

# The effect of a hindered amine light stabilizer on the aging behavior of moisture-curable polyurethane as a cultural relics consolidant

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**Abstract:** This paper aims to study the effect of a hindered amine light stabilizer (HALS 770), on the aging behavior of moisture-curable polyurethane (MCPU). MCPU is specifically developed by ourselves for the reinforcement of fragile organic cultural relics in high-humidity environments, but its aging resistance is insufficient. To improve the aging resistance of MCPU, HALS 770 was used to prepare a modified MCPU (MMCPU). A colorimeter, an infrared spectrometer and a thermal analyzer were used to characterize the color and structure changes of MCPU and MMCPU during aging and to determine their aging kinetics. The results show that the activation energy for the thermal decomposition increased from 91–109 kJ/mol to 135–151 kJ/mol. When the color change is used as the indicator for aging, the lifetime of MMCPU under UV aging is 133% longer than that of MCPU, the lifetime of MMCPU under thermal aging at 293 K is 41.3 times that of MCPU. The addition of HALS 770 to MCPU significantly inhibits the aging behavior.

**Keywords:** moisture-curable polyurethane, hindered amine light stabilizer HALS 770, consolidant, cultural relics, aging, light stabilizer.

## Wpływ aminowego stabilizatora światła z zawadą przestrzenną na starzenie utwardzanego wilgocią poliuretanu stosowanego jako konsolidator zabytków

**Streszczenie:** Zbadano wpływ dodatku aminowego stabilizatora światła z zawadą przestrzenną (HALS 770) na starzenie się poliuretanu utwardzanego w kontakcie z wilgocią (MCPU). MCPU opracowano specjalnie do wzmacniania delikatnych organicznych zabytków kultury w środowiskach o dużej wilgotności, jednak jego odporność na starzenie jest niewystarczająca. W celu zwiększenia odporności na starzenie MCPU modyfikowano (otrzymano MMCPU) dodatkiem aminowego stabilizatora światła z zawadą przestrzenną (HALS 770). Zmiany koloru, przyjęte jako wskaźnik starzenia, i struktury MCPU oraz kinetykę procesu oceniano z wykorzystaniem kolorymetru, spektrometru podczerwieni i analizatora termicznego. Wyniki wskazują, że dodatek HALS 770 w istotnym stopniu hamuje procesy starzenia MCPU – stwierdzono zwiększenie energii aktywacji rozkładu termicznego, z 91–109 kJ/mol MCPU do 135–151 kJ/mol – MMCPU. MMCPU w procesie starzenia UV był o 133% stabilniejszy niż MCPU i 41,3 razy bardziej odporny na starzenie termiczne w 293 K.

**Słowa kluczowe:** poliuretan utwardzany w kontakcie z wilgocią, aminowy stabilizator światła HALS 770, konsolidator, relikty kulturowe, starzenie, stabilizator światła.

Certain archeological sites, such as tombs and grottos, are usually very humid, and the relative humidity is generally above 90%. After an extended burial, the status of organic cultural relics is extremely poor. Such artifacts would easily break with a single touch or scatter on

one blow. Sometimes, the transfer of relics from tombs is impossible without damaging them. Therefore, these fragile cultural relics are usually consolidated with reinforcement materials before they are taken out and transferred to museums. The commonly used materials for

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conservation of cultural relics include acrylic resin [1], poly(vinyl butyral) [2, 3], organic silicon [4] and epoxy resin [5]. However, these materials are mainly used under normal atmospheric humidity conditions. In high-humidity environments, their use commonly results in a series of problems, such as a difficulty in curing, failure to solidify, whitening after solidification, and poor compatibility with organic cultural relics. Moisture-curable polyurethane is a material specially developed to address these problems in the reinforcement and conservation of fragile organic cultural relics in high-humidity environments [6]. The consolidant is colorless and transparent, but its aging resistance is insufficient.

Commonly used stabilizers for polymer materials include ultraviolet absorbers (UVA) [7], HALS (hindered amine light stabilizer) [8], and light shielding agents [9]. For the conservation of cultural relics, UVA is typically used to reduce the aging of protective materials [10]. However, HALS is rarely used for this purpose. HALS 770 (Tinuvin 770) is a hindered amine light stabilizer with a significant inhibitory effect against the aging of polymers [11]. This study used HALS 770 to modify the self-synthesized MCPU (moisture-curable polyurethane) to yield a modified MCPU (MMCPU) and studied the effect of HALS 770 on the aging behavior of polyurethane, providing a reference for studies on the stability of materials employed for the conservation of cultural relics.

## EXPERIMENTAL PART

### Materials

Isophorone diisocyanate (IPDI, 99%), and poly(ethylene glycol) [is also known as *poly(ethylene oxide)* (PEO)] 600 (PEG600) were purchased from Aladdin company. Dibutyltin dilaurate (DBTDL, AR) was produced by Chengdu Kelong.

Bis (2,2,6,6-tetramethyl-4-piperidiny) sebacate (98%) (HALS 770) was obtained from Dongguan Wenhua.

Ethyl acetate (AR) was produced by Tianjin Kemiou Chemical Reagent Co., Ltd.

### Preparation of MCPU and MMCPU solutions

MCPU was synthesized with a 1.11 : 1 : 0.01 mass ratio of IPDI/PEG600/DBTDL. The reaction took place at 60°C for 3 h until the MCPU prepolymer was obtained. And then the prepolymer was dissolved in ethyl acetate to get a 20 wt % MCPU solution.

HALS 770 (1 wt % of MCPU prepolymer) was added to a MCPU solution to get a MMCPU solution.

### Preparation of the MCPU and MMCPU films

3 cm<sup>3</sup> of MCPU solution or MMCPU solution was dropped on a slide and placed in the environments with relative humidity levels about 99%, respectively. The

films were cured for 24 h, and then the colorimetric values and Fourier transform infrared (FT-IR) spectra were measured.

### Methods of aging

Each sample film was placed 5 cm below a 254 nm UV lamp (Zijing, Tianjin China) and exposed to the UV irradiance (245 μW/cm<sup>2</sup> on average) for UV aging and in an oven (DHG-9035A, Shanghai, China) for thermal aging at 373 K or 393 K, respectively.

### Methods of testing

#### Colorimetric measurement

The colorimetric values of the thin films were measured using a Kangguang SC-80C colorimeter (Beijing, China) with a D65 standard light source and an observation angle of 10°. Each sample film was measured on the top of the standard whiteboard of the colorimeter.

#### Infrared spectroscopy analysis

FT-IR spectra of the samples were acquired using the attenuated total reflectance (ATR) accessory of a LUMOS FTIR microscope (Bruker, Germany).

## RESULTS AND DISCUSSION

### Results of UV aging

Light is one of the most important factors affecting the aging of materials for the conservation of cultural relics. In this experiment, 254 nm UV radiation was selected for accelerated aging. During UV aging, the cured film gradually became yellow, but no other aging phenomena, such as bubble formation, brittleness, and tackiness, occurred. Meanwhile, considering the selection of materials for the conservation of cultural relics, the principle of "not altering the original appearance of cultural relics" should be followed; therefore, color was chosen as the evaluation indicator for aging. The chromaticity was described using the CIELab (1976) system. The color difference is expressed as  $\Delta E$  [12, 13]:

$$\Delta E = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2} \quad (1)$$

where:  $\Delta E$ ,  $\Delta L^*$ ,  $\Delta a^*$ ,  $\Delta b^*$  indicate the changes of the color, the  $L^*$  value, the  $a^*$  value and the  $b^*$  value after and before aging respectively.  $L^*$  is used to describe the lightness of the color (0 means black, while 100 means white), the  $a^*$  parameter indicates the green or red axis (negative means green, while positive means red), and the  $b^*$  parameter is used to describe differences in the blue or yellow axis (negative means blue, while positive means yellow).

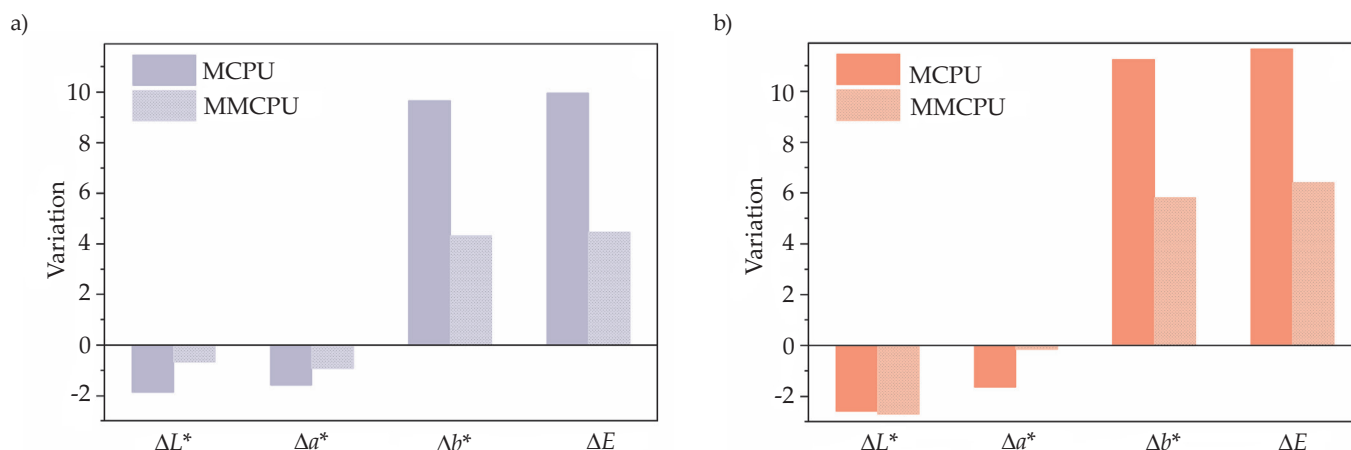


Fig. 1. Changes in the colorimetric values of the MCPU and MMCPU films attributed to aging: a) UV aging for 72 h, b) thermal aging for 21 h at 120°C

When  $\Delta E$  exceeds 6, the color changes significantly. The experimental results show that during the aging process,  $\Delta L^*$  and  $\Delta a^*$  did not change significantly, while  $\Delta b^*$  was substantially increased; in addition, the  $\Delta b^*$  value exceeded 90% of  $\Delta E$  value basically (Fig.1). Therefore,  $\Delta b^* = 6$  was used as the lifetime endpoint in this study.

The  $\Delta b^*$  values of MCPU and MMCPU present linear relationships with time for UV aging (Fig. 2). The slope of the fitted line for the MCPU samples is 0.1338/h, and the lifetime is 45 h, whereas the slope of the fitted line for the MMCPU samples is 0.0575/h, and the lifetime is 104 h. Therefore, after adding HALS 770, the aging rate of MMCPU is reduced by 57%, and the lifetime value of MMCPU is 231% of the original lifetime.

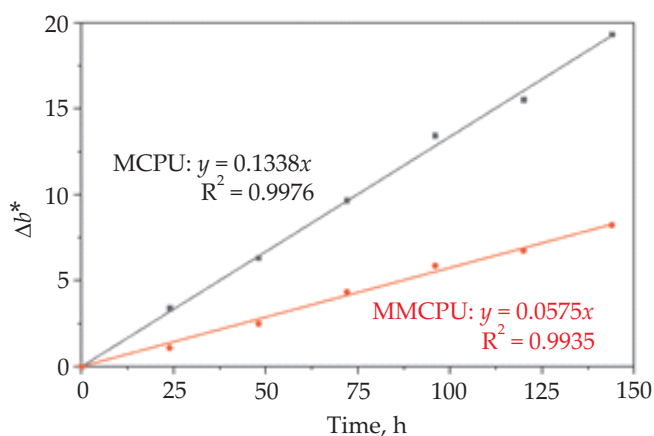


Fig. 2. Relationships between  $\Delta b^*$  of the MCPU and MMCPU films and time during UV aging

### Results of thermal aging

Thermal aging is inevitable in the preservation of cultural relics. When the ambient temperature rises, the thermal motion of molecules inside a material is exacerbated due to the influence of the temperature increase in the material. The reactant molecules acquire more

energy, which can even lead to chain scission. During the thermal aging process, the MCPU films gradually turned yellow, but there were no significant changes in their mechanical properties. The  $\Delta b^*$  values of the MCPU and MMCPU films thermally aged at 373 K and 393 K are shown in Fig. 3. When  $\Delta b^* = 6$  is used as the lifetime endpoint, MCPU exhibits a lifetime of 39 h at 373 K and a lifetime of 10 h at 393 K, whereas MMCPU presents a lifetime of 141 h at 373 K and a lifetime of 22 h at 393 K, which are 3.6 and 2.2 times the values obtained before modification, respectively.

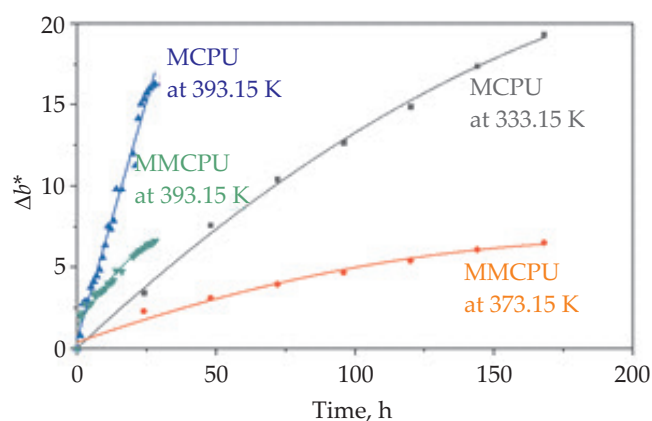


Fig. 3. Relationships between  $\Delta b^*$  of the MCPU and MMCPU films and time obtained during thermal aging

Dakin proposed an empirical equation for thermal aging:

$$\lg \tau = a'/T + b' \quad (2)$$

where:  $T$  is the ambient temperature (K),  $\tau$  is the expected lifetime (h) in the environment at temperature  $T$ , and  $a'$  and  $b'$  are constants.

By introducing the lifetimes of the samples at 373 K and 393 K into the Dakin equation, the lifetime equations for MCPU [Eq. (3)] and MMCPU [Eq. (4)] are obtained:

$$\lg \tau = 4479.1154/T - 10.4138 \quad (3)$$

$$\lg \tau = 5895.7752/T - 13.6503 \quad (4)$$

Consequently, when the temperature was lower, the lifetimes of MCPU and MMCPU were longer, and as the temperature increased, the lifetimes of MCPU and MMCPU decreased sharply; when the temperature was higher, the lifetimes of MCPU and MMCPU were shorter, and the changes in lifetimes with temperature became shallower (Fig. 4). In the 293 K (room temperature) environment, the expected lifetimes of MCPU and MMCPU are 8 y and 330 y, respectively. According to the stability classification of materials for the conservation of cultural relics (Table 1) [14], MCPU and MMCPU can be classified as class C and excellent materials, respectively. The lifetime of the MMCPU is 41.3 times that of MCPU, indicating that the modification greatly improves the thermal stability of MCPU.

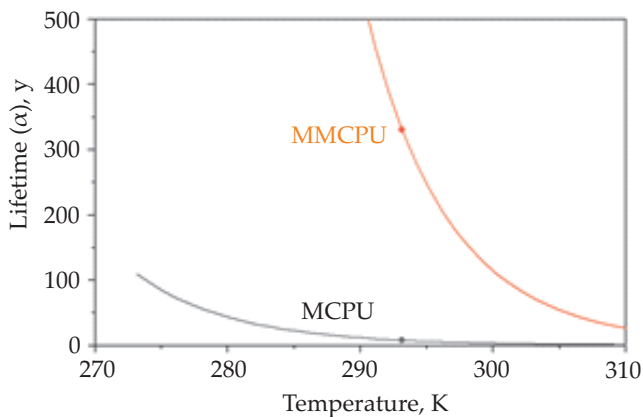


Fig. 4. Relationships between the expected lifetime and temperature for MCPU and MMCPU when using color as the indicator

Table 1. Classification of materials for the conservation of cultural relics according to their stability

Lifetime year	Class	Remarks
0–20	C	Stability needs to be improved
20–100	B	Can be selectively applied for the conservation of cultural relics
100–200	A	Can be applied for the conservation of cultural relics
>200	Excellent materials	Stable materials that are preferred for the conservation of cultural relics

### Aging kinetics

Thermal analysis is an effective means to measure the thermal stability of solid materials and can be used to study the aging kinetics of materials. According to the Coats-Redfern method [15], when  $-\lg [-\lg (1-\alpha) \cdot T^{-2}]$  is linearly related to  $1/T$ , the reaction is first order, in which

$\alpha$  is the conversion rate and  $T$  is the thermodynamic temperature.

In Fig. 5, the data points  $\{-\lg [-\lg (1-\alpha) \cdot T^{-2}], 1/T\}$  for different heating rates are fitted by straight lines ( $R > 0.99$ ). These plots indicate that the reaction orders for the thermal decompositions of MCPU and MMCPU are unrelated to the heating rate; the thermal decomposition reactions at the heating rates of 5, 10, and 15 K/min are all first-order reactions.

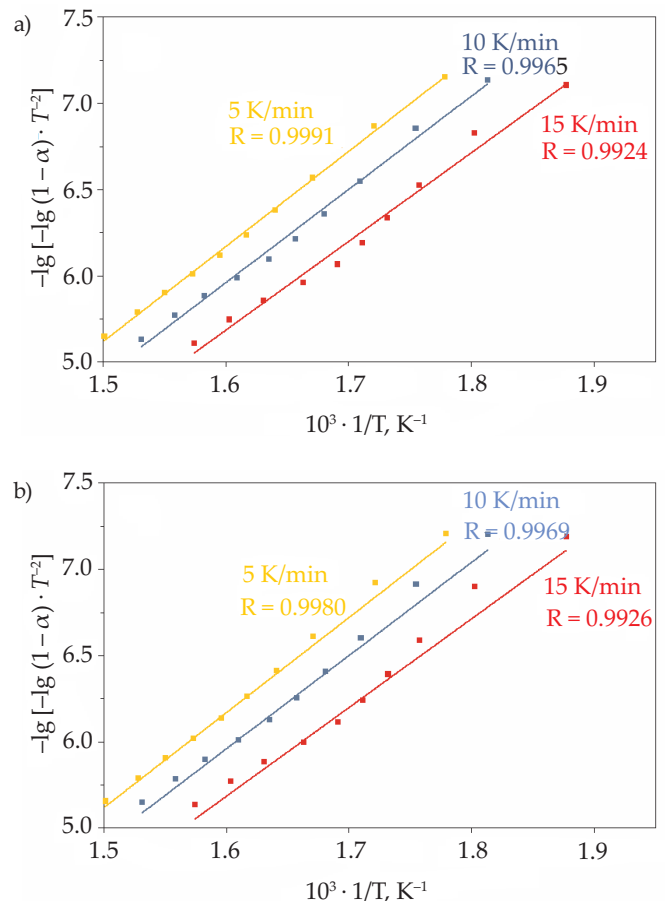


Fig. 5. Kinetic plots of the thermal decompositions of MCPU and MMCPU obtained using the Coats-Redfern method: a) MCPU, b) MMCPU

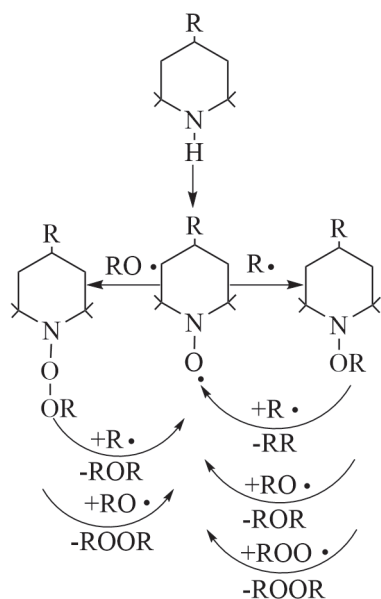
Based on the Arrhenius equation, the transformation of the reaction kinetics equation using Doyle's approximation yields the following equation [16]:

$$\lg \beta = -\frac{0.4567E_a}{RT} + \lg [-AE_a/R \ln(1-\alpha)] - 2.315 \quad (5)$$

where:  $\alpha$  is the conversion rate,  $T$  is the thermodynamic temperature (K),  $\beta$  is the heating rate (K/min),  $A$  is the pre-exponential factor ( $\text{min}^{-1}$ ),  $E_a$  is the activation energy (J/mol), and  $R$  is the ideal gas constant. The plot of  $\lg \beta$  vs.  $1/T$  is a straight line at a fixed conversion rate; thus, the activation energy  $E_a$  can be obtained from the slope, and the pre-exponential factor  $A$  can be derived from the intercept. The activation energy of the thermal decomposition of MCPU is 91–109 kJ/mol, and that of MMCPU is 135–151 kJ/mol (Fig. 6), which indicates that the activation







Scheme A

radicals, and free peroxy radicals, respectively. HALS 770 also reacts with the hydroperoxides produced in the aging process of MCPU and converts them to stable alcohols and ketones. Meanwhile, the generated free nitroxyl radicals further participate in reactions to capture free radicals. This action is the reason why the expected lifetime and stability of MMCPU increases greatly after the HALS 770 modification.

## CONCLUSIONS

During UV and thermal aging processes, the ether bonds of MCPU broke, and the samples gradually turned yellow. After modification with HALS 770, the activation energy for the thermal decomposition of MMCPU became 135–151 kJ/mol, which is approximately 40% higher than that of MCPU. When  $\Delta b^* = 6$  was used as the lifetime endpoint, the lifetime of MMCPU during UV aging was 104 h, which represents 231% of the value for the unmodified MCPU (45 h), whereas the lifetime of MMCPU during thermal aging at 373 K and 393 K are 3.6 and 2.2 times that of the unmodified MCPU. The expected lifetime of MMCPU in the 293K (room temperature) environment was found to be 330 y, which is 41.3 times that (8 y) of the unmodified MCPU. The alicyclic amines in the HALS 770 molecules are converted to free nitroxyl radicals that can be regenerated. The free nitroxyl radicals can effectively capture the free radicals generated during the aging of MCPU and prevent the process from proceeding, thereby stabilizing MCPU. This study shows that HALS 770 significantly inhibits the aging behavior of MCPU, providing a reference on the antiaging of materials for the conservation of cultural relics.

In the future, studies on the aging of MCPU under natural conditions and inside cultural relics will be conducted.

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