



# Preparation and characterization of yellowing resistance and low volume shrinkage of fluorinated polysiloxane urethane acrylate



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## ABSTRACT

Fluorinated polysiloxane urethane acrylates were synthesized by 1H,1H,2H,2H-Perfluorooctanol (F13), polysiloxane (PSi), isophorone diisocyanate (IPDI) and 2-hydroxyethyl acrylate (HEA). The molecular structure was characterized by FTIR, GPC, and XPS. The yellowing resistance was measured by sphere Spectrophotometer and ultraviolet-visible spectrophotometer. The volume shrinkage was measured by laser displacement sensor (LDS). The glass-transition temperature ( $T_g$ ) and storage modulus ( $E'$ ) were measured by dynamic mechanical analysis (DMA). Real time infrared (RTIR) spectroscopy was used to investigate the reaction kinetics of photopolymerization of synthesized fluorinated polysiloxane urethane acrylate (PSi-IPDI-HEA-F13). It was proved that the introduced of 1H,1H,2H,2H-Perfluorooctanol into the system of polysiloxane urethane acrylates (PSi-IPDI-HEA) could increase the yellowing resistance and decrease the volume shrinkage. Thermal stability was reduced by a small amount.

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## 1. Introduction

Generally, polyurethane acrylates (PUAs) are composed of polyol or diol, diisocyanate and hydroxyalkyl acrylate. They can perform to transformation from solvent-free liquid to solid almost instantaneously upon UV irradiation and show a range of properties available through the judicious choice of the component of PUAs. This high production rate, energy efficiency and versatility of properties have made them ideal materials for a wide range of applications, including protective coatings for optical fibers, thin film coatings, and photolithography [1–4].

However, two major drawbacks of pretty high yellowing and polymerization shrinkage exist. Yellowing is caused by photo-oxidation or photo-degradation of polymers/coatings upon UV irradiation, which is a common phenomenon especially for those with aromatic structures. Therefore, it is important to impart light stability to the PU coatings by introducing the light stable segments [5].

It is a well-known fact that polysiloxanes (PSi) possesses unique properties, such as good resistance to high temperature, low surface tension and energy, low dielectric constant and high resistance to ozone [6–9]. The introduction of polysiloxane into the PUAs could enhance the thermostability of the UV-cured film and reduce the dispersion surface energy by the change of the microstructure [10]. More importantly, the Si–O–Si as the backbone of polysiloxane will occur much less oxidation or yellowing, for no unsaturated bond and less UV absorption [11]. In addition, isophorone diisocyanate (IPDI) instead of aromatic isocyanates would avoid involving the scission of the urethane group or oxidation of the central methylene group with quinone (yellow) formation as a chromophoric reaction product [12–14].

And polymerization shrinkage is 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, and would lead to materials failures and shorten service life of photopolymerized materials [15–17].

To decrease the polymerization shrinkage, new structures are also the most important and essential way. It was proved in our previous work that reducing the double bond density by introducing long alkyl chain could reduce the volume shrinkage comparing with shorter ones due to lower double bond

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density and higher flexibility, which is believed as one of economic and effective methods [18,19]. The 1H,1H,2H,2H-Perfluorooctanol (F13) also contains the long carbon chain, which should be possible to decrease the polymerization shrinkage. In addition, introduction of fluorinated groups into the PUAs is very attractive because of the peculiar characteristics provided by the presence of fluorine atoms: hydrophobicity, chemical stability, weathering resistance, good release properties, low coefficients of friction, water impermeability, and low refractive indices. At present, fluorinated monomers are used for many coating applications [20–23].

In the present paper, polysiloxane urethane acrylate (PSi-IPDI-HEA) was synthesized by polysiloxane (PSi), isophorone diisocyanate (IPDI) and 2-hydroxyethyl acrylate (HEA) and with or without 1H,1H,2H,2H-perfluorooctanol (F13) as long chain modifier. It was found that the system of PSi-IPDI-HEA has excellent yellowing resistance. Besides, it was proved that the introduction of F13 into the system could help in increased yellowing resistance and reduced the volume shrinkage. In addition, the thermal stability is reduced to a small amount. The photopolymerization properties, glass-transition temperature ( $T_g$ ) and the storage modulus ( $E'$ ) of UV-cured films of PSi-IPDI-HEA and PSi-IPDI-HEA-F13 were evaluated.

## 2. Experimental

### 2.1. Materials

*iso*-Bornyl acrylate (*i*BOA) and aliphatic urethane acrylate (CN9001NS) were supplied by Sartmoer Co., USA. 2-Hydroxyethyl acrylate (HEA), dibutyltindilaurate (DBTDL) and *p*-methoxyphenol (MEHQ) were supplied by Sigma-Aldrich Co. LLC, USA. Isophorone diisocyanate (IPDI) was supplied by Wanhua Chemical Group Co., China. Polysiloxane of X-22-4039 (PSi) was supplied by Shin-Etsu Chemical Co., Japan (Mn: 5000 g/mol, hydroxyl group value: 58.0 mg KOH/g). The molecular structure of polysiloxane (PSi) was showed in Scheme 1. 1H,1H,2H,2H-Perfluorooctanol (F13) was purchased from Hengtong Fluorine Co., China. 2-Hydroxy-2-methyl-phenyl-propan-1-one (Photoinitiator: 1173) was supplied by Tianjing Jiuri Chemical Co., Ltd. China.

### 2.2. Instrument

The Fourier transform infrared (FTIR) spectra was recorded on a Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA), scanned between range from 650 to 4000  $\text{cm}^{-1}$ . 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 385 nm UV-LED source (UVEC-4, Lamplic, China) at room temperature. The light intensity on the surface of samples was 40  $\text{mW}/\text{cm}^2$ , which were 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:

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

where  $A_0$  is the =C–H absorbance around 810  $\text{cm}^{-1}$  and  $A_t$  is the absorbance value at irradiation time  $t$  [24].

The elemental composition and surface morphology of the UV-cured films was observed by using X-ray photoelectron spectroscopy (XPS, and Thermo Electron Corporation, Escalab 250, Germany).

The molecular weight of the prepolymer was determined by a Waters 515-2410 gel permeation chromatograph (GPC, Waters). Tetrahydrofuran, 1.0 mL/min, was used as the mobile phase. The

GPC instrument was calibrated by using multiple linear polystyrene (PS) standards.

The yellowness index was measured by SP60 Portable Sphere Spectrophotometer (X-Rite Instrument, X-Rite Company, USA). Five points of each cured film was measured and averaged in the ultraviolet aging test before and after. Optical transmission spectra were measured by SP752-PC ultraviolet-visible (UV-vis) spectrophotometer over the wavelength range from 350 to 900 nm [10].

Thermo gravimetric analysis (TG) was conducted on a Q500 thermogravimetric analyzer (TA instruments, USA) at the scanning rate of 10  $^{\circ}\text{C}/\text{min}$  in a nitrogen flow. Measurements were collected from 30 to 750  $^{\circ}\text{C}$ .

Dynamic mechanical thermal analysis was performed on dynamic mechanical thermal analyzer (NETZSCH 242C, Germany) at a heating rate of 5  $^{\circ}\text{C}/\text{min}$  in the range between –120 to 150  $^{\circ}\text{C}$  with the sheet of dimensions 10 mm  $\times$  5 mm  $\times$  3 mm. The glass transition temperature ( $T_g$ ) was defined as the peak of  $\tan \delta$  curve.

The volume shrinkage was directly measured by a self-designed real time volume shrinkage measuring apparatus based on the laser displacement sensor (LDS) [25]. It was performed by using a LKG10 laser navigator (KEYENCE, Japan). The thickness of the sample layer was controlled to around 150  $\mu\text{m}$  by coating the sample on the glass slices (1 mm thickness). The  $\phi 30 \mu\text{m}$  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 done by irradiating using UV spot light source same as the real time FTIR measurement. Five samples were used for each experiment.

The test method for adhesive strength was according to ASTM D3359 and the pencil hardness was tested according to ASTM D3363. The flexibility was measured on a film cylindrical bending test device (QTY-type, Shanghai Instrument Co., China), according to GB/T 1731-93 (National Standard of China) [18].

### 2.3. Synthesis of fluorinated polysiloxane urethane acrylate (PSi-IPDI-HEA-F13)

The synthesis of PSi-IPDI-HEA-F13 (Scheme 1) was carried out in a four-necked glass reactor equipped with a stirrer, a thermometer, an addition funnel and a reflux condenser. IPDI, DBTDL and MEHQ were poured into the four-necked glass reactor, polysiloxane was dropped into the reactor slowly at 40  $^{\circ}\text{C}$  with a small amount of chloroform as solvent (the weight ratio of solvent and polysiloxane were less than 10%). The mixture was stirred quickly for 10 min, then the temperature of above reaction mixture was raised to 45  $^{\circ}\text{C}$ , 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 [26]. When the –NCO value decreased to 50% of original value, the first step reaction was finished. Then the reaction temperature was dropped to 40  $^{\circ}\text{C}$ , mixed HEA and F13 together and dropped them into the reactor. The mixture was stirred quickly for 10 min, then the temperature was raised to 55  $^{\circ}\text{C}$ , until the FTIR peak at 2267  $\text{cm}^{-1}$  for the –NCO group disappeared, the reaction was finished. Table 1 listed the formulas of fluorinated polysiloxane urethane acrylates.

### 2.4. Sample preparation

The UV-cured film was prepared by mixing oligomer (O1, O2 and O3, 70 wt%) and monomer with a certain weight ratio (*i*BOA, 30 wt%) respectively, 1173 of 1 wt% was added to the mixture to form a stock photosensitive liquid, named Samples 1, 2 and 3 (S1,

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