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STUDY ON THE BEHAVIOR AND MECHANISM OF ACCELERATED AGING OF POLYUREA COATING UNDER XENON LAMP

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Abstract : In this paper, the surface properties, mechanical properties, microstructure and chemical composition of polyurea coating under Xenon lamp for 1000 h was investigated, these aging behavior were characterized and aging mechanism was analyzed through SEM and FTIR. The results indicated that the tensile strength, tear strength only showed a slight decrease after aging for 1000h while contact angle and gloss showed a trend of decrease 15.64% and 22.19%, respectively. FTIR results showed that C-N bond, N-H bond and C-O-C bond be partly broken, and the degree of total hydrogen bonding decreased. As a result, the force of the molecular bond of the coating decreased.

1. Introduction

Concrete structures are widely fabricated in the harbours, submarine tunnels, and over sea bridges. Numbers of marine structures are constructed with the exploitation of the marine resources and utilize of the marine spaces. However, the marine structure corrosion occurs gravely due to environmental factors, which diminish the safety and durability of marine concrete structure fearfully. In recent years, polyurea coatings are widely known for their corrosion resistance, ageing resistance, good mechanical properties, and strong adhesion to substrates [1-4]. They have been increasingly used in marine protection projects such as sea-crossing bridges, undersea tunnels, docks, and offshore highways [5-7]. According to [8-10 research[8-10], the outdoor protective life of polyurea coating can reach 100 years, and the protective effect is remarkable, which provides effective measures for the realization of many major projects with ultra-long life[11, 12].

Research on aging in the marine environment of coatings has become an important issue for coating losing its protective performance in a complex environment. More and more studies use artificial accelerated aging to study the aging behavior of coating [13-16]. For example, s. Bhargava et al. [17]studied the UV aging mechanism of waterborne polyurethane coatings. The results showed that the functional groups such as C-O-C, C=O, C-H and CO-NH were fractured. Zhu[5] studied the aging mechanism of aliphatic polyurethane coatings and acrylic polyurethane coatings under ultraviolet light irradiation. The results showed that the acrylic polyurethane was mainly cleaved by C-O bond, and the aliphatic polyurethane was mainly cleaved by C-N bond. As a special polyurethane coating, previous researches have been limited to chemical bond cleavage [6, 18-22]. There were few studies on the degree of hydrogen bonding and the relative content of soft and hard segments before and after aging.

Therefore, the natural exposure experiment of marine environment was simulated by Xenon arc lamp irradiation. SEM, FTIR were used to study the degree of hydrogen bonding and the chemical change of polyurea coating before and after aging. Furthermore, the aging mechanism of coated Xenon lamp under aging is obtained.

2. **Experimental section**

2.1Material

The polyurea coating used in this experiment was manufactured by Qingdao Shamu Advanced Material Co., Ltd., China. The sprinkler uses the PHX-40 proportional spray gun and the AP-2 spray gun from Polyurethane Machinery of the United States. The spray temperature and pressure are 65 ° C and 2500 psi, respectively. The coating thickness was about 2 mm and it was completely cured for 7 days.

2.2 Experimental method

Samples with a size of 40cm×20cm were prepared and placed in a Xenon weather-resistant aging lamp (Suzhou Zhihe Environmental Testing Equipment Co., Ltd., Suzhou, China) for aging. The temperature was set to 40 ℃, the humidity setting value was 50%, and the light setting value was 600 W/m^2.

2.3 Characterization

2.3.1Mechanical properties test

Tensile strength, tear strength and elongation at break of the coating were tested by MZ-4000D1 universal testing machine, Jiangsu Mingzhu Testing Machinery Co., Ltd., China. The tensile speed was 500±5mm/min, and the minimum stroke was 750mm to ensure that the measured value was between ranges of 30-70%. The accuracy was not less than 1%. The tearing speed was 200 mm/min.

2.3.2 Thickness test

Thickness gauge was produced by Jiangsu Mingzhu Company, the minimum division value was required to be 0.01mm, the pressure weight was (100±10) g, the diameter of the measuring surface was (10±1) mm and the dial value was 0-100HA.

2.3.3 Gloss test

The sample was tested by XGP series mirror gloss meter produced by Tianjin Xintong Guangda Technology Development Co., Ltd.

2.3.4 Contact angle test

Using SDC-200 static contact angle tester, Dongguan Shengding Precision instrument Co., Ltd. Wipe the sample with anhydrous ethanol and remove the floating dust on the surface of the sample. Inject proper amount of distilled water into the syringe, but place the sample on the loading table, place it flat and drop the liquid. Distilled water drops stay on the surface of the sample for a few seconds, waiting for the droplet to stabilize, and then capture the digital image of the droplet profile.

2.3.5 Scanning electron microscope:

The microstructure of the samples before and after aging was observed by JSM-7500F scanning electron microscope, Japan electronics Co., Ltd. The resolutions were 1.0nm (15kv) and 1.4nm (1kv), respectively. The acceleration voltage range was from 0.1kv to 30kV, the electron gun uses tungsten wire lamp and the range of the magnification was from 25 times to 1000000 times.

2.3.6 FTIR

Vertex 70 FTIR spectrometer (Brooke Optics, Germany) was used to study the ATR-FTIR (attenuated total reflection) spectra of samples before and after aging with 32 scans and 4cm^{-1} resolution. The spectral region from 4000 to 500cm^{-1} was cleaned with anhydrous ethanol and used to measure the surface of the sample. The degree of degradation can be detected by detecting the change of dipole moment related to the telescopic vibration of functional groups

3. Results and Discussion

3.1Glossniss

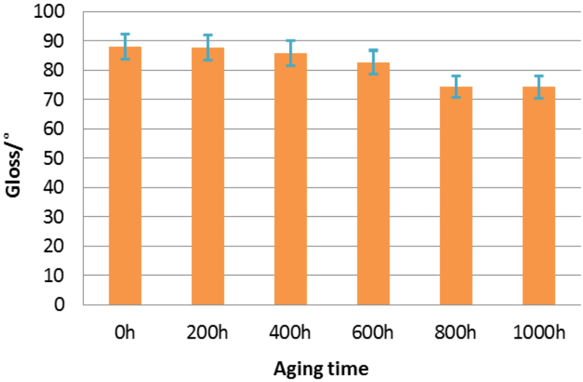

Fig.1. Change of gloss for aging 1000h

The gloss was measured by the light reflection principle, and was one of the important means to characterize the roughness of the coating[23]. Figure 1 showed the glossiness of the xenon arc lamp with the lightcollecting coating on the illumination of 200h, 400h, 600h, 800h and 1000h. As can be seen from the figure, before the xenon lamp was irradiated, the glossiness was 87.97±2.8°, the irradiation time reached 1000 hours, and the glossiness was 74.21±3°, which was decreased by about 15.64%. The results showed that the surface roughness of the coating increases after 1000 h of Xenon arc lamp irradiation, which may be due to micropores and microcracks on the surface of the coating during aging.

3.2 Contact angle and surface energy

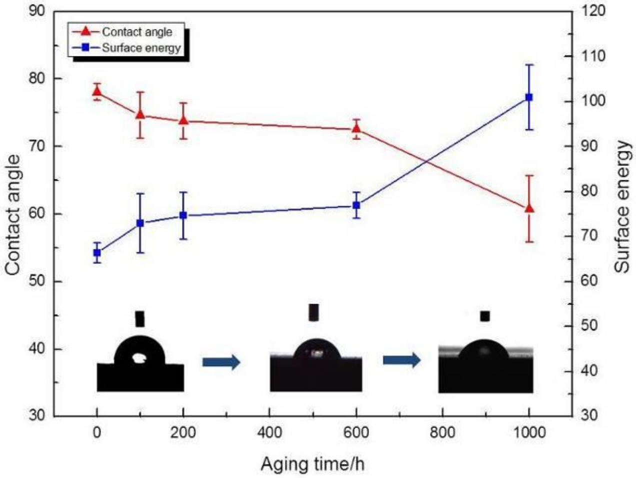

Fig.2. Change of contact angle and surface energy

Figure 2 showed the change of water contact angle on the xenon lamp for 100h, 200h, 600h and 1000h, and the surface energy was calculated using Fowkes polarity analysis. When the aging time was 0h, 100h, 200h, 600h and 1000h, The contact angles was 78.05±1.2°, 74.65±3.4°, 73.74±2.6°, 72.56±1.4° and 60.73±5.9°, respectively, which decreased by about 22.19%. The literature[24] showed that the contact angle was correlated with the wetting properties of the coating surface, and the results showed that the wettability of the coating was enhanced. The surface energy of the coating increased with the aging time, and it was 66.34±2.27°, 72.89±6.5°, 74.65±5.2°, 76.90±3.8° and 100.94±12.17° at 0h, 100h, 200h, 600h and 1000h respectively. The hydrophilicity of the surface of the coating increased, which greatly increased the adhesion of dust and other contaminants; the surface polarity increased, indicating that the functional groups on the surface increase and the molecular structure changed after the coating ages.

3.3 **Mechanical properties**

3.3.1 Change of hardness and thickness

Tab.1

Change of hardness and thickness

Aging time/h	0	200	400	600	800	1000	Rate of change
Hardness A	90.67	91.00	90.67	89.33	89.30	89.63	1.14%
Thickness/mm	2.45	2.47	2.43	2.34	2.23	2.34	4.89%

Table 1 showed that the hardness and thickness of the coating change during the aging process of 1000 h. The effect of Xenon lamp irradiation on the hardness of the coating was not obvious, but the hardness of the coating was basically unchanged after aging, which only decreased by 1.14%. Aging had a slight effect on the thickness of the coating, which may be due to the degradation of macromolecules on the surface of the coating under the aging of the Xenon lamp, which led to the decrease of the thickness of the coating.

3.3.2 Tensile strength, tear strength and elongation at break

The tensile strength, tear strength and elongation at break over time of the coating under the xenon lamp for 100 h, 200 h, 600 h and 1000 h, respectively, were given in Figure 3. It can be clearly seen from the drawing that the tensile strength, tear strength, and elongation at break tendency of the coating during the irradiation of the xenon lamp are consistent.

When irradiated for 200h, the mechanical properties of the coatings showed an upward trend to a certain extent. The reason for this phenomenon was that in the early stage of irradiation, ultraviolet light, temperature and other factors would promote the cross-linking between polyurea macromolecules. In combination, this process competes with the cross-linking of molecules and the breakage of molecular bonds, and the cross-linking effect was significantly greater than the breaking bond, which increased the mechanical properties.

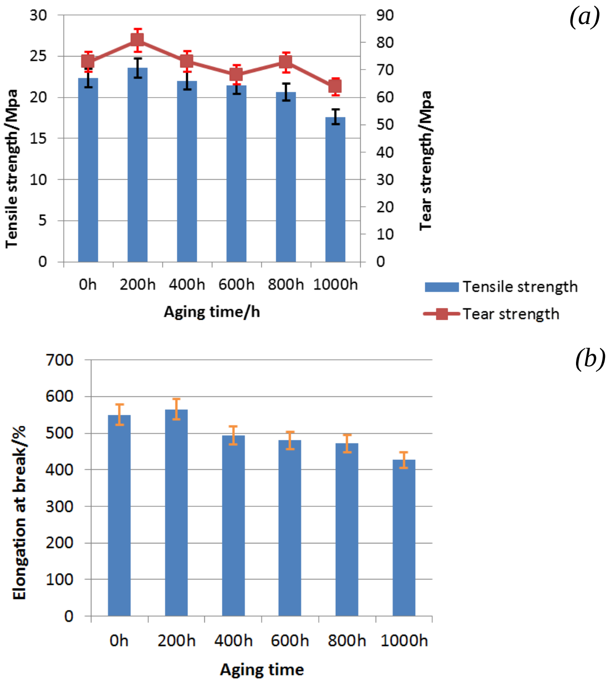

Fig.3 Change of (*a*) tensile and tear strength; (*b*) elongation at break

After irradiation for 400 h, the mechanical properties of the coating began to decrease. However, the tensile strength, tear strength decreased by 4.68MPa and 9.17Mpa, respectively when the irradiation time reached 1000h the coating still had good mechanical properties.

3.4 SEM

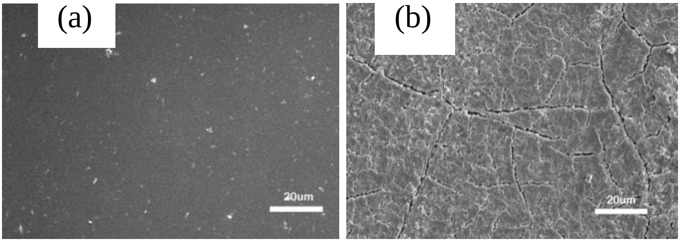

Fig.4. SEM of polyurea (a) before and (b) after 1000h aging

Figure 4 showed the surface morphology of the coating before and irradiated with Xenon lamp for 1000 h. It can be seen from the diagram that the surface of the coating was smooth and flat before aging, and there were no obvious defects. After aging for 1000 hours, cracks, holes and other defects appeared on the surface of the coating, and white powder impurities are attached to the surface. This was due to the degradation of macromolecules on the surface of the coating irradiated by Xenon lamp.

3.5 FT-IR

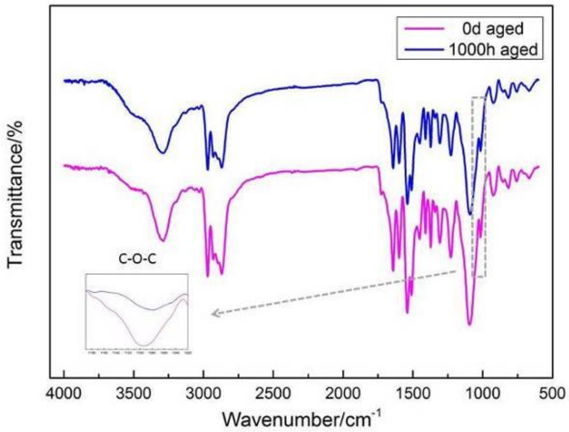

Fig.5. FTIR of polyurea coating before and after aging

FT-IR spectroscopy has been utilized to study the functional group change of polyurea coating before and after aging. As shown in Fig. 6, all spectra were characterized by a major band centered at 3287 cm^{-1}, ascribed to the N-H groups, and another peak at about 1540 cm^{-1}, which was assigned to the C-N bond. The peaks due to the carbonyl stretching bands were characterized by bands at 1600-1700 cm^{-1}. The above peaks proved the existence of -NH-CO-NH-[3].

The major difference between the spectra corresponding to the unaged and aged sample was only their intensity of bands. A decrease in the intensity signal of the aged compared to the unaged sample was observed and it indicated the beginning of the disappearance of such bands. So such structural modifications, namely chain scissions, have provided evidence that the xenon lamp aging provokes a harmful effect on the material resistance. This result confirmed again the mechanical degradation previously described in Refs[10]. In the vicinity of 3287 cm^{-1}, 1540 cm^{-1}, respectively, representing N-H, C-N stretching vibration peak was slightly weakened, and the urea carbonyl absorption band of about 1600-1700 cm^{-1} also had a certain degree of downward trend. Therefore, the bond between N-H, C-N and C=O had different degrees of fracture.

Quantitative analysis of hydrogen bonding characteristics of the segmented copolymers was conducted by using Fourier transform infrared spectroscopy[25]. The carbonyl stretching bands were deconvoluted into components corresponding to different free and hydrogen bonded groups， as shown in Table 2. The proportion of ordered hydrogen bond and disordered hydrogen bond was 59.26% and 21.17%, respectively. While the ordered after aging changed to 53.49%, disordered changed to 21.03%. The total hydrogen bonding degree of the coating decreased from 80.43% to 74.52% after 1000 h irradiation with Xenon lamp. The literature[26] showed that the degree of hydrogen bonding was related to the intermolecular force of the coating, that was to say, the higher the degree of hydrogen bonding of the coating molecule was, the greater the intermolecular interaction force was. The experimental results showed that the intermolecular force of the coating decreases after aging. The macroscopic performance was the decrease of the mechanical properties of the coating.

Table 2

Percentage of hydrogen bonding before and after aging

Aging time/h	Wavenumber	Assignment	Area	Percentage of hydrogen bonding (%)		
	(cm^{-1})			X_o	X_{diso}	X_b
0	1633-1643	Ordered hydrogen bonding	5.9026	59.26		80.43
	1651-1665	Disordered hydrogen bonding	2.1083		21.17	
	1674-1686	free	1.9597			
1000	1628-1645	Ordered hydrogen bonding	3.7821	53.49		74.52
	1652-1668	Disordered hydrogen bonding	1.487		21.03	
	1675-1683	free	1.8013			

4. Conclusion

The aging behavior of polyurea coating irradiated by Xenon arc lamp for 1000 h was studied in this paper. The results show that the surface morphology, gloss, contact angle and mechanical properties of the coating were changed. The tensile strength, tear strength and elongation at break all increased at first and then decreased. When the aging time reached 1000 h, the tensile strength and tear strength decreased 4.68 and 9.17MPa, respectively. Gloss and contact angle also showed a downward trend, which decreased by 15.64% and 22.19% respectively. FTIR study showed that there exited bond breakage between C-N, C-H and C=O bond. After aging, the hydrogen bonding degree of the coating decreased, which resulted in the decrease of molecular force.

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УДК 624.012

DETERMINATION OF CRITICAL STRESS FIBER INTENSITY FACTOR OF CONCRETE BY TEARING OFF WITH A SPLITTING

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Annotation. There are no particular obstacles for crack propagation in high-strength concrete. However, in the dispersion-reinforced concrete obstacles in the form of fibers hamper the spread of the crack. It is clear that under the action of the load, the development of a crack is inevitable, but additional energy is expended on overcoming each obstacle in the form of a fiber, so the process of cracking can gradually fade. Thus, the fibers in the concrete are crack inhibitors. Crack resistance is a local physico-mechanical property of a solid that characterizes the ability to resist the propagation of cracks in it. Fiber concrete is a building material for which a distinctive feature is the improvement of crack resistance characteristics. The determination of the stress intensity factor makes it possible to correctly assess the resistance of the material during the formation and development of cracks. The stress intensity factor is one of the most important indicators of the crack resistance of a material such as fiber-reinforced concrete. For this reason, the methods and methods for determining this indicator should most fully disclose all the features of work under load and the quality of fiber-reinforced concrete. To determine the stress intensity factor in the laboratory, you can use the technique of Leonovich S.N., Piradov K.A., Guzeev E.A. The essence of the method consists in determining the maximum loads destroying control