

## WATERBORNE POLYURETHANE-ACRYLIC HYBRID POLYMER BASED ON PTMEG: PHYSICAL AND MECHANICAL PROPERTIES

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### Abstract

A series of waterborne polyurethane-acrylic (PUA) hybrid dispersions, with potential use as adhesives and coatings, derived from polytetrahydrofuran glycol (PTMEG) were prepared. The influence of the NCO/OH ratio and DMPA content on the properties of both the PUA aqueous dispersions and their films were evaluated. The structures and some mechanical performances of the PUA films were employed with FT-IR and mechanical measurements. The experimental data demonstrated a non-linear relationship between the properties of the obtained products and the NCO/OH ratio and the DMPA content. When the DMPA content was up to 8.0%, the PUA achieved the minimum particle size of 8.2nm and maximum tension strength of 2.53MPa, respectively.

### 1. Introduction

Waterborne polyurethane (PU) has been found to possess excellent physical and chemical properties, and could be prepared from many

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Keywords and phrases: polyurethane-acrylic, dispersion, in-situ polymerization, mechanical property.

Received June 13, 2012

commercially available polyols, isocyanates, and chain extenders [1, 4, 8]. This environment-friendly material is often used in various industry parts, such as coatings for wood and automobiles, biologic materials, textiles, leather and printing inks, and so on [3, 6]. However, pure suffers from highly costing, poor chemical resistance, and low gloss because of the hydrophilic group such as carboxyl group in their molecule chains, which has restricted their use in many industrial applications [5]. Polyacrylate polymers are known to show an outstanding performance in the weather-ability, chemical resistance, adjustable mechanical properties, and low cost. Therefore, in an attempt to combine polyurethane with polyacrylate, a more elegant way is expected to synthesize the polyurethane-acrylate (PUA) hybrid polymer with an effective chemical technology to increase the performances of the final eco-friendly materials [9], in which both polyurethane and polyacrylate are present in a single dispersion particle, and the PUAs are expected to provide the advantages of both polyacrylate and polyurethane. In recent years, researches on preparation and characterization of PUA hybrid dispersions have seen an important progress. Majid et al. [7] found that the PU modified with acrylic resin showed the lowering of cost and the improvements of properties.

Although many of the journal articles on PUA in the literature appear to focus almost exclusively on the application of these interesting systems [2, 10], there are relatively little systematic publications on PUA to generate basic data aimed at providing primary insights into the relationships among the polymer structure, fundamental physical and mechanical properties of these dispersions and their films during use. In this work, various aqueous PUA hybrid dispersions based on PTMEG polyether polyol were prepared by in-situ polymerization technology, with the aim of broadening the understanding of these PUA's structure-properties relationships. Moreover, influence of the NCO/OH ratio and the DMPA content on the properties of the PUA was investigated.

## 2. Experimental

### 2.1. Materials

Polytetrahydrofuran glycol polyether polyol (PTMEG,  $M_n = 2,000$ ), was produced by Yutian Petrochemical Co. in Qingdao, China. Dimethylol propionic acid (DMPA) was produced by PERSTOP Co. in Switzerland and dried before use. Isophorone diisocyanate (IPDI) was supplied by HUL Co. in Germany. Hydroxyethyl methyl acrylate (HEMA) was provided by Yinlian Chemical Ltd. in Wuxi, Jiangsu, China. Methyl methacrylate (MMA), butyl acrylate (BA), N-methyl-pyrrolidone (NMP), triethylamine (TEA), and azobisisobutyronitrile (AIBN) were obtained from Guoyao Chemical Ltd. in Shanghai, China. Acetone was obtained from Solvent Co. in Shanghai, China.

### 2.2. Preparation of waterborne PUA dispersions

A calculated amount of PTMEG, DMPA, and IPDI were first added into a dry 250mL four-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser. Then, DBLT was added as catalyst when the mixture was heated to 60°C.

The mixture was heated to 85°C for 4h until the content of NCO group reached a theoretical value. The content of -NCO was monitored by the standard dibutylamine titration method. During the prepolymerization, a little catalyst di-*n*-butyltin dilaurate was needed, and appropriate acetone was also added into the system to reduce the viscosity. Then, the reactants were cooled down to 60°C. HEMA was added into the system and reacted at 60°C for 5h. When the temperature was cooled down to 40°C, TEA were added into the flask subsequently and reacted at 40°C for 30min. Subsequently, a mixture of calculated BA and MMA was added into the prepolymer, and the prepolymer/monomer mixture was then dispersed into deionized water under vigorous stirring. Finally, AIBN was added into the dispersion subsequently, extension of prepolymer and the copolymerization of vinyl monomers at 70°C. Steady PUA-I aqueous dispersion was prepared after being reacted for 4h. The solid content of the obtained dispersion was about 30%.

PUA films were prepared by casting the aqueous dispersions into a poly (tetrafluoroethylene) mold, laying aside at room temperature for 2-3 days.

### 2.3. Characterization

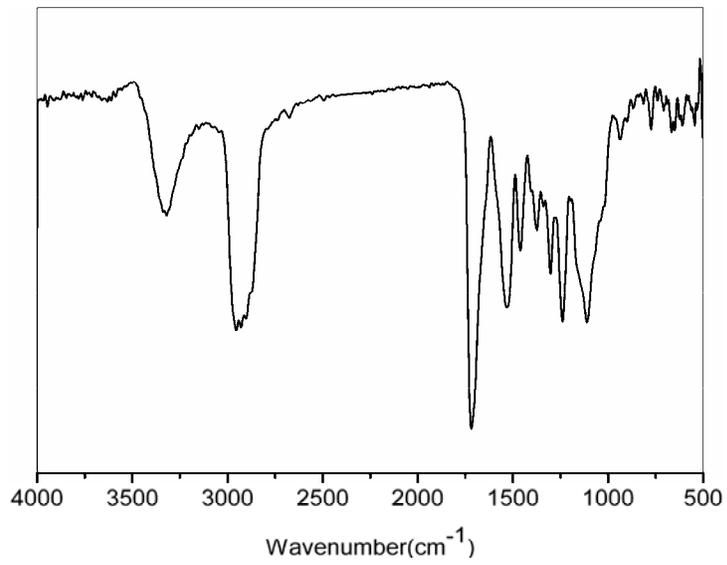
The FT-IR spectra of the PU aqueous dispersions were recorded by using a Nicolet Magna-IR 550 FTIR spectrometer at 25°C. The particle size of the PUA aqueous dispersion was measured by a Microtrac UPA 150 Particle Size Analyzer. The viscosity of the PUA aqueous dispersion was measured by an NDJ-79 rotation viscometer at 25°C and a shear rate of 2000s<sup>-1</sup>.

The mechanical properties for all samples were conducted on an Instron 4465 testing machine under 50mm/min crosshead rate, and the samples were made in accordance with GB1040-79. The hardness of the modified PUA films was measured according to GB/G1703-93.

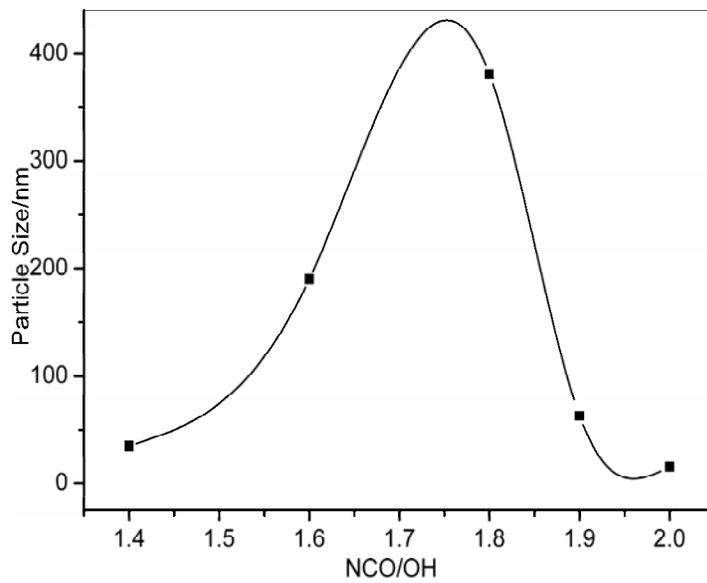
## 3. Results and Discussions

### 3.1. Characterization of the structure for PUA film

The chain structure of PUA was confirmed by Fourier transform infrared (FTIR) spectroscopy. It was mainly used to check the completion of polymerization reaction, in terms of disappearance of the NCO band at 2270cm<sup>-1</sup> illustrating the NCO had basically been reaction. Besides, the FTIR spectra of PUA showed the absorption peaks of typical polyurethane at 3322cm<sup>-1</sup>( $\nu_{\text{N-H}}$ ), 2895–2971cm<sup>-1</sup>( $\nu_{\text{C-H}}$  of CH<sub>2</sub> and CH<sub>3</sub>), 1711cm<sup>-1</sup>( $\nu_{\text{C=O}}$ ), and 1101cm<sup>-1</sup>( $\nu_{\text{C-O-C}}$ ), respectively. It indicated that both PU and PA structure had formed in the modified PUA.



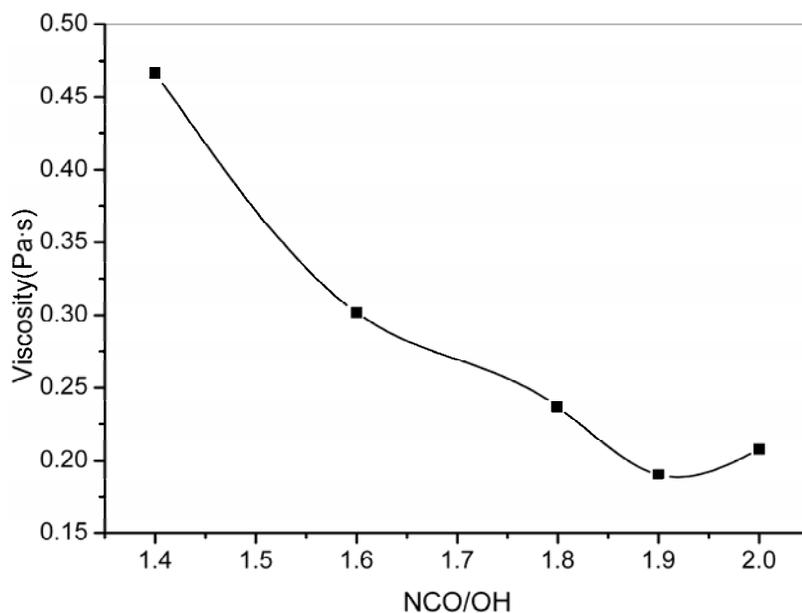
**Figure 1.** FTIR spectroscopy of PUA.



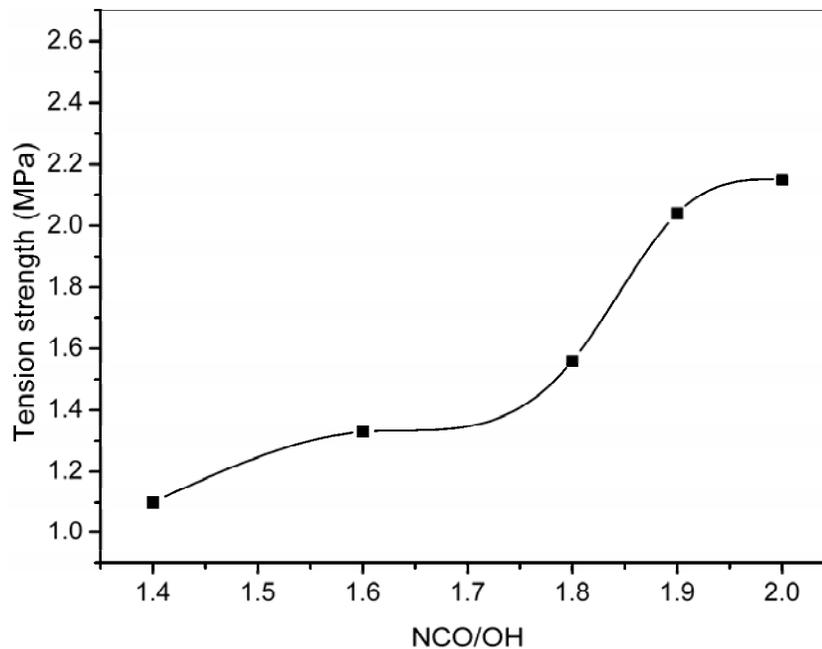
**Figure 2.** Particle size of PUA at different R.

### 3.2. Influence of NCO/OH ratio on the properties and PUA dispersions and their films

Figure 2 showed particle size of the aqueous PUA dispersions at different R. It indicated that with the increasing of the R, the particle size of PUA firstly increased then decreased, it may be due to the changes of hard segment content in the polyurethane with different R. On the other hand, a decrease in the viscosity of PUA dispersions was produced by increasing R, which inhibited the fragmentation of the microphase into smaller particles during its dispersion in water, shown as in Figure 3. The tension strength for different PUAs was listed in Figure 4. Due to the formation of cross-linked structure between PU and PA and intermolecular hydrogen bonds among PUA molecules, the PUA films showed an increasing tensile strength at higher R.



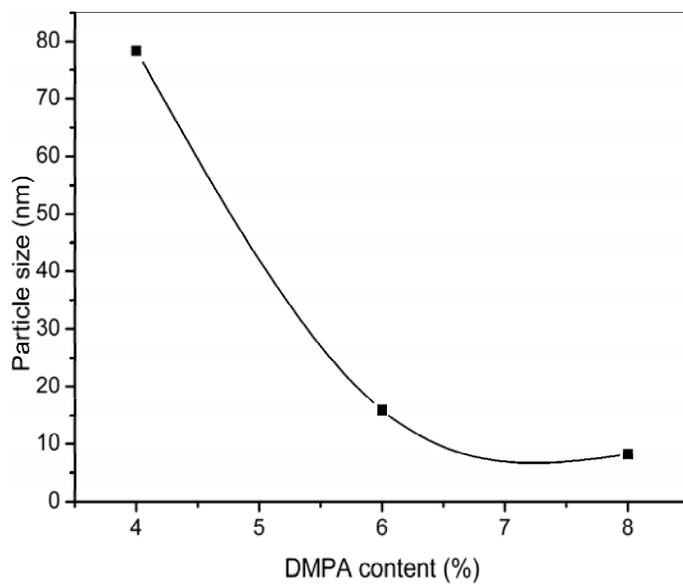
**Figure 3.** Viscosity of PUA dispersions at different R.



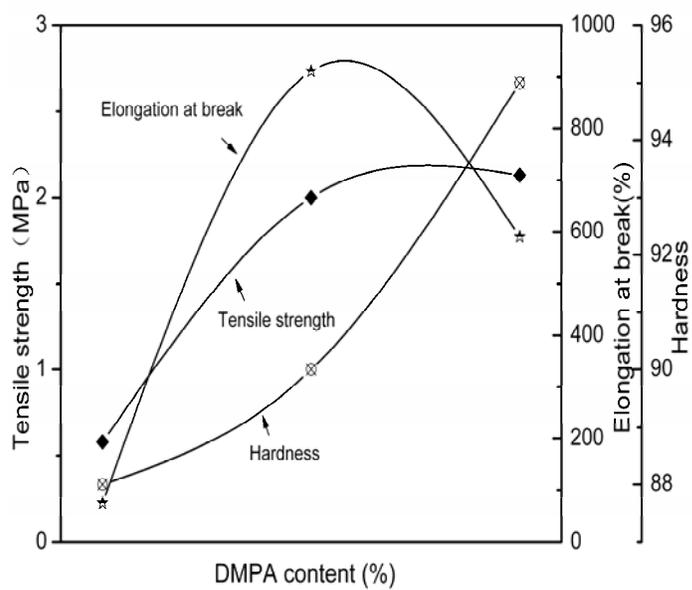
**Figure 4.** Tension strength of PUA at different R.

### 3.3. Influence of DMPA content on the properties and PUA dispersions and their films

At a constant R of 2.0, the particle size and mechanical properties of PUA were analyzed, as shown in Figures 5 and 6. With the increasing of DMPA content, the particle size of PUA dispersions decreased and the mechanical properties of the corresponding films enhanced, and showed a minimum particle size of 8.2nm and maximum tension strength of 2.53MPa, respectively, resulting from the hydrophilic of DMPA chains and hydrogen bonds among hard segments.



**Figure 5.** Particle size of PUA.



**Figure 6.** Mechanical properties of PUA.

#### 4. Summary

Waterborne polyurethane-acrylic (PUA) hybrid dispersions based on isophorone diisocyanate (IPDI), polytetrahydrofuran glycol (PTMEG), dimethylol propionic acid (DMPA), and hydroxyethyl methyl acrylate (HEMA) were prepared. The NCO/OH ratio and DMPA content were varied, and their effects on PUA properties were studied. The results indicated that with the increasing of the R, the particle size of PUA firstly increased then decreased, the viscosity of PUA dispersions decreased and the PUA films showed an increasing tensile strength at higher R. The obtained PUA have great potential application, such as coatings, leather finishing, adhesives, sealants, plastic coatings, and wood finishes.

#### Acknowledgement

This work was financially supported by China Postdoctoral Science Foundation (2011M500865), Jiangsu Planned Projects for Postdoctoral Research Funds (grant no. 1002033C), Agricultural Independent Innovation of Jiangsu Province (CX(11)2032), and Jiangsu Province Key Laboratory of Fine Petro-chemical Technology (213164).

#### References

- [1] A. Barreiro, Y. Carotenuto, N. Lamari, F. Esposito, G. Romano, A. Ianora, A. Miralto and C. Guisande, *Journal of Experimental Marine Biology and Ecology* 401 (2011), 13.
- [2] S. M. Cakic, J. V. Stamenkovic and I. S. Ristic, *Polymer Degradation and Stability* 94 (2009), 2015.
- [3] M. M. Clara, G. O. Fernando, P. A. Isabel, C. Javier, F. Ignacio and R. Vicente, *Journal of Molecular Biology* 367 (2007), 1431.
- [4] E. H. Kim, Y. G. Jung and U. Paik, *Thin Solid Films* 518 (2009), 1424.
- [5] X. Kong, S. M. Li, J. Q. Qu and H. Q. Chen, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 47 (2010), 368.
- [6] H. T. Lee, S. Y. Wu and R. J. Jeng, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 276 (2006), 176.

- [7] K. Majid, *Advances in Polymer Technology* 22 (2003), 218.
- [8] H. Martin, H. Kind, N. Mitchell and S. Howorka, *Journal of the American Chemical Society* 129 (2007), 9640.
- [9] A. K. Nanda, D. A. Wicks and J. U. Otaigbe, *Macromolecules* 39 (2006), 7037.
- [10] C. Sow, B. Riedl and P. Blanchet, *Progress in Organic Coatings* 67 (2010), 188.

