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Preparation and assistant-film-forming performance of aqueous polyurethane dispersions

Lei Wang [a], Yanan Zhu [b], Jinqing Qu [a],*

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, Guangdong, China
[b] Carpoly Chemical Group Co. Ltd., Jiangmen 529085, Guangdong, China

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ABSTRACT

A series of novel trimethylol propane monoesters were synthesized to prepare aqueous polyurethane dispersions (PUD), which were used as a polymer coalescent to assist the film forming of high T_g poly-acrylate latexes (PA). The effects of trimethylol propane monoester categories, NCO/OH molar ratios, soft segment contents, dimethylolpropionic acid (DMPA) contents, and diamine chain extenders on assistant-film-forming performance of PUD were investigated. The surface microstructures of PA/PUD blend latexes were also characterized with scanning electron microscopy (SEM) and transmission electron microscope (TEM). The results showed that the PUD prepared from trimethylol propane monolaurare (TMPLA) with long-chain alkyl groups displayed excellent assistant-film-forming ability. The assistant-film-forming ability of PUD was increased with decreasing of NCO/OH molar ratios and hard segment proportions. The optimum preparation process of better assistant-film-forming PUD was that isophorone diisocyanate (IPDI), polyether 220 (N220), trimethylol propane monoester (TMPLA) and adipic acid dihydrazide (ADH) as reactants, 1.5 of the NCO/OH molar ratios, 55/45 of the soft/hard segment mass ratio and 5% of ω (DMPA). The high T_g polyacrylate latexes with PUD could form a continuous transparent film at 5 °C with 30 g L^{-1} of the volatile organic compounds (VOC) contents and display good film performance.

1. Introduction

Nowadays, with ever-increasing environmental protection and health awareness, the ultralow or even zero volatile organic compounds (VOC) waterborne coating has become an important developing trend of coating industry [1–4]. For waterborne coating industry, polyacrylate (PA) coatings are widely used in coating industry due to possessing good performance including weather-resistance and physical and chemical properties.

However, waterborne coatings industry owning high film hardness and good chemical resistance need polyacrylate latexes with high glass transition temperature (T_g), amount of organic small molecule solvents are necessarily used as coalescents to assistant PA formation the excellent film at low temperature (below 5 °C), thus increased the VOCs contents in the waterborne coatings [5,6]. During the past several decades, some methods have been discussed to low or eliminate organic coalescent including using reaction active coalescent, core-shell polymer emulsions and hard/soft latex blends [7–9]. Emmons found that

a methacrylic dicyclopenadiene-oxygen-ethyl ester (DPOMA) carrying vinyl groups as a coalescent could both assist film-forming of PA and also react with oxygen catalyst with an organic cobalt salt, while it tremendously decreased the storage times of latexes [7]. The core-shell polymer latexes are intensively studied because these exhibit low minimum film forming temperature (MFFT) and are promising candidates for low VOC coatings [10–12]. Hughes and Michael demonstrated that the polyacrylate latexes with core/shell structures could significantly decrease the MFFT and VOC contents of latexes and coatings [10,11]. Cui found that there was no obvious boundary between core and shell part in polymer latexes and possibly existed more complex structures including interpenetrating network, grafted and ionic bonding [12]. However, it was very difficult to coordinate the balance of MFFT and T_g of polyacrylate latexes. As a result, the small molecular organic coalescent were also added to improve the film properties during film-forming process of waterborne industry coatings. Hard/soft latex blending methods which were explained that the high glass transition temperature (T_g) (i.e., hard latex) blended with a suitable amount of low-T_g latex (i.e., soft latex) could form a good continuous film at low temperature (below 5 °C) [13]. It has already become the most potential methods to prepare the ultralow and zero VOC contents waterborne wood coatings [14]. Jensen and Colombini reported

Table 1
The appearance, yields of mono-ester, di-esters and tri-esters of the trimethylol propane monoester.

monoester	appearance	Yield,%	di-ester yield,%	Tri-ester yield,%
TMPOA	Deep yellow	85.7	7.3	7.0
TMPBA	yellow	84.6	10.5	1.1
TMP-tBA	yellow	87.8	11.1	1.1

that the ratios of particle size between hard and soft latexes and the hard/soft blending composition had not only a great effect on MFFT and film properties, but also an obvious influence on blending morphology and viscoelastic [15,16]. Although the hard/soft latex blends could form a continuous and transparent film under low temperature, the proportion of soft latexes (*low T_g*) in blend systems often exceed that of hard latex (*high T_g*) and obviously decrease chemical resistance and hardness. We have previously synthesized a soft low T_g polyacrylate latexes ($T_g = -20\,°C$) and prepared hard/soft latex blends with a 65/35 of the mass ratio, and discovered that it could form a continuous and transparent film with good performance without addition of any small molecules organic coalescent [17].

On the other hand, aqueous polyurethane dispersions (PUD) have attracted an increasing attention in a broad range of applications due to their perfect properties including flexibility and excellent physical and mechanical properties [18–20]. Moreover, polyurethane as a type of block copolymer display excellent film-forming properties owing to the soft segment T_g low up to $-60\,°C$ [21]. Meanwhile, it is able to significantly change the film-forming ability and compatibility with other polymers by adjusting the ratios and structure between hydrophobic and hydrophilic groups [22]. Polyurethane-acrylic hybrid latexes (PUA) which introduced polyacrylate moieties in polyurethane may lead to form the synergistic effect of polyacrylate and PU, many literatures reported the preparation methods and relationships of structures and properties [23–25]. However, few studies reported PUD replaced the small molecular organic coalescent to assistant polyacrylate latexes film formation. In this paper, we first synthesized a series of trimethylol propane monoesters as a novel diol chain-extender (Scheme 1), and prepared aqueous polyurethane dispersions (Scheme 2), which were used as a polymer coalescent to assist the film forming of high T_g polyacrylate latex. The effects of its basic building blocks on the assistant-film-forming performance of PUD were investigated, we also demonstrate the relationship of the structure of PUD and its assistant-film-forming ability, and prepare good performance waterborne wood coatings with ultralow VOCs contents.

2. Experimental section

2.1. Materials

Polyacrylate latex (PA) (solid content = 47%, MFT = 50 °C, η = 2370 mPa·s, average particle size = 129 nm) was obtained from Carpoly Chemical Group Co., Ltd. Polypropylene glycol (N220, M_w = 2000), Polytetra-methylene-ether-glycol (PTMG, M_w = 2000), Polycaprolactone (PCL, M_w = 2000), Castor oil (C. O.) and dimethylol propionic acid (DMPA) were purchased from Perstorp Industrial Surfaces Co., Ltd. (Sweden). Toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), Hexamethylene diisocyanate (HDI) were offered by Degussa and bio-based aliphatic isocyanate polymer (FLO100) was offered by Vencorex. *p*-Toluenesulfonic acid was purchased from Adamas. Triethylamine (TEA, Aldrich). 1,4-Butyleneglycol (BDO, Perstorp), trimethylol propane (TMP), Lauric acid (LA), Oleic acid (OA), Benzoic acid (BA), and 4-*tert*-Butylbenzoic acid (tBA) were supplied by Aladdin. Ethylenediamine (EDA), diethylenetriamine (DETA), adipic acid dihydrazide (ADH) and 3-aminomethyl-3,5,5-trimethylcyclohexylamine (IPDA) were

purchased from Acros. Unless otherwise stated, reagents were purchased and used without purification.

2.2. Synthesis of trimethylol propane monolaurare (TMPLA)

A 500 mL three-necked flask was equipped with a three-way stopcock and a magnetic stirring bar, and flushed with dry nitrogen. Trimethylol propane (134 g, 1 mol), Lauric acid (200 g, 1 mol), xylene (30 mL) and *p*-toluenesulfonic acid (0.3 g) were fed in the flask. The mixture was stirred at 180 °C until the acid value upto 5 mg KOH/g. Then, the solvent was removed under reduced pressure and the partly crude product was purified by silica gel column chromatography using dichloromethane/methanol (20:1, v/v) as an eluent to afford the product of monoester. A light yellow liquid was obtained with a yield of 88.3%. Di-ester and Tri-ester were obtained with a yield of 9.8% and 1.9%, respectively. Trimethylol propane monooleic (TMPOA), trimethylol propane monobenzoic (TMPBA), and trimethylol propane mono-4-*tert*-butylbenzoic (TMP-tBA) were synthesized in a manner similar to TMPLA. The appearance, yields of mono-ester, di-esters and tri-esters of the trimethylol propane monoester were listed in Table 1.

The spectrum data and elemental analysis were given as follow.

2.2.1. TMPLA
IR (v^{-1}, KBr): 3428, 2943, 2873, 1490, 1382, 1256, 1175, 1089, 1033, 1005, 890, 837, 792, 747.
^{1}H NMR (400 MHz, δ in ppm, DMSO-d_6): 4.39 (s, −OH), 3.82 (s, −CH$_2$), 3.38 (m, −CH$_2$), 2.25 (m, −CH$_2$), 1.51 (m, −CH$_2$), 1.27 (m, −CH$_2$), 0.87 (m, −CH$_3$).
^{13}C NMR (100 MHz, δ in ppm, DMSO-d_6): 176.03, 62.44, 60.21, 41.47, 32.89, 31.31, 29.76, 28.88, 22.76, 21.19, 13.67, 8.83.
Elemental analysis: calculated C, 68.31; H, 11.47; Founded C, 68.47; H, 11.29;

2.2.2. TMPOA
IR (v^{-1}, KBr): 3419, 2977, 2895, 1607, 1403, 1270, 1161, 1107, 1029, 995, 903, 821, 785, 716.
^{1}H NMR (400 MHz, δ in ppm, DMSO-d_6): 5.48 (d, −CH=CH-), 4.01 (m, −OH), 3.65 (s, −CH$_2$), 3.45 (m, −CH$_2$), 2.32 (d, −CH$_2$CH), 2.17 (m, −CH$_2$CH), 1.64 (m, −CH$_2$), 1.30 (m, −CH$_2$), 0.84 (m, −CH$_3$).
^{13}C NMR (100 MHz, δ in ppm, DMSO-d_6): 173.01, 129.79, 65.53, 62.68, 43.47, 34.03, 33.31, 31.55, 29.63, 29.28, 29.12, 29.07, 25.29, 22.88, 21.19, 13.67, 8.83.
Elemental analysis: calculated C, 72.31; H, 11.63; Founded C, 72.16; H, 11.90;

2.2.3. TMPBA
IR (v^{-1}, KBr): 3420, 2988, 2930, 2871, 1805, 1600, 1010, 911, 827, 734.
^{1}H NMR (400 MHz, δ in ppm, DMSO-d_6): 8.05 (m, −ArH), 7.66 (t, −ArH), 7.56 (m, −ArH), 4.17 (s, −OH), 3.64 (s, −CH$_2$), 3.45 (m, −CH$_2$), 1.69 (s, −CH$_2$), 0.91 (m, −CH$_3$).
^{13}C NMR (400 MHz, δ in ppm, DMSO-d_6): 166.73, 133.45, 131.27, 129.88, 128.61, 67.32, 64.09, 43.04, 22.92, 7.78.
Elemental analysis: calculated C, 65.53; H, 7.61; Founded C, 65.33; H, 7.50;