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Exploration for decreasing the volume shrinkage for photopolymerization

Tongzhou Jiang, Yong He*, Yu Jian, Jun Nie

State Key Lab of Chemical Resource Engineering and Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

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ABSTRACT

This article explored one method to decrease the volume shrinkage for photopolymerization including synthesis of a series of methacrylate–vinyl ether hybrid monomer, combination initiator system and introduction of chain transfer agent. Its photopolymerization kinetics was monitored by Fourier transform real-time infrared spectroscopy (FTIR) and the volume shrinkage is measured by using laser displacement sensor (LDS), the adhesion strength is also evaluated. The results indicated that the volume shrinkage could be adjusted in some degree on demand which is good for adhesion strength.

1. Introduction

It is well known that the volume shrinkage is one of the primary reasons leading to some deficiencies of photopolymerization materials. Because when the inherent polymerization shrinkage strain is frustrated by sufficient interfacial adhesion between the polymer and base substrate, stress is conveyed to the substrate. If the stress exceeds the adhesive strength of any component of the system, the micro- or macro-defect can emerge [1–3]. But the bulk volume shrinkage in photopolymerization is an unavoidable result of the formation of new covalent bonds taking place the van der Waals force. Recently, many works have been focused on it [4,5].

Numerous studies have been carried out to reduce the polymerization volume shrinkage, which could be divided into three types: changes in monomer structure or chemistry [6], addition of fillers or additives [7–9], and changing process condition [10–12]. The chemical methods are most important and convenient way. It is proved that the free radical/cationic hybrid system, such as (meth)acrylate/vinyl ether, is efficient to decrease the volume shrinkage due to the two polymer network formation, especial for those flexible structure containing system [13–16]. Another selection is epoxy photocuring system, because expansive ring open reaction could decrease the shrinkage [17–19]. It was also demonstrated that introduction of ordered liquid crystal structure leading to amorphous polymer could decrease shrinkage and stress [20]. Furthermore, the thiol–vinyl system could be a good candidate for its step polymerization mechanism [21–24]. It is apparent that the key point to decrease the polymerization volume shrinkage is to adjust the chemical component and control the polymerization kinetic character.

In this study, we construct a hybrid monomer system consisted of methacrylate double bond and vinyl ether double bond simultaneously, similar with we have reported previously [25,26]. We try to control the double bond conversion and kinetic of photopolymerization to adjust the shrinkage via combination initiator and chain transfer agent. We hope to improve the adhesion ability of this system to some usual substrate easily and give some instructive information for application in high resolution material.

2. Experimental

2.1. Materials

Ethylene glyol monovinyl ether (EGE), 4-hydroxybutyl vinyl ether (HVE), and diethylene glycol monovinyl ether (DGE) were used as received (TCI, Japan). 1,4-cyclohexanedimethanol vinyl ether (CVE) was used as received (J&K Chemical, China). CN710 (Sartomer, USA) was also used without further purification. The comparing monomers, ethylene glycol dimethacrylate (A*), 4-hydroxybutyl dimethacrylate (B*), diethylene glycol dimethacrylate (C*) were donated by Eternal Chemical Company (Taiwan, China). The triarylsulfonium salt (45 wt% solution in propylene carbonate, UVI-6976) and 2-hydroxy-2-methyl-1-phenyl-1-propanone (Irg1173) were donated by Runtec Chemical Company

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* Corresponding author.
E-mail address: heyong@mail.buct.edu.cn (Y. He).

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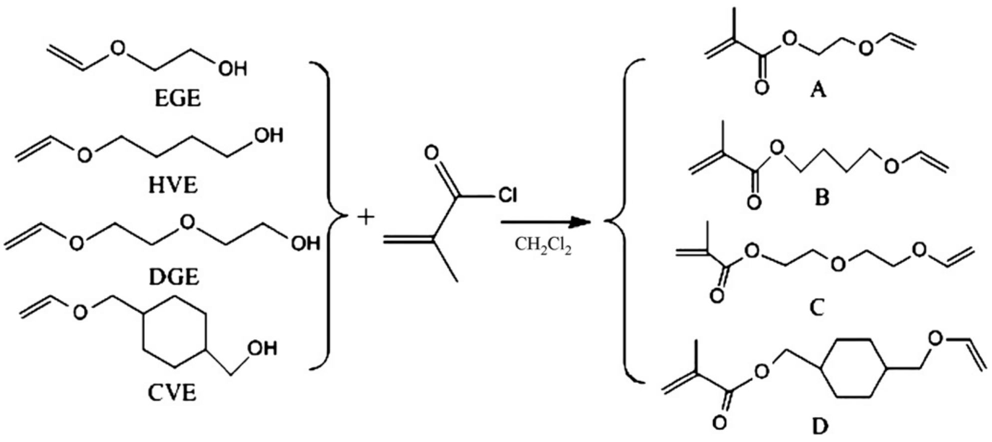

Fig. 1. Synthetic route of the hybrid monomers.

(Changzhou, Jiangsu, China). Methacryloyl chloride, triethylamine, 1-dodecanethiol and other reagents were of analytical grade (Beijing Chemical Reagent Company) and were used without further purification.

2.2. Synthesis of the hybrid monomers

For hybrid monomer 2-(vinyloxy)ethyl methacrylate (A), a mixture of 0.5 mol of ethylene glycol monovinyl ether (EGE) and 0.7 mol of triethylamine dissolved in 100 mL of dichloromethane was added into a three-necked flask equipped with stirrer, thermometer, and dropping funnel. Under cooling condition (0–5 °C) by ice-salt bath, 0.65 mol of methacryloyl chloride dissolved in 20 mL of dichloromethane was added over 2 h. The precipitate was filtered off and washed twice with 20 mL of dichloromethane. Then the organic layers were combined and washed with water, 1 mol/L hydrochloric acid and 0.5 mol/L $NaHCO_3$ and dried over night with anhydrous sodium sulfate. The dichloromethane was removed by rotary evaporation. The crude product was purified by silica gel column chromatography using dichloromethane/petroleum ether (3/1, m/m) as eluent and yield is 60%.

The hybrid monomers 4-(vinyloxy)butyl methacrylate (B), 2-(2-(vinyloxy)ethyloxy)ethyl methacrylate (C) and (4-((vinyloxy)methyl)cyclohexyl)methyl methacrylate (D) were all synthesized by the similar esterification method. The synthesis process is shown in Fig. 1.The product was identified by FTIR and ^1H NMR.

IR (cm^{-1}): A: 3039.1 ($\nu_{=C-H}$), 2950.8, 2915.4, 2869.7 ($\nu_{=C-H_2}$, $\nu_{=C-H_3}$), 1722.9 ($\nu_{C=O}$), 1664.7 ($\nu_{C=C}$), 1636.8 ($\nu_{C=C}$), 1191.6 (ν_{C-O}), 813.1 ($\nu_{C=C}$). B: 3040.7 ($\nu_{=C-H}$), 2949.7, 2917.3, 2870.3 ($\nu_{=C-H_2}$, $\nu_{=C-H_3}$), 1719.4 ($\nu_{C=O}$), 1666.2 ($\nu_{C=C}$), 1635.6 ($\nu_{C=C}$), 1192.0 (ν_{C-O}), 815.3 ($\nu_{C=C}$). C: 3040.1 ($\nu_{=C-H}$), 2950.1, 2916.2, 2868.9 ($\nu_{=C-H_2}$, $\nu_{=C-H_3}$), 1719.6 ($\nu_{C=O}$), 1667.7 ($\nu_{C=C}$), 1637.0 ($\nu_{C=C}$), 1191.6 (ν_{C-O}), 815.7 ($\nu_{C=C}$). D: 3037.3 ($\nu_{=C-H}$), 2948.6, 2913.9, 2867.9 ($\nu_{=C-H_2}$, $\nu_{=C-H_3}$), 1718.3 ($\nu_{C=O}$), 1663.5 ($\nu_{C=C}$), 1635.8 ($\nu_{C=C}$), 1190.8 (ν_{C-O}), 813.2 ($\nu_{C=C}$).

^1HNMR δ (ppm): A: 6.48, 6.14 (d, 2H, $CH_2{=}$), 6.45 (d, 1H, $-OCH{=}CH_2$), 4.19, 4.04 (d, 2H, $-OCH{=}CH_2$), 4.37 (t, 2H, $-COOCH_2-$), 3.93 (t, 2H, $-CH_2OCH{=}$), 1.94 (d, 3H, $-CH_3$). B: 6.47, 6.43 (d, 2H, $CH_2{=}$), 6.09 (d, 1H, $-OCH{=}CH_2$), 4.19, 4.15 (d, 2H, $-OCH{=}CH_2$), 3.99 (t, 2H, $-CH_2OCH{=}$), 3.97 (t, 2H, $-COOCH_2-$), 1.93 (d, 3H, $-CH_3$), 1.79 (m, 2H, $-CH_2CH_2OCH{=}$), 1.74 (m, 2H, $-COOCH_2CH_2-$). C: 6.48, 6.45 (d, 2H, $CH_2{=}$), 6.46 (d, 1H, $-OCH{=}CH_2$), 4.18, 4.16 (d, 2H, $-OCH{=}CH_2$), 4.29 (t, 2H, $-COOCH_2-$), 3.83 (t, 2H, $-CH_2OCH{=}$), 3.76 (m, 2H, $-CH_2CH_2OCH{=}$), 3.72 (m, 2H, $-COOCH_2CH_2-$), 1.93 (d, 3H, $-CH_3$). D: 6.50, 6.44 (d, 2H, $CH_2{=}$), 6.47 (d, 1H, $-OCH{=}CH_2$), 4.15, 3.96 (d, 2H, $-OCH{=}CH_2$), 4.11 (t, 2H, $-COOCH_2-$), 3.50 (t, 2H, $-CH_2OCH{=}$), 1.94 (d, 3H, $-CH_3$), 1.86 (m, 1H, $=COOCH_2-CH-$), 1.82 (m, 1H, $=CH-CH_2OCH{=}$), 1.28, 1.28, 1.17, 1.17 (d, $-4H$, CH_2CH_2-).

2.3. Characterization

2.3.1. NMR

^1H NMR spectra were recorded on a Bruker AV600 unity spectrometer operated at 600 MHz using TMS as an internal reference, with $CDCl_3$ as the solvent.

2.3.2. FTIR

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA). Real-time infrared spectra (RTIR) were used to determine the conversions of double bond. The mixture of monomer and initiator was applied between two KBr crystals and irradiated with UV spot light source (Omnicure S100, EXFO 100 W mercury arc lamp with 5 mm crystal optical fiber, Canada) at room temperature. The light intensity on the surface of samples was 30–50 mW/cm^2, which was detected by radiometry (UV-A, Beijing Normal University, China). Three samples were used for each experiment.

Conversion data of free radical and cationic polymerization could be obtained by monitoring the decay of methacrylate double bond (MDB) peak and the vinyl ether double bond (VEDB) peak. Upon irradiation, the decrease of the methacrylate double bond absorption peak area from 797.5 to 829.3 cm^{-1} and the vinyl ether double bond absorption peak area from 1610 to 1625 cm^{-1} accurately reflect the extent of free radical and cationic polymerization, respectively. 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 function groups could be calculated by measuring the peak area at each time of the reaction by using the following equation [27,28].

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

DC is the conversion at t time, A_0 and A_t are the peak areas of function group before irradiation and at t time respectively.

2.3.3. The measurement of the volume shrinkage

A self designed real time volume shrinkage measuring apparatus was made to directly measure the photo-cure shrinkage 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 μm by coating the sample onto the glass slices (1 mm thickness). The ø30 μm