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Synthesis and properties of poly(acrylates-co-urethane) adhesives for low surface energy materials

Minrui Li [a], Zhen Zheng [a], Shujuan Liu [a], Yuezeng Su [b], Wei Wei [a], Xinling Wang [a],*

[a] Department of Polymer Science and Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, PR China
[b] School of Aeronautics and Astronautics, Shanghai Jiao Tong University, Shanghai 200240, PR China

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ABSTRACT

The series of poly(acrylates-co-urethane) were synthesized based on the copolymerization between 2-hydroxyethyl acrylate terminated polyether (or polyester) urethane and acrylate monomers initiated by tri-n-butylborane (TBB). The effects of the soft segment of polyether (or polyester) urethane diacrylate on the copolymer properties were mainly discussed. Polyether (or polyester) urethane was relatively well dispersed in polyacrylate continuous phase, and was intended to aggregate with the increase of soft segment polarity and content. The adhesion to low surface energy materials and loss factor (tan δ) of copolymers were almost not influenced by the soft segment content, but decreased with the increase of soft segment polarity within the scope of the study. On the other hand, the working life of copolymers as adhesives was shortened with the increase of soft segment polarity, but prolonged with the increase of soft segment content. The copolymers with different structures of polyether (or polyester) urethane diacrylate were also shown to be good candidates as adhesives at room temperature.

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1. Introduction

Low surface energy materials, such as polypropylene (PP), polyethylene (PE) and polytetrafluorethylene (PTFE), have been used in many fields because of their excellent performances. Due to their low energy surface, these materials demonstrate poor adhesion. Traditional methods to improve their bonding, such as plasma treatment, corona discharge, radiation, acid etching, grafting and so on [1–5], have limitations in utilization because most of them are complex, costly, and particularly unsuitable to apply by the retail consumer. Using primer can promote adhesion to these materials [6,7], but the cost is increased and the surface treatment is often needed. However, these traditional methods have been still applied in coating or bonding low surface energy materials until now.

It was encouraging that radical polymerization initiated by organoborane at room temperature was put forward by Brown and Ghosez since 1967 [8,9]. With the technology, polyacrylate adhesives initiated by organoborane to bond low surface energy materials have been reported by Schoutchi, Zharov, Pocius Sonnenschein and Kneafsey et al. since the early 1990s [10–17]. The promoting mechanism was formulated by us and Sonnenschein, Zhang, Hirokazu et al. [18–22]. However, brittleness and poor film-forming properties remain to be problematic. Thus, this kind of acrylate adhesives have been modified by many methods including cross-linking polyacrylates, copolymerizing acrylates with other monomers and blending polyacrylates with other polymers [23–27]. Generally, acrylates with low glass transition temperature (T_g) are used to improve those performances at the expense of cohesive strength of adhesives.

Sonnenschein et al. [26] reported a class of poly(acrylate/epoxy) hybrid adhesives for bonding low surface energy materials. The introduction of epoxy increased the cohesive strength of adhesives greatly, but the brittleness also increased sharply. In order to improve the brittleness of adhesives, they reported another class of poly(acrylate/siloxane) hybrid adhesives in their following work, but the cohesive strength decreased again [27]. Because of the excellent performances of polyurethane (PU), it is prone to improve the brittleness and cohesive strength of polyacrylate together [28–36]. Deviny and Pocius et al. reported a class of polyacrylates adhesives containing PU that was introduced into the adhesive system by decomplexer containing urethane oligomer or another polyether glycol reacted with decomplexer diisocyanate [28–31]. However, the copolymerization of acrylates and urethane oligomer terminated by unsaturated bond, which is expected to improve phase distribution of polyacrylate and urethane oligomers, has not been reported by others so far.

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* Corresponding author. Tel.: +86 2154745817; fax: +86 2154741297.
E-mail address: xlwang@sjtu.edu.cn (X. Wang).

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In our previous paper, we showed 2-hydroxyethyl acrylate terminated polyether urethane could improve the adhesion of polyacrylates to low surface energy materials [37]. Generally, the structure or content of soft segment in PU exerted great influences on polymer properties. In this paper, poly(tetramethylene glycol) (PTMG) or poly(1,4-butanediol adipate) diol (PBA) with different polarity was used as soft segment to synthesize polyether (or polyester) urethane diacrylate with different soft segment contents. Then, poly(acrylates-co-urethane) was synthesized with polyether (or polyester) urethane diacrylate as monomer which copolymerized with acrylates initiated by TBB. The effects of soft segment of polyether (or polyester) urethane diacrylate on the copolymer properties were explored.

2. Experimental part

2.1. Materials

Poly(tetramethylene glycol) (PTMG-1000, M_n=1000 g mol^{-1}; PTMG-2000, M_n=2000 g mol^{-1}, Dupont Co.) and poly(1,4-butanediol adipate) diol (PBA-1000, M_n=1000 g mol^{-1}; PBA-2000, M_n=2000 g mol^{-1}, Eternal Technologies Co.) were dewatered for 2 h under 200 Pa vacuum at 120 °C. Toluene diisocyanate (TDI), dibutyltin dilaurate (DBTDL), hexamethylene diamine, 2-hydroxyethyl acrylate (HEA), methyl methacrylate (MMA), butyl acrylate (BA), polypropylene (PP, density: 0.92 g cm^{-3}, 4 mm thickness) and polyethylene (PE, density: 0.96 g m^{-3}, 2 mm thickness) plates were described elsewhere [37]. The PP or PE plates were washed with isopropyl alcohol before being used. Tri-n-butylborane (TBB) was synthesized according to the document [38].

2.2. Synthesis and characterization of copolymers

The synthesis of polyether (or polyester) urethane diacrylate with different soft segments (the [NCO]/[OH] is 2/1) or soft segment contents (with PTMG-1000 as soft segment) was the same with that of polyether urethane diacrylate described elsewhere [37]. The products were characterized by Fourier transform infrared spectroscopy (FTIR). FTIR experiment was performed on a Perkin-Elmer 1000 FTIR spectrometer ranging from 700 to 4000 cm^{-1}. The FTIR samples were prepared by coating film (N, N-dimethylformamide as solvent) on the KBr wafer and dried in vacuum. The scanning frequency was 64 times and the resolution was 4 cm^{-1}.

The preparations of TBB/hexamethylene diamine complex and copolymer adhesives were described elsewhere [37]. Lap-shear specimens were prepared by coating the copolymer adhesives on two PP or PE plates. A clamp was used to fix the lapped area and control the bonding thickness. The lapped area was 25 × 12.7 mm^2, and the adhesive thickness was controlled to 0.2 mm with piano string (diameter 0.2 mm). After curing at room temperature for 48 h, the lap shear strength (LSS) of lapped samples was tested on INSTRON 4465 universal electromechanical tester (with high-temperature cabinet) according to ASTM D-1002. Five replicates for each adhesive were tested. The crosshead speed was 10 mm/min, and testing temperature and environment humidity were 23 ± 1 °C and about 50%, respectively. Failure mode was recorded according to ISO-10365:1992.

Working life of copolymer adhesives was tested according to GB/T 7123.1-2002, and was defined as the time in which the service performance (LSS) of the adhesive could be maintained. The test samples were prepared through making an adhesion sample at some time intervals. The beginning time was recorded as the time when components of adhesives started to mix. All samples were cured for 48 h before LSS test were performed.

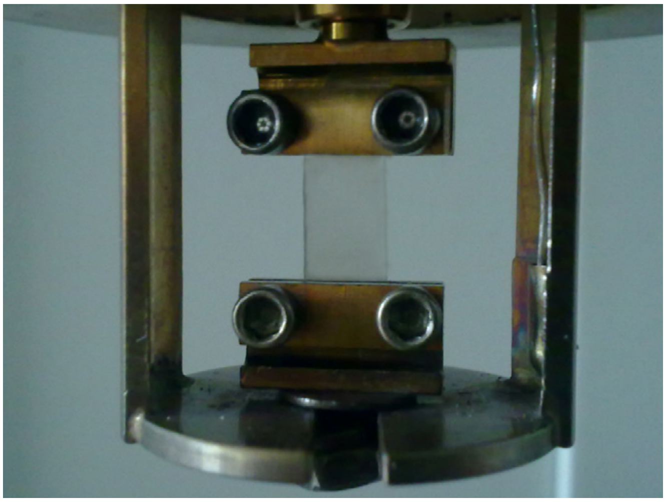

Fig. 1. Schematic diagram of tension mode of DMA.

Dynamic mechanical analysis (DMA) of copolymers was carried out on Perkin Elmer DMA 7e Dynamic Mechanical Analyzer from −80 to 130 °C. The test frequency was 1 Hz, and the rate of temperature ramping was approximately 3 °C/min. Tension was adopted as mode of force as shown in Fig. 1. The size of DMA samples was 11.0 × 4.0 × 1.5 mm^3.

Microscopy samples of the copolymers approximately 100 nm thick were obtained at −80 °C with a Leica ULTRACUT UC6 cryoultramicrotome, and were collected on a copper supporting grid. The electron micrographs of the prepared sections were observed in a JEM-2100 transmission electron microscopy running at an accelerating voltage of 200 kV.

3. Results and discussion

The FTIR spectra of the synthesized polyether (or polyester) urethane diacrylate are shown in Fig. 2. From Fig. 2, the characteristic absorption of NCO at about 2273 cm^{-1} disappears in all spectra, indicating that all the polyether (or polyester) urethane diacrylates are synthesized successfully, which were then used as the monomer that copolymerized with acrylates initiated by TBB (20 wt% polyether (or polyester) urethane diacrylate). The synthesized copolymers were named "Ta-b/c" (or "Ba-b/c"), where "T" and "B" represent PTMG and PBA as the soft segment of polyether (or polyester) urethane diacrylate, respectively, "a" represent the thousand unit of M_n of soft segment and "b/c" represent the ratio of [NCO]/[OH]. The typical copolymer structure is shown in Fig. 3.

3.1. Transmission electron microscopy (TEM)

Fig. 4 shows the transmission electron microscopy micrographs of the copolymers with different structures of polyether (or polyester) urethane diacrylate. The dark and white zones in the picture represent the urethane oligomer phase and polyacrylate phase, respectively. Fig. 4 indicates that urethane oligomer phase is relatively well dispersed in polyacrylate continuous phase. The urethane oligomer phase appears to aggregate in Fig. 4b because of the stronger interaction between PBA segments. So, the dispersion of urethane oligomer in polyacrylate phase with PTMG as soft segment is better than that with PBA as soft segment. Fig. 4c shows the urethane oligomer domain size gets

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