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Preparation and Application of Polyurethane Coating Material Based on Epoxy Cyclohexane Protective for Paper

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Abstract: Paper is important to most historical and cultural relics, however, these paper heritages are facing a crisis of disappearance, damage and aging. For increasing the paper strength, delaying the paper aging, and improving the weak stability and permeability of former resins used for paper, another material is necessary to be produced on preservation and protection of the paper items. The synthesis of epoxy cyclohexane polyetherpolyol was as follows: Epoxy cyclohexane was as the starting material, ethylene glycol was as the initiator, boron trifluoride ether was as catalyst, and dichloromethane was as the solvent. The synthesized homopolyether was characterized by infrared (IR) spectroscopy and proton nuclear magnetic resonance (^{1}HNMR) spectroscopy to determine the structure. Then the epoxy cyclohexane homopolyether reacted with the hexamethylene diisocyanate (HDI) trimer, and the polyurethane was obtained. With the tests of the physical and chemical properties of paper samples, it showed that the paper processed with 10% polyurethane liquid had excellent performance, the increase in the tensile strength was from 1105 to 2317 N/m, and the increase in the folding endurance was from 20 to 504 times. What's more, the paper processed with 10% polyurethane liquid had good brightness and gloss. The results of the paper samples for the test have shown that the synthesized material simultaneously has the advantages of epoxy cyclohexane homopolyether and polyurethane, possessing excellent performance in paper reinforcement. Thus, the synthesized polyurethane material has broad application prospect in paper protection field.

Keywords: polyether polyol; polyurethane; paper protection

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1. Introduction

Paper, recording a considerable number of historical information, has gone through for about 2 thousand years. It indicates that archives and libraries worldwide currently have nearly 2.5 million km of paper works for storage [1–6]. After hundreds of years of preservation, a large number of works on paper become weak and brittle. Thus, another material is necessary to be produced on preservation and protection of the paper items.

In the 1950s, conservators used organic polymer materials in the protection of paper because of their water resistance, corrosion resistance, high strength, excellent processing performance and various forms of application [7,8]. Among these materials, although polyurethane resin has good impact strength, a low curing temperature and abrasion resistance, it is easy to produce yellowing characteristics and instability. Polyether polyols are important raw materials in the preparation of polyurethane materials. Polyether polyols are polymers in which the polymeric molecular chain contains an ether linkage (R–O–R) and the terminal group is an –OH group. In the presence of a catalyst, a compound containing an active hydrogen atom (such as a group containing –OH or $–NH_2$) is used as a

starting agent, and a small molecule compound with an epoxy structure is prepared by ring-opening polymerization [9]. Traditional polyurethane materials will turn yellow after long-term outdoor exposure. Transparent polyurethane materials not only have the excellent properties of ordinary polyurethane, but also have high transparency, so transparent polymer materials have been researched in recent years [10]. The reason why conventional polyurethane is opaque is that the microscopic incompatibility between the soft segment and the hard segment causes microphase dispersion, which causes the surface light to be dispersed. For this reason, conventional polyurethane is mainly used in fields where the transparency requirement is not very high [11]. The main factors affecting the opacity of polyurethane are the type of isocyanate, the composition of the chain extender, the composition and molecular weight of the flexible segment, the crystallization of the flexible rigid segment, the thermal history and the synthesis method [12–15]. The crystallization of the segments is an important factor affecting the transparency of polyurethane. If the soft segment and the hard segment are crystallized, the transparency will be affected. Usually, polyether polyol is used to synthesize transparent polyurethane [16,17]. The rigid six-membered ring of epoxy cyclohexane can improve the anti-reciprocating folding ability of paper under a certain tension, and the synthesized polyurethane based on epoxy cyclohexane homopolyether has better transparency. Comparing to our previous study of the paper strength method by resin, hexamethylene diisocyanate (HDI) trimer penetrated more easily into the paper fiber and offered wettability into the fiber for its low molecular weight [18]. It increases the paper strength, delaying the paper aging, and improving the weak stability and permeability of former resins, more over, avoids the weakness of the resin molecular weight on luster and texture.

So far, the epoxy cyclohexane homopolyether reacted with the hexamethylene diisocyanate (HDI) trimer, and the polyurethane was obtained. With the tests of the physical and chemical properties of the paper samples, it showed that the synthesized material simultaneously has the advantages of epoxy cyclohexane homopolyether and polyurethane, possessing excellent performance in paper reinforcement [19].

2. Materials and Methods

2.1. Materials

The epoxy cyclohexane used was of industrial grade and obtained from Shenma Group (Pingdingshan, China). Dichloromethane was purchased from Tianjin Komeo Chemical Reagent Co., Ltd. (Tianjin, China). Boron trifluoride diethyl etherate, sodium hydroxide and anhydrous ethanol were procured from Tianjin Chemical Reagent Plant 3 (Tianjin, China). Ethyl acetate, dibutyltin dilaurate and N,N-dimethyl formamide were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the above reagents were of analytical grade, with no more purification. The HDI trimer, industrial grade, obtained from Bayer (Leverkusen, Germany). Xuan paper were purchased from the Xuan Paper Company (Xuancheng, China).

2.2. Preparation of Epoxy Cyclohexane Homopolyether

According to the mechanism of cationic ring-opening polymerization of epoxy compounds, glycol is used as an initiator, boron trifluoride ether is used as a catalyst, and epoxy cyclohexane is a monomer molecule with chain growth. Glycol reacts with boron trifluoride ether, then an oxonium ion with a positive charge at the active center was produced between the intermediate product that is generated and epoxy cyclohexane [20]. The reaction temperature was controlled below 10 °C. 5 h later, 20 mL of distilled water was added to stop reaction establishment, then the product was poured out, washed by sodium hydroxide solution. When the product was reversed into a single-necked flask, vacuum distillation started. Through removing the unreacted raw materials and solvent, the ultimate product was obtained [6].

2.3. Preparation of Polyurethane Based on Epoxy Cyclohexane Homopolyetheryl

HDI trimer (40 g) and epoxy cyclohexane homopolyetheryl (5 g) were mixed into acetic ether (30 g), tiny amounts of dibutyltin dilaurate (0.2 g) was then added as the catalyst. The content of isocyanate (–NCO) was measured regularly during the reaction, once the content of –NCO increased to 15%, the synthesis was terminated.

2.4. Preparation of Paper Samples

For futher evaluating the effect of polyurethane, Xuan paper, similar to the paper used for cultural heritages, were adopted as paper samples. Xuan paper were cut into the standard size (210 mm × 297 mm). With immersion in different concentrations of the polyurethane liquids for 2–5 min, then the coated paper samples were dried at room temperature. A set of samples were as the blank test, the other set of samples were coated with obtained polyurethane material.

2.5. Analysis and Testing Methods

The tensile strength determination of the paper was processed refering to the Chinese standard GB/T 12914-2008 (ISO 12914-2:1994, MOD) [21] by PN-TT300 (Hangzhou Pin Heng Technology Co. Ltd., Hangzhou, China), with a speed of 20 mm per minute. The paper samples were 24.0 cm in length and 1.5 cm in width. The folding endurance determination of paper was processed at a force of 4.9 N refering to the Chinese standard GB/T 457-2008 (ISO 5626:1993, MOD) [22] by a PN-NZ135 double-fold instrument (Hangzhou Pin Heng Technology Co. Ltd, Hangzhou, China). The test specimens were 15.0 cm in length and 1.5 cm in width, and the applied force was 4.91 N. The tearing strength determination of the paper samples was processed refering to the Chinese standard GB/T 455-2002 (equiv. ISO 1974:1990) [23] by PN-TT1000 (Hangzhou Pin Heng Technology Co. Ltd., Hangzhou, China), and the paper samples were 6.5 cm in length and 5.0 cm in width. The gloss determination of the paper was processed refering to the Chinese standard GB/T 8941-2013 (ISO 8254-1-2009, MOD) [24] by a PN-GM glossmeter (Hangzhou Pin Heng Technology Co. Ltd., Hangzhou, China) with 75° geometries. The brightness determination of the paper was processed refering to the Chinese standard GB/T 7974-2013 (ISO 2470:1999, MOD) [25] by a brightness tester PN-48B (Hangzhou Pin Heng Technology Co. Ltd., Hangzhou, China). The reflectance mode was applied in configuration, and the spectral range increased from 457 nm with a step of 10 nm. In addition, the brightness was shown by R457 in the study [6,20].

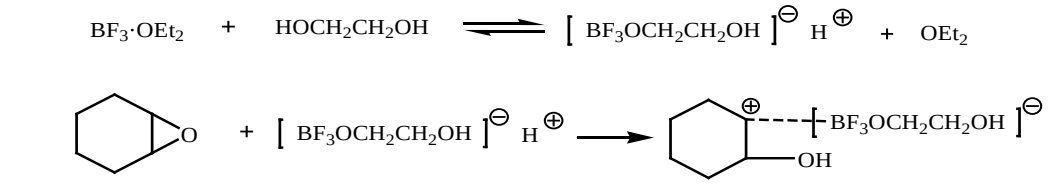
3. Results and Discussion

3.1. The Reaction Mechanism of Epoxy Cyclohexane Homopolyether

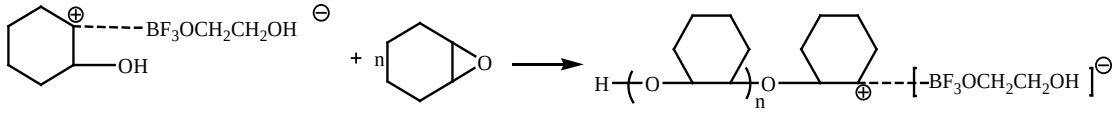
By catalytic reaction, the epoxy cyclohexane homopolyether was synthesized between the catalyst boron trifluoride ether and the initiator glycol. The reaction mechanism of polymerization is similar to that of the cationic ring-opening polymerization of epoxy compounds [6,26]. The reaction mechanism is as follows: Glycol reacts with boron trifluoride ether, and the intermediate product that is generated reacts with epoxy cyclohexane to form an oxonium ion with a positive charge at the active center [20]. The ring-opening polymerization process with the active oxygen group of epoxy cyclohexane is divided into the chain initiation stage, chain growth stage and chain termination stage. The polymerization mechanism is shown in Scheme 1.

The synthesis process of epoxy cyclohexane homopolymer is shown in Figure 1. The product of the synthetic epoxy cyclohexane homopolymer is colorless and transparent, as shown in Figure A1 (Appendix A).

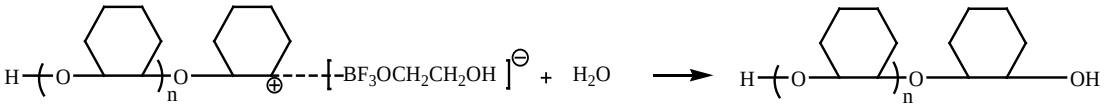
First step:



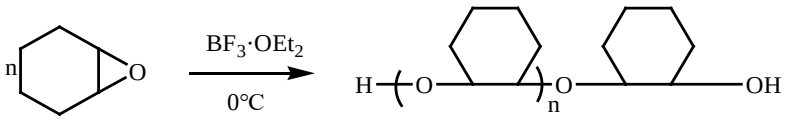
Second step:



Third step:



The total equation is as follows:



Scheme 1. The reaction mechanism of epoxy cyclohexane homopolyether.

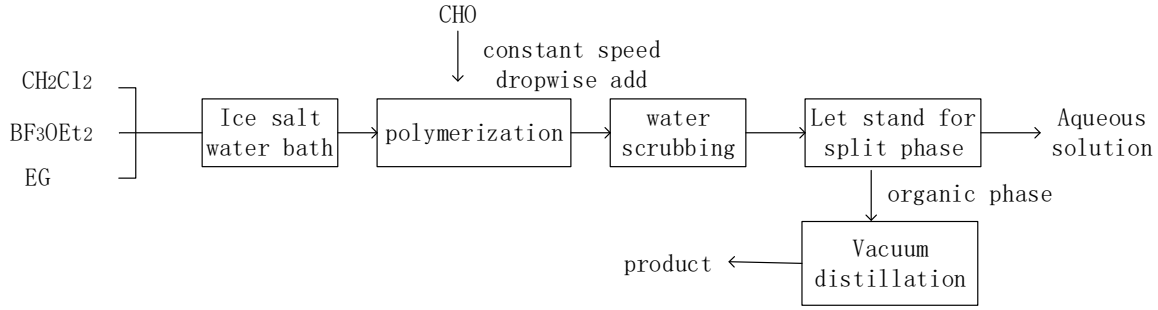


Figure 1. Synthesis of epoxy cyclohexane homopolymer.

The IR spectrum of epoxy cyclohexane homopolymer is shown in Figure 2. As can be seen from Figure 2, the characteristic absorption peak of O–H is at 3442 cm^{-1}. The strong absorption peaks at 2933 and 2864 $cm^{-1}$are the absorption peaks of the methylene and methine groups. The characteristic vibration absorption peak of the C–H bond is at 1451 cm^{-1}. There is a strong absorption peak at 1092 cm^{-1}, which is not only the absorption peak of the aliphatic ether bond, but also the absorption peak belongs to the iconic functional group of the obtained product. The absorption peaks of the C–C skeleton are at 850 and 551 cm^{-1}. From the analysis, it was shown that the epoxy cyclohexane was subjected to ring-opening polymerization to form a terminal hydroxyl polyether structure.

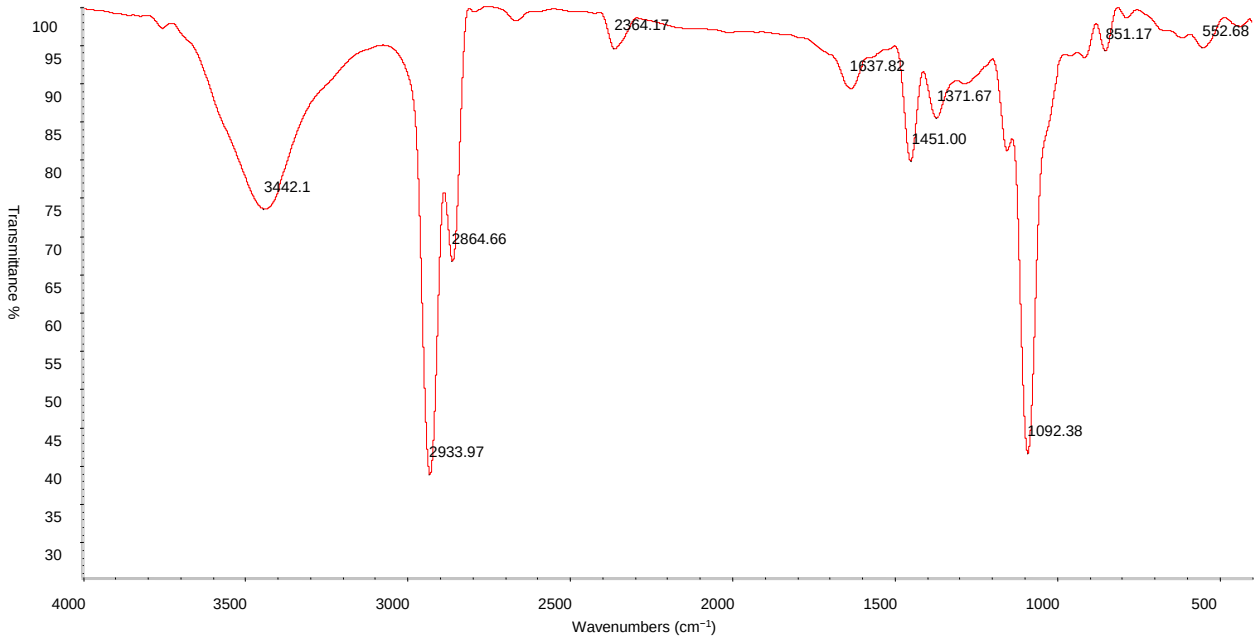


Figure 2. Infrared (IR) spectroscopy of synthetic epoxy cyclohexane homopolymer.

The proton nuclear magnetic resonance(^{1}HNMR) spectroscopy of epoxy cyclohexane homopolymer is shown in Figure 3. As can be seen from Figure 3, there is a proton peak at δ 3.4, which is the proton peak of the C connected to the O in epoxy cyclohexane. There is a proton peak at δ 1.0−2.0, which is the proton peak of the C unconnected to the O in epoxy cyclohexane, and the proton peak at δ 3.0 belongs to the terminal hydroxyl group. The peak of the solvent is at δ 7.26.

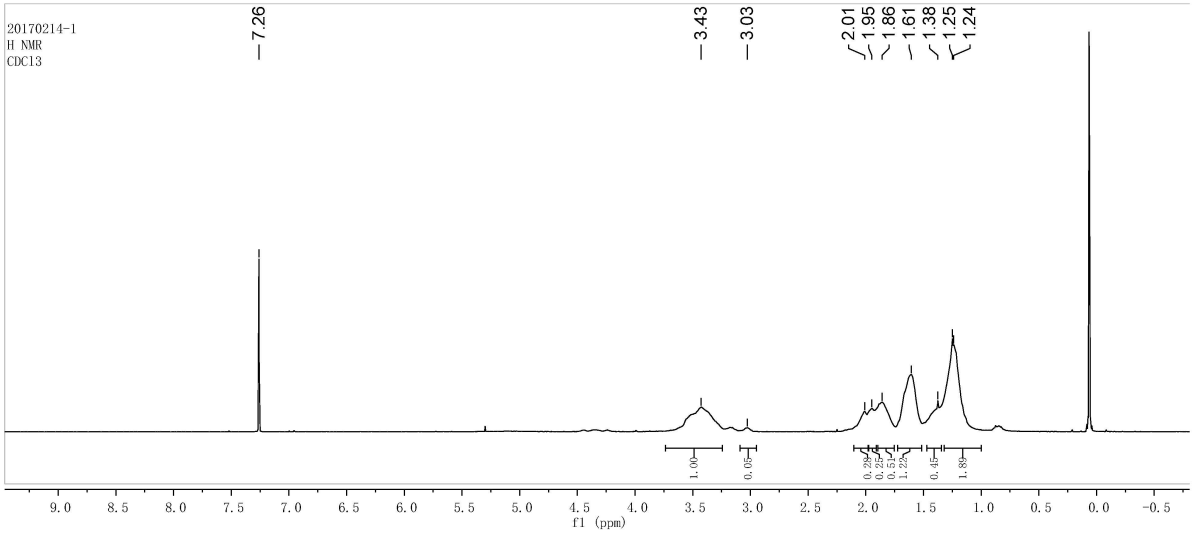


Figure 3. Proton nuclear magnetic resonance (^{1}HNMR) of synthetic epoxy cyclohexane homopolymer.

Epoxy cyclohexane homopolyether was dissolved in N,N-dimethyl formamide, then gel permeation chromatography was performed. The results are as follows:

$$\overline{Mw} = 1386.7,\ \overline{Mn} = 1066.9,\ D = \overline{Mw}/\overline{Mn} = 1.30.$$

$\overline{Mw}$: The average molecular weight; $\overline{Mn}$: Number-average molar weight; D: Molecular weight dispersion.

The gel permeation chromatogram of epoxy cyclohexane homopolyether is shown in Figure 4.

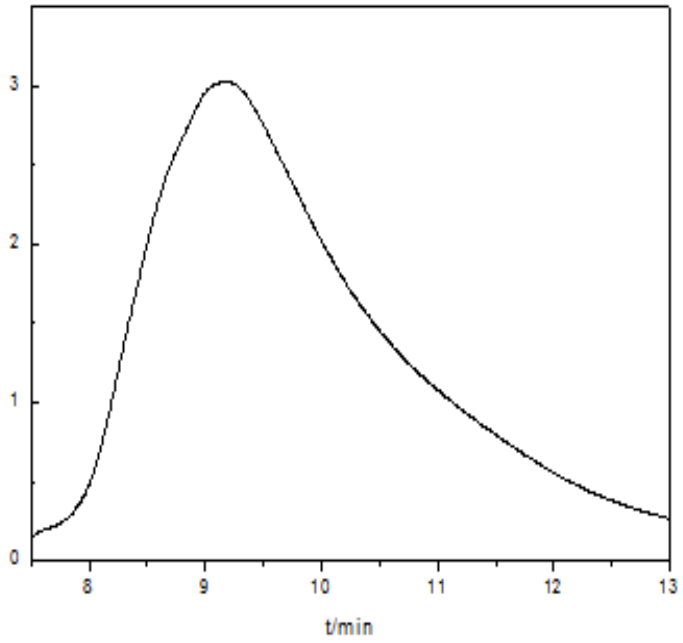
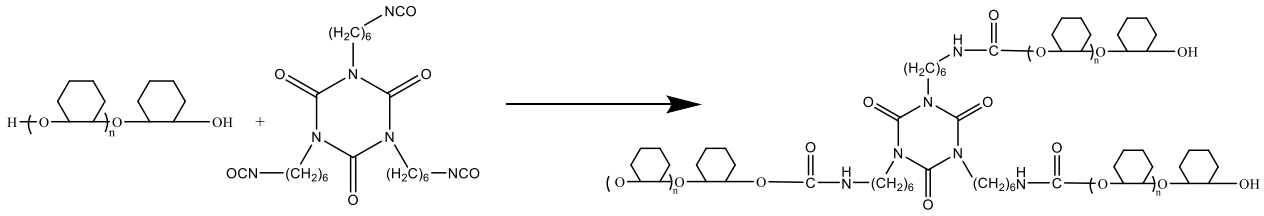


Figure 4. Gel permeation chromatogram of synthetic epoxy cyclohexane homopolyether.

3.2. Properties of Polyurethane Based on Epoxy Cyclohexane Homopolyether

The polyurethane material was produced by epoxy cyclohexane homopolyether and HDI trimer in low-molecular-weight, particularly, it has good performance in the protection of the paper. The reaction mechanism can be seen in Scheme 2. In the use of catalyst dibutyltin dilaurate, the isocyanate group in the HDI trimer showed a high activity with hydroxyl groups of epoxy cyclohexane homopolyether.



Scheme 2. The reaction mechanism of polyurethane based on epoxy cyclohexane homopolyether.

The physical properties of polyurethane based on epoxy cyclohexane homopolyether as a protective material are shown in Table 1. After 1 month of storage, the 25% polyurethane reinforcement fluid exhibited only a small amount of lamination, indicating the fluid was provided with excellent stability.

Table 1. Physical properties of polyurethane at different concentrations.

Sample	5%	10%	15%	20%	25%
Storagestability (>1 month)	stable	stable	stable	stable	lamination
Viscosity/mPa·s	0.9	1.16	1.24	1.3	2.0

In addition, the viscosity is consistent in the permeability of the protective material. The penetration of the paper is inversely proportional to the viscosity, that is, lower viscosity is profitable for penetration. A viscosity range of 0.9 to 2.0 mPa·s is shown in Table 1, which met the demand of the paper.

3.3. Application of Polyurethane Based on Epoxy Cyclohexane Homopolyetheryl as Protective Material for Paper Samples

In this section, mechanical properties of Xuan paper were researched, it was affected by polyurethane based on epoxy cyclohexane homopolyetheryl in different concentrations. As seen in Figure 5a, it shows that the tensile strength of the coated paper improved effectively, indicating that polyurethane based on epoxy cyclohexane homopolyetheryl could strengthen the fibers of the paper. At the same time, with the increase of mass concentration, the tensile strength of the paper treated with polyurethane liquid firstly increased, when the mass concentration was 25%, the tensile strength decreased. As the mass concentration of polyurethane increasing to 20%, the tensile strength of paper increased from 1105 to 3039 N/m. This is due to the fact that the paper and polyurethane may form a network, but when the quality score continues to increase, the paper may become brittle. However, when the paper was treated with a higher concentration of polyurethane, the tearing strength and folding endurance decreased. Thus, for the reinforcement of precious papers, many mechanical indicators of the paper should be considered. Elongation is another important tensile property of paper. The trend of the elongation adjusted to the mass concentrations can be seen in Figure 5b. It has Similar trend to Figure 5a. While mass concentration rising, the elongation displays rising and then decline. The reason may be that the hydrogen bonds are replaced by carbamate bonds in the fibers, enhancing the bonding force in the paper fiber. The folding endurance of paper in concentration growth is depicted in Figure 5c. As can be seen that the folding endurance of the coated paper is higher than that of the blank paper samples, it due to that the fibers of the coated paper have more capability of holding the original flexibility during the folding process. When the mass concentration of polyurethane reached to 10%, the folding endurance of paper increased from 20 to 504 times, approximately 24.2 times higher than that of the blank paper. The tearing strength of the paper was tested via a mechanical rupture process initiated and propagated at a high stress concentration, which then caused a cut. And the tearing strength was researched, shown in Figure 5d, similarly, it was affected by mass concentration. Specifically, when the mass concentration was at 10%, a maximized tearing strength of the paper was obtained [6,19]. It indicates that the broken fibers were interconnected by polyurethane. This is confirmed in the SEM image.

The gloss and brightness of the paper were further determined, for finding the effect of polyurethane reinforcement liquids on the appearance of the paper. The results are listed in Table 2. G75 gloss was determined at 75°. The brightness of R457 represents the papers' reflection ability of the light of around 457 nm. After the treatment, the brightness and gloss of the paper samples did not change significantly.

Overall, taking all factors (e.g., folding endurance, tensile properties, brightness and gloss, tearing strength) into consideration, the optimal mass concentration of polyurethane based on epoxy cyclohexane homopolyetheryl is 10%.

For comparing the effect of the protective materials on thickness of the paper, the thickness of the paper samples was determined five times by a micrometer. The series of blank paper samples were categorized as group A. The series of paper samples that coated with 10% polyurethane based on epoxy cyclohexane homopolyetheryl were categorized as group B. Then the thickness was determined, and the results are shown in Table 3. The difference in thickness is 0.0018 mm. It indicates the effects of polyurethane on paper thickness are negligible.

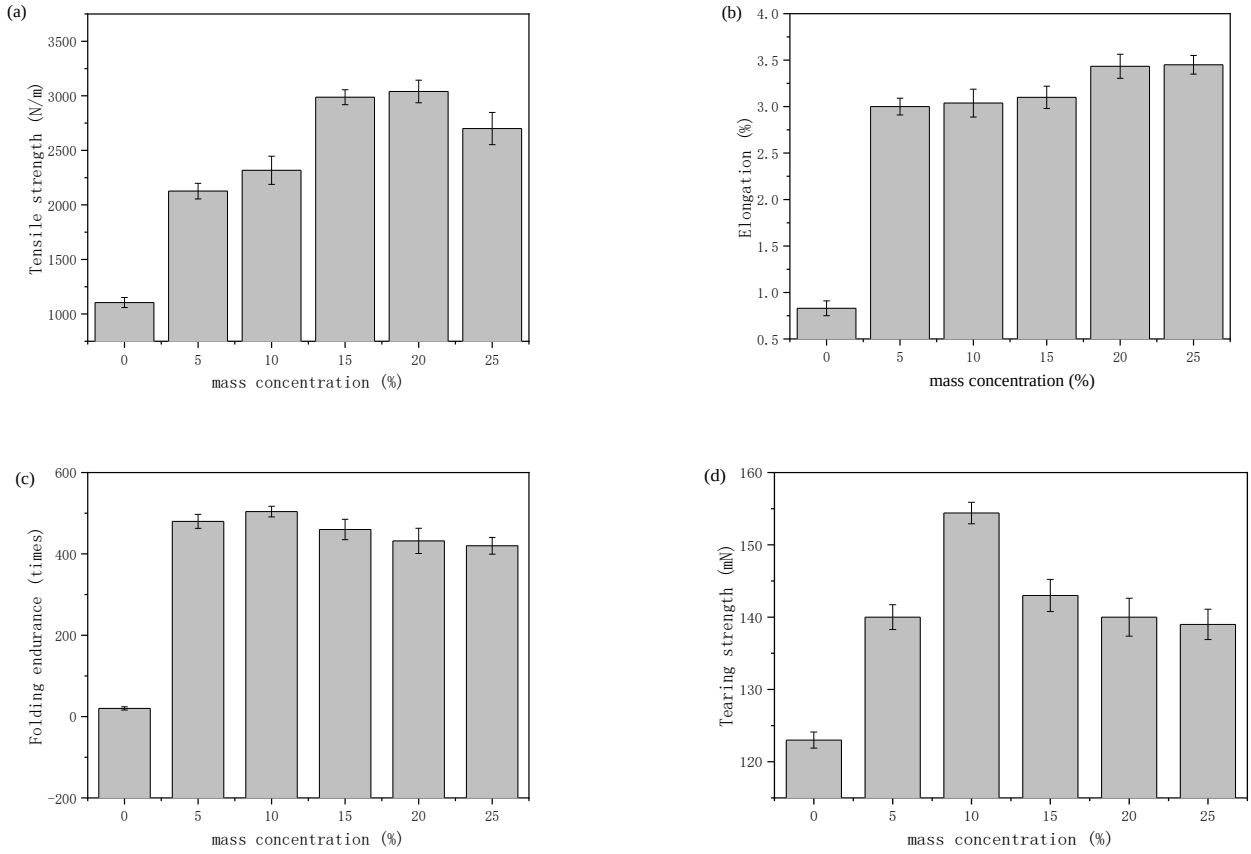


Figure 5. Mechanical properties of the paper treated with different concentrations of polyurethane: (**a**) Tensile strength of the treated paper; (**b**) Elongation of the treated paper; (**c**) Folding endurance of the treated paper; (**d**) Tearing strength of the treated paper.

Table 2. Brightness and gloss of the paper treated with different concentrations of polyurethane.

Mass Concentration (%)	0	5	10	15	20	25
R457—brightness (%)	75.9 ± 0.1	74.4 ± 0.1	73.0 ± 0.1	72.9 ± 0.1	72.6 ± 0.1	69.9 ± 0.1
G75—gloss	5.0 ± 0.1	5.0 ± 0.1	4.9 ± 0.1	4.8 ± 0.1	4.6 ± 0.1	4.5 ± 0.1

Table 3. Thickness of paper samples.

Sample	Thickness/mm				Average/mm
A	0.087	0.088	0.088	0.089	0.0880
B	0.089	0.089	0.090	0.091	0.0898
Thickness difference	0.002	0.001	0.002	0.002	0.0018

Finally, the synthesized epoxy cyclohexane polyurethane was dried to form a coating on the surface of the paper, filling the gaps in the paper fibers, enhancing the binding force between fibers and improving paper performance. Due to the rigid six-membered ring of epoxy cyclohexane, coating the synthetic polyurethane on the surface of the paper helps the paper to resist external forces, and the tensile strength, folding endurance, elongation and tearing strength are improved. At the same time, because of the ring-opening polymerization of cyclohexane, the synthesized epoxy cyclohexane polyurethane has a six-membered rigid chain structure with large steric hindrance, so the molecular chain is disordered, hard to crystallize, and transparent, with good brightness and gloss.

A scanning electron microscope (SEM) was applied to determine the surface and cross-section of the paper samples. The SEM images of the surface of the paper samples are shown in Figure 6. The SEM image of the untreated paper sample showed closely packed cellulose fibers, with an interwoven network with no deformation. As shown in Figure 6b, there is a layer of high molecular connection between the fibers. The broken fibers of the paper sample were interconnected and strengthened. The result demonstrates that polyurethane based on epoxy cyclohexane homopolyetheryl can satisfy the request of the paper protection.

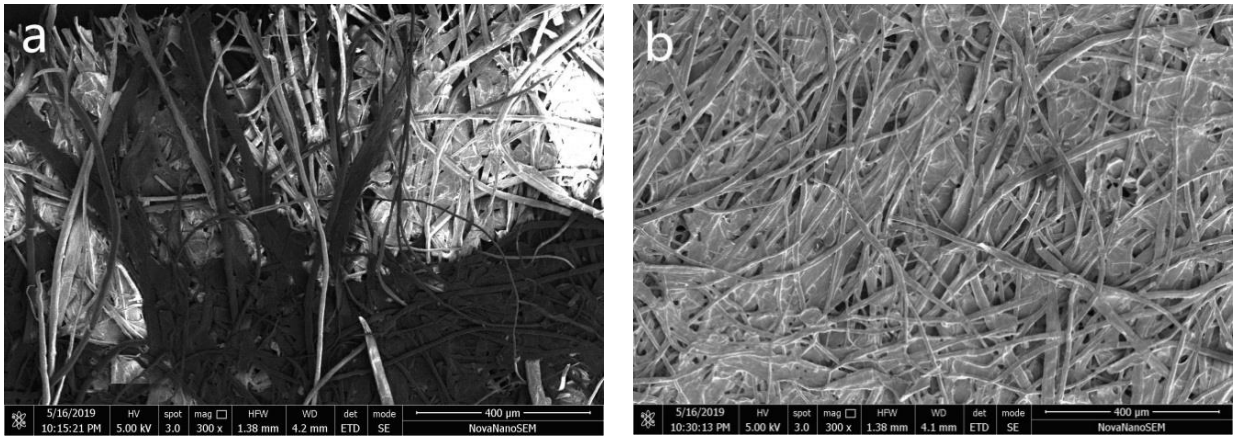


Figure 6. Scanning electron microscope (SEM)images showing the surface of the Xuan paper before (**a**) and after (**b**) treatment with polyurethane liquid.

4. Conclusions

In this study, polyether polyol was obtained from epoxy cyclohexane. The homopolymer of epoxy cyclohexane was characterized by IR spectra and ^{1}HNMR spectroscopy. The synthesized polyurethane was characterized by its physical properties (storage stability and viscosity), and its application in paper protection and preservation was researched. The results showed that epoxy cyclohexane achieved ring opening, and a homopolymer of epoxy cyclohexane with a hydroxyl end was obtained. Moreover, the polyurethane material prepared using the homopolymer is stable at room temperature, and the paper treated with it has excellent mechanical properties. This study provides an innovative solution for paper conservation.

Author Contributions: Conceptualization, H.L. and S.-S.J.; methodology, H.L. and S.-S.J.; validation, H.L., J.L., and S.-S.J.; formal analysis, S.-S.J. and J.L.; investigation, H.L. and S.-S.J.; resources, Y.-P.Q. and Y.-F.S.; data curation, S.-S.J., J.L., Y.-P.Q., and Y.-F.S.; literature retrieval and chart making, J.L.; writing—original draft preparation, S.-S.J., J.L., and H.L., revision of manuscripts, S.-S.J., J.L., Y.-P.Q., Y.-F.S., and H.L.; writing—review and editing, H.L.; supervision, H.L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compound epoxy cyclohexane homopolymer are available from the authors.

Abbreviations

The following abbreviations are used in this manuscript: HDI: hexamethylene diisocyanate, IR: infrared, ^{1}HNMR: proton nuclear magnetic resonance.

Appendix A

The product of the synthetic epoxy cyclohexane homopolymer is colorless and transparent, as shown in Figure A1.

Figure A1. The production of synthetic epoxy cyclohexane homopolyether.

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