Aging behavior of the three-proof polyurethane coating under UV radiation

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Abstract: The influence of UV radiation on the gloss, structure (SEM, FTIR), thermal (TGA, DTG) and mechanical properties of polyurethane resins and the three-layer protective coating made of them was investigated. The gloss of the resins was greater than that of the protective coating. UV radiation has been proven to reduce gloss (at 1,200 hours irradiation, 81.3° to 8.9° for resins, and 61.1° to 2.8° for coating).The tensile strength of the resins decreased during aging, and the relative elongation at break after reaching the minimum was increased (at the irradiation time of 100 h). In the case of coating, both the tensile strength and elongation decreased during aging and, after reaching the minimum they increased (at the irradiation time of 800 h), reaching the maximum (at the irradiation time of 1000 h), and then decreased.

Keywords: polyurethane, ultraviolet, coating, resin.

Wpływ promieniowania UV na starzenie trójwarstwowej powłoki poliuretanowej

Streszczenie: Zbadano wpływ promieniowania UV na połysk, strukturę (SEM, FTIR), właściwości termiczne (TGA, DTG) i mechaniczne żywic poliuretanowych oraz wykonanej z nich trójwarstwowej powłoki ochronnej. Połysk żywic był większy niż powłoki ochronnej. Potwierdzono, że promieniowanie UV zmniejsza połysk (przy naświetlaniu przez 1200 godzin, w przypadku żywic z 81,3° do 8,9°, a w przypadku powłok z 61,1° do 2,8°). Wytrzymałość na rozciąganie żywic zmniejszała się w trakcie starzenia, a wydłużenie względne przy zerwaniu po osiągnięciu minimum zwiększało (przy czasie naświetlania 100 h). W przypadku powłoki zarówno wytrzymałość na rozciąganie, jak i wydłużenie zmniejszały się w trakcie starzenia i po osiągnięciu minimum zwiększały (przy czasie naświetlania 800 h), osiągając maksimum (przy czasie naświetlania 1000 h), a następnie zmniejszały.

Słowa kluczowe: poliuretan, ultrafiolet, powłoka, żywica.

The three-proof polyurethane protective paint is one of protective paints, which are used to protect the surface of the circuit boards. It is anti-humid and heat-, mildew-, salt-fog- and UV-proof, although the circuit on the circuit board may be easily eroded by the external environment. Therefore, research into protective paints should be intensified, focusing on reducing the erosion of the external environment and extending the service life of objects such as circuits.

Another important factor which may cause coating failure is sunlight, especially ultraviolet [1], whose wavelength is relatively short [2] (295–400 nm). The energy of 300 nm ultraviolet light reaches 399 kJ/mol generally and the energy of polymers bonds is usually 250–420 kJ/mol, so the ultraviolet radiation may destroy chemical bonds in polymer. However, the process of polymer decomposition caused by UV is relatively slow. It may be an effect of very small UV absorption rate of polymers [3].

At present, there are two main mechanisms of photoaging: free radical fracture caused by ultraviolet irradiation and reaction of hydrophilic groups in polymers under water vapor. Many researchers studied aging mechanism of organic coatings. Luo *et al.* [4] conducted an aging test of polyurethane coating in the marine environment and atmosphere. It was found that after four years the main functional groups in polyurethane coating almost disappeared,

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T a b l e 1. Materials

Material	Manufacturer	Name/Comment
Flexible three polyurethane finish Component A	Aladdin Chemical Co., Ltd	Acroleic acid
Flexible three polyurethane finish Component B	Aladdin Chemical Co., Ltd	Water-based polyurethane
Polyurethane resin Component A	Shandong Manhang Technology Co., LTD	Diisocyanate
Polyurethane resin component B	Shandong Longhua Chemical Co., Ltd	Trihydroxymethyl-propane and epoxy resin
Silicone insulated primer Component A	Lanabai Chemical Co., Ltd	Dimethyldichlorosilane (DMCS)
Silicone insulated primer Component B	Zheng Yangming New Materials Co., Ltd	N-butyl acetate
Epoxy anticorrosion primer Component A	Shandong Longhua Chemical Co., Ltd	Epoxy resin
Epoxy anticorrosion primer Component B	Shandong Dexiang International Trade Co., Ltd	Diethylene triamine
Defoamer	German BYK chemical company	BYK-054/ to eliminate bubbles
Leveling agent	German BYK chemical company	BYK-333/to reduce surface tension and increase smoothness and wettability
Butyl acetate	Beijing Chemical Plant	Solvent
Xylene	Beijing Chemical Plant	Solvent
Alcohol	Beijing Chemical Plant	–
Glue	Tianjin Yanhai Chemical Co., Ltd	HY-914

and the aging of resin started with the photochemical reaction of weak molecular bonds. The break of molecular chain in the resin was possibly due to ultraviolet and water influence and resulted in defects in coating and further aggravation. Yang *et al.* [5, 6] explained the blistering phenomenon of the coating surface which was caused by the ultraviolet light, water and oxygen together: these three factors degraded the coating surface and induced hydrophilic groups which further, in contact of coating with water, resulted in microporous defects of the surface. Under the condition of alternating cold, heat, dry and wet, the blistering phenomenon of coating occurred. Xu *et al.* [7] showed that the carbon chain fracture in polyurethane caused by ultraviolet irradiation occurs mainly in C-O and C-N bonds and induces new hydrophilic groups, leading to the aging failure of the coating. Yang *et al.* [8] analyzed the microstructure of thermoplastic polyurethane UV-aged elastomer and concluded that when the aging time is long enough, UV irradiation may break down C-N bond of urethane group and generate enamine, making the coating yellow.

At present, in order to improve the anti-aging properties of polyurethane products under UV light [9], physical modification and chemical grafting are suggested. Xu *et al.* [10] performed wet curing of PUR with carbon black as a filler, which improved the hydrolysis, heat, and light resistance of the material. Zhang *et al.* [11] modified polyurethane with nanocrystalline cellulose (NCC), which significantly improved the yellowing and wear resistance. Pan *et al.* [12] grafted the fluorine-containing resin on the surface of hollow glass beads and after that added the grafted beads to polyurethane resin

as a filler, improving aging resistance of polyurethane coating.

In this work, the behavior and damage mechanism of three-proof polyurethane resin in a simulated marine atmospheric environment, as well as useful properties of three protective paints were investigated. Artificial UV aging of the resin and coating was performed simultaneously to investigate the effect of UV agents on aging.

EXPERIMENTAL PART

Materials

Materials used in the experiments are listed in Table 1.

Equipment

Equipment used during the experiments is listed in Table 2.

T a b l e 2. Experimental equipment

Experimental equipment	Manufacturer
Laboratory basket-type dispersion grinder	Shanghai Ffulai Energy Technology Co., Ltd
Electric stamping machine	Yangzhou Jingzhuo Test Machinery Factory
Air dry oven	Shanghai Hengyi Technology Co., Ltd
Scanning electron microscope	Tskana, Czechoslovakia
Fluorescent ultraviolet aging box	Biuged Precision Instrument Co., Ltd

Preparation of resin and coating samples

During the research components A and B of the elastic three-proof polyurethane resin and components A and B of the epoxy anti-corrosion primer were used (Table 1).

The surface of 6 lids of 1 L white plastic buckets (with inner diameter of 110 mm) was wiped with alcohol and dried. 54 g of component A and 9 g of component B (which allows for maintenance of ratio A:B = 6:1) were put together into a 1 l plastic tank and after that 12.6 g of butyl ester (20% solvent), 0.13 g of defoamer (0.2%), 0.13 g of leveling agent (0.2%), and 0.13 g of organic bismuth catalyst (0.2%) were added and stirred well. The mixed resin was poured into the white lids, about 6–7 g per lid, and placed horizontally into a fume hood for surface drying after leveling.

Four pieces of 5 × 12 cm carbon steel plates were polished with 400-grit sandpaper and their surface was wiped with anhydrous ethanol and dried. 36 g of resin component A and 6 g of component B (ensuring ratio A:B = 6:1) were taken and butyl ester, antifoaming agent, leveling agent, and organic bismuth catalyst were added, mixed well, sprayed with a spray gun to the surface dry on the carbon steel plate, and placed in a fume hood for surface drying.

In addition, 12 g of component A and 2 g of component B of epoxy anti-corrosion primer (ensuring ratio A:B = 6:1) were diluted with a mixed solvent of butyl ester and xylene, and the carbon steel sample was brushed. The edges were sealed, brushed and dried in the fume hood.

The surface-dried pouring paint film and sprayed samples were put into a vacuum oven at 60°C for solid drying, and the cured paint film samples and templates were taken off the oven after 48 hours of solid drying.

The paint film poured into the lid was cut into pieces (dumbbell-shaped with dimensions 4 mm x 75 mm) using an electric punching machine. 24 pieces of resin splines with a uniform thickness were prepared.

Preparation of three-proof polyurethane topcoat film and sample

In the experiments, components A and B of epoxy anti-corrosion primer and components A and B of elastic three-proof polyurethane topcoat were used (Table 1).

The surface of 6 lids of 1 L white plastic buckets (with inner diameter of 11cm) was wiped with alcohol and dried for later use. 45.09 g of component A and 5.01 g of component B (according to ratio A:B = 9:1) were taken, put into a 1 l plastic tank, and 10.02 g of butyl ester (20% solvent), 0.10 g of defoamer (0.2%), 0.10 g of leveling agent (0.2%), and 0.10 g of organic bismuth catalyst (0.2%) were added and stirred well. The mixed resin was poured into the white lids, about 6–7 g per lid, and placed horizontally in the fume hood for surface drying after leveling.

Four pieces of carbon steel plates (5 × 12 cm), were polished with 400-grit sandpaper and their surface was wiped with anhydrous ethanol and dried. 36 g of resin component A and 4 g of component B (which correspond to the ratio A:B = 9:1) were taken and butyl ester, defoamer, leveling agent, and organic bismuth catalyst were added, mixed well, sprayed with a spray gun to the surface and dried on the carbon steel plate. The sprayed plate was placed in a fume hood for surface drying.

In addition, 12.6 g of component A and 1.4 g of component B of epoxy anti-corrosion primer (according to the ratio A:B = 9:1) were diluted with a mixed solvent of butyl ester and xylene, and the surface was dried well. The carbon steel sample was brushed back and edge was sealed, and after brushing placed in a fume hood to dry.

The surface-dried pouring paint film and sprayed samples were put into a vacuum oven at 60°C for solid drying. After 48 hours of solid drying they were taken out.

The paint film after removal from the lid was cut using an electric punching machine to the dumbbell-shaped pieces with dimensions of 4 × 75 mm. 24 resin splines with uniform thickness were selected for tests.

Preparation of three-proof polyurethane topcoat matching primer

Components A and B of the silicone thermal insulation primer (Haihua Institute) and the components A and B of the three-proof polyurethane topcoat (Table 1) were used.

Six pieces of 5 × 12 cm carbon steel plate were ground with 400-grit sandpaper and their surface was wiped with absolute ethanol and dried. 45 g of component A and 5 g of component B of the thermal insulation primer (which ensures the ratio A:B = 9:1), were taken and 12 g of butyl ester was added and the mixture after mixing well was sprayed on the carbon steel plate and dried at 60°C in a fume hood for 7 hours.

In addition, 90 g of component A and 10 g of component B of the three-proof topcoat (according to the ratio A:B = 9:1) were taken, and butyl ester, defoamer, leveling agent, and organic bismuth catalyst were added, mixed evenly and sprayed on the surface with a spray gun. The sprayed plate was placed in a fume hood for surface drying.

30 g of component A and 5 g of component B of epoxy anti-corrosion primer (according to the ratio A:B = 6:1) were diluted with a mixed solvent of butyl ester and xylene, and afterwards the back was brushed and the sample was sealed. After brushing it was placed in a fume hood to surface dry.

The surface-dried samples were put in a vacuum oven at 60°C for 48-hours long hard drying.

Methods of testing

UV aging test method

The UV aging test method was carried out on the way of artificial climate aging exposure of paints and var-

nishes to UV fluorescent line and water (according to GB / T 23987-2009) [13]. Two ends of 15 resin strips and 15 coating strips were gently stick to the polytetrafluoro-ethylene plate with double-sided adhesive tape (the plate size was 5 × 12 cm). Two other prepared resin samples and two coating samples and were put into the fluorescent ultraviolet aging box (light source: UVA-340 nm, cycle mode: 4 h illumination + 4 h condensation, illumination blackboard temperature: 60°C, condensation blackboard temperature: 50°C) and the ultraviolet aging test was started.

The test was conducted for 1200 h and every 200 h samples were taken. Each time, 3 resin and coating samples were taken and placed in a 60°C oven for 30 min of drying. After cooling down to the room temperature, mechanical properties and the gloss and color difference of the samples were tested and recorded. After the tests, samples were put back into the UV aging box.

Mechanical properties test method

Mechanical properties were measured using a universal tensile machine. The thickness of the paint film was measured using a vernier caliper and it was kept between 0.2 mm and 0.4 mm. The spline was a standard width of 4.0 mm and the crosshead speed was 100 mm/min. During the tests tensile strength and elongation at break were recorded. Three samples were taken for a measurement and the measurement results were averaged.

Light loss rate

The gloss test of resin paint films and coating was carried out in accordance with GB/T 9754-2007 "Paints and varnishes 60° specular gloss". The AG-4446 triangular gloss tester (BYK, Germany) was used to measure resins and varnishes. Variation in gloss at a 60° angle of the coating surface was measured. Five points were selected on the sample plate for each measurement and the maximum and minimum values were removed and the average was taken. The gloss loss was calculated according to GB/T 1766 "Grading method for aging of paint and varnish coatings".

Chromatic aberration test method

The color difference tests were conducted using SP60 color difference meter (X-rite, United States) in accordance with GB/T 11186.2 "Measurement method of coating color, part 2 color measurement". The initial sample was used as the standard for testing of resins and coating of each node. The coating discoloration grade (change of chromatic aberration) was divided into 0–5 according to GB/T 1766, where grade 0 was the lightest degree of discoloration, indicating no discoloration, and grade 5 was the greatest degree of discoloration, indicating severe discoloration.
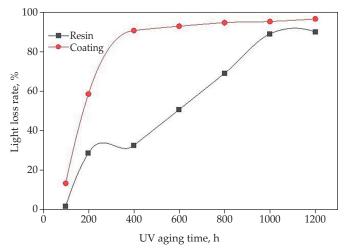

Fig. 1. Light loss rate of resin and coating during UV aging

Fourier transform infrared

Fourier transform infrared (FTIR) was performed using NICOLET iN10 micro-infrared spectrometer (Thermo Fisher, United States). The test wavelength range was 800–4000 cm^{-1} and the attenuated total reflection test was used. Each functional group in the sample was qualitatively determined by the position of the characteristic absorption peak in the infrared spectrum and the change of the functional group was determined according to the intensity change of the peak intensity and the peak area.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a comprehensive thermal analyzer. The measurement sample weight was 5–8 mg, the test gas was N_2, the test temperature range was 50–600°C, and the heating rate was 10°C/min. The mass of the measured sample varied with temperature. The weight loss change of the sample was determined before and after aging.

Scanning electron microscopy

The scanning electron microscopy (SEM) was conducted using TESCAN VEGA3 scanning electron microscope (Tskana, Czechoslovakia). The magnification of the sample was 500–2000 times and the surface of the coating was scanned by a high-energy electron beam to obtain its microscopic morphology.

RESULTS AND DISCUSSION

Light loss rate

The light loss rate of resin and coating films was calculated according to GB / T 1766-1995 [14], and the light loss rate grade of film was evaluated. Table 3 and Fig. 1 show the change of gloss of resin and coating with UV aging test time.
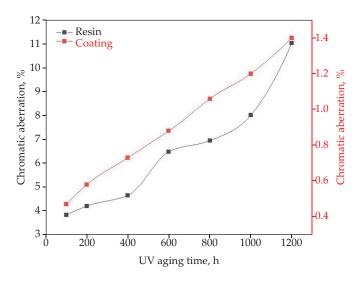
Fig. 2. Change of color difference of resin and coating during UV aging

After 200 h of UV irradiation the light loss rate of the resin increased sharply to 28.66% and the light loss reached grade 2, which means a slight light loss. After 400 h of UV irradiation, the light loss reached grade 3, which means an obvious loss of light. The light loss rate measured after 800 h of irradiation was 69.13%, and reached grade 4 of light loss standard, which means the serious light loss. After 1000 h of irradiation the light loss rate of the coating reached 89.05%, which became a complete light loss state. This shows a very obvious effect of the UV irradiation on the gloss of resin; the pure resin sample completely lost light after UV irradiation for a long time.

The initial gloss of the coating was 61.1° and the gloss loss rate reached 13.26% after 100 h, 58.59% after 200 h, and 90.84% after 400 h of UV irradiation, which means that the coating completely lost its gloss and the light loss reached grade 5. This shows that the influence of ultraviolet light on the gloss of coating is obvious in the early

stage of the experiment, and the coating completely lost its gloss after 400 h of UV irradiation. Based on Fig. 1 it may be stated that the influence of ultraviolet light on the coating was slow in the later stage and the UV light had a great influence on the gloss of the resin and coating. The resin lost light completely after 1000 h and the coating lost light completely after 400 of UV irradiation.

Chromatic aberration

The color difference change (Fig. 2) of paint film of resin and coating was determined by comparison between the aged and the non-aged sample plates according to GB / T 1766-1995 [14], so that the color change grade of paint film could be evaluated.

Fig. 2 shows the change of color difference of resin and coating in time during UV aging test. It can be seen that the color difference of resin and coating increased linearly with the time, but the color difference of resin sample changed faster than that of coating. The color difference (compared with the initial sample) of the resin sample after 100 h of UV aging was 3.83%, reaching grade 2 of the discoloration standard, which means a slight discoloration phenomenon. After 600 hours of aging, the color difference reached 6.48%, grade 3 of the color loss standard. After 1200 h of aging, the color difference was 11.03% reaching grade 4 of the color loss standard, which means a large loss of color. The color change of the coating during the UV aging was greater. After 1200 h of aging the color difference of the coating was 1.4% and still no discoloration [15].

It shows that UV irradiation has an obvious effect on the color change of resin, and a little effect on the color change of coating and supporting system coating. It may be due to the fillers and additives significant enhancement of the color change which is resistant in UV environment. Moreover, the color change resistance of the coating is also significantly enhanced after being used
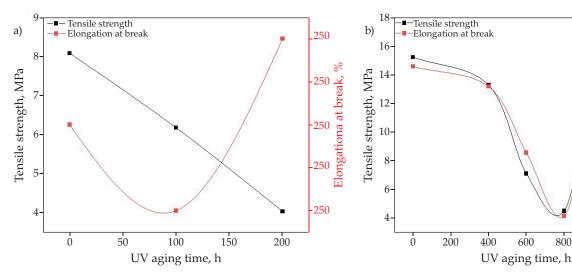

Fig. 3. Tensile properties of: a) resin, b) coating

Fig. 4. FTIR spectra of resin in the initial state and after 200 h of UV aging
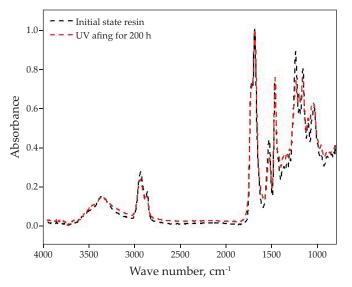

Fig. 5. FTIR spectra of coating in the initial state and after 200 h and 800 h of UV aging

together with the primer and the coating can still maintain its color after 1200 h of UV aging.

Mechanical properties

During the UV aging test, the changes of tensile strength and elongation at break were measured by fixed-point sampling of resin and coating samples, as shown in Fig. 3.

The variation diagram of tensile strength and elongation at break of resin spline under UV aging is shown in Fig. 3a. It could be seen that the UV aging of resin took only 200 h, because the spline couldn't be sampled after 400 h of aging and the mechanical test couldn't be carried out. However, only after 200 h of aging the tensile strength of the resin spline decreased from 8.08 MPa to 4.03 MPa (decrease of 50%), indicating the UV irradiation great impact on the mechanical properties of the pure resin paint film and the strength of destructive force.

Fig. 3b shows the changes of the tensile strength and elongation at break of the coating as a function of the UV aging. Both the tensile strength and elongation decreased during aging and, after reaching the minimum at the irradiation time of 800 h, they increased, reaching the maximum at the irradiation time of 1000 h. In the last period of 1000–1200 h, both parameters decreased.

It is shown that UV irradiation has a great impact on the mechanical properties of the polyurethane resin and coating. It may be due to the fact that the UV action destroys the chemical bonds in the resin and coating, resulting in the hardness and brittleness of the paint film. After the UV destroy of the molecular structure of the paint film, the water vapor present in the environment is more likely to enter the paint film and join its failure.
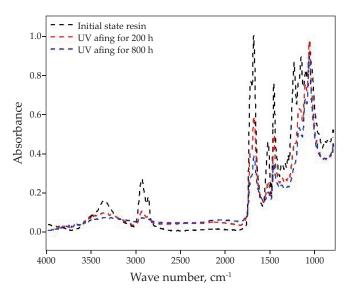
Fourier transform infrared spectroscopy (FTIR)

According to the inflection points of physical properties such as mechanical properties, and gloss and color difference, the resin and coating samples were analyzed by infrared spectroscopy at initial state, after 800 h and 1200 h of UV aging.

The infrared comparison diagram of the initial state of the resin sample and after 200 h of aging is shown Fig. 4. Band at wavenumber 3361 cm^{-1} is a characteristic peak of O-H and N-H, bands at wavenumber 2935 cm^{-1} and 2866 cm^{-1} are the characteristic peaks of CH$_3$ and CH$_2$, respectively, band at wavenumber1712 cm^{-1} is a characteristic peak of ester C=O, band at wavenumber 1684 cm^{-1} is a characteristic peak of amide C=O, band at wavenumber 1528 cm^{-1} is the deformation vibration of (CO)NH, band at wavenumber 1461 cm^{-1} is a characteristic peak of CH$_2$, band at wavenumber 1235 cm^{-1} is a superposition peak of C-C and C-N, band at wavenumber 1196 cm^{-1} is a characteristic peak of C-O, band at wavenumber 1099 cm^{-1} is a characteristic peak of Si-O-Si, and band at wavenumber 1040 cm^{-1} is a characteristic peak of C-F.

It could be observed that in the infrared spectrum of the resin sample after 200 h of UV aging, CH$_3$ and CH$_2$ had an obvious weakening trend, (CO)NH absorption peak at band at wavenumber 1528 cm^{-1}, C-C and C-N absorption peak at band at wavenumber 1235 cm^{-1}, and C-O absorption peak at band at wavenumber 1196 cm^{-1} also weakened significantly, Si-O absorption peak at band at wavenumber 1101 cm^{-1} weakened as well, while O-H and C=O absorption peaks at bands at wavenumber 3361 cm^{-1} and 1684 cm^{-1} increased significantly. This shows the UV irradiation fracture of C-N and C-O bonds in the paint film, while a new C=O was generated.
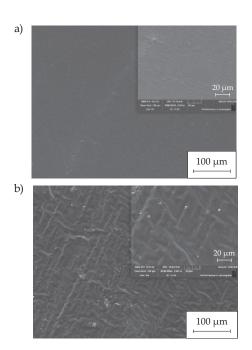
a)

b)

Fig. 6. SEM images of resin: a) in the initial state, b) after 200 h of aging

a)

b)

c)

Fig. 7. SEM images of coating: a) in the initial state, b) after 200 h, c) after 800 h of UV aging

In Fig. 5, band at wavenumber 3309 cm^{-1} is a characteristic peak of O-H and N-H, bands at wavenumber 2930 cm^{-1} and 2863 cm^{-1} are the characteristic peaks of CH$_3$ and CH$_2$, respectively, band at wavenumber 1715 cm^{-1} is a characteristic peak of ester C=O, band at wavenumber 1684 cm^{-1} is a characteristic peak of amide C=O, band at wavenumber 1528 cm^{-1} is the deformation vibration of (CO)NH, band at wavenumber 1461 cm^{-1} is a characteristic peak of CH$_2$, band at wavenumber 1236 cm^{-1} is a superposition peak of C-N and C-C, band at wavenumber 1185 cm^{-1} is a characteristic peak of C-O, band at wavenumber 1111 cm^{-1} is a characteristic peak of Si-O-Si, and band at wavenumber 1066 cm^{-1} is a characteristic peak of C-F.

It could be noticed that after the UV aging test, each absorption peak of the coating basically showed an obvious weakening trend, but the characteristic C-F peak at 1066 cm^{-1} wavenumber was significantly enhanced, indicating the UV irradiation great impact on the coating. It may be due to solid particles added to the coating, which increase the degree of pulverization and cracking of the coating under UV irradiation, resulting in severe damage to the coating.

Scanning electron microscopy (SEM)

The morphology of resin and coating samples in the initial state and after 800 h and 1200 h of UV aging was observed using scanning electron microscope and the results are shown in Fig. 6 and Fig. 7.

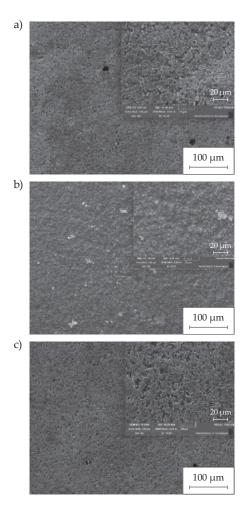In the initial state of resin sample, under the magnification of 500 times, the paint film was flat and smooth, and under the magnification of 2000 times, some shallow folds on the surface were observed. After 200 h of UV aging, the surface of the resin paint film was seriously wrinkled, uniform and dense, and under magnification of 500 times there was a gap between the substrate and the paint film.

In Fig. 7, from left to right, the surface morphology of the coating in the initial state and after 200 h and 800 h of UV aging is visible. It could be observed that the coating surface particles in the initial state were obvious and evenly distributed, and the paint film was glossy, free of cracks and relatively smooth. After 200 h of UV aging the surface of the coating was very dry and rough, almost with no luster, and the gap between particles was obvious. After 800 h of UV aging the surface of the coating was not only dry and rough, but also had small cracks at magnification of 500 times. At higher magnification it could be seen that the surface of the paint film had obvious dry cracks, many cracks, with different lengths and depths, and obvious small pits. It was shown that the UV irradiation could significantly reduce the gloss of the coating surface, dry cracks, pits and voids on the paint film surface, which could accelerate the environment factors to affect the coating, causing the failure of the coating.
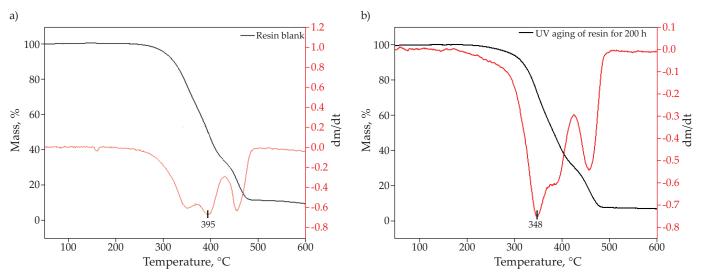
a)

b)

Fig. 8. TGA and DTG curves of resin samples: a) in the initial state, b) after 200 h of UV aging

T a b l e 4. TGA results of resin samples

	$T_{1\%}$, °C	T_{max}, °C	Termination of decomposition temperature, °C	Residue, wt%
Blank sample	263.6	394.5	538.7	11.3
UV-aged for 200 h	249.7	347.7	507.5	7.6

Thermogravimetric analysis (TGA)

Thermogravimetric analysis reflects the weight change of resin and coating with temperature and time to explain the change of weight loss before and after aging. Generally, the higher the degree of crosslinking of the coating, the lower the weight loss.

Fig. 8 and Table 4 show the TGA curve and DTG curve of resin samples in the initial state and after 200 h of UV aging. It could be seen that the initial decomposition temperature ($T_{1\%}$) of blank resin sample was 263.6°C and the maximum weight loss was 88.7%. The initial decomposition temperature of sample UV-aged for 200 h was 249.7°C and the maximum weight loss was 92.4%. This shows the great impact of UV aging on thermal stability and crosslinking degree of the polyurethane resin. After UV aging, thermal stability and crosslinking degree of the resin decreased significantly.

Figure 9 and Table 5 show the TGA curve and DTG curve of the coating in the initial state and after 200 h and 800 h of UV aging. It could be seen that the initial decomposition temperature of the three samples was higher than 250°C, indicating that there were almost no hydrated molecules in the coating samples.

The initial decomposition temperature of blank coating sample was 257.7°C and the maximum weight loss was 55.5%. The initial decomposition temperature of the samples UV-aged for 200 h was 264.6°C and the maximum weight loss was 59.8%. The initial decomposition temperature of the sample aged for 800 h was 268.4°C and the maximum weight loss was 55.4%.
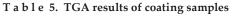
It was shown that the UV irradiation had a significant impact on the thermal stability and crosslinking degree of the coating, and the coating samples aged for 800 h had the best thermal stability, followed by the samples aged for 200 h, and the blank samples which had the worst thermal stability. The change of the crosslinking degree of the sample shown by the weight loss of the sample was as following: the coating sample without UV aging had the highest crosslinking degree, than the coating sample aged for 800 h and the coating sample aged for 200 h had the lowest crosslinking degree, which was also related to the change of its mechanical properties.

CONCLUSIONS

When simulating the influence of ultraviolet light on polyurethane resin and coating in the ocean atmosphere, we found its great influence and destructive effect on both resin and coating.

The research on UV light aging behavior of polyurethane resins and coating showed that UV irradiation had a great impact on polyurethane materials. The resin and coating lost their light after UV aging for 1000 h and 400 h, respectively. The resin reached grade 4 of discoloration after 1200 h of the experiment, however the coating was still discolored at grade 0 after 1200 h of UV aging, indicating that the addition of fillers protected the coating from UV light. The SEM images showed that the resin had obvious wrinkling after 200 h of UV irradiation, and the coating had surface dried and cracked after 800 h. Combined with the TGA curve, it was showed that the crosslinking degree of the coating increased after 800 h

T a b l e 5. TGA results of coating samples

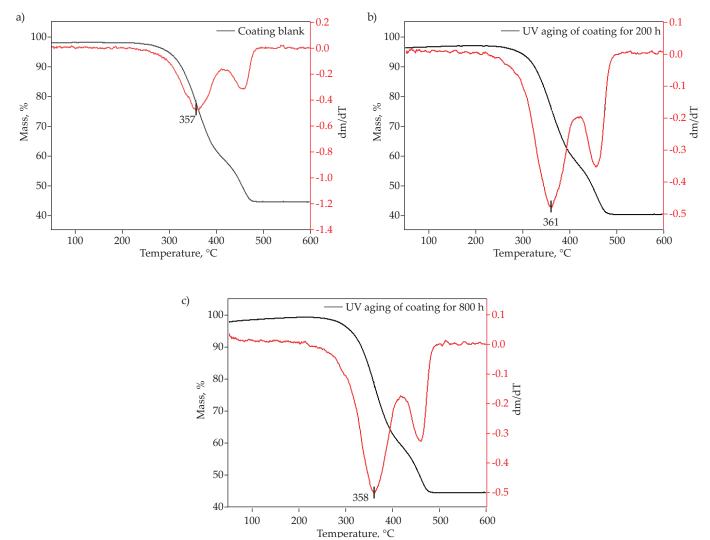|	Temperature of initial decomposition, °C	Max. pyrolysis rate temperature, °C	Termination of decomposition temperature, °C	Residue, wt%
Blank sample	258	357	510	44.5
UV-aged for 200 h	265	361	512	40.2
UV-aged for 800 h	268	358	506	44.6

Fig. 9. TGA and DTG curves of coating: a) in the initial state, b) after 200 h, c) after 800 h of UV aging

of UV aging, and the infrared spectrum analysis showed that the peak of C-C bond and the C-N bond of the polyurethane decreased sharply under the UV irradiation environment. The results show that the surface of the resin and coating was seriously damaged by UV irradiation, but the addition of fillers could protect the coating to a certain extent. Structural damage results in reduced protective properties of resins and coating.

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