Preparation and properties of polyurethane acrylates modified by saturated alcohols

Lili Qin, Yong He, Baihua Liu, Yu Jian, Chunguang Li, Jun Nie*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing, 100029, PR China

ABSTRACT

Polyurethane acrylates (PUAs) modified by saturated alcohols were synthesized by saturated alcohols, isophorone diisocyanate (IPDI), 2-hydroxyethyl acrylate (HEA) and polycaprolactone triol (PCL). The molecular structures were identified by Fourier transform infrared (FTIR) spectroscopy. Real time infrared (RTIR) spectroscopy was used to investigate the conversion vs. irradiation time plots of photopolymerization of synthesized PUAs. The volume shrinkage was measured by using laser displacement sensor (LDS). The adhesion in the glass, polycarbonate (PC) and polyvinyl chloride (PVC) substrates was tested by the laser micrometer and universal testing machine. The glass-transition temperature (Tg) and storage modulus (E') were measured by dynamic mechanical analysis (DMA). The pendulum hardness, pencil hardness and flexibility were also tested. The results showed that the synthesized PUAs had low volume shrinkage and excellent adhesion in glass, PC and PVC substrates.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Because of the distinct advantages, such as less environmental pollution, low VOC, fast curing speeds at ambient temperature, excellent film quality, high chemical stability, energy conservation and high production efficiency, the UV curing technology had become commercially important in applications ranging from printing inks, coatings, adhesives, dental composites to photoresist [1–4]. Polyurethane acrylates (PUAs) were widely used as oligomers to control the polymerization kinetic and mechanical properties for UV coatings, due to their excellent physical and chemical properties such as adhesion to substrates, impact property, flexibility, chemical and scratch resistance and weatherability [5–7].

However, one major drawback was their polymerization shrinkage, which was due to the substitution of weak and long distance intermolecular van der Waals bonds of the resin-monomers by strong and short covalent bonds during polymerization [8–10], and would lead to materials failures and shorten service life of photopolymerization materials.

The reduction of photopolymerization volume shrinkage had been the subject of numerous studies which could be summarized in two categories: addition of fillers or additives [11–16], and changes in monomer structure. The chemical methods were the most important and convenient way. It was proved that

reducing the double bond density by improving the molecular weight or reducing the double bond functionality of the monomer or oligomer was efficient to decrease the volume shrinkage [17–20]. Another selection was introducing rigid groups which were difficult to deform in photopolymerization [21]. It was also demonstrated that the introduction of ring-opening polymerization monomers such as the monomers with spiro ring or epoxy structure leading to volume expansion could reduce the volume shrinkage in photopolymerization [22–25]. Introducing flexible fragment into the molecular chain and improving the flexibility of molecules were also proved to be effective methods to reduce the volume shrinkage. Hilonga et al. [26] found that the volume shrinkage of the aerogels prepared by long chain alkyl group solvents was lower than that in alkyl groups with shorter chains. Jiang et al. [27] found that the volume shrinkage decreased with the increase of monomer chain, because the longer chain length could lead to the lower double bond density and improve the flexibility of molecules. The saturated long chain alcohols had high flexibility, if it was introduced into the oligomer structure, a part of the volume shrinkage generated by photopolymerization was expected to be offset. Furthermore, according to the molecular bonding adhesion mechanism [28], the adhesion between cured film and substrate would also be improved. Therefore, it was expected that low volume shrinkage and high adhesion polymer films would be obtained when the flexible long chain was incorporated into PUA structure.

In this study, a series of PUAs modified by saturated alcohols with different chain length were synthesized to study the relationship between the chain length of saturated alcohols and volume shrinkage. It was expected that these PUAs had low

---

* Corresponding author. Tel.: +86 10 6442 1310; fax: +86 10 6442 1310.
E-mail address: niejun@mail.buct.edu.cn (J. Nie).

volume shrinkage and excellent adhesion and would exhibit broad prospects for industrial applications.

2. Experimental

2.1. Materials

2-Hydroxyethyl acrylate (HEA), 1,6-hexanedioldiacrylate (HDDA) and CN9001NS were supplied by Sartomer Co., USA. Isophorone diisocyanate (IPDI) was purchased from shanghai First Reagent Co., China. Dibutyltindilaurate (DBTDL) and p-methoxyphenol (MEHQ) were supplied by Tianjin Fucheng Chem. Co., China, 2-hydroxy-2-methyl-phenyl-propan-1-one (Irg1173) was supplied by ChangZhou Runtec Chemical Co. (Changzhou, China). Polycaprolactone triol was donated by Shenzhen Guanghua Albert Industrial Co. Ltd., China. Saturated alcohols (n-butanol, n-octanol, cetyl alcohol, stearyl alcohol) were supplied by Beijing Chemical Plant (Beijing, China).

2.2. Instrumentation

The determination of the free isocynate-group contents was calculated according to HG/T2409-92, using surplus of diisobutylamine reacted with the free isocynate-groups, titrated back with HCl. Bromophenol Blue was added into the sodium hydroxide solution as a chemical indicator. The reactions were described as follows:

$$R-NCO + (C_4H_9)_2NH \rightarrow RNHCON(C_4H_9)_2$$

$$(C_4H_9)_2NH + HCl \rightarrow (C_4H_9)NH \cdot HCl$$
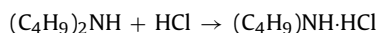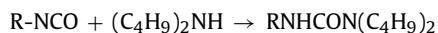
FTIR spectrum was recorded on a Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA). Real-time infrared (RTIR) spectra were used to determine the conversions of double bond. The mixture of monomer and initiator was applied between two KBr crystals and irradiated by UV spot light source (Rolence-100 UV, Taiwan, China) at room temperature. The light intensity on the surface of samples was $30\,mW/cm^2$, which was detected by UV Radiometer (Beijing Normal University, China). For each sample, the series RTIR runs were repeated three times. Because the decrease of absorption of the peak area was directly proportional to the number of polymerized double bond, the degree of conversion (DC) of the =C—H could be expressed as follows:

$$DC(\%) = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 is the =C—H absorbance around $810\,cm^{-1}$ and A_t is the absorbance value at irradiation time t.

The volume shrinkage was directly measured by a self designed real time volume shrinkage measuring apparatus based on the laser displacement sensor (LDS) [29]. It was performed by using a LK-G10 laser navigator (KEYENCE, Japan). The thickness of the sample layer was controlled to around $150\,\mu m$ by coating the sample onto the glass slices (1 mm thickness). The ø30 μm laser beam, initially zeroed on the glass slice, reflected off the surface of the sample to give the thickness of sample layer. The LDS detected the displacement of the sample (dimensional change) due to the shrinkage of photopolymerization by recording the motion of mirror reflecting laser with the fixed reflection angle on charge-coupled device (CCD). The sampling interval was 20 ms. Photopolymerization was irradiation by UV spot light source same as the real time FTIR measurement. Five samples were used for each experiment. CN9001NS from Sartomer was used to compare with the synthesized PUAs, which was aliphatic polyurethane acrylate of two functionalities, as the same with the synthesized PUAs.

The contact angles were measured with $5\,\mu L$ of distilled water droplet placed automatically on the cured film by OCA20 (Dataphysics, Germany).

The adhesion of PUA in glass, PVC, PC substrates was tested by a universal testing machine (Model 1185, Instron, USA). 40 μm thick sample was uniformly spread on the surface of different substrates. The pieces of substrates were overlapped in 10 mm in which the sample was spread and the area of bonding was 10 mm × 20 mm. The UV cured samples were tested by using the testing machine with a crosshead speed of 5 mm/min at room temperature. Five samples were measured for each experiment, and the average of these values was recorded.

Dynamic mechanical thermal analysis was performed on dynamic mechanical thermal analyzer (METZSCH 242C, Germany) at a heating rate of $5\,°C\,min^{-1}$ in the range of −50 to 120 °C with the sheet of 10 mm × 5 mm × 1 mm. The glass transition temperature (Tg) was defined as the peak of tan δ curve. The crosslink densities were calculated from the following formula based on the kinetic theory of rubber elasticity [30]: $v_e = E'/(3RT)$, where E' is the elastic storage modulus on the rubbery plateau region; R is the gas constant and T is Kelvin temperature.

The flexibility property was carried out on a film cylindrical bending test device (QTY-type, Shanghai Instrument Co., China), according to GB/T 1731-93 (National Standard of China).

The pencil hardness was tested according to GB/T 6739-1996. The pendulum hardness was measured according to GB/T 1730-93(B).

2.3. Synthesis process of polyurethane acrylate (PUA)

The synthesis of PUA was carried out in a four-necked glass reactor equipped with a stirrer, a reflux condenser, a thermometer, and an addition funnel. IPDI, HDDA, MEHQ and DBTDL were poured into the glass reactor. PCL was dropped into the reactor slowly at 40 °C. The mixture was stirred quickly for 10 min, then the temperature of above reaction mixture was raised to 50 °C, until the NCO content was below the calculated point. The change of NCO value during reaction was determined by using the dibutylamine back titration method according to HG/T 2409-92 (Industry Standard of China). When the NCO value decreased to 50% of origin value, the first step reaction was finished.

Then, the reaction temperature was dropped to 40 °C, HEA was dropped into the reactor. The mixture was stirred quickly for 10 min, then the temperature of above reaction mixture was raised to 70 °C, until the NCO value decreased to 16.7% of origin value, the second step reaction was finished.

After that, the reaction temperature was dropped to 40 °C, the saturated alcohol (n-butanol, n-butanol, cetyl alcohol or stearyl alcohol) was added into the reactor. The mixture was stirred quickly for 10 min, then the temperature of above reaction mixture was raised to 70 °C, until the FTIR peak at $2267\,cm^{-1}$ for the —NCO group disappeared. The synthetic route was shown in Fig. 1 (take n-butanol as example).

Different kinds of saturated alcohols (n-butanol, n-octanol, cetyl alcohol, stearyl alcohol) were added respectively to prepare oligomer PUA with different chain length. The physical properties of CN9001NS and these synthesized PUAs were shown in Table 1, the Mn and concentration of double bonds were calculated.

2.4. Sample preparation

The UV curing sample was prepared by adding 1173 into the synthesized PUA (which had been added into 20 wt% HDDA) at the mass ratio of PUA:1173 as 97:3, named S_1, S_2, S_3 and