Progress on Modified Polyurethane for Preservation of Paper Cultural Relic

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Abstract:

Paper cultural relics have extremely high value in research and collection. However, as the time goes on and the environment changes, there will be unfavorable conditions on paper relics, like yellowing, moulding, chalking, aging and embrittlement to some extent. Nowadays, the protection and repair of paper cultural relics are the research emphasis in the field of relics protection. The modified Polyurethane (PU) is an effective material for protecting paper cultural relics and overcome the disadvantages of traditional PU material, including poor polar-solvent resistance and poor heat resistance. Therefore, in this article, the synthesis, properties, applications of modified PU material were summarized and prospects for the research development in the future were look forward.

1. Introduction:

Polyurethane (PU) material is an important material which is synthesized via reaction between polyisocyanate and compounds with terminal hydroxyl groups. The backbones of PU macro-molecules contain urethane groups. PU macro-molecules contain a large number of strongly-polar groups and soft segments like polyether and polyster, which grants PU material with high mechanical strength, oxidation stability, fine solvent resistance, water resistance and fire resistance. PU material has wide applications for its outstanding properties. The isocyanate groups with high reactivity on PU macro-molecules could crosslink with hydroxy groups on paper fiber under room temperature. Thus, PU material can be applied in reinforcing the paper relic, to improve the mechanical strength of the paper relic and prolong its life. Furthermore, the modified Polyurethane could hold better properties to satisfy the requirements of paper relic protection.

2.Modified methods of PU material:

Common materials used for modified PU include: organosilicone, nano-SiO2, acrylic resin, epoxy resin and some natural products.

1). Organosilicone modification:

Modified PU with organosilicone could improve the flexibility and the surface hydrophobicity of PU glue, thereby the water resistance and mechanical property of paper relics could be improved. [1]

Methods of modified PU with organosilicone include: simple bleeding method, in-situ polymerization method and co-polymerization method. The co-polymerization method is better than the others. According to the molecular structure of organosilicone, the co-polymerization method could be divided into: silanol modified

method, aminoalkyl polysiloxane modified method, hydroxyalkyl polysiloxane modified method and alkoxy silane modified method. [2]

However, the organosilicone is expensive and some researches indicate that organosilicone couldn't dissolve uniformly in PU material. Thus, in the field of paper relics protection, organosilicone modified method need to be optimized via combining different methods.

2). Nano-SiO_2 modification:

Nano-SiO2 is small in dimension and is apt to distribute between macro-molecular chains. Meanwhile, there are a large number of active hydroxyl groups existing on the surface of nano-SiO2. These active hydroxyl groups are prone to form hydrogen bond with PU molecules. Nano-SiO2 modification could improve the adhesive property, mechanical property and heat resistance of PU material.

Methods of modified PU with nano-SiO2 include: sol-gel method, in-situ polymerization etc.

Gao Lijun's team utilized Diphenyl-methane-diisocyanate (MDI), polyneopentylene-hexamethylene adipate glycol (PHA), Poly-1,4-butylene adipate (PBA) as ingredients, utilized nano-SiO2 as modified material, single component wet curing PU was prepared [3]. The research indicates that, the PU property is best when w(nano-SiO2) =1.2%.

Gao Yanfei used 3-triethoxysilyl-1-Propanamine (KH550) and tetraethyl orthosilicate (TEOS) as materials, nano-SiO2 was lead into the PU, and a solvent-free PU for paper/plastic flexible packing was prepared. The research shows that, the peel strength of modified PU is relatively high in the case of w(nano-SiO2)=0.8%. Besides, nano-SiO2 could be used for surface modification in advance; thus its surface property is optimized and makes it distribute uniformly [4].

modified PU by nano-SiO2 possesses outstanding comprehensive performances. Besides, nano-SiO2 won't contaminate paper relics. So, nano-SiO2 is an ideal modifier for PU applied in preservation of paper relics. Also, nano-TiO2, nano-CaCO3 and other inorganic nano material could be utilized as modifiers. The main disadvantage of nano-SiO2 modification is that: nano-SiO2 is prone to coalesce because of its high surface energy. So it should be modified in advance to decrease the number of active hydroxyl groups on its surface. It could also be dispersed with ultrasonic to make it distribute uniformly in PU prepolymer.

3). Acrylic resin modification:

Acrylic resin possesses outstanding properties like: weather resistance, water resistance and alkali resistance. Modified PU with acrylic resin could make up for the disadvantages of PU in these aspects.

Modified methods include: blending modification, copolymerization method and graft modification.

Li Zhihua's team utilized isophorone diisocyanate (IPDI), acrylic acid, butyl acrylate, methyl methacrylate, polyether glycol (GE230) and dihydromethyl propionic acid (DMPA) as materials, modified water polyurethane by acrylic resin was synthesized via blending modification, copolymerization method and graft modification

[5][6][7]. The properties of three products were compared. After analysis on particle size, transparency, chemical resistance, molecule structure and micro-structure of those emulsions, it is found that PU molecules have good compatibility with acrylic resin molecules and they could achieve complementary advantages. The comprehensive properties of PU material got improved, and the property for modified PU via graft method is better than the others.

4). Epoxy resin modification:

Epoxy resin molecule contains more than two epoxy groups along with some hydroxy groups. The epoxy resin could bring more branched structures to the backbones of PU molecules and form partial-mesh structures, which can improve the mechanical property, water resistance and chemical resistance of PU material. Epoxy resin modified methods includes: blending method, graft copolymerization method and epoxy open loop method.

Zheng Fei utilized polytetramethylene glycol (PTMG) and isophorone diisocyanate (IPDI) as main ingredients, modified PU material by epoxy resin was synthesized [8]. First, epoxy resin with terminal hydroxyl groups via reaction between epoxy resin and diglycolamine was synthesized. Then, epoxy resin modified waterborne PU material via copolymerization method was synthesized. The results indicate that: the epoxy resin modified waterborne PU material has better stability when w (epoxy resin) < 5%. As the content of epoxy resin increases, the tensile strength of PU material increases and the elongation at break decreases. Besides, epoxy resin modification improved the heat resistance of waterborne PU.

However, the β carbon atom on expoxy group is prone to be attacked by nucleophile (like hydroxy group and water) and electrophile (like Lewis acid), and the epoxy group could get opened, which makes the quality of PU unstable. So, modified PU by epoxy resin is not suitable for paper relic protection.

5). Natural products modification:

Zhang Hao blended waterborne PU (WPU) with nanocrystalline cellulose (NCC) modified by organosilicon coupler, and synthesized NCC/WPU composite material possessing well-distributed structure [9]. The result indicates that, the yellowing resistance and abrasive resistance of modified PU material got improved prominently.

As the main component of paper, cellulose could modify PU adhesive without bring any contamination to paper relics, which has good prospect in paper relics protection area.

Other natural products modifier include: lignin, montmorillonite etc.

6). Other modifier:

Light aging is a challenge for paper relics protection. The modified PU by ultraviolet absorbent was prepared, and the optimal condition was obtained after testing and evaluating [10].

3. Forecast:

As a historic country of culture, China possesses a large number of precious paper relics. The protection of paper historical relics is urgent need for development. PU adhesive has broad prospect in protection of paper culture relics for its outstanding mechanical properties and chemical resistance. There are two aspects need optimizing: ①Select suitable isocyanate which could permeate well in paper, dry fast and has good comprehensive properties. ②Select suitable modifier and modify PU via single or composite methods to improve the comprehensive properties of PU adhesive, so as to meet the requirements of paper relics protection.

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