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Improvement of biodegradability of UV-curable adhesives modified by a novel polyurethane acrylate

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ABSTRACT

Ultraviolet (UV)-curable adhesives were prepared with a biodegradable polyurethane acrylate (BPUA) using isophoronediisocyanate, polycaprolactonediol, and hydroxyethyl acrylate via a two-step method with dibutyltindilaurate as catalyst under appropriate reaction conditions. These adhesives can be applied in liquid crystal display panels and electronic components. Biodegradability of the adhesives was examined through microbiological cultivation for potential application as environment-friendly materials. Mechanical properties of the UV-curable adhesives were measured to investigate the effects of BPUA in curing behavior. Results showed that biodegradability increased with the increasing content of BPUA. When the content of BPUA reached 55–60%, the adhesives exhibited the best adhesion strength (8.95 MPa) and gel fraction (93.04%).

1. Introduction

As increasing demand for reducing volatile organic compounds (VOCs) and hazardous air pollutants emissions, UV-curing technique are gradually replacing thermo-curing for their lower toxicity. UV-curing technique provides many advantages such as instant drying, broad formulating range, reduced energy consumption, high curing rate and low space and capital requirement for curing equipment. UV-curing technique represents a major advance in the development of adhesives [1]. UV-curable adhesives consume small amount of energy and are environment friendly because they involve a non-solvent and room-temperature process [2,3]. These adhesives have been widely used in areas such as printed circuit board production, plastic adhesion, liquid crystal display installation, electronic component integration, and many other fields [4–6].

However, UV-curable adhesives cannot be decomposed by microbes because of their special chemical structure and properties that are acquired after UV curing, which often results in long-term retention problems [7]. Natural polymer and synthetic polymer are the mainly matrix resin of biodegradable adhesives, natural polymer including starch, polyhydroxyalkanoates (PHA), vegetable protein, and synthetic polymer are mainly polylactic acid (PLA) and so on. The biggest advantage of the natural biodegradable polymer were exhibiting good storage stability and application process, and can quickly degrade after discarding. Therefore, Czech et al. [8] investigated biodegradable pressure-sensitive adhesive tapes containing a starch carrier, which were completely biodegradable after 42 days of soil test. The biodegradable UV-curable adhesives have gained increasing benefits due to their special advantages such as less environment pollution, low energy consumption, high chemical stability, and high curing speed even at room temperatures. However, natural biodegradable polymers, and polylactic acid cannot be UV cured, also the biodegradable adhesives exhibited poor storage stability and bonding strength, synthesizing a novel biodegradable UV-curable polymer is particularly necessary.

UV-curable adhesives are based on an oligomer (epoxy, polyurethane, or polyester acrylate) with double bond functionalities [9]. Compared with other oligomers prepared in industry, polyurethane acrylate (PUA) is one of the most widely and diversely applied in UV-cured adhesive field because of its unique properties, such as excellent abrasion resistance, low glass transition temperature, flexibility, hardness, and solvent resistance [10,11]. Therefore, looking for more new structure and special property PUA would play the key role in the development of UV-curable adhesives. Biodegradable polyurethane oligomers could be used to synthesis biomedical tissues for their good mechanical strength and the biocompatibility of the nature material [12]. Numerous research and developments on biodegradable polyurethane

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oligomers have been reported. Thus, BPUA, which can be synthesized from degradable polyols, such as polyethylene glycol (PEG) and polycaprolactone-diol (PCLD) [13,14], are incorporated in UV-curable adhesives to enhance biodegradability in microbial environment. PCLD has drawn increasing interest as a promising biodegradable material because it can degrade in microbial environments and it exhibits extreme elasticity, tensile strength, and adhesion strength as a result of the formation of hydrogen bonds among polyurethane chains [15,16]. Therefore, UV-curable adhesives containing BPUA based on PCLD have remarkable potential for environment-friendly applications. Moreover, they are also expected to exhibit similar performance as that of conventional UV-curing adhesion systems [17]. Likewise, polyurethanes prepared from aliphatic diisocyanates are more biodegradable than those prepared from aromatic diisocyanates.

In this study, a series of PCLD-based PUA was prepared and characterized. Then, the optimized biodegradable PUA was selected to be used in preparing the UV-curable adhesives. Results showed that most products exhibited good biodegradation property and outstanding mechanical properties.

2. Experimental

2.1. Materials

Isophoronediisocyanate (IPDI) and polycaprolactonediol (PCLD) (M = 2000 g/mol) were supplied by Sanpoly Chemical Co., Ltd., China. Hydroxyethyl acrylate (HEA), isobornyl methacrylate (IBOMA), dibutyltindilaurate, photoinitiator 1173, and photoinitiator 184 were provided by Guoling Instrument Co., Ltd., China. Plasticizer (DINP) and coupling agent (KH-560) were purchased from Zhongjie Chemical Technology Co., Ltd., China.

2.2. Instrumentation

The adhesives were cured by a UV-curing equipment with a 1000 W middle-pressure mercury lamp (main wavelength: 365 nm, Guangzhou JinPeng Electron Co., Ltd.). The FT-IR spectra were obtained by an AVATAR360 (Nicolet) spectrometer within a spectral range of 400–4000 cm^{-1} and the synthesized biodegradable polyurethane acrylates (BPUA) samples were coated on KBr pellets. Tensile and adhesion strengths were performed by a Electronic Universal Testing machines (UTM 4000, Sunthink Science Technology Development Co., Ltd., Shenzhen, China). The surface of the films after biodegradation was viewed with a scanning electron microscope (FEI-XL30, Philips Electron Optics Co., Ltd.) at 20 kV. The thermal analysis was performed by a DTA-TG thermal analyzer (DTG-60, Shimadzu) and heated from 50 °C to 600 °C at a rate of 10 °C/min in N_2 atmosphere.

2.3. Synthesis of UV-cured BPUA oligomers

BPUA oligomers were synthesized through a two-step method based on IPDI, PCLD, and HEA. Appropriate reaction conditions were investigated by measuring the changes in NCO conversion rate with reaction time in different temperatures, contents of catalyst, and ratio of raw materials using din-butylamine titration method every 0.5–1 h (data not shown). Optimum reaction condition was obtained as follows: IPDI and PCLD were added to a four-necked flask equipped with a stirrer, condenser, and an addition funnel. The reaction temperature was controlled between 50 to 60 °C. After reacting for 1 h, dibutyltin dilaurate was added in the reactor. The reaction was continued for 2–3 h. Then, HEA was dropped in the reactor slowly. The reaction continued for another 2–3 h at 60–80 °C. The end of the reaction was determined by the disappearance of the NCO group peak at 2260 cm^{-1} in the Fourier transform infrared (FTIR) spectrum. The mixture was then cooled and collected. The synthetic route of UV-BPUA is shown in Fig. 1.

2.4. Preparation of biodegradable UV-curable adhesives

Collected BPUA oligomers and IBOMA were initially stirred well. Photoinitiators (1173, 184), DINP and KH-560 were added and mixed using a mechanical stirring bar in 500 rpm for 30 min. Two-step blending process was performed to obtain a homogeneous mixture. The mixture was coated in a glass plate and cured in the UV-curing apparatus with a high-pressure mercury lamp (2000 W). The distance between light source and glass plate was 15 cm.

2.5. Characterization

2.5.1. Tensile strength

The biodegradable UV-curable adhesives were scraped into a particular thickness and were cured using UV-curing equipment. The tensile strength of the cured films was determined by an Electron Universal Testing machine at a speed of 2 mm/min. All measurements had an average of three runs, whereas the film sample has a width of 15 mm, length of 50 mm and thickness of 0.2 mm.

2.5.2. Adhesion strength

On the glass (75 mm × 25 mm × 1 mm) surface, 0.1 g of the biodegradable UV-curable adhesives was coated and covered with PE film (75 mm × 25 mm × 0.2 mm). The adhesion strength measurement was then tested using the Electron Universal Testing machine at a speed of 5 mm/min. All measurements were thrice the average.

2.5.3. Gel fraction

The UV-cured films were cut into a size of 20 mm × 20 mm × 1 mm and were soaked in toluene at room temperature for 48 h. The insoluble part was dried at 60 °C to a constant weight. The gel fraction was calculated based on following formula:

$$\text{Gelfraction}(G) = (W_1/W_0) \times 100\%$$

where W_0 is the weight of the film before soaking in toluene, and W_1 is the weight after drying.

2.5.4. Soil burial respirometric test

The biodegradation degree of adhesives was tested by respirometric biodegradation methods [18,19]. Soil burial respirometric test [19] was carried out in 500 mL sealed cylindrical glass vessels containing a multilayer substrate. The films (0.35 g) cut into pieces after UV-curing, mixed with mature compost (5 g) and supplemented with 25 mL $(NH_4)_2HPO_4$ solution (0.1%), were sandwiched between two layers of 10 g perlite wetted with 30 mL distilled water. The vessels were kept in the oven at 58 °C in a well-ventilated environment. In order to absorb CO_2 evolved from samples, each vessel was equipped with a beaker containing 10 mL KOH solution (0.25 mol/L), and replaced with fresh KOH solution every 3–5 days. The replaced KOH solution was back titrated with HCl (0.25 mol/L) and the amount of CO_2 adsorbed was determined. The tests were carried out in triplicate.

2.5.5. Fungal biodegradation test

To observe the biodegradable behavior of the UV-curable adhesives after UV curing, the films were cut into 20 × 20 × 1 mm sizes, and then ultrasonically cleaned in ethanol and distilled water. The produced films were placed in Petri dishes inoculated with 20 mL of solid sterilized media and supplied with 100 μL 10^{-2} of soil dilution liquid. Petri dishes were then set to incubate in a climatic chamber