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Short communication

Synthesis and properties of PDMS modified waterborne polyurethane–acrylic hybrid emulsion by solvent-free method

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ABSTRACT

A new type of polysiloxane modified polyurethane–acrylic hybrid emulsion was synthesized by solvent-free method and the polysiloxane was introduced into the soft segment of polyurethane chains using dihydroxybutyl-terminated polydimethylsiloxane (PDMS). The formed film from the hybrid emulsion could provide obviously higher water-resistance property. The preparation technologies such as the content of carboxy group and acrylic monomer, the rate and the time of emulsification were discussed systematically. The chain structure and the particle size were confirmed by the analysis of Fourier transform infrared spectroscopy and transmission electron microscopy, respectively. The effect of PDMS content on the water resistance and the mechanical property were investigated by absorbed water ratio, water contact angle and dynamic mechanical measurement.

1. Introduction

Polyurethane materials are known to offer high performance with their toughness, abrasion resistance, mechanical flexibility and chemical resistance. Waterborne polyurethane has become one of the major research and development fields in recent years because of its environmental friendliness. During the synthesis of waterborne polyurethane, the water is used as dispersant instead of organic solvent, therefore the emission of volatile organic compounds can be largely reduced. However, in some cases, acetone or other organic solvent has to be added in the synthesis process to reduce the high viscosity of reactive system, and these organic solvents must be removed at last [1–10]. This method not only adds the cost of organic solvent and equipment investment, but also pollutes the atmosphere. In order to resolve the problem, solvent-free process was proposed and has attracted more and more attention [11–20].

Galgoci et al. [20] discussed the cost/performance advantages and disadvantages for the urethane–acrylic hybrid polymer dispersions (HPDs) and *N*-methylpyrrolidone (NMP)-free versions of HPDs, and found that due to the true hybrid nature similar to an interpenetrating network, NMP-free HPDs could perform favorably in their preparation and some good physical properties compared to analogous solvent-containing HPDs.

In this work, we make modifications of the polyurethane–acrylic (PUA) hybrid emulsion by polysiloxane using the solvent-free method. We used dihydroxybutyl-terminated polydimethylsiloxane (PDMS) to incorporate the polysiloxane into the soft segment of polyurethane chains and obtained a new material of PDMS modified waterborne polyurethane–acrylic (Si-PUA). The preparation technology was discussed systematically and the effect of PDMS content on Si-PUAs was investigated.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI), Junsei Chemical Co., Ltd.; dimethylol propionic acid (DMPA) and 1,6-hexanediol (HDO) were the products of Aldrich Chemical Company; dihydroxybutyl-terminated polydimethylsiloxane (PDMS), C_{OH} = 60 mgKOH/g, Dow Chemical Company; polypropylene glycol (PPG), M_n = 2000, Daicel Chemical Industries, Ltd.; hydroquinone used as an inhibitor, Luoyang Chemical Reagent Company; butyl acrylate (BA), *n*-butyl methacrylate (BMA), triethylamine (TEA) used as neutralization agent, di-*n*-butyltin dilaurate (DBT) used as catalyst, ammonium persulfate (APS) used as initiator and sodium bicarbonate ($NaHCO_3$) used as pH buffer solution were all purchased from Shanghai Chemical Reagent Co., Ltd. DMPA, PDMS, PPG and HDO were vacuum desiccated and IPDI was vacuum distilled before using. BA and BMA were used as received.

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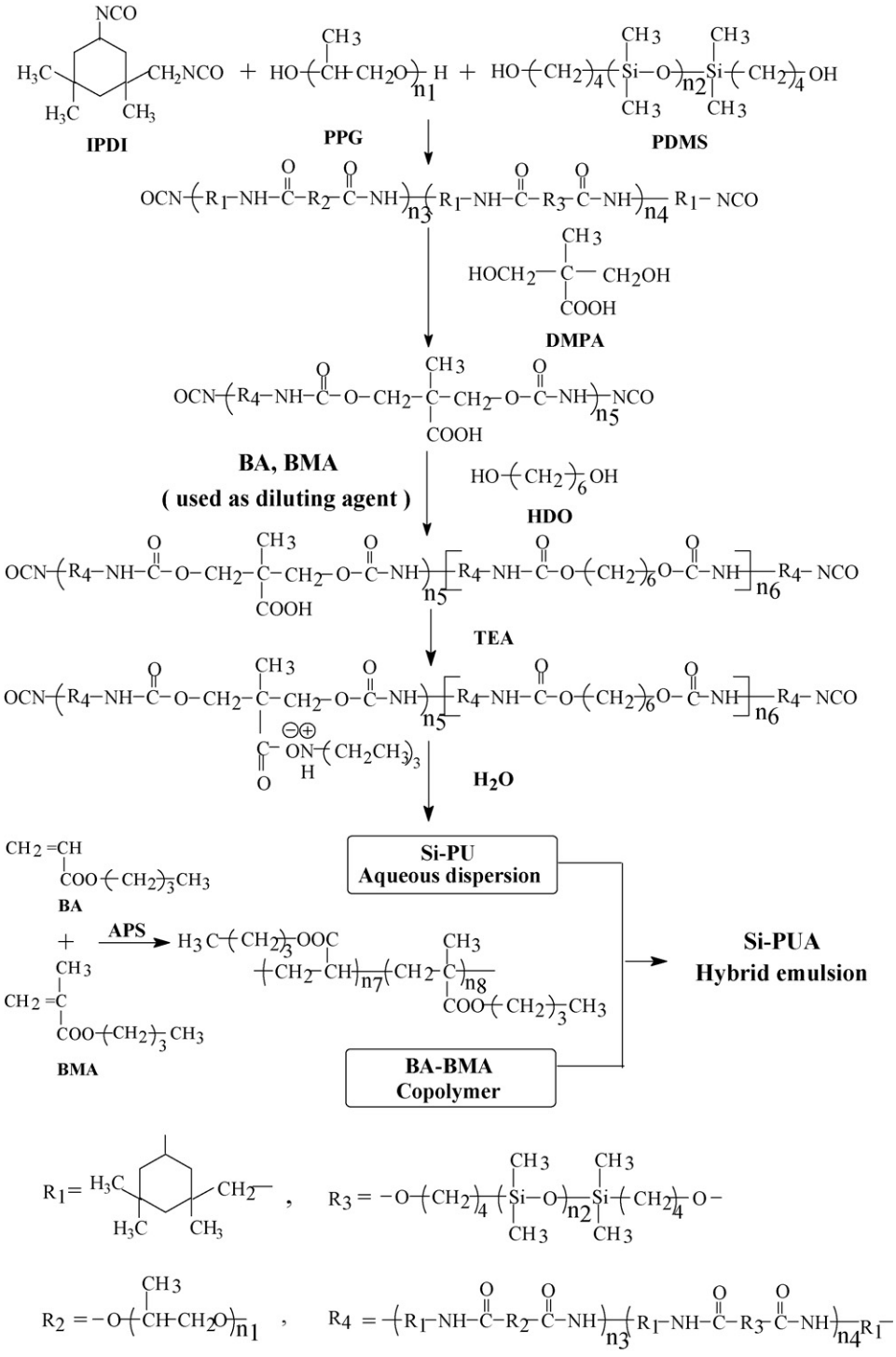

Scheme 1. Preparation process of Si-PUA hybrid emulsion.

2.2. Preparation of Si-PUAs

The hybrid emulsion of Si-PUA was prepared according to the procedure shown in Scheme 1. IPDI, PPG and PDMS were first added into a dry vessel equipped with a reflux condenser, a mechanical stirrer and a thermometer. The prepolymerization of polyurethane was carried out at 90 °C under N_2 atmosphere until the NCO content reached a theoretical value *A*. Then DMPA as a chain extender was added into the system and reacted at 80 °C until the NCO content reached a theoretical value *B*. After it was diluted with suitable acrylic monomer, HDO and catalyst DBT were added to react for another 5 h at 70 °C. During the process, suitable inhibitor was needed, and TEA as a neutralization agent was used to react with carboxy group in the side chain of prepolymer at 35 °C. Finally high speed shearing was used to emulsify the solution after suitable deionized water was added into the reaction system. The PDMS modified polyurethane (Si-PU) aqueous dispersion containing acrylic monomer was obtained. Continued the next