulting in the product of the quinone structure which can make polyether PU fibers yellowish [13].
To investigate the effect of UV irradiation on hydrogen bonding between segments, deconvolution is intended among hydrogen bonding bands of polyether PU fibers in IR spectrum, and C=O bands are mainly analyzed considering few hydrogen bonds between C-O-C and NH appear in Fig. 2a. Fig. 3 illustrates the comparison between C=O bands of polyether PU fibers with various irradiation from 1600cm\(^{-1}\) to 1775cm\(^{-1}\) (Fig. 3a) and its deconvolution results (Fig. 3b). After deconvolution, the C=O band appears at 1673cm\(^{-1}\) in IR spectrum of the unaged sample, which indicates the presence of residual isocyanate in prepolymerization and further verifies the reaction producing new segments occurred. The C=O band appears at 1662cm\(^{-1}\) in IR spectrum of the QUV aged samples, which is attributed to carboxylic acids and alcohols formed during QUV aging [23].

**Figure 2.** FTIR plots of polyether PU fibers with various UV irradiation from 2650cm\(^{-1}\) to 3450cm\(^{-1}\) (a), Reactions to form quinone products (b)

**Figure 3.** FTIR spectrum of polyether PU fibers with various UV irradiation from 1600cm\(^{-1}\) to 1775cm\(^{-1}\) (a), Deconvolution results of polyether PU fibers with various UV irradiation from 875cm\(^{-1}\) to 1175cm\(^{-1}\) (b).
3.2. The Effect of UV Irradiation on the Micro Domain Structure of Polyether PU Fibers

The detailed micro domain structure including the micro phase separation and segments changes in the polyether PU fibers is investigated using the SAXS method. Fig.4 shows the Lorentz corrected SAXS plots and AFM images, it can be seen from Fig.4a that there are specific peaks ($q_{\text{max}}$) of all polyether PU fibers which are associated with inter domain spacing ($d$) of hard segment domains in a microphase separated structure. The peak firstly moves to the left (0.6W/m$^2$-0.9W/m$^2$) and then to the right (1.2W/m$^2$-1.5W/m$^2$) indicating the long-range period $d$ firstly increases (0.6W/m$^2$-0.9W/m$^2$) and then decreases (1.2W/m$^2$-1.5W/m$^2$), [24], [25], [26]. AFM images from Fig.4b to Fig.4f display three different phases, while lighter phase (c3, d3, e3) and darker phase (c2, d2, e2, f2) signify the soft segment domain and hard segment domain of polyether PU fibers, and others (b1, c1, d1, e1, f1) are related to mixture of soft and hard segments [27]. With the increase of UV irradiation, the region with segments mixture of unaged polyether PU fibers in Fig.4b firstly transforms to larger domains in the region, as shown in Fig.4c and Fig.4d (0.6W/m$^2$, 0.9W/m$^2$). Moreover, it is followed by the disappearance of domains in the region, as shown in Fig.4e (1.2W/m$^2$) and Fig.4f (1.5W/m$^2$). As a consequence, larger hard segment domains and ordered soft segments formed due to the generation of new soft and hard segments promote the degree of micro-phase separation under low UV irradiation (0.6W/m$^2$-0.9W/m$^2$). Disordered soft segments and destroyed hard segment domains formed due to the break-up of chemical and hydrogen bonds cause hard segments dispersed within soft segment matrix, which deteriorates the degree of micro-phase separation under higher UV irradiation (1.2W/m$^2$-1.5W/m$^2$).

Figure 4. SAXS patterns after Lorentz function of polyether PU fibers with various UV irradiation (a), AFM images of polyether PU fibers with various UV irradiation(b, c, d, e, f)

4. Conclusion

This paper presents an experimental study about the effects of QUV exposure on the structure and mechanical properties of polyether PU fibers. Regarding FTIR analysis, three-stage reactions have been hypothesized for this system under QUV aging. The break up of chemical bonds caused by QUV exposure is considered as a primary reaction, and a secondary reaction to explain hydrogen peroxide formed in the presence of UV irradiation, water and oxygen environment, while a tertiary reaction shows the re-polymerization occurred under accumulation of aging products (carboxylic acids and alcohols). At low UV irradiation (0.6W/m$^2$, 0.9W/m$^2$), the mechanism mainly includes primary and
secondary reactions while a parallel reaction occurs to produce new polyurethanes by the residual isocyanate in pre-polymerization stage and alcohols formed under QUV aging. Under higher UV irradiation (1.2W/m², 1.5W/m²), primary and tertiary reactions dominate. With the respect of SAXS and AFM analysis, at low UV irradiation (0.6W/m², 0.9W/m²), more hard segments gathers to form larger domains, which promotes micro phase separation of polyether PU fibers. Under higher UV irradiation (1.2W/m², 1.5W/m²), chemical bonds are destroyed and segments become disordered, resulting in the decrease of micro phase separation of polyether PU fibers.

5. Acknowledgement
This work was totally supported by NSAF (Grant No. U1430107).

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