

FULL PAPER

Research on the aging mechanism of polyurea-based coatings due to effects of UV radiation exposure

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Accelerated aging of polyurea coatings by UV radiation under laboratory conditions is tested. The results of coating color and gloss measurements indicate that the gloss and color of the polyurea coating are significantly changed. The coating gloss is decreased sharply from 72.12 GU to 1.93 (decreased by 97.3%) GU after 1000 hours of aging under UV radiation. The total color difference ΔE^*_{ab} is increased up to 13.67 after 1000 hours of testing, and the color of the coating tends to change to yellow. Based on the SEM imaging method, it shows that the microscopic surface of the coating is cracked. Such cracks increase in terms of quantities, numbers, and width with deeper propagation into the coating when increasing the aging time by UV radiation. Through the IR spectrum analysis method, it also demonstrates that the bonds of functional groups characterized by polyurea are also destroyed. The polyurea chain destruction is increased with the increase of UV aging time, some bonds of the N-H group, and the C=O group in polyurea are completely destroyed when increasing the aging time to 1000 hours.

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KEYWORDS

Accelerated aging; polyurea coating; UV radiation; coating gloss; total color difference.

Introduction

Polyurea is formed from the reaction of diisocyanates with an amine-based curing agent by polymerization. Polyurea, as a thermoplastic elastomer, has special properties due to its phase structure and physical bonding [1-3]. Thanks to its exclusive mechanical and physical properties, it has chemical-resistant and water-proofing properties with effective weather and abrasion resistance. Polyurea has been widely applied in many different sectors of the

industry, marine, and military, such as anti-corrosion coatings for metal structures, waterproof for construction and marine works, explosion-proof coating, and bulletproof armor in the military sector [1,2,4].

Polyurea has a special molecular structure consisting of a soft segment and a hard one of which, the soft segment includes of long-chain aliphatic polyether and forms amorphous regions, while the hard segment consists of a urea bond (NH – CO – NH). The molecular structure of polyurea is shown in Figure 1.

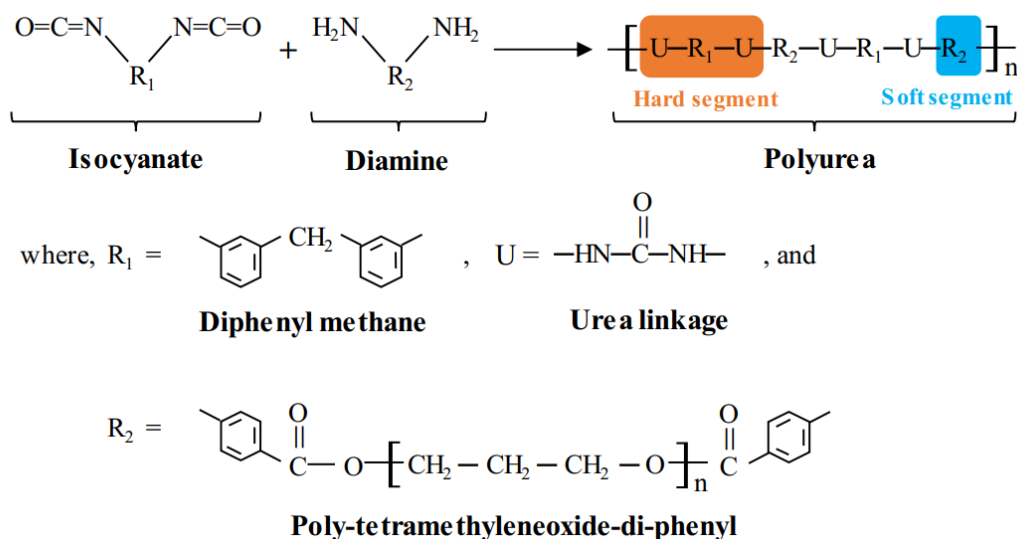


FIGURE 1 Molecular structure of polyurea [5]

Researches show that the fragmented structure of polyurea leads to the formation of special physical properties such as high tensile strength and higher elongation.

It is reported that when polymeric materials, in general, and polyuretic materials, in particular, are exposed to harsh environments (such as UV radiation, harsh temperature, oxygen, etc.), it causes changes in their physical, chemical, and mechanical properties [6,7]. Many researches demonstrate that most polymers absorb solar ultraviolet radiation, causing the degradation due to photothermal and oxidative reactions [8, 9]. Under natural conditions, the impacts of climatic factors lead to variations in the coating properties. As a result, it not only destructs the coating, but also damages assets and the safety of structures [10,11].

Researches on the aging of coatings in natural conditions have become an urgent request with increasing numbers of researches that apply the artificial accelerated aging method to study the aging of coatings [12-14]. For example, Bhargava *et al.* [15] studied the UV aging mechanism of the polyurethane coatings in water. The results showed that functional groups such as C-O-C, C = O, C-H, and CO-NH are broken. Zhu [16] studied the aging mechanism of aliphatic

polyurethane coatings and acrylic polyurethane coatings under the ultraviolet light radiation. The results revealed that acrylic polyurethane is mainly cleaved by the C-O bond, and aliphatic polyurethane is mainly cleaved by the C-N bond. According to this research direction, the study of properties and structures of polyurea is gradually receiving great attention. Youssef [17] studied the effect of UV radiation on the mechanical properties of polyurea samples and found that the elastic modulus is increased when the UV exposure time is increased. Whitten [18] studied the color change from white to tan after prolonged exposure to ultraviolet light.

Polyurea coating is a special type of polyurethane coating; however, there are very few researches on the aging mechanism of this coating under the effects of UV radiation. This research focuses on studying the aging of polyurea coatings under the effects of the UV radiation by the accelerated method under laboratory conditions.

Materials and methods

Materials

The polyurea coating used in this study is manufactured by Line-X, U.S.A. Viscosity at 250 °C for curing agent component

(Component A) is 550 ± 100 (cPs); plastic component (Component B) is 1100 ± 100 (cPs). Polyurea is sprayed onto a CT3 steel plate with dimensions of 150x75x2 mm by a specialized heating spray gun REACTOR E10HP (USA) at a temperature of 65 °C and a pressure of 2500 psi, the weight ratio of components A and B is 1:1. The coating thickness is about 1.0 mm, after coating samples; they are placed to dry naturally at room temperature for 7 days before testing.

Test mode

The test sample is placed in a UV test cabinet (UV test, Atlas); the test mode is according to ASTM D4587-11(2019) with a radiation intensity of 0.38 W/m² at 340 nm wavelength. Test cycle: Lighting time by UV lamp is 8 hours, black plate temperature is 70 ± 2.5 °C; condensation time is 4 hours, black plate temperature is 50 ± 2.5 °C. Samples are measured coating properties after periodic intervals of 200, 400, 600, 800, and 1000 hours.

Measurement methods

Scanning electron microscope

To measure the SEM images, a Hitachi S-4800 Field Emission Scanning Electron Microscope operating at 10 kV with the magnification of 80000-1000000 times is used.

IR spectrum

Infrared spectroscopy is used to determine the characteristic functional groups of polyurea. Spectra of samples are measured by a Nicolet 6700 FT-IR spectrometer within the wavelength range of 4000-400 cm⁻¹, a resolution of 8 cm⁻¹ and 64 times of scanning.

The gloss

To measure the gloss, a British hand-held gloss meter (Novo Gloss Trio Glossmeter) with 3

angles of 20/60/85 degrees, and a scale with an angle of 60°: 0 - 1000 GU; an angle of 20°: 0 - 2000 GU; and an angle of 85°: 0 - 199 GU, 0,1 GU resolution is used. The standard ASTM D523-14(2018) is applied to measure the gloss. The results are averaged at 5 different locations on the specimen surface.

The colors

The colors of samples are measured by a handheld X-RITE spectrophotometer, series Ci62 (USA). Standards of ASTM D2244 are applied to measure colors. Colors are defined according to the CIE 1976 L*a*b* (CIELAB) color space. The total color difference ΔE^*_{ab} between two colors, given each color according to the parameters L*, a*, and b* is calculated as follows:

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

$$\text{In which, } \Delta L^* = L^*_B - L^*_S \quad (2)$$

$$\Delta a^* = a^*_B - a^*_S \quad (3)$$

$$\Delta b^* = b^*_B - b^*_S \quad (4)$$

Where L*_s, a*_s, and b*_s are color indices of samples after testing and L*_B, a*_B, and b*_B are color indices of original samples. The signs of the components ΔL^* , Δa^* , and Δb^* have the following approximate meanings.

$$+ \Delta L^* = \text{lighter} \quad (5)$$

$$- \Delta L^* = \text{darker} \quad (6)$$

$$+ \Delta a^* = \text{redder (less green)} \quad (7)$$

$$- \Delta a^* = \text{greener (less red)} \quad (8)$$

$$+ \Delta b^* = \text{yellow (less blue)} \quad (9)$$

$$- \Delta b^* = \text{bluer (less yellow)} \quad (10)$$

Results and discussion

Color changes

Figure 2 displays the color changes of samples after testing under the UV radiation within different intervals. Table 1 expresses the color parameters of polyurea samples after different testing periods.

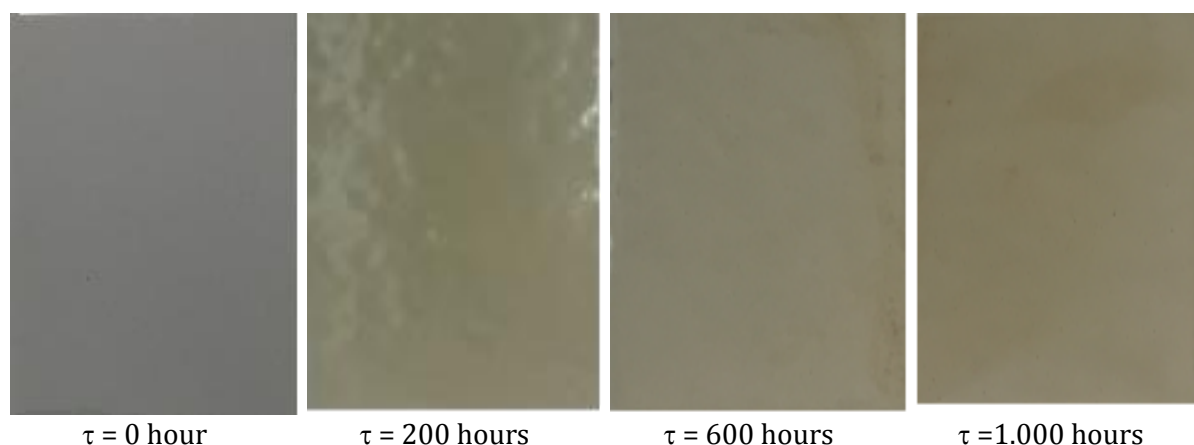


FIGURE 2 Images of changed colors of polyurea samples after different testing periods (0, 200, 600, and 1000 hours)

Based on images of Figure 2 and color measurement data table in Table 1, it indicates that the color change of polyurea samples under the effects of UV radiation is very significant. The color change is clearly visible to the naked eye after 200 hours of testing ($\Delta E^*_{ab} = 12.03$). The color tends to turn yellow, this is indicated in Table 1, parameter values L^* and a^* (characterized by white/black and red/green, respectively) do

not change significantly, in which the parameter b^* (characterized by yellow/blue) has a clear change from the value of -1.06 to 10.76 after 200 hours of testing. The sample is less likely to change its colors when increasing the test time under the effects of UV radiation, and the total color difference changes from 12.03 to 13.67 when increasing the test time from 200 to 1000 hours.

TABLE 1 Color parameters of polyurea samples

Testing time	L^*	a^*	b^*	ΔE^*_{ab}
$\tau = 0$ hours	58.45	-0.66	-1.06	0
$\tau = 200$ hours	56.27	-1.13	10.76	12.03
$\tau = 400$ hours	56.18	-1.40	11.53	12.81
$\tau = 600$ hours	56.75	-1.27	11.88	13.06
$\tau = 800$ hours	56.20	-1.48	11.96	13.23
$\tau = 1000$ hours	56.55	-0.88	12.48	13.67

Gloss changes

Figure 3 represents the gloss change of polyurea samples at an angle of 60° over different testing periods. Retained gloss is defined as the percentage change in the gloss

of the sample during testing compared to that of the original sample. The gloss of samples is decreased clearly after 200 hours of testing (decreased by 33%). The gloss is gradually reduced when increasing the testing time under the effects of UV radiation.

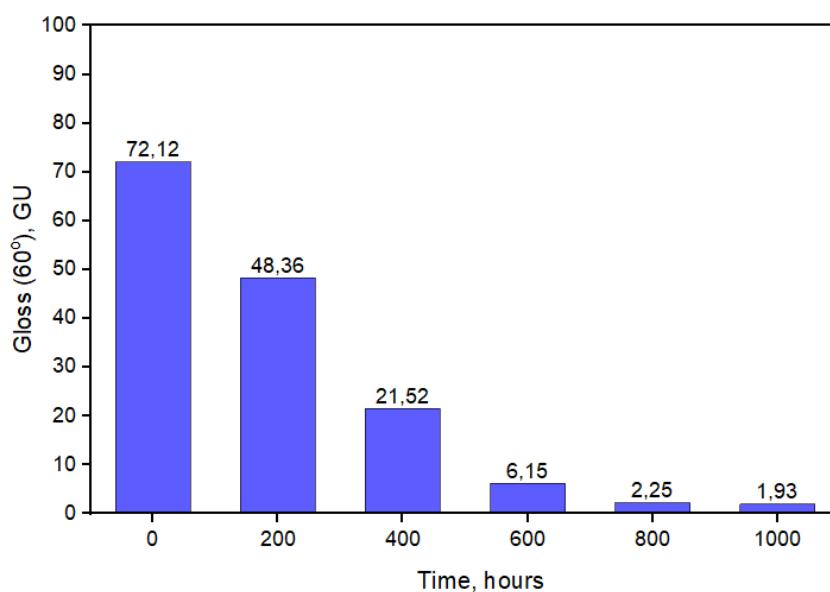


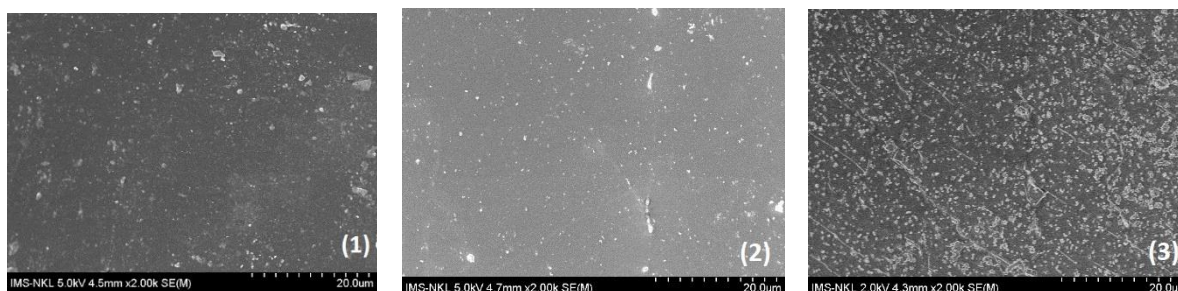
FIGURE 3 Gloss change of the polyure coating after different testing periods

Gloss gradually decreases from 72.12 GU to 48.36 (33%), 21.52 (70%), 6.15 (91.5%), 2.25 (96.9%), and 1.93 (97.3%) GU when gradually increasing aging time under UV lamp as 200, 400, 600, 800, and 1000 hours, respectively. A decrease in the gloss of the coating is a sign of coating aging due to the effects of UV radiation. UV radiation causes polymer chain disruption and, as a result, reduces the gloss of the coating [19]. Cracks in the coating surface show the result of polymer chain breakdown process in the coating. Observing the surface by SEM method (Figure 4), it is clear that the number and magnitude of the marks increase with increasing aging time under UV radiation.

Morphology of sample surface

To assess the mechanical damage during the testing process, the morphology of the UV-exposed surface is surveyed by a scanning electron microscope. Figure 4 displays the

surface morphologies of aging and un-aging polyurea coatings under the effects of UV radiation for different time periods (200, 400, 600, 800, and 1000 hours). It can be seen that small cracks started to be appeared on the surface of samples after 400 hours of testing. Cracks are increased in terms of quantities and width with deeper propagation into the coating when the time of UV exposure is increased. The micro-cracks on similar materials have been researched previously when exposed to ultraviolet light [20, 21]. The surface cracking due to aging causes the breakage of polymer chains. This result is consistent with the statements by Woo *et al.* [22] when studying the UV-induced aging of some polymer materials.



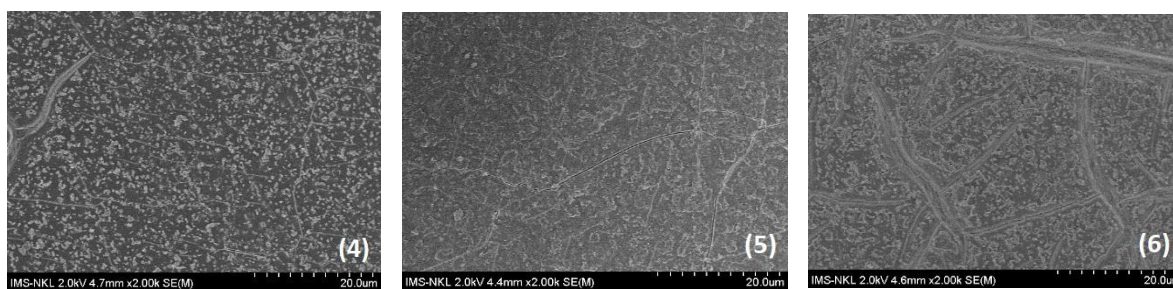


FIGURE 4 Sample surface morphology: (1) before testing, (2) after 200 hours, (3) after 400 hours, (4) after 600 hours, (5) after 800 hours, and (6) after 1000 hours

IR spectrum

The IR spectrum of original polyurea coatings not impacted by the UV radiation is illustrated in Figure 5. The spectrum map shows typical absorption peaks of polyurea. In which, the absorption peak at 3300 cm^{-1} is characterized by deformation vibrations of N - H bonds. At the absorption peaks between 2870 cm^{-1} and 2970 cm^{-1} are generated by symmetrical deformation oscillations of CH_2 bonds [5, 23]. Absorption peaks in the region from 1600 cm^{-1}

to 1726 cm^{-1} are characterized by elongation oscillations of the C = O group in polyurea. The absorption peaks in the region from 1017 cm^{-1} to 1095 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the C - O - C bonds, respectively. Bending oscillations in and out of the plane of the C-H bond on the benzene ring produce absorption peaks of nearly 1018 cm^{-1} and 920 cm^{-1} , respectively. Furthermore, absorption peaks in the vicinity of 770 cm^{-1} are mainly caused by out-of-plane bending oscillations of the O = C - O bonds.

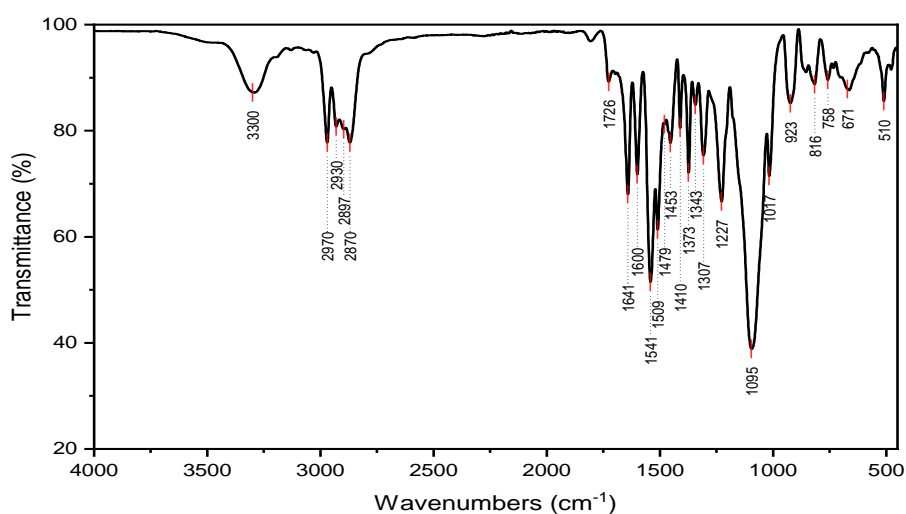


FIGURE 5 IR spectrum of the original Polyurea coating

The IR spectra of polyurea coatings over different aging periods are depicted in Figure 6. Based on IR images, a sharp decrease of signal intensity of the characteristic absorption peaks of polyurea is observed when increasing the aging time. The decrease

of signal intensity of the samples when increasing the aging time indicates the presence of chain cleavage and the disappearance of certain functional groups [24].

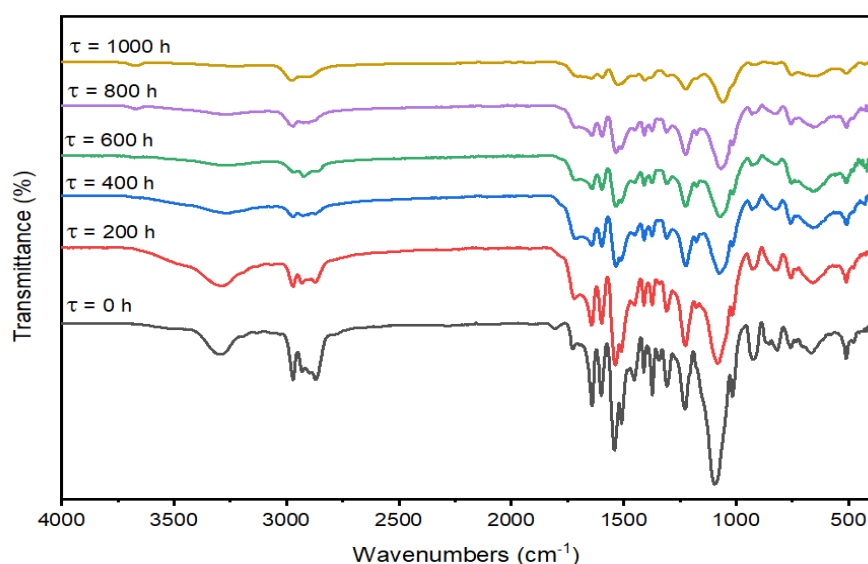


FIGURE 6 IR spectrum of polyurea coatings before and after aging

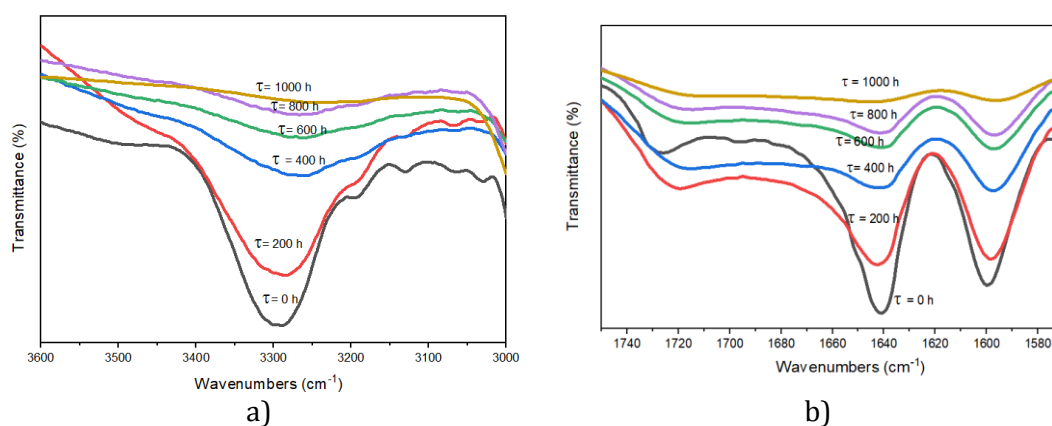


FIGURE 7 IR spectrum of the group N - H (a), and C = O (b) group in polyurea

For example, at the absorption peak of 3300 cm^{-1} , it is characterized by the N - H group, and at the absorption peaks from 1600 cm^{-1} to 1726 cm^{-1} , it is characterized by the elongation oscillation of the C = O group, it has been gradually decreased and almost disappeared when increasing the aging time from 0 to 1000 hours (Figure 7). This expresses the existence of the cleavage of N - H bond and C=O bond in polyurea. These results are also consistent with the SEM images as demonstrated in Figure 4.

Conclusion

The accelerated aging test of polyurea coatings under the effects of UV radiation for 1000 hours has shown the following points:

Polyurea coatings are strongly discolored, and the total color difference ΔE^*_{ab} after 200, 400, 600, 800, and 1000 hours are 12.03, 12.81, 13.06, 13.23, and 13.67, respectively.

Gloss gradually decreases from 72.12 GU to 48.36 (33%), 21.52 (70%), 6.15 (91.5%), 2.25 (96.9%), 1.93 (97.3%) GU when gradually increasing aging time under UV lamp respectively 200, 400, 600, 800 and 1000 hours, respectively.

Based on the SEM imaging method, it is shown that the microscopic surface of the coating is cracked. Cracks increase in terms of quantities and width with deeper propagation into the coating when increasing the aging time under the effects of UV radiation.

The IR spectrum analysis method further demonstrates that the bonds of functional groups that are characterized by polyurea are destroyed. The polyurea chain destruction is increased when increasing the UV aging time; some functional groups are completely destroyed when increasing the aging time up to 1000 hours.

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