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Recent Advances in Synthesis of Waterborne Polyurethane and Their Application in Water-based Ink: A Review

Xing Zhou [1], Yan Li [1], Changqing Fang [1,2,*], Shujuan Li [1], Youliang Cheng [2], Wanqing Lei [2], Xiangjie Meng [3]

[1] School of Mechanical and Precision Instrument Engineering, Xi'an University of Technology, Xi'an 710048, China
[2] Institute of Printing and Packing Engineering, Xi'an University of Technology, Xi'an 710048, China
[3] Ship Design & Research Institute, Bohai Shipbuilding Heavy Industry Co., Ltd., Huludao 125004, China

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Over the last few years, waterborne polyurethane (WPU) was applied to various fibers, adhesives, primers for metals, caulking materials, emulsion polymerization media, paint additives, defoamers, associate thickeners, pigment pastes, textile dyes and biomaterials, resulting in the increasing enthusiasm of researchers to design and synthesize novel WPU with unique properties. Thus, various processes and raw materials have been developed to prepare WPU. This review gives an overview on the developments of WPU mainly derived from novel polyols, analyzes the potential application in water-based inks and presents the probable future research area about water-based inks. Notably, the poly(ε-caprolactone) and poly(lactic acid) are the versatile materials used in WPU synthesis and supply the potential special performance for preparing WPU. Meanwhile, addition–fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP) processes provide an opportunity to control the chain sequence of WPU and obtain products with the desired performance.

1. Introduction

Due to global limitation to the amounts of volatile organic compounds (VOCs) released to the atmosphere, environmentally friendly products are becoming popular and acceptable in industries. Low VOCs technologies have also gained a larger share in industry. Among these low VOCs products and technologies, water is the best choice to be used as a medium to synthesize and produce chemical products. Actually, water was regarded as a cheap, safe, non-toxic and environmentally benign solvent, which may enhance the rates and efficiencies of a wide variety of organic reactions[1].

Printing ink plays an important role in printing industry. In packaging area, printing inks is demanded increasingly all over the world. It is reported that more than one million tons of ink are produced in Europe annually[2]. According to the global ink report of Pira International, printing industry tends to be more sustainable. Water-based ink has been considered as the most potentially sustainable printing ink due to the advantages of environmentally benign, high solid content and gloss, low viscosity, etc. It is composed of four types of ingredients: colorant, vehicle or binder, additives and water. The vehicles or binder, known as the "Heart" of printing ink, have multiple functions in the ink. They disperse the pigments in the support material and bind it on the printing stock. Moreover, they can modify the rheological and mechanical properties of the printing inks. Nowadays, water-based inks are required to have increasing performance, environmental benign and non-toxicity, but the traditional binders are mostly phenolic resins, which are derived from tall oil rosin (colophony) or alkyd resins and cannot meet the requirement. The only way to improve the ink performance is to apply new resins as the binders, which refers to the water-based material, namely waterborne polyurethane (WPU).

WPU has sparked much interest in research in the past years. In fact, WPU are one of the most rapidly developing and active branches of polyurethane chemistry[3]. The reaction to produce WPU belongs to the representative organic reactions in water. It is a broad class of polymers produced through the reaction between polyurethane prepolymer and water[4]. The most widely used synthesis route of WPU is structural modification, i.e., modifying hydrophobic polyurethane backbone with built-in hydrophilic

* Corresponding author. Prof., Ph.D.; Tel.: +86 29 82312038; Fax: +86 29 82312512.
E-mail address: fcqxaut@163.com (C. Fang).

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groups[5]. Then deionized water is added to emulsify and disperse the hydrophilic WPU prepolymer, with the process of chain extension[6–8]. In synthesizing WPU, water plays the role of chain extender, emulsifier and solvent to react with WPU prepolymer.

Actually, due to the limited effect on the environment and numerous structural features which result in many useful and intriguing properties[9], WPU has been widely used as coatings for various fibers, adhesives for alternative substrates, primers for metals, caulking materials, emulsion polymerization media for different monomers, paint additives, defoamers, associate thickeners, pigment pastes and textile dyes[10]. Meanwhile, previous studies[7,11,12] have confirmed that WPU dispersions are able to apply in water-based ink. In WPU, there are numerous −NHCOO− groups; also there may be urea (−NH−CO−NH−) and even carbamic acid ester and carbodiimide groups, which are by-products that may confuse the structure and properties of WPU. To frustrate the side reaction, a vast number of efforts have been performed on the raw materials and scheme for preparing WPU. The raw materials of WPU dispersions are diisocyanates, polyols, chain extender (hydrophilic chain extender and difunctional low molecular chain extender), neutralizer and water. Notably, diisocyanates and polyols are the most important for constructing structure of WPU, which constitute hard segment and soft segment, respectively. Diisocyanates used to synthesize WPU can be either aromatic or aliphatic with different chemical reactivities. As a result, WPU coatings made from aliphatic isocyanates are of light stability[10,13,14], while that made from aromatic isocyanate are light degradation easily[4,15]. Meanwhile, chemical reactivities of isocyanate groups (primary and secondary NCO) on some diisocyanates are different[15,16], which is able to influence performance of WPU. Various types of diisocyanates have been used to synthesize WPU. They have been reviewed previously[10], and there is nearly no research about new diisocyanate. Therefore, unnecessary details about diisocyanate will not be given in this review. Polyols, which is available as reaction partners for diisocyanate, are mainly dihydroxy terminated long chain macroglycols with a wide range of molecular weight (M_w = 400–6000 g/mol). The most used conventional polyols in WPU synthesis are polyethers, polyesters, polydienes and polyolefins, which are critical for the performance of final products[10]. Due to the changeable structure of polyols, most attention has been paid to the polyols but not to diisocyanates in WPU industries and researches. A large amount of new polyols for special application have been synthesized and employed in WPU synthesis recently, which will be presented in section 2 in detail.

The main goal of this review is to give an overview of academic study in the field of WPU based on novel oligomer polyols and the potential application in the water-based ink. Especially, polyols obtained from the vegetable oils, which is the renewable resources, have a great research value and enormous potential application in the synthesis of WPU and water-based ink. To our best knowledge, no literature has provided a thorough review on the novel polyols and water-based ink recently. Thus, this review also aims to guide the beginner devoting to the WPU and water-based ink to find the research direction. The main content of this review is depicted in Fig. 1.

2. Synthesis Approaches

Various synthesis approaches have been developed for preparing WPU, including acetone, prepolymer emulsification, melt, and cetimine-cetazine processes[10]. The most widely used are acetone and prepolymer emulsification process. A great deal of literature has taken one of them or the mixing process for the synthesis of WPU[17–20]. Apart from these methods, several new processes have been developed for the synthesis of novel WPU, such as homogeneous solution polymerization (HSP)[21], miniemulsion polymerization process (MEPP)[22–25], addition–fragmentation chain transfer (RAFT) polymerization, and atom transfer radical polymerization (ATRP).

As known, WPU dispersion is commonly prepared by dispersing an isocyanate-terminated prepolymer in water using a tertiary amine to produce ionic centers, thus stabilizing the polymer particle. According to Otaigbe et al.[20], water and surfactant were mixed together to form a homogeneous solution to disperse the prepolymer, followed by adding the solution (20 wt%) of hexamethylenediamine (HMDA) in water. This process is called the homogeneous solution polymerization (HSP), as shown in Scheme 1[21]. Poly(ε-caprolactone) diol, dimethylolpropionic acid (DMPA) and methylene diphenyl diisocyanate were employed to obtain the dispersions in acetone followed by solvent exchange with water. The synthesis reaction could be divided into two steps. The first one is the formation of NCO-terminated prepolymer and the second one is the chain extension and dispersion in the mixture of water and surfactant (4 wt% based on the total solid) over 10 min periods. The properties of dispersions and films were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and hydrolytic degradation measurements. The results obtained revealed that the particle size of WPU decreased rapidly with increasing DMPA content. This ascribed to that the DMPA enhanced the hydrophobicity of the poly(ester-urethane), thus increasing DMPA content and leading to an improved poly(ester-urethane), resulting in smaller particle sizes. The explanation of relation between DMPA content and particle size is different from others[26], for which the DMPA enhanced the hydrophilicity of WPU, resulting in smaller particle size.

Recently, a one-step procedure, called miniemulsion process, was developed to synthesize WPU dispersions in water. Miniemulsions can be obtained by the combination of a high shear device, water-insoluble and monomer-soluble component, water and a surfactant[27]. To synthesize polyurethane of high molecular weight, Landfester et al.[22,23] controlled the reaction between isocyanate and hydroxyl (chain extension) and the reaction between isocyanate and water (foaming reaction) to a large extent via the aqueous miniemulsion process (Fig. 2). In this miniemulsion process, firstly, isophorone diisocyanate, finely divided dodecanediol, hexadecane, sodium dodecyl sulfate and water were mixed and stirred together for 1 h at room temperature. Then, the key procedure that the mixture was ultrasonicated for several minutes at low temperature to prevent the polymerization was carried out. After that, temperature was increased and catalyst was added to complete the polyaddition. The shortage of this process was that the properties of obtained polyurethane dispersions were defective. To improve the properties, such as mechanical stability, toughness, solvent and chemical resistance, etc., the mixture with polyacrylic system was used. Landfester et al.[22,23] and El-Aasser et al.[24] synthesized the blend of polyacrylic and polyurethane with good performance and nanoparticles in perfect morphology (Fig. 3). Apart from the synthesized process, the recipe (Table 1) and procedure for the preparation of blend of PU and poly(n-butyl methacrylate) (PBMA) hybrid miniemulsion has been reported by El-Aasser et al.[24], which provided a way for others to obtain the high performance polyurethane dispersion.

Meanwhile, Gaudin and Zydowicz[28] developed the miniemulsion process by interfacial step polymerization to prepare poly(urethane-urea) nanocapsules of 70 nm in mean diameter. According to the interfacial step polymerization in miniemulsion process, it was possible to reduce the size of polyurethane nanocapsules. The morphology and thermal properties of the nanocapsules were studied. Compared with the nanocapsules of 200 nm