



Investigation of a non-isocyanate urethane functional monomer in latexes by emulsion polymerization



Lei Meng^a, Mark D. Soucek^{a,*}, Zhen Li^b, Toshikazu Miyoshi^b

^a Department of Polymer Engineering, University of Akron, Akron, OH 44325, USA

^b Department of Polymer Science, University of Akron, Akron, OH 44325, USA

ARTICLE INFO

Article history:

Received 14 February 2017

Received in revised form

27 April 2017

Accepted 1 May 2017

Available online 9 May 2017

Keywords:

Emulsion polymerization

Hybrid latex

Emulsion

Core-shell

Polyacrylate

Polyurethane

ABSTRACT

A urethane methacrylate monomer, 2-[(butylcarbamoyl)oxy]ethyl methacrylate (BEM), methyl methacrylate (MMA), and butyl acrylate (BA) were used to prepare latexes. The effects of polymer process (batch versus semi-batch), polymer composition, and the locus (core-shell) of urethane functionality in the latex particles were studied. Urethane functional latexes were evaluated by FT-IR, solid state nuclear magnetic resonance (SS-NMR), dynamic light scattering (DLS), gas chromatography (GC), differential scanning calorimetry (DSC), tensile and dynamic mechanical thermal analysis (DMTA). A compositional drift was observed for the batch polymerization which resulted in early formed polymers rich in MMA and BEM. This accounted for the higher modulus and tensile strength in latexes derived from batch polymerization. Both homogeneous and core-shell structures were prepared. The tensile modulus, tensile strength and elongation-at-break were all dependent on BEM content.

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1. Introduction

Polyacrylates [1] (PA) is one of the most widely used families of polymeric binders for waterborne coatings, and polyurethanes [2] (PU) are one of the most widely used high performance polymeric binders used in coatings. As a consequence, there has been much effort to create hybrid coatings with some of the characteristics of each. To the extent that these two polymeric binders are miscible, physical blending can be a practical method. Although some benefits have been obtained using a blending approach, the properties are less than linear as predicted from the simple “rule of mixtures” and direct blending of acrylic emulsions with PUs can result in a diminution of coatings properties [3,4].

Various methods of improving the mixing of hybrid polyurethane/polyacrylate (PUA) materials have been explored [5], including intimately mixing [6,7], grafting [4,8–14], interpenetrating polymer networks (IPNs) [15–20] and core-shell morphology [21–24]. An interesting approach to intimately mix PUAs is to polymerize acrylic monomers in the presence of a polyurethane dispersion to obtain hybrid emulsions [3,12,25]. A series of PUA hybrid latexes without external surfactant were

prepared by *in situ* polymerization [6]. The optimum acrylic monomer content was found to be about 30 wt%. In another study, hybrid polymers were prepared when acrylates were embedded into polyurethane dispersions (PUD)s during a emulsion polymerization [7]. The optimum performance properties for coating applications derived from the hybrid synthesized with a 50:50 wt ratio of PU and PA components.

Another approach is grafting between the polyurethane and acrylic emulsion [4,10–14]. The presence of grafted copolymer helps improve the compatibility of acrylic-polyurethane hybrid emulsions [4,10–13]. Zhang et al. had successfully prepared a series of PU/PA hybrid emulsions by solvent free method using γ -ray initiation [14]. The FT-IR result, showed that the PUA grafting initiated by γ -ray irradiation was superior than grafting by potassium persulfate. Larock et al. prepared a variety of new hybrid latexes prepared from a soybean oil-based waterborne PU and acrylic methyl methacrylate (MMA)/butyl acrylate (BA) copolymers [13]. The thermal and mechanical properties were enhanced by the extensive grafting of the acrylic onto the PU and subsequent interpenetration between the acrylic and the PU phases. Grafting was attributed to chain transfer from the propagating free radical to PU or copolymerization between the radical and the double bonds in the soybean oil-based.

IPN-like approaches have been developed by mixing urethane

* Corresponding author.

E-mail address: msoucek@uakron.edu (M.D. Soucek).

pre-polymers and acrylic monomers and concomitantly polymerizing the pre-polymers and monomers, respectively [26–29] to form PUA IPNs. A broad glass transition range indicated an interpenetrating network of PA and PU chains [20]. In terms of a semi-batch approach, Chai et al. prepared core–shell PUA composite with PU as the shell and with PA as the core. The particle sizes were not influenced by the type of initiators or PU/PA weight ratio [22]. Chai et al. also found that homogeneous interpenetrating PUA was better than the core-shell PUA in terms of wet rub fastness, solvent resistance, adhesive resistance, whereas the core-shell PUA was better at flex resistance. In another study, urethane/acrylic latexes with 30–40% solid content were synthesized by core-shell emulsion polymerization with PU as the seed [23]. Kulkarni et al. compared the performance properties of core-shell hybrids and latex IPNs. The experimental results showed better performance properties of PUA core-shell hybrid than that of the homogeneous latex IPN hybrids [24].

An acrylic carbamate monomer synthesized from TDI was first copolymerized with acrylic monomers to form a PU/PA composite about 20 years ago [5]. The tensile strength of polymer films was increased significantly. The copolymerization of urethane and acrylic monomers in the same backbone overcome the poor compatibility of polyurethane and polyacrylate on the molecular level and was shown to improve the toughness, strength, and scratch resistance of acrylate. In fact, the incorporation of urethane functionality into a polymer has been widely demonstrated to improve the mechanical properties in both biological [30–32] and engineering [33–35] applications. All these urethane acrylate or methacrylate monomers were synthesized through an isocyanate route [31]. However, isocyanates have recently become the focus of safety concerns [36].

Recently, non-isocyanate urethane di-methacrylates had been prepared and used as reactive diluents for making UV-curable polyurethane coatings. The non-isocyanate urethane reactive diluents reduced the viscosity of the coating formulation, and improved the impact resistance and tensile properties of the final cured coatings [37]. More recently, a series of new mono-methacrylates were prepared using a similar approach [38]. Herein, a non-isocyanate urethane mono-methacrylate was prepared via a cyclic carbonate pathway and used to prepare latexes. Urethane functional latexes were prepared by semibatch monomer-starved emulsion polymerization of 2-[(butylcarbamoyl)oxy]ethyl methacrylate (BEM) with MMA and BA. The effect of monomer concentration and the location of urethane functionality in the latex particles, were studied. Urethane functional latexes were evaluated by FT-IR, solid state nuclear magnetic resonance (SS-NMR), dynamic light scattering (DLS), gas chromatography (GC), differential scanning calorimetry (DSC), tensile tests and dynamic mechanical thermal analysis (DMTA).

2. Experimental

2.1. Materials

Ethylene carbonate (EC, 98%), butyl amine (BA, 99%), methacrylic anhydride (MAA, 94%), dichloromethane (99%), hydroquinone (99%), triethylamine (TEA, 99%), dimethyl sulfoxide- d_6 (DMSO- d_6 , 100%), anhydrous magnesium sulphate (99%), hydrochloric acid (HCl, 36.5–38 wt%), methyl methacrylate (MMA, 99%), butyl acrylate (BA, 99%), ammonium persulfate (APS), sodium bicarbonate (NaHCO₃), Triton X-200 and Triton X-100, all purchased from Sigma-Aldrich, and except for the acrylic (and methacrylic) monomers were used as received. 4-(dimethylamino) pyridine (DMAP, 99%) was obtained from Acros Organics. Acrylic and methacrylic monomers were purified by using Alfa Aesar™

inhibitor removal resin purchased from Fisher Scientific before use. The purified monomers were stored in the refrigerator before synthesis. Deionized water with conductivity below 15 μ S/cm was used in the preparation of the latexes. The latexes were purified by using the Spectrum™ RC Dialysis Membranes (MWCO 12000–14000) purchased from Fisher Scientific.

2.2. Instrumentation

The nuclear magnetic resonance (NMR) spectra were taken in a Varian Mercury 300 MHz spectrometer for liquid samples and Bruker Avance III 300 NMR spectrometer for solid samples. Fourier Transform Infrared Spectroscopy was obtained on a Nicolet 380 FT-IR instrument (Thermo Electron Corp.). Molecular weight was determined by gel permeation chromatography (GPC) using high-resolution Waters columns with THF at 1 mL/min with polystyrene as the calibration standard. Electrospray ionization (ESI) mass spectra were acquired on a HCT Ultra II quadrupole ion trap mass spectrometer (Bruker Daltonics, Billerica, MA). Gas Chromatography (Varian CP-3800) with a flame ionization detector was used to quantify the unreacted monomers. Particle size and distributions were obtained on dynamic light scattering (DLS) using a PSS NICOMP (Santa Barbara, CA) equipped with a He–Ne laser operating at 652 nm and a triple detector. Particle imaging was performed on JSM-1230 TEM (JEOL). A PC 700 Benchtop meter (Oakton) was employed for pH and conductivity. Thermal analysis was performed using 1000 DSC (Q1000, TA Instruments). Tensile tests were performed on an Instron 5567 (Instron Corp., Grove City, PA). The viscoelastic properties were measured on a dynamic mechanical thermal analyzer (DMTA, Q800, TA Instruments). Linear oscillatory shear, melt-rheology measurements were performed with an Advanced Rheometric Expansion System (ARES G2, TA Instruments).

2.3. Synthesis of the non-isocyanate urethane functional methacrylate monomer (BEM)

The synthesis process of BEM consists of two steps. Ethylene carbonate (88.06 g, 1.00 mol, EC) was dissolved in 300 mL dichloromethane in a 1 L three-neck flask. Then, butylamine (80.46 g, 1.10 mol) was dropwise added into the EC-CH₂Cl₂ mixture at 0 °C by using the ice bath under N₂ atmosphere and magnetic stirrer. The mixture was then stirred at room temperature for 24 h. The slightly yellow liquid (yield: 98%), hydroxyalkylcarbamate was obtained after removal of the dichloromethane. In the second step, hydroxyalkylcarbamate, BA-EC (80.6 g, 0.5 mol) was dissolved in 300 mL dichloromethane at 0 °C under N₂ atmosphere and magnetic stirrer. 4-(dimethyl-amino) pyridine (DMAP) catalyst (610 mg, 5 mmol), and hydroquinone inhibitor (98.4 mg, 0.8 mmol) were then added, followed by dropwise addition of triethylamine (TEA) (70.8 g, 0.7 mol), and then dropwise addition of methacrylic anhydride (98.4 g, 0.6 mol). The reaction mixture was stirred at 0 °C for 24 h. After 24 h reaction, an additional 200 mL dichloromethane was added. Purification of BA-EC-MAA was obtained via an extraction process as followings: the saturated brine (300 mL) was added to the reaction mixture to obtain a two phase separated mixture; the product (bottom layer) was collected, washed with 1 M hydrochloric acid solution (300 mL \times 3) saturated sodium bicarbonate solution (300 mL \times 3) and saturated brine (300 mL \times 1), and dried in anhydrous magnesium sulfate. After the dichloromethane was evaporated, the product was put into the vacuum oven at 35 °C until there was no change of weight. A light yellow liquid product was obtained with yield 60–70%. ¹H NMR (500 MHz, DMSO- d_6) δ (ppm) = 0.84 (t, J = 6.9 Hz, 3 H, -CH₃), 1.26 (m, 2 H, -CH₂CH₃), 1.36 (m, 2 H, -CH₂CH₂CH₃), 1.87 (s, 3 H, -CH₃), 2.97 (m,

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