



Micromorphology and mechanism of polyurethane/polyacrylate membranes modified with epoxide group

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ABSTRACT

Polyurethane/polyacrylate (PUA) composite emulsions were synthesized based on the presence of pre-formed polyurethane chains. Glycidyl methacrylate (GMA), an acrylate monomer, was introduced into the system. Surface tension measurements assured the surface activities of the polyurethane emulsion. Dynamic light scattering (DLS) result showed that the average diameters and polydispersity were increased with the increment of GMA content. X-ray photoelectron spectroscopy (XPS) result indicated that the upper surface was rich in PU phase. The peak deconvolution results of XPS also confirmed the formation of PUA. The crosslinking degree and tensile strength were both enhanced due to the reaction between the carboxyl groups and the epoxide groups. Thermo gravimetric analysis (TGA) of the membranes showed that the thermal stability enhanced and the decomposition temperature was much higher than the pure PU membrane. X-ray diffraction (XRD) analysis, together with differential scanning calorimetry (DSC) results, demonstrated the amorphous nature of the PU matrix. Atomic force microscopy (AFM) observation performed the extremely flat membrane.

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1. Introduction

Polyurethane (PU) has excellent physical and chemical properties and therefore is widely used in a variety of applications, such as coatings, adhesives, binders, sealants and textile [1,2]. However, the PU has some drawbacks. Weak water-resistance and poor membrane performance are showed, resulting from the presence of hydrophilic moieties in polymer backbone chains [3]. In general, acrylic polymers (PA) are widely used because of their excellent toughness, compatibility and miscibility. However, some of the physical and mechanical properties of acrylic polymers are inferior to those of PU. An approach to achieving the best properties of both systems is to synthesize the polyurethane/polyacrylate (PUA) composite latex particles. The composite emulsion has the excellent flexibility of PU and the chemical resistance of acrylic polymers. In this system, the PU dispersion is used as seed for subsequent radical emulsion polymerization, resulting in intimately mixed composite particles; that is, both polymers are present in a single latex particle and form core-shell structure. Notably, the quality of the

membrane is often lower, which is attributed to a low compatibility between the two components [4,5]. Glycidyl methacrylate (GMA) was chosen to enhance the properties of the PUA membranes.

GMA, acrylate monomer exhibits polymerizable methacrylic unsaturation and an epoxy group. GMA has been used extensively into a large number of chemical reactions due to the reactivity of epoxide groups. The monomer is copolymerized by means of free radical initiators, and the pendent epoxy group is found to be very effective to bring about the modification process [6]. When the aqueous dispersions are casted as membranes, the pH of the reaction medium decreases and makes the epoxide ring-opening reaction more favorable to happen. These epoxide groups are reactive with carboxylic acid group and can react at low temperature, e.g. 20–40 °C. So the crosslinking reaction between the carboxyl group and the epoxide group occurs [7,8]. Li et al. discussed a heterogeneous-phase reaction mechanisms between the water-soluble chondroitin sulfate (CS) and the water-insoluble GMA in an aqueous medium at room temperature. Both of the reaction mechanisms, including a rapid reversible transesterification and a slow irreversible ring-opening conjugation, took place simultaneously. Over the initial stage of the reaction, there is a predominant formation of the resultant products of the transesterification. With the evolution of the reaction, there is a decrease in pH of the reaction medium that limits the transesterification and makes the epoxide ring-opening mechanism more favorable. For a long period of

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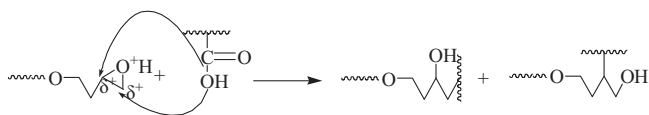


Fig. 1. The ring-opening mechanism of GMA with carboxylic acid group.

reaction, the formation of the resultant products of the epoxide ring-opening mechanism would be predominant over that of the transesterification mechanism. The quantitative analysis was carried out by the ^1H NMR data. The ring-opening reaction contributed to more than 80% of the total substitution efficiency, but the products of transesterification were reduced to less than 20% [9]. Reis et al. reported a detailed examination of the reaction mechanisms of poly-(vinyl alcohol) (PVA) and poly-(acrylic acid) (PAAc) by GMA in water. The chemical reactions of GMA with carboxyl groups and alcohols of the macromolecules in an aqueous solution under transesterification and epoxide ring-opening reaction were discussed. The proportion of the reaction products of transesterification and epoxide ring-opening were also calculated by the ^1H NMR data. The ring-opening reaction product contributed to 85.7% [10]. The chemical reaction of the GMA with acid groups ($-\text{COOH}$) of the macromolecules in an aqueous solution is shown in Fig. 1.

Although there have been some reports demonstrating the benefit of these composite emulsions, the average diameter of the composite emulsions was mostly in the range of micron scale [11,12]. Even though there are a few reports concerning the synthesis and characterization of the nanograde core-shell composite PUA emulsion, there are no systematic reports concerning the surface tension property of the polyurethane emulsion [12,13,3].

In this article, aqueous polyurethane dispersion was prepared by using carboxyl acid group to make the polyurethane dispersible and then nanograde core-shell composite emulsions were obtained. PU was used as seeds in the soap-free emulsion polymerization. Surface tension, dynamic light scattering (DLS), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), electronic tensile machine, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (XRD) and atomic force microscopy (AFM) were employed to investigate the structures and properties of the composite emulsions and their membranes. The influences of GMA content on the solvent swell and gel content were studied. The epoxide group in GMA was found to be very effective to bring about the ring-opening reaction with carboxylic acid group.

2. Experimental

2.1. Materials

Isophorone diisocyanate (IPDI), Polycaprolactone polyol (PCL, $M_n = 1000$), 2,2-Bis(hydroxymethyl) propionic acid (DMPA) were purchased from Qingdao Runcang Chemical Co., Ltd.; Trimethylol propane (TMP) was supplied by Sinopharm Chemical Reagent Co., Ltd.; Dibutyltin dilaurate (DBTDL), N-Methyl-2-pyrrolidone (NMP), Triethylamine (TEA) were produced by Tianjin Hongyan Chemical Reagent Co., Ltd.; Methyl methacrylate (MMA), 2-Hydroxyethyl acrylate (HEA), Acetone, Tetrahydrofuran (THF), Potassium persulfate (KPS), Butyl acrylate (BA) were supplied by Peking Chemical Reagent Co., Ltd.; Glycidyl methacrylate (GMA) was supplied by Suzhou Anli Chemical Factor. All raw materials are laboratory grade chemicals and were used as received without further purification. PCL were dried in vacuum at 100°C before use [14,15].

2.2. Preparation of PUA composite emulsions

2.2.1. Preparation of PU dispersion

The synthesis of the polyurethane seed dispersions was carried out in a four-necked glass reactor equipped with a mechanical stirrer, a thermometer, a nitrogen inlet and a condenser with a CaCl_2 drying tube. Polyurethane prepolymer based on IPDI, PCL, DMPA and TMP were prepared with NMP as solvent and DBTDL as catalyst. The reaction was carried out at 80°C in a water bath under a nitrogen atmosphere for 2 h. Then, HEA was added sequentially into the reactor and reacted for 1.5 h. The double bond-end capped polyurethane prepolymer was obtained. After the prepolymer temperature dropped to room temperature, the prepolymer was neutralized by TEA for 15 min and the degree of neutralization was 100%. The PU dispersions with solid content of 30 wt% were obtained by adding an adequate amount of distilled water.

2.2.2. Preparation of core-shell PUA composite emulsion

The core-shell PUA composite emulsions were prepared by soap-free emulsion polymerization. The above-synthesized anionic aqueous PU dispersion was used as seed emulsion. The PU dispersion acted as not only macromonomers but also macromolecular emulsifier. The mixture of MMA, BA, GMA and HEA were used in the radical polymerization stage for obtaining core-shell PUA. The polymerization was carried out with KPS as initiator. The aqueous solution of KPS was dropped into the reactor at 80°C within 2 h. When KPS was added into the dispersion, the acrylate monomers swollen in PU dispersion were initiated. After the addition, the polymerization was kept at 80°C for 3 h. After completing copolymerization, core-shell structure was obtained. The synthesis process of PUA aqueous solution is summarized in Scheme 1. The sample designation and composition was shown in Table 1.

Homogeneous membranes were prepared by pouring the emulsions onto a flat Teflon disk and drying under ambient conditions for some days and then at 60°C for 24 h. After demoulding, the membranes were stored in desiccators to avoid moisture.

2.3. Characterization

Surface tensions were measured by the ring method with XJZ-200 surface tensiometer (Chengde Jin Jian Testing Instrument) at 25°C . The polyurethane surfactant aqueous solutions in a series of concentrations had been prepared without further cleaned purification at room temperature and were placed in a vessel. Double distilled water ($\gamma = 72.1 \pm 0.01$ mN/m) and absolute alcohol ($\gamma = 22.3 \pm 0.01$ mN/m) were used to calibrate the instrument. To increase the accuracy of the surface tension measurements, an average of triplicates was determined.

Particle size of dispersions was determined using a Malvern instruments (Malvern Zetasizer Nano ZS) by Dynamic Light Scattering (DLS) method. Samples were diluted with water into an appropriate concentration as indicated by the instrument. The mean particle size was characterized by z-average diameter (D_z) and the particle size distribution was characterized by polydispersity index (PDI). They were automatically calculated by the computer, connected to the machine.

The transmission electron microscope (TEM) observations were carried out on an H-600 electron microscope (Hitachi Co., Japan) with an acceleration voltage of 120 kV. The emulsions prepared were diluted with deionized water to about 0.2 wt%. The samples were prepared by depositing a drop of well diluted blend suspension onto a 200-mesh copper grid and allowing it to set for 10 min. After drying, the samples were stained with phosphotungstic acid for another 10 min.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) were taken at ambient temperature using a model V70

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