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Synergistic effect of anionic and nonionic monomers on the synthesis of high solid content waterborne polyurethane

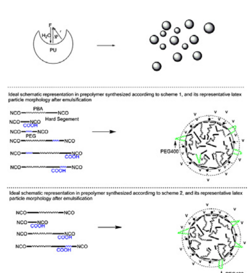
Hou Lijie[a,b,1], Ding Yongtao[b], Zhang Zhiliang[c], Sun Zhongsheng[b], Shan Zhihua[a,*]

[a] Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University, Chengdu 610065, China
[b] Chemistry and Chemical Engineering College, Yantai University, Yantai 264005, China
[c] Research Center of Analysis and Test, Qilu University of Technology, Jinan 250353, China

HIGHLIGHTS

- The synergistic effect of anionic and nonionic monomers on the properties of PUDs.
- An effective method to synthesize high solid content PUDs.
- A method makes the hydrophilic monomers in PU have the best emulsifying property.
- The effect of incorporating PEG on the properties of the derived films.

GRAPHICAL ABSTRACT



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ABSTRACT

High solid content waterborne polyurethane dispersions (PUDs) were synthesized via to the combination of ionic and nonionic monomers, in which the effect of the molecular mass of poly (ethylene glycol) (PEG) and its connection relationships of those hydrophilic groups in polyurethane with dimethylol propionic acid (DMPA) (through changed the synthetic schemes of PUDs) were researched. It is found that the molecular mass of PEG has obvious effect on combining with DMPA to synthesize PUDs. The incorporation of small molecular mass PEG200 (Mn = 200) had little effect on improving the dispersion and stability properties of anionic PUDs. But as the molecular mass of PEG increasing, they (PEG400, PEG600, PEG1000 and PEG2000) have obvious effect on improving the dispersion and stability properties, and can decrease the required dosage of DMPA to stabilize PUDs, moreover, cam improve the solid content of the latex. However, the effect of PEG2000 is less prominent than that of PEG400, PEG600 and PEG1000. The connection relationships of PEG with DMPA also have a certain effect on the property of the latex. When the small molecular mass one (PEG400) directly connects with DMPA, the synergistic effort is enhanced and the required dosage of DMPA to stabilize latex decreases to 2.0% (using DMPA alone needs 2.4%). As a result, the solid content of PUDs increased from 42% (using DMPA alone) to 52%, and the water resistance of PUDs is also improved. The thermal, dynamic mechanical and tensile-strength properties of derived films of PUDs were also analyzed, and the results show the incorporating PEG into polyurethane decrease the glass transition temperature of soft segments (T_{gs}), as well decreases the crystallinity and the extent of phase separation, which both cause the decrease of heat resistance. But

* Corresponding author. Tel.: +86 13018245966.
E-mail addresses: houlijie2007@sina.com (H. Lijie), ytding@ytu.edu.cn (D. Yongtao), zhzhl0531@163.com (Z. Zhiliang), sunzhongsheng120@sina.com (S. Zhongsheng), leather512@sohu.com (S. Zhihua).
[1] Tel.: +86 013475354815.

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through the combination, the synthetic formulas of PUDs with better tensile strength and elongation ratio than using DMPA alone were obtained. Besides, it is found that the molecular mass of PEG and the connection relationships of PEG with DMPA also had some influence on the properties of the derived films.

1. Introduction

Owing to strict environmental and legislative pressures, the conventional solvent-based systems have steadily been discouraged. Waterborne polyurethane dispersions (PUDs) are a kind of waterborne polymer colloids, use water as dispersing medium, contain little or no solvent, nontoxic, nonflammable, do not pollute the air, are considered a class of green material by the coatings and adhesives industry. In the last decade, PUDs have been widely used in the leather making, automobile, textiles, papers, wood, and footwear industries due to its environmentally friendly property [1–3]. The synthesis of PUDs is predominant to embed hydrophilic monomers, as inner emulsifiers (self-emulsification), in hydrophobic polyurethane backbone and to obtain the PUDs with fine dispersing in water. Anionic PUDs are commercially predominant, in which the dimethylol propionic acid (DMPA) as hydrophilic monomer is most often encountered in literature [4–6]. Anionic PUDs have fine particles size, stability and film-forming property, show good mechanical and adhesion properties, but are sensitive to pH value and electrolytes. Cationic PUDs are relatively few, but show excellent adhesion to anionic-substrates such as glass and leather. Nonionic hydrophilic monomers, normally containing oxyethyl segments, also are employed to synthesize PUDs [7,8]. Nonionic dispersions are stable against frost, pH change, electrolytes, mechanical influence and solvent, however, are thermosetting possibly with the temperature rising, moreover, the casting film of nonionic dispersions is more water sensitive than the one of ionic ones, so the advantage is often offset by its disadvantage, and it is few alone as internal emulsifier to synthesize PUDs [1]. Fortunately, the combination of ionic and nonionic monomers has the synergistic effect, can obtain PUDs with fine particles size [9], stable dispersion at low overall hydrophilic groups, and satisfactory resistance to frost and electrolytes [10–12].

Although having many advantages, PUDs also have some demerits. Compared to the conventional solvent-borne polyurethane, the derived film of popular PUDs is inferior in mechanical property, water and solvent resistance, which is due to containing some content of hydrophilic groups and its linear structure. Those problems can be resolved by proper molecular design [13–15], employing internal [16,17] or external crosslinking agent [18–21] and hybridization with other materials [22,23] in some degree. Besides those demerits, PUDs exhibits slow drying rates and adhesion due to the enthalpy of vaporization of water higher than that of solvent. In this regard, increasing solid content, or reducing the volume of water in PUDs, is an effective method to resolve the problem since most of the PUDs products solid contents are below 40%.

"High solid content and low viscosity latex" means fast drying, low energy cost, efficient transport and low cost, is always the aim both to academia and to commerce [24]. Although some companies can produce high solid content (about 50%) PUDs, for commercial secrecy, there are few open documents about high solid content PUDs.

The swelling of latex particles [1], which is caused by the electric double layer, along with the electroviscous effect of latex particles, which leads to the increase of viscosity [25], together make the decrease of solid content. So to decrease the dosage of ionic monomers in polyurethane, can increase the solid content. Lee and Kim [26] designed ionic groups in soft segments and chain terminal of polyurethane, which makes the hydrophilic groups easily enter the surface of particles, decreases the dosage of DMPA (down to 2%) and increases solid content up to 45%. But the decrease of ionic groups possibly leads to poor dispersion and instability of latex. Saw and his co-workers researched to the relation between phase inversion process and DMPA content, and the research shows when —COOH content in polyurethane is above 0.2 mmol/g (2.7% DMPA), the latexes are stable. The water addition to make phase inversion process increases (means the possible limit of solid content decreases) as the content of —COOH increases. When the content of —COOH decreases to below 0.2 mmol/g, the latex forms mixture structures including PU/W, W/PU/W and PU/W/PU/W types latex particles, at the same time it needs more water addition to make phase inversion happen compared to the sample containing 0.2 mmol/g DMPA, besides, the latexes become unstable [27]. Other relative research work by Y. Chen and Y.L. Chen verifies that a minimum content (0.178 mmol/g or 2.4% DMPA) of —COOH is required to form stable dispersions [28]. From existing research and experience, employing ionic monomers alone as hydrophilic groups has great limit in developing high solid content PUDs.

It is well known that the combination of ionic and nonionic surfactants (can make CMC and surface tension decrease) is an effective method to enhance the efficiency of surfactants. As to the synthesis of PUDs, the combination of ionic and nonionic monomers also has been attempted and got finer particle size than using ionic monomers alone [9], which implies that the combination has positive effect on the dispersion and stability properties of PUDs. We always hope to get stable and fine particles size latex with the least hydrophilic groups, which means the less swelling of latex particles and then PUDs with higher solid content and better water resistance can be obtained. So it needs the incorporated hydrophilic monomers make the best effort on the emulsifying properties of PUDs. Besides, the location of the hydrophilic groups in the molecular chain of emulsifiers has important effect on the properties of emulsifiers, the connection relationships of anionic and nonionic monomers or the position of those hydrophilic groups in polyurethane should also have an influence on the dispersion and stability properties of PUDs.

But so far, there is inadequate understanding to the influence of those facets. Therefore, there is need to do a more detail research into the combination of anionic and nonionic monomers. In this study, we used different molecular mass nonionic monomers (PEG) combining with anionic monomer (DMPA) as hydrophilic groups in polyurethane, and changed the connection relationships of them through different synthetic schemes, to analyze the effect of PEG (including its molecular mass) and the connection relationships on the properties of latex, as well the properties of derived films. The main objective of the work reported here is to get a further understanding to the combination of anionic and nonionic monomers to synthesize PUDs, to make those hydrophilic monomers have the best emulsifying properties, and to use the least hydrophilic monomers to synthesize stable PUDs, as well to obtain PUDs with high solid content and fine water resistance. Of course, the research here should contribute to the synthesis of other kinds waterborne polymer colloids, especially to the ones (e.g., polyurethane, polyesters, and epoxy resins) made by phase variation process, to get excellent dispersion and stability properties.