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Properties and paper sizing application of waterborne polyurethane emulsions synthesized with isophorone diisocyanate

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ABSTRACT

In this work, a two-step synthesis methodology has been used to synthesize a series of waterborne polyurethane (WPU) emulsions with isophorone diisocyanate (IPDI), poly-caprolactone diol (PCL) and dimethylol propionic acid (DMPA) as monomers and ethylenediamine (EDA) as the chain extender, respectively. The influences of the NCO/OH molar ratio, DMPA content, chemicals-adding sequence, and acetone content on the physical properties of the resultant emulsions have been investigated in detail. The results show that the emulsion viscosity increases with an increase in the NCO/OH molar ratio or DMPA content whereas it declines sharply as the acetone amount increases. The emulsion particle size is seen to increase with the NCO/OH molar ratio but it decreases as the DMPA content increases. The chemicals-adding sequence is observed to strongly affect the particle size and viscosity of the resultant emulsions. For cast films, with an increase in the NCO/OH molar ratio, the elongation monotonically decreases while the tensile strength is seen to increase at first and then deceases. The film water absorption capacity is found to go up as the DMPA content increases. Furthermore, after sized with the emulsions, the paper water resistance is markedly improved and the 30s Cobb value is seen to decrease by 63% as compared to the unsized counterpart. The paper folding resistance and the tensile index are also improved to certain extents. For producing well-performed WPU emulsions for sizing paper sheets, an NCO/OH molar ratio of 1.6–1.8 and a DMPA content of 6.0–7.0 wt.% are preferably chosen.

1. Introduction

Paper products are mainly used for writing upon, printing upon and drawing but also extensively used for various packaging purposes. To satisfy these application requirements, the paper sheets must be able to provide a receptive surface for receiving ink such as from printers and copiers, apart from bearing a good surface appearance. Once the water component in the ink could readily penetrate into paper fibers the ink after being dried would become blurring. Thus well-performed water resistance should be required for the paper sheets to avoid the ink blurring. In order to reduce the tendency of the dried paper sheets to absorb liquid or water, paper sizing treatment must be taken during paper manufacture, for the purpose of allowing inks and paints to precisely remain on the surface of the paper sheets rather than be absorbed into the paper inside [1]. If not sized, the paper sheets made may easily absorb aqueous liquids by capillary action of the cellulose fibers, resulting in poor performance. For such reasons, a lot of surface sizing agents are used for producing high quality paper products [2,3].

Surface sizing agents are expected to be a kind of surfactants that are supposed, after sized on the surface of papers, to cover the paper cellulose and form a continuous film, with the hydrophilic tail facing the fiber and the hydrophobic tail facing outwards, subsequently creating a water-repellent paper surface [4]. Until now, the sizing agents that are the most frequently employed for paper manufacturing include alkyl ketene dimer (AKD) [5–7], starch [3,8], rosin [4,9], alkenyl succinic anhydride (ASA) [7,10], polyvinyl alcohol (PVA) [3,11], chitosan [3,12], carboxymethyl cellulose [3] and water-dispersible synthetic polymers [13]. The application of these materials has demonstrated that the application of the sizing agents could have greatly promoted the paper waterproof performance.

Waterborne polyurethane (WPU) emulsions, used as paper surface-sizing agents, have recently received increasing concerns in the papermaking industry [13]. Because of their environment-friendly nature and excellent mechanical properties, WPU materials have been abundantly used in the paint and ink industries as well [14–19]. Polyurethane macromolecules are known to comprise alternative sequences of soft and hard segments,

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and the soft segments are mainly stemming from high molecular weight polyol components while the hard segments are contributed by isocyanates, low molecular weight diols like short diols or DMPA, urethane and urea bond sequences [20]. Thus controlling the relative amounts of soft and hard segments in polymer chains may render WPU emulsions to be appropriately employed in a number of surface coating applications. However, there are still a lot of preparation variables, such as solid content, acetone content, NCO/OH ratio, DMPA content, second component, degree of pre-polymerization or neutralization and chain extension, that could strongly affect the emulsion particle sizes and distributions, and viscosity of the WPU emulsions and the properties of thin films made from them [21–27]. For examples, García-Pacios et al. [21] have investigated the synthesis of the WPU dispersions based on polycarbonate polyol, and they found that broader particle size distribution could be resulted as the NCO/OH ratio increases whereas both the dispersion viscosity and the dry film crystallinity decrease. Similarly, Otts and Urban [22] have reported that changing the NCO/OH ratio from 1.0 to 2.2 could significantly affect the film morphology, and that the cast films with higher NCO/OH ratio might possess increased glass transition temperature and surface roughness. Early, Kim and Lee [23] have considered the synthesis of the WPU dispersions from phthalic anhydride, neopentyl glycol, isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA) according to a prepolymer-mixing process, and their results show that the particle size decreases almost linearly with the DMPA concentration, and that the emulsion viscosity increases slowly at low DMPA concentration but it goes up rapidly at high DMPA concentration. More recently, Guo et al. [24] have detailed the influences of the NCO/OH molar ratio and DMPA content on the properties of the WPU emulsions synthesized with 2,4-Toluene diisocyanate (TDI) and IPDI. For better controlling the emulsion particle size, Mequanint and Sanderson [25] suggest that increasing the amount of ionic groups in the WPU emulsions could lead to smaller particles.

In recent works [24,27], we have attempted to synthesize different WPU emulsions for the purpose of being used as sizing agents for papermaking applications. To this end, a series of the WPU emulsions have been considered in this study. The emulsions used were synthesized with IPDI, PCL and DMPA as monomers and EDA as the chain extender by means of a two-step synthesis method consisting of pre-polymerization and chain-extending reaction. To our knowledge, the influence of chemical addition sequence on the WPU emulsions has less frequently been addressed and the paper sizing applications of WPU emulsions have been far less reported. In present work, the influences of NCO/OH molar ratio, DMPA content, chemicals-addition sequence, and acetone content on the physical properties of the resultant emulsions have been investigated in detail. Furthermore, the physical properties of the surface-sized paper sheets have been tested and compared with those of the pristine paper sheets.

2. Experimental

2.1. Materials

Poly-caprolactone diol (PCL, number-average molecular weight of 2000) was supplied by Shanghai Maotong Trading Co. Ltd., China. Dimethylol-propionic acid (DMPA) and isophorone diisocyanate (IPDI) were obtained from Aldrich, USA. N-methyl-2-pyrrolidinone (NMP), triethylamine (TEA), ethylenediamine (EDA) and acetone were purchased from Tianjin Guangfu Fine Chemical Co. Ltd., China. Double-distilled and deionized water was self-made and used through all the experiments.

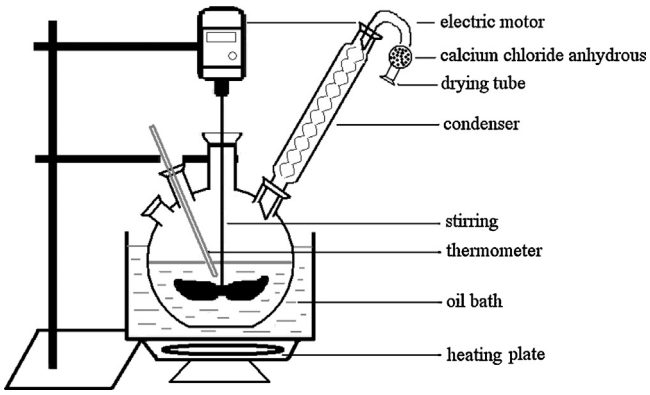

Fig. 1. Apparatus for preparing WPU emulsions.

Before conducting the WPU synthesis, PCL, DMPA and IPDI were all carried out drying treatment for water residual removal [24]. As well, NMP and acetone were both dehydrated by immersing 4 Å zeolite in the solvent for more than 1 week prior to any use.

2.2. Preparation of emulsion dispersions

Fig. 1 shows the apparatus used in this study for synthesizing WPU emulsions, including a 500-mL four-neck flask armed with a reflux condenser, a mechanical stirrer, a thermometer and a nitrogen gas inlet. Fig. 2 graphically shows the detailed protocol for preparing the WPU emulsions with IPDI, PCL and DMPA as the monomers and EDA as the chain-extending agent. Briefly speaking, the WPU emulsions were synthesized with two steps: pre-polymerization step and chain-extending reaction step. In step one, the monomers of IPDI, PCL and DMPA were reacted to obtain a low-molecular-weight NCO-terminated prepolymer. In step two, the prepolymer thus obtained was further reacted with a chain-extending agent of EDA to result in final WPU polymers with high molecular weight. Table 1 presents the detailed formulae used in this study for having synthesized different WPU emulsions. The procedure of preparing WPU is similar to that reported earlier [24] and may be given as follows.

The PCL after measured was added into the 500-mL flask, and then heated up to 80 °C. When all the PCL melted, IPDI at given amount was added under stirring with N_2 protection. After 1 h reaction, the DMPA solution in NMP (mass ratio of DMPA/NMP = 1:2) was added to the above system at the same temperature and maintained for another 3 h, subsequently resulting in the low-molecular-weight prepolymer. Note that the prepolymer molecules were all NCO-terminated and all hydroxyl groups from PCL and DMPA, as assumed, were theoretically consumed by NCO groups. Then the chain-extending reaction step began. The flask was cooled down from 80 to 50 °C, and acetone and TEA were subsequently added under continuous stirring. The former was used for reducing the system viscosity and the latter for neutralizing the carboxylic acid groups stemming from the DMPA monomer. After kept for 0.5 h, the flask was further cooled down to below 10 °C using an ice water bath, followed by addition of water and EDA into the flask. The resultant mixture was then warmed up to 70 °C for further chain extension reaction and acetone removing for 1 h, and yielding the final WPU emulsions with a theoretical solid content of 35 wt.%. Table 2 shows the specification, observations and stability of the resultant emulsions. Our results show that WPU emulsions synthesized in this work are mostly transparent and bear blue color, and they are satisfactorily stable after stored ambient for 6 months.