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Synthesis and properties of UV-curable self-healing oligomer

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ABSTRACT

A novel UV-curable self-healing oligomer was designed on the basis of a quadrupolar hydrogen bond system. The oligomer is formed by reacting a mixture of a hydrogen bonding group and a photosensitive monomer with three-arm polyols. The structure was identified using ^{1}H NMR and the real-time FTIR was used to observe the conversion of double bonds. The self-healing property was monitored by optical microscopy and atomic force microscope, and the gloss induced by damaging and healing processes was tested using a glossmeter. Furthermore, a thermogravimetric analyzer was used to test the thermostability. The healing performance was considerably improved with the increasing content of the ureido-pyrimidone dimer. The results revealed that the reversibility of the quadrupolar hydrogen bond system is beneficial to the healing capacity.

1. Introduction

The concept of self-healing materials was proposed in 1981 [1] as a method for healing invisible microcracks to prolong their service life and ensure safety in the process of using them. In 2001, White [2] proposed the liquid encapsulation concept: a self-healing effect from the combination of an encapsulated healing agent and a dispersed catalyst. Since then, several related encapsulation approaches for anticorrosive coating applications have been reported [3–8]. Although self-healing coatings are a promising means of improving the anticorrosion performance of materials, some limitations should not be ignored: the healing with these methods just can happen only once and the healing agent dispersed in the matrix may affect the general performance of the coating. The storage stability of microcapsules is a crucial factor in their applications. For these reasons more people focus on the research of intrinsic healing approaches: [9–12] using reversible physical or chemical bonds to help materials flow to damaged areas and achieve repairing. This method does not require the addition of healing agent and repeated repairing can be allowed in the same area. The concept of hydrogen bonds in healing applications [13,14] is worth investigating because of high healing efficiency and moderate repairing condition. Mahesh V. et al. [15] reported light-healable nanocomposites based on a telechelic poly (ethylene-co-butylene) that was functionalized by using hydrogen-bonding ureido-pyrimidone (UPY) and cellulose nanocrystals decorated with the same binding motif. The research revealed that on the basis of the hydrogen bond principle, the sample exhibited improved mechanical properties compared with the supramolecular polymer alone and demonstrated easier healing with higher healing efficiency.

UV-curing technology is an environmental protection, energy saving and efficient green technology. It avoids the defect of thermal curing, which can cause damage at high temperature for some heat-sensitive substrates. In recent years, UV-curing has developed rapidly in many applications. The technology is now extensively used for coating, [16,17] electronic engineering [18] and printing industries, [19] et al.

In this study, we combined the UV-curing technology and self-healing concept to design a novel UV-curable self-healing oligomer which was based on a quadrupolar hydrogen bond system. The healing ability was demonstrated through optical microscopy observations, atomic force microscope and gloss measurements. It is found that the coating is easy to heal the broken areas and the self-healing process could be repeated several times. The UV-curing process was monitored using real-time FTIR. Furthermore, thermostability was tested using a thermo gravimetric analyzer (TGA).

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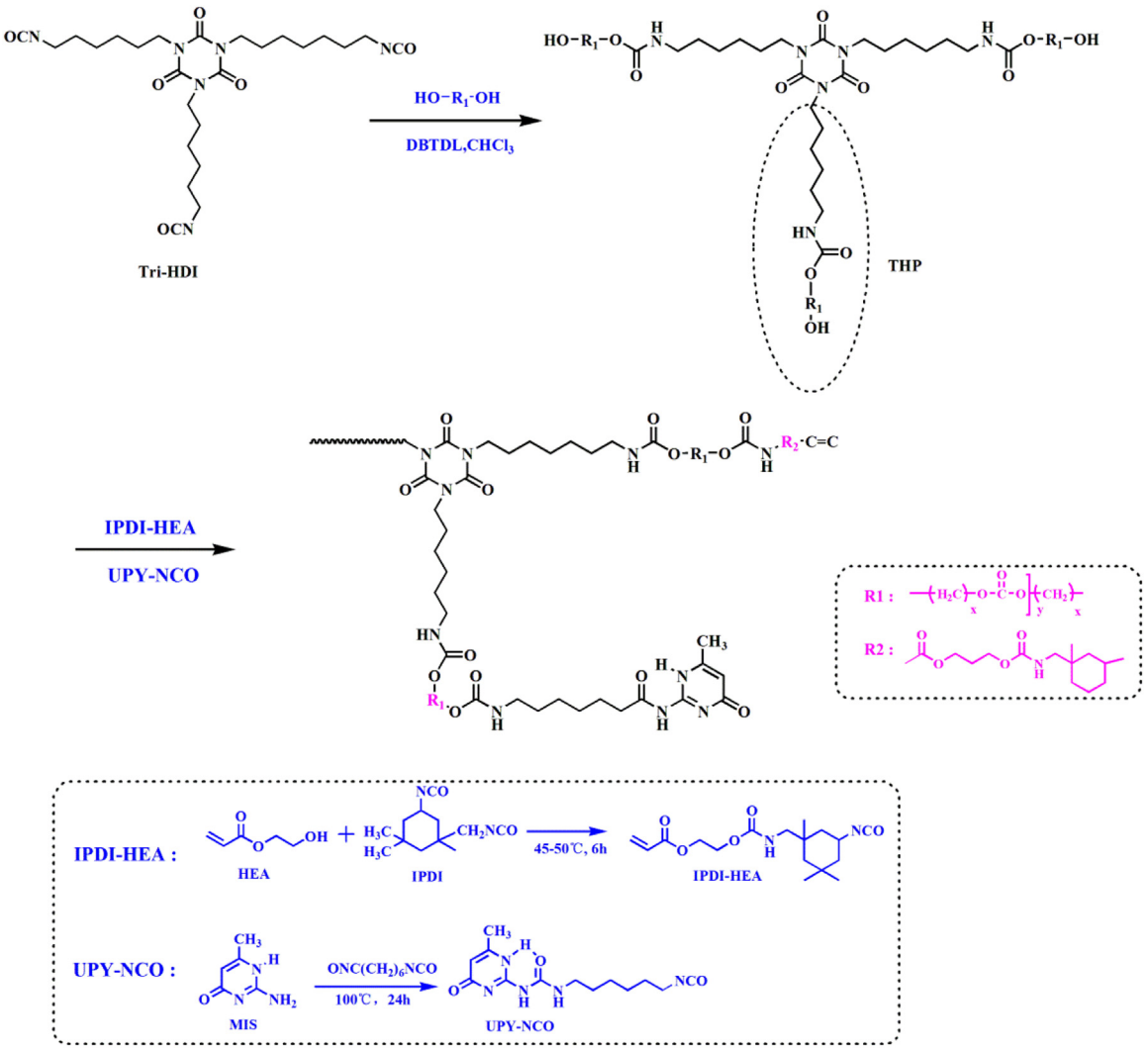

Fig. 1. The synthetic of $THPU_XC_Y$.

2. Experimental

2.1. Materials

A tri-functional homopolymer of hexamethylene diisocyanate (Tri-HDI) was supplied by Bayer Materials Science Company. Polycarbonate diols (PCDL500, M_W = 500) was obtained from Asahi-KASEI. 4-Methoxyphenol (MEHQ), dibutyltin dilaurate (DBTDL) and chloroform were purchased from Sinopharm Chemical Reagent Co. Ltd. 6-Methylisocytosine (MIS) was acquired from TCI Shanghai.

2.2. Synthesis of UPY-NCO and IPDI-HEA

A mixture of 0.01 mol 6-Methylisocytosine (MIS) and 0.062 mol HDI was stirred at 100 °C for 24 h. After the reaction, the mixture was added to hexane. The resulting precipitate was filtered and washed with hexane more than three times. The obtained white powder was dried at 30 °C under vacuum and designated as UPY-NCO.

Isophorone diisocyanate (IPDI) (0.05 mol) with catalyst DBTDL and inhibitor 4-methoxyphenol were placed in a four-necked round-bottom flask equipped with an additional funnel, a condenser and a mechanical stirrer. Then, 0.055 mol 2-hydroxyethyl acrylate (HEA) was added to IPDI at a constant and slow speed to ensure that the isocyanate content was constant during the reaction. The product was IPDI-HEA.

2.3. Synthesis of $THPU_xC_y$ resin

UV-curable self-healing oligomers were prepared through a two-step route as depicted in Fig. 1. Tri-HDI was added at a constant and slow speed into a mixture of PCDL and catalyst DBTDL in chloroform ($CHCl_3$) at 60 °C for several hours until all the isocyanate was used. The product was three-arm polyols (THP). THP, UPY-NCO and IPDI-HEA were mixed and reacted at 60 °C until all the isocyanate was used, thereby obtaining $THPU_xC_y$ resins.

2.4. Preparation and testing of coatings

Q-panel (75 mm × 50 mm) was used as the coating substrate and cleaned with acetone before use. $THPU_xC_y$ resin was mixed with Irgacure 184 (3 wt%) to form a UV-curable coating. Coatings were daubed as 120 μm thickness to the aluminum plates with a doctor blade. The viscosity of each sample was adjusted with an additional solvent. The panel was placed at room temperature for 6 h and then baked for 5 h at 60 °C to remove the solvent. Finally, each sample was cured in air on a Fusion LC6 B bench top conveyor with an F300 UVA lamp (UVA intensity of 120 mW/cm^2 measured using a