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Synthesis and properties of waterborne fluorinated polyurethane-acrylate using a solvent-/emulsifier-free method

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ABSTRACT

Pristine waterborne polyurethane-acrylate [pristine WPUA, soft-segment content: 64 wt%, dimethylol propionic acid (DMPA): 20 mol%/4.95 wt%] emulsions were synthesized using an acetone process from 4,4′-dicyclohexymethane diisocyanate ($H_{12}MDI$)/poly(tetramethylene oxide glycol) (PTMG,2900 g/mol)/DMPA/2-hydroxyehthyl metacrylate (HEMA) without an external emulsifier. A series of waterborne fluorinated polyurethane-acrylate hybrid [WFPUA: WFPUA10, WFPUA20 WFPUA 30 and WFPUA 40, where the numbers indicate the total content of acrylic monomers] emulsions as antifouling coating materials were synthesized from vinyl group-terminated urethane prepolymer (pristine WPUA components)/[isobornyl acrylate (IBOA)/*n*-butyl acrylate (BA)/perfluorodecyl acrylate (PFA) (IBOA/BA/PFA: 4/3/3 wt ratio)] by radical polymerization using an emulsifier-free/solvent-free method. The as-polymerized hybrid emulsion containing 50 wt% of acrylic monomer content was found to be unstable, indicating that near 50 wt% of acrylic monomer content was beyond the limit value of self-emulsifying ability. The gradient concentration of fluorine in the film structures from the film-air surface to the film–dish interface was characterized by Fourier transform infrared spectroscopy and x-ray photoelectron spectroscopy. As the total acrylic monomer/PFA content of hybrid materials increased, the water/methylene iodide-contact angles, lower temperature T_g and elongation at break increased, however, the higher temperature T_g, water swelling, tensile strength/modulus and hardness decreased. The contact angles of hybrid film samples increased with increasing total acrylic monomer/PFA content up to about 30 wt%/9 wt%, and then almost leveled off. The optimum total acrylic monomer/PFA content was found to be about 30 wt%/9 wt% to obtain high performance water/oil repellent coating materials.
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1. Introduction

Generally, waterborne acrylic resins are inferior to their solvent-based counterparts because of the need for external surfactants that are introduced to impart dispersion stability in water to these resins. Water dispersions (lattices or emulsions) of polyurethane ionomers (ion-containing polyurethanes) without external surfactant allow the application of polyurethane from aqueous media. Waterborne polyurethanes are environment-friendly materials with good adhesion, elasticity and chemical resistance [1–10]. However, dried films of waterborne polyurethanes are generally water sensitive because of the presence of the ionic groups. Therefore, the ionic content should be kept to minimum for the formation of water-resistant materials. We found that it was very difficult to obtain stable waterborne polyurethane–urea dispersions with low content of ionic moieties (<10 mol%, 2 wt%) [11].

Acetone process and prepolymer mixing process are mostly used to synthesize waterborne polyurethanes. The synthesis of solvent-free waterborne polyurethanes via these processes is not possible because the synthesis of the isocyanate-terminated prepolymer leads to gelation in the melt. Solvents such as *N*-methyl-2-pyrrolidone (NMP) and prepolymer thinner are expensive, and NMP residues in the dried film tend to cause yellowing and are capable of dissolving or swelling a wide range of protective equipment in an industrial environment. With reference to one of the California Propositions, all products containing NMP require special labeling, describing the NMP content [12]. Therefore, it is beneficial to synthesize waterborne polyurethane emulsions using a solvent free method.

Waterborne polyurethanes have the drawbacks of high cost, low pH stability and limited outdoor durability, whereas acrylic polymers have an excellent water and weather resistance, good

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pigmentability and lower cost. As a result, formulators have sought ways of combining the advantages of waterborne polyurethane and acrylic polymer [13,14]. The most popular strategy is to blend the waterborne polyurethane dispersion with an acrylic emulsion. Generally, the performance of these blends is lower than what would be predicted from the arithmetic rule of mixtures [13,15]. One possible explanation is that, at the molecular level, the acrylic polymers are insoluble in the waterborne polyurethane. Therefore, so-called hybrid systems were developed to overcome this problem. The hybrids incorporate both urethane and acrylic polymers into the same emulsion particle with a multiphase structure using a range of techniques, such as core–shell type polymerization technology, seeded polymerization or interpenetrating network formation. Kukunja et al. compared the performance of acrylic–polyurethane hybrid emulsions with that of physical blends, and found that hybrid emulsions provide improved performance in coatings [14]. Hirose and Kadowaki prepared polyurethane/polyacrylate hybrid emulsions with a core–shell structure [16]. Polyurethane/polyacrylate hybrid emulsions with an interpenetrating polymer network (IPN) were prepared by the polymerization of acrylic monomers/PU prepolymer dispersion [17–19]. Most reports of acrylic–polyurethane hybrid emulsions are in the form of patents, which have potential application in coatings; only a few publications report the results of a systematic study [20–26].

Fluorinated polymers have many useful and desirable features, such as unique surface properties and high resistance to thermal, chemical, and weather attack, owing to the low polarizability and strong electronegativity of the fluorine atom. Polytetrafluoroethylene is one of polymeric solids with the lowest surface energy. Therefore, its critical surface tension/water contact angle of wetting of 18.5 mN/m/108° are the characteristics of a surface consisting essentially of closed packed perfluoromethylene $-CF_2-$ groups [27]. Generally, the surface tension/contact angle of material is used as criteria of antifouling property. The lower critical surface energy of many polymers containing fluorocarbon side chains has been attributed mainly to the higher content of CF_3 groups on their surfaces [28–31]. Therefore, fluoroalkyl acrylate homopolymers with long side chains have very low critical surface tension, ranging from 10 to 11 mN/m [28]. The main disadvantage of a fluorinated monomer is its relatively high cost. Therefore, the content of fluorinated monomers should be minimized whilst maintaining reasonable surface tension (water/oil repellency). In particular, acrylic co-polymers with fluorine-containing groups or perfluoroalkyl groups can provide materials with low surface energies, and the acrylic groups ensure that the polymers can adhere well to a range of substrates. Thus, they have been used a progressively greater extent in surface coatings for water/oil repellency for textiles, paper and leather [32–35].

A combination of polyurethane with an acrylic polymer-containing fluorine component is expected to be effective in increasing the performance of the resulting materials. Those materials combine some of the virtues of polyurethane and fluorinated acrylate/acrylate polymer, such as high thermal stability, good chemical resistance, low water absorptivity (water resistance) and attractive surface properties, excellent flexibility, good wearability, and high weatherability [31,36,37]. Some studies have reported the preparation and properties of these hybrid materials [17–19]. However, there has been little research on hybrid materials of waterborne polyurethane-polyacrylates containing fluorine component.

In this study, a series of waterborne fluorinated polyurethane-acrylate emulsion were prepared from vinyl end-capped polyurethane prepolymer containing a fixed content of ionic moieties and an acrylate/perfluoroalkyl acrylate mixture by emulsifier-free emulsion copolymerization and a solvent-free method. The resulting waterborne fluorinated polyurethane-acrylates containing a 0, 10, 20, 30 and 40 wt% of acrylic monomer content were characterized by Fourier transform infrared (FTIR) spectroscopy with an Attenuated total reflectance (ATR) apparatus, X-ray photoelectron spectroscopy (XPS), Brookfield viscometer, particle size analyzer, dynamic mechanical analysis (DMA) and contact angle measurements. This study focused on the effect of total acrylate monomer/PFA content on the surface/thermal/mechanical properties of pristine WPUA/WFPUA hybrids as antifouling coating materials.

2. Experimental

2.1. Materials

Poly(tetramethylene oxide glycol) (PTMG, number-average molecular weight = 2900 g/mol; Aldrich Chemical, Milwaukee, WI) was dried at 85 °C under 1–2 m/108 mmHg for several hours until no bubbling was observed. Dimethylol propionic acid (DMPA, Aldrich Chemical, Milwaukee, WI) was dried in a vacuum oven at 100 °C for 5 h 4,4′-dicyclohexymethane diisocyanate (H_{12}MDI, Aldrich Chemical, Milwaukee, WI) and triethylamine (TEA, Aldrich Chemical, Milwaukee, WI) were used after dehydration with 4-Å molecular sieves for 1 day. Dibutyltin dilaurate (DBTDL, Aldrich Chemical, Milwaukee, WI), distillated deionized water, 2-hydroxyehthyl metacrylate (HEMA, Aldrich Chemical, Milwaukee, WI), isobornyl acrylate (IBOA, Aldrich Chemical, Milwaukee, WI), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate (PFA, Aldrich Chemical, Milwaukee, WI), butyl acrylate (BA, Aldrich Chemical, Milwaukee, WI), and ammonium persulfate (APS, Aldrich Chemical, Milwaukee, WI) were used as received.

2.2. Preparation of pristine waterborne polyurethane-acrylate (WPUA) emulsion and waterborne fluorinated polyurethane-acrylate (WFPUA) hybrid emulsions

Pristine waterborne polyurethane-acrylate (Pristine WPUA) was prepared using the acetone process. However, a series of waterborne fluorinated polyurethane-acrylate (WFPUA) hybrid emulsions were synthesized using a solvent-/emulsifier-free method (Scheme 1). This process was divided into three steps. (1) The first step is the formation of vinyl-terminated polyurethane prepolymer by reacting HEMA (24 mol %) with NCO-terminated urethane prepolymer prepared from H_{12}MDI (44 mol%)/PTMG (Mn = 2900, 12 mol%, soft-segment content: 64.24 wt%)/DMPA (20 mol %/4.95 wt%): PTMG and DMPA were placed in a four-neck, round-bottom flask equipped with a thermometer, mechanical stirrer, condenser with a drying tube, an inlet for dry nitrogen and a heat jacket, and was degassed in a vacuum at 90 °C for 1 h. The mixture was allowed to cool to 45 °C with moderating stirring (175–200 m/108 rpm). H_{12}MDI was then dropped slowly into the flask, and the reaction mixture was allowed to react at 85 °C until the theoretical NCO content was reached. The change in NCO value during the reaction was determined using the standard dibutylamine back-titration method (ASTM D 1638). The reaction mixture of NCO-terminated urethane prepolymer was cooled to 45 °C, and HEMA was added dropwise. To obtain a vinyl-terminated urethane prepolymer, the capping reaction of NCO-terminated urethane prepolymer with HEMA was continued until the NCO-content reached zero, as evidenced by the disappearance of the IR NCO peak. (2) The second step is the neutralization of vinyl-terminated urethane prepolymer using tertiary amine TEA and the formation of mixtures of neutralized vinyl-terminated urethane prepolymer and acrylic monomers (IBOA/BA/PFA) to allow copolymerization between vinyl-terminated polyurethane prepolymer and the acrylic monomers: The acrylic monomer mixture (IBOA/BA/PFA: 10–50 wt

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