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From rosin to high adhesive polyurethane acrylate: Synthesis and properties

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ABSTRACT

A high adhesion polyurethane acrylate (HPUA) was synthesized from isophorone diisocyanate (IPDI), hydroxyethyl acrylate (HEA) and hydrogenated rosin. The chemical structure was characterized by ^{1}H NMR and FTIR; storage modulus and glass transition temperature (T_g) were measured with dynamic mechanical analyzer. Real time infrared spectroscopy (RTIR) was used to investigate the effect of different concentrations of photoinitiator on the double bond conversion of HPUA. Real time volume shrinkage and adhesion on glass, poly(ethylene terephthalate) (PET), polycarbonate (PC) and polyvinyl chloride (PVC) substrates were also measured by laser micrometer and universal testing machine. Results showed that this kind of HPUA has a high photopolymerization rate, low volume shrinkage and high adhesion compared with commercial polyurethane acrylate competitor.

1. Introduction

Owing to its numerous distinct advantages, such as instant drying, broad formulating range, reduced energy consumption, curing under mild conditions, and less space and capital requirement, UV-radiation technology has quickly developed in many high technical fields [1–3].

In a free radical UV-curing system, one of the biggest problems is low adhesion ability compared with solvent drying or thermo curing counterparts, which can be attributed to larger volume shrinkage and weaker bonding ability. It could lead to worse application properties and low fabrication resolution. The adhesion ability of UV-cured materials can be improved by a number of strategies including introducing organic-inorganic hybrid systems [4], long-chain structure compounds [5,6], and adding adhesion promoters [7] or inorganic nanoparticles [8,9]. However, even with such modifications, deficiencies still exist.

The most important component of UV curable formulations is the oligomer, which decides the polymerization kinetics and the mechanical properties of the cured material, such as hardness, adhesion, flexibility and solvent resistance [10–12]. Polyurethane acrylates, which are usually synthesized from polyols or diols, together with diisocyanates and hydroxyalkyl (meth)acrylates, are the most widely used oligomer types due to their diverse properties and characteristics. Thus, the design and synthesis of new polyurethane acrylates by the use of novel polyols or diols could be one of a promising range of solutions to alleviate this problem.

Rosin is a widely harvested and biodegradable natural product [13–15] which has been applied in many industrial fields. Hydrogenated rosin is the dominant variety of modified rosin with lower toxicity than rosin due to its bulky and high rigid alicyclic structure. This kind of alicyclic structure can decrease volume shrinkage during polymerization in comparison with linear analogues. Also, the carboxylic group of the hydrogenated rosin can react with a variety of groups resulting in structures which can, for example, lead to better adhesion to various materials via the molecular bonding adhesion mechanism [16]. It has been reported that reactions between carboxylic acid and isocyanate groups can result in the formation of amide and imide-urea moieties with the introduction of second isocyanate groups, which can form hydrogen bonding and chemical bonding with the polar groups such as hydroxyl, carboxyl on substrates surface [17–20]. Therefore, low volume shrinkage and high adhesion polymer films could be obtained when the hydrogenated rosin moiety is incorporated into an oligomer structure.

In this study, we aimed to synthesize a new type of bifunctional polyurethane acrylate by hydrogenated rosin, diisocyanate and hydroxyethyl acrylate. It is expected that this new polyurethane acrylate could exhibit smaller volume shrinkage caused by alicyclic structure and better adhesion resulting from imide-urea groups.

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2. Experimental

2.1. Materials

Triethylene propylene glycol diacrylate (TPGDA), 2-hydroxyethyl acrylate (HEA) and CN9001 (an aliphatic urethane acrylate with good adhesion) were supplied by Sartomer (Warrington, PA, USA). Isophorone diisocyanate (IPDI) and hydrogenated rosin were purchased from Shanghai First Reagent Co., (Shanghai, China). Magnesium chloride and butyl acetate were analytical reagent grade and provided by Beijing Chemical Plant (Beijing, China). Dibutyltin dilaurate (DBTL) and p-methoxyphenol (MEHQ) were analytical reagent grade and supplied by Tianjin Fucheng Chemical Plant (Tianjin, China). 2-hydroxy-2-methyl-phenyl-propan-1-one (Darocur1173) was supplied by Ciba (Basel, Switzerland). Butyl acetate was processed with standard method and all other reagents were used as received.

2.2. Synthesis of high adhesion polyurethane acrylate (HPUA)

HPUA was synthesized via a three-step reaction. IPDI (0.1 mol), DBTL (700 ppm) and MEHQ (1000 ppm) were added into a four-necked flask equipped with a mechanic stirrer, thermometer, reflux condenser and dropping funnel. HEA (0.105 mol) was slowly added dropwise to the IPDI through a dropping funnel and temperature was maintained at no more than 40 °C. The progress of reaction was determined by measuring the NCO value using the di-n-butylamine back titration method according to HG/T2409-92 (Industry Standard of China). When the NCO value decreased to 50% of the original value, the first step reaction was regarded as complete.

The reaction temperature was then raised to 75 °C and the hydrogenated rosin (0.05 mol) dissolved into 50 mL butyl acetate with $MgCl_2$ (0.1 wt%, as catalyst) was added. The second step reaction was monitored by FTIR. When the COOH peak (around 1690 cm^{-1}) disappeared, the second step reaction was regarded as complete.

Finally, the reaction temperature was raised to 100 °C and the mixture stirred at this temperature until the FTIR peak at 2267 cm^{-1} for the –NCO group disappeared. The reactant was precipitated by petroleum ether, filtrated and dried under a vacuum system, which was then purified by column chromatography with combination eluent of 70 wt% ethyl acetate and 30 wt% petroleum ether, giving a faint yellow solid HPUA after vacuum drying at 30 °C at 10 mmHg for 24 h. The synthetic route for this process is shown in Scheme 1.

2.3. Measurement

The ^{1}HNMR spectrum was recorded by a Bruker AV600 unity spectrometer operated at 600 MHz using $CDCl_3$ as solvent.

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 5700 instrument (Thermoelectric, USA). Real-time infrared spectroscopy (RTIR) was used to determine conversion of double bonds. The formulations (Table 1) were applied between two KBr crystals and irradiated with UV radiation with a UV spot light source (Rolence-100 UV, Taiwan, China) with 25 mW/cm^2 light intensity at room temperature. The degree of conversion (DC) of the double bond was calculated from the peak area at each reaction time by the following equation [21].

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

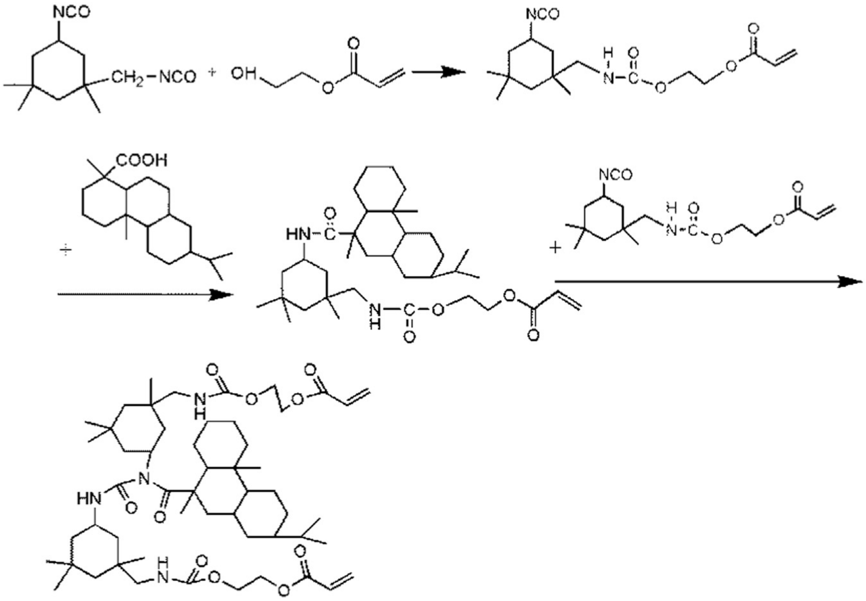
DC is the degree of conversion of double bonds at time t, A_0 and A_t are the peak area of the double bond around 810 cm^{-1} before irradiation and at time t.

Glass transition temperature (T_g) was indicated by the peak in the tan δ curve measured through dynamic mechanical analyzer (METZSCH 242 C, Germany) with 1 Hz frequency and 5 mm strain amplitude. Temperature scans were carried out in a N_2 atmosphere from −50 to 140 °C with a heating rate of 5 °C/min. Specimen dimensions were $10 \times 5 \times 1$ mm^3. Specimens were irradiated by a UV plane light source (RW-UVAC301-40bh, Runwo Co., China) under light intensity at 30 mW/cm^2 for 60 s.

The photopolymerization volume shrinkage of the various formulations investigated were obtained using a LK-G laser micrometry technique developed by our lab [22]. The thickness of

Table 1
Formulations investigated (wt%).

Component	S1	S2	S3	S4	S5	S6
CN9001	80	60	50	40	20	0
HPUA	0	20	30	40	60	80
TPGDA	20	20	20	20	20	20



Scheme 1. Reaction route for the synthesis of HPUA.