Preparation and properties of high storage stability polyester polyol dispersion for two-component waterborne polyurethane coating

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Abstract. A new type of polyester polyol dispersion with good storage stability was prepared based on a hydrophilic monomer 5-sodium sulfodimethyl isophthalate (5-SIPM), and frequently-used monomers such as neopentyl glycol (NPG), dimethyl terephthalate (DMT), dimethyl phthalate (DMP) and trimethylolpropane (TMP) by the transpolycondensation and polycondensation method. The polyester polyol dispersion was characterized by FTIR and GPC. The proper content of these monomers were determined by the performance of polyester dispersion: the content of TMP was 15wt%, the content of NPG was 7.5wt% and the hydrophilic monomer 5-SIPM content was 5wt%. Two-component waterborne polyurethane (2K-WPU) coatings were prepared by Bayhydur® XP2487/1 and polyester polyol dispersions, which were stored before and after at 40 °C for 6 weeks, the prepared films have no differences in drying time, adhesion, pencil hardness, gloss and chemical resistance, the result also reveals that the polyester polyol dispersion have excellent storage stability resistance.

1. Introduction

Nowadays, as increasing demand for minimizing volatile organic compounds (VOCs) and hazardous air pollutants emissions, substantial waterborne systems have been introduced gradually to meet the requirements for environment-friendly coats, with lower toxicity and VOCs emissions compared to solvent-based products. Two-component waterborne polyurethane (2K-WPU) coatings appear better properties than one-component waterborne polyurethane coatings due to higher crosslinking density in coatings. 2K-WPU with the high performances of mechanical properties, chemical resistance and outdoor durability, has been used in industrial metal coating, plastics coating and automotive finishing [1-2]. Consequently, 2K-WPU coatings composed of polyisocyanate component and polyol dispersion component have attracted great interest from researchers. However, polyester polyol dispersion is the most widely used of polyol dispersion component. The structure of polyester polyol dispersion component has a significant effect on properties of 2K-WPU coatings, such as adhesion, hardness and impact resistance. Unfortunately, there are a lot of easily hydrolyzed ester bond in polyester polyol dispersion [3]. These ester bond hydrolysis reduces film properties and storage stability of polyester polyol dispersion. Hence, it is key to improve the storage stability of waterborne polyester in polyester polyol dispersion research. Yue [4] used trimellitic anhydride (TMA) as a hydrophilic monomer, synthesized polyester polyol dispersion by esterification process. The stability and properties of polyester polyol dispersion was decreased by the decarboxylation of TMA. Yasuhiko [5] used 2,2-dimethylol propionic acid (DMPA) as a hydrophilic monomer and avoiding decarboxylation,
synthesized polyester polyol dispersion by esterification process. But the difficulty of the process is
that the reaction of carboxyl group on DMPA is hard to control and reaction system is easy to be
gelation, because the carboxyl group of DMPA is partially reaction with hydroxyl group of other
monomer at the late stage of esterification reaction when temperature exceeding 200°C.

In this work, our group use 5-sodium sulfodimethyl isophthalate (5-SIPM) as hydrophilic monomer,
trihydroxy methyl propane (TMP) and neopentylglycol (NPG) with high sterically hindered neoamyl
structure to synthesize a novel type of polyester polyl dispersion through transpolycondensation and
polycondensation process. The polyester polyl dispersion has superior storage stability due to high
resistance ester bond. The influences of TMP, NPG and 5-SIPM content on the properties of polyester
polyl dispersion were investigated. Then the polyester polyl dispersion was applied to the
preparation of a new 2K-WPU coating with the Bayhydur® XP2487/1 polyisocyanate hardener. The
basic properties of that 2K-WPU coating using polyester polyl dispersion before and after storage for
6 weeks at 40 °C were studied. The results demonstrate that the properties of 2K-WPU coatings have
no obvious change in store of polyester polyl dispersion, including drying time, pencil hardness,
gloss, adhesion and chemical resistance.

2. Experimental

2.1. Materials
Dimethyl phthalate (DMP), dimethyl terephthalate (DMT), 5-sodium sulfodimethyl isophthalate (5-
SIPM), trihydroxy methyl propane (TMP) and neopentylglycol (NPG) were obtained from Tianjin
Kermel Chemical Reagent Co., China. Zinc acetate and antimony trioxide were provided by Aladdin
Industrial Co., China. Bayhydur® XP2487/1 polyisocyanate hardener (100% solid content) was kindly
supplied by Bayer Co., Germany. The agent BYK-028 and BYK-346 were purchased from BYK Co.,
Germany. All these reagents were used as such without any further purification.

2.2. Synthesis of the polyester polyl dispersion
The polyester polyl dispersion was prepared according to transpolycondensation (Figure 1) and
polycondensation process (Figure 2) with basic formulation (Table 1). The reaction was carried out in
four-necked flask equipped with a variable speed stirrer, a thermometer, nitrogen gas inlet tube, and
Allihn condenser. A Dean-Stark apparatus was used to remove the methanol and water of reaction.

| Table 1. Basic formulation to prepare the polyester polyl dispersion |
|----------------------|------------------|
| Materials            | Content          |
| DMT, DMP and 5-SIPM  | 1 mol (in total) |
| NPG and TMP          | 2 mol (in total) |
| Zinc acetate         | 0.04 wt%         |
| Antimonomous oxide   | 0.05 wt%         |
Experimental polyester polyol dispersion had been synthesized according to the following steps: DMT, DMP, TMP, NPG and 5-SIPM were placed in 250 mL four-necked round bottom flask. The mixture was heated to 140 °C and maintained for 0.5 h to get rid of the water contained in the raw materials under N₂ atmosphere. Zinc acetate as the catalyst for transpolycondensation, was then added and slow heating flask to 195 °C for 2 h, methanol produced in transesterification process was distilled from flask to Dean-Stark apparatus. Continuing to heat up to 200 °C and adding antimony trioxide as the catalyst for polycondensation. Then the flask was evacuated to 0.1MPa and maintained until all the dihydric alcohol was distilled from flask to Dean-Stark apparatus. At last, the flask was cooled to 120 °C and diluted with Butyl Cellosolve to 85% solids, and then distilled water was added in flask with stirring at 2000 rpm about 1 h to form the polyester polyol dispersion dispersion with 52±2% solid content.

Bayhydur® XP2487/1 (100% solid content) was chosen as polyisocyanate hardener for the preparation of 2K-WPU coating with the polyester polyol dispersion. Table 2 illustrates the properties of 2K-WPU coating.

| Components                      | Weight/g |
|---------------------------------|----------|
| Polyester polyol dispersion     | 69.36    |
| Byk-346                         | 0.3      |
| Byk-028                         | 0.4      |
| Water                           | 12.61    |
| Bayhydur® XP2487/1              | 17.33    |
2.3. Characterizations

2.3.1. Characterization of the polyester polyol dispersion

Fourier transformation infrared (FTIR) spectra of the polyester polyol dispersion was recorded on a Nicolet MAGNA-IR 560 FTIR spectrometer. Hydroxyl value of the polyester polyol dispersion was determined by chemical analysis in terms of standard methods HG/T 2709-95. Molecular weights and polydispersity of the polyester polyol dispersion were measured by gel permeation chromatography (GPC, Model PerkinElmer series 2000). DMF was used as a solvent and flow rate of 1.0 mL·min⁻¹ at 30 °C.

2.3.2. Characterization of 2K-WPU composed of polyester polyol dispersion

The water and solvent resistance of 2K-WPU films was measured as follows [6]. The 2K-WPU films were cut into 3×3 cm pieces and determined their dry weight. These films were immersed in water or solvent after a certain period of time, and were weighed immediately when the water or solvent attached to the surface was wiped off.

Other physical properties of 2K-WPU films were evaluated according to standard test methods [7] (dry time GB/T 1728-89, gloss GB/T 1743-89, adhesion ASTM D 3359, pencil hardness ASTM D 3363).

3. Results and discussion

3.1. Characterization of polyester polyol dispersion

In Figure 3, the following stretching vibrations are observed: The broad band at 3469 cm⁻¹ is due to -OH groups. Typical absorption peaks of 2963 cm⁻¹ to 2888 cm⁻¹ due to -CH₃ and -CH₂- stretching vibration are observed. Obvious sharp band at 1731 cm⁻¹ is due to C=O groups of ester linkage. In addition, other representative absorption peaks of 1175 and 1030 cm⁻¹ are due to asymmetric and symmetric stretching vibrations of S=O groups, and it illustrate that the formation of the desired polyester polyol dispersion containing sulfonic acid sodium groups (-SO₃Na⁺) through the transpolycondensation and polycondensation process [8].

Molecular weight including weight average weight (M₀), number average weight (Mₙ), Z-average molecular weigh (M_z) and polydispersity (PD) of samples was measured by GPC (Table 3). Table 3 shows the number average molecular weight of the polyester polyol dispersion is 2266, the polydispersity is 1.44, the molecular weight and polydispersity is desired.
Table 3. GPC results of polyester

|        | $M_n$/Da | $M_w$/Da | $M_z$/Da | PD ($M_w/M_n$) |
|--------|----------|----------|----------|----------------|
|        | 2266     | 3269     | 5055     | 1.44           |

3.2. Influence of TMP content

To investigate TMP content influence, a series of polyester polyol dispersions were synthesized based on different TMP content, the same ratio of other raw materials and experimental conditions. Their hydroxyl values and TMP contents are showed in Figure 4. It indicates that MPP synthesized at higher TMP content has a higher hydroxyl value. Generally, the hydroxyl value of polyester polyol dispersion is 100~150 mg·g⁻¹ to ensure that there is sufficient cross-linking point to prepare 2K-WPU coating. Hence, the optimal content of TMP was determined to 15% for the synthesizing reaction.

Figure 4. The relationship between the content of TMP and hydroxyl value

3.3. Influence of NPG content

The NPG content plays an important role in the synthesizing of polyester polyol dispersion, which can some what influence structure of high resistance ester bond and storage stability of the final products. Four samples of polyester polyol dispersions were synthesized at NPG content of 5, 7.5, 10 and 12.5wt%, respectively, and the results of influence of NPG content are exhibited in Table 4. As can be seen, when the NPG content exceeds 10wt%, the reaction system is very easy to gel. Because that carbon atoms in the side chain of NPG will also be involved in the condensation reaction at high temperatures. With the increase of NPG content, the proportion of hydrophilic monomer decreased, and the hydrophilic property was not enough to stabilize the resin in water. On the other hand, increasing of NPG content, the particle size of the polyester polyol dispersion increases and the stability decreases. Because the relatively less hydrophilic property was not enough to stabilize the polyester polyol in water with increasing of NPG content. Therefore, the optimum NPG content is found to be 7.5wt%.

Table 4. The impact of the ratio of NPG

| NPG content/wt% | Appearance                  | Storage stability (40 °C, 7d) | Particle size of dispersions/nm |
|-----------------|-----------------------------|-------------------------------|--------------------------------|
| 12.5            | gel                         | -                             | -                              |
| 10              | white, flocculation partly  | sediment                      | 221                            |
| 7.5             | white, without flocculation partly | good                       | 148                            |
| 5               | white, with blue light      | good                          | 91                             |
3.4. Influence of 5-SIPM content

A series of polyester polyol dispersions were prepared at different 5-SIPM content. The influence of 5-SIPM content on particle size, stability and water resistance of polyester polyol dispersion are presented in Table 5. It can be demonstrated that 5-SIPM content increasing leads to decreased particle size and water resistance, increased the stability of polyester polyol dispersion.

The number of hydrophilic -SO\(_3\)Na\(^+\) groups in polyester polyol dispersion increases with increasing 5-SIPM content. The -SO\(_3\)Na\(^+\) groups attract the water molecules forming a water layer on the surface of polyester polyol dispersion particles. Then the relative size of the water layer to total particle size increases with reducing polyester polyol dispersion particle size. With reducing polyester polyol dispersion particle size, the relative size of the external water layer to total dispersion particle size increases. Meanwhile, there is an increase in the number of total dispersion particles with reducing particle size [9]. The study of stability and water resistance of polyester polyol dispersion displays that polyester polyol dispersion based on the 5-SIPM content of 5 wt% has best comprehensive performance.

Table 5. The impact of the content of 5-SIPM

| 5-SIPM content/wt% | Appearance                  | Storage stability | Water resistance (60 ℃ 3h) | Particle size of dispersions/nm |
|--------------------|-----------------------------|-------------------|---------------------------|-------------------------------|
| 4.5                | milky white and opaque      | sediment          | unchanged                 | 202                           |
| 5                  | milky white and translucent | without sediment  | unchanged                 | 148                           |
| 5.5                | milky white and translucent | without sediment  | slight white              | 110                           |
| 6                  | brown and translucent       | without sediment  | white                     | 96                            |
| 6.5                | brown and transparent       | without sediment  | white, vesicle            | 78                            |

3.5. The storage stability of the polyester polyol dispersion

Table 6 presents that the appearance, solid content, acid value and pH value of polyester polyol dispersion have no obvious change in 6 weeks at 40 °C store condition. It indicates that the polyester polyol dispersion has excellent storage stability.

Table 6. Properties of the polyester polyol dispersions (before and after storage at 40 °C, 6 weeks)

| Items                  | Before storage   | After storage  |
|------------------------|------------------|----------------|
| Appearance             | milky white, with blue light | milky white, with blue light |
| Solid content/%        | 43.7             | 43.7           |
| Acid value/mg KOH/g    | 1.1              | 1.3            |
| pH value               | 6.0              | 5.3            |

3.6. The properties of 2K-WPU coating

Table 7. Properties of film in different the polyester polyol dispersions

| Properties                  | Before storage | After storage |
|-----------------------------|----------------|---------------|
| Surface drying time/min     | 30             | 40            |
| Hard drying time/h          | 5              | 6             |
| Adhesion/grade              | 0              | 0             |
| Pencil hardness/grade       | 2H             | 2H            |
| Gloss(20°)/%                | 92.7           | 92.5          |
| Gloss(60°)/%                | 97.3           | 98.0          |

Bayhydur® XP2487/1 (100% solid content) was chosen as polyisocyanate hardener for the preparation of 2K-WPU coating. Table 7 and 8 illustrate the some properties of 2K-WPU coating.
Drying time, adhesion, hardness, gloss and chemical resistance of 2K-WPU coatings using polyester polyol dispersions before and after storage for 6 weeks at 40 °C have no obvious change. It demonstrates that polyester polyol dispersion has the high content of hydroxyl groups, the high crosslinking and excellent storage stability.

Table 8. Chemical resistance of film in different the polyester polyol dispersions

| Chemical name   | Immersion time/min | Before storage | After storage |
|----------------|--------------------|----------------|--------------|
| 90# gasoline    | 10                 | 0              | 0            |
| Xylene          | 10                 | 2              | 2            |
| Ethanol         | 20                 | 2              | 2            |
| Acetone         | 10                 | 3              | 3            |
|                 | 20                 | 4              | 4            |

0 represents the best effect, 5 represents the worst effect.

4. Conclusion

(1) The FTIR result reveals the polyester polyol dispersion are in line with expectations. The GPC results indicate the number average molecular weight is 2266 and polydispersity is 1.44.

(2) The proper content of TMP was 15 wt%, the proper content of NPG was 7.5 wt% and the proper content of 5-SIPM was 5wt%.

(3) Drying time, adhesion, hardness, gloss and chemical resistance of 2K-WPU coatings using Bayhydur® XP2487/1 and the polyester polyol dispersions which were stored before and after at 40 °C for 6 weeks, the prepared films have no obvious change. It indicates that the polyester polyol dispersion has outstanding storage stability.

References

[1] García-Pacios V, Jofre-Reche JA, Costa V, Colera M and Martin-Martínez JM 2013
[2] Coatings prepared from waterborne polyurethane dispersions obtained with polycarbonates of 1,6-hexanediol of different molecular weights Prog. Org. Coat. 76 1484-1493
[3] Fan W, Du W, Li Z, Dan N and Huang J 2015 Abrasion resistance of waterborne polyurethane films incorporated with PU/silica hybrids Prog. Org. Coat. 86 125–133
[4] Hawkins C A, sheppard A and Wood T 1997 Recent advances in aqueous two-component systems for heavy-duty metal protection Prog. Org. Coat. 32 253-261
[5] Mehdipour-Ataei S and Zigheimat F 2007 Soluble polyesters with preformed ether and imide units: synthesis and properties Des. monomers polym. 10 145-152
[6] Wu J R and Chen, D J 2016 Synthesis and characterization of waterborne polyurethane based on covalently bound dimethylol propionic acid to e-caprolactone based polyester polyol Prog. Org. Coat. 97 203-209
[7] Huang K, Liu Y and Wu D 2014 Synthesis and characterization of polyacrylate modified by polysiloxane latexes and films Prog. Org. Coat. 77 1774–1779
[8] Wu G M, Kong Z W, Chen J, Huo S P and Liu G F 2014 Preparation and properties of waterborne polyurethane/epoxy resin composite coating from anionic terpene-based polyol dispersion Prog. Org. Coat. 77 315–321
[9] Lee H T, Wu S Y and Jeng R J 2006 Effects of sulfonated polyol on the properties of the resultant aqueous polyurethane dispersions Colloids Surf., A 276 176–185