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Preparation and Characterization of Low-gloss Waterborne Polyurethane Coatings

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Abstract—In this research, a series of anionic low-gloss waterborne polyurethanes were prepared, and their surface structures were studied. Samples were prepared with terminal hydroxyl polydimethylsiloxane (PDMS), polyethylene glycol (PEG) of different molecular weight, toluene diisocyanate (TDI), dimethylolpropionic acid (DMPA), in the presence of dibutyltin dilaurate (DBTDL) catalyst, neutrallized by triethylamine (TEA). Preparation process was optimized to get better emulsion stability and matting effect of coating. The preparation process is: at 90 ℃, react terminal hydroxyl polydimethylsiloxane, polyethylene glycol, toluene diisocyanate and dibutyltin dilaurate catalyst together for 4h. Cool the performed polymer to 50 ℃, then add quantified dimethylolpropionic acid and solvent such as tetrahydrofuran, heat to 70 ℃ and react for 2h. Cool polymer to room temperature, add quantified triethyl-amine and deionized water to make emulsions. Matting aqueous polyurethane under the conditions of R = 1.2, DMPA mass fraction of 6%, PEG molecular weight of 1000, PEG / PDMS molar ratio = 1: 3, catalyst mass fraction of 0.5%, neutralization degree 100%, latex solid content of 20%, gets the best overall performance, 60 ° gloss of 3.3, in line with matting standards.

Keywords-Waterborne Polyurethane; Polydimethylsiloxane; Polyethylene Glycol; Copolymerization; Low-gloss

I. INTRODUCTION

Waterborne polyurethane uses water as solvent, eliminating the danger of flammable and combustible solvent-based polyurethane in production and transportation. Furthermore, it is environmental friendly and will not harm people's health. Therefore, research on waterborne polyurethane is a hot zone [1]. In the matter of leather finishing, waterborne polyurethane has advantages of good air permeability and good moisture-penetrability [2] [3]. In leather products market, the pursuit of natural style and sense of genuine leather is a great trend, so the demand of leather that has a sense of genuine leather and low-gloss is increasing. Matting waterborne polyurethane leather finishing agents can reduce the gloss of leather surface, eliminating plastic sense caused by too bright leather surfaces, form soft, natural, elegant look [4] [5].

Matting performance of coatings mainly depends on appropriately formed surface roughness [6]. Micron roughness on membrane surface makes a strong scattering and diffusion of incident light, and reduces the amount of light reflected into the eyes of people by matting coating surface, so as to achieve the purpose of matting. At present, preparation of matting polyurethane coatings is to add micron-sized silica matting agent [7] into WPU dispersion, but adding inorganic components into the emulsion will reduce system stability and scratch resistance and bending resistance of the coating. US6331582 B1 [8] described a thermally activated coating composition comprising a solvent-based acrylic or polyester binder resin, a colorant and a polyvinyl acetal matting agent. EP0841992 A2 [9] disclosed a low-gloss solvent-based crosslinkable coating composition comprising a combination of polar polymers, non-polar polymer and crosslinking agent. US5744522 [10] disclosed a low-gloss powder coating composition comprising acrylic copolymer, aromatic polyester and specific isocyanurate curing agent. However, the solutions above use organic solvents to form dispersion, or add complex organic matting particles.

This article prepared self-emulsifying waterborne matting polyurethane dispersion without using matting agent, with excellent coating matting performance, good emulsion stability, water resistance, scratch resistance, etc., it can be widely used in Polyvinyl chloride (PVC), polyurethane (PU) leather surface finishing.

II. EXPERIMENTAL

A. *Materials*

Polyethylene glycol (PEG, Mn=400, 600, 1000, 2000), purchased from Xilong Chemical ltd., CP; terminal hydroxyl polydimethylsiloxane (PDMS, Mn=2000), purchased from Canada Siltech co., industrial; toluene diisocyanate (TDI), purchased from Bayer co., industrial; dimethylolpropionic acid (DMPA), purchased from Baishun Chemical co., CP; dibutyltin dilaurate (DBTDL), purchased from Xilong Chemical ltd., AR; triethylamine (TEA), purchased from Beijing Chemical Factory, AR; tetrahydrofuran (THF), purchased from Beijing Chemical Factory, AR.

B. *Synthesis Procedures*

Add quantified PEG and PDMS into a 250 ml three-necked flask with thermometer, blender, and condenser tube, then dehydrate at 100 ℃ in vacuum for 1h. Cool to 90 ℃, add quantified TDI and DBTDL, react for 4h. Cool to 50 ℃, add quantified DMPA and THF, heat to 70 ℃, react for 2h. Cool to room temperature, add quantified TEA to neutralize prepolymer, then add deionized water to make the emulsion.

Pour the emulsion into glass petri dishes at room temperature, wait until it forms a film, and dehydrate the films at 60 ℃ in vacuum for 24h to get the samples.

C. *Measurements*

FTIR spectra were recorded on a Nicolet 8700 FTIR spectrometer (Thermo Scientific), using KBr method, region 4000cm-1~500 cm-1.

Coating gloss was tested by Sheen 101N 60° vancometer, according to ISO 2813:2014 < Paints and varnishes – Determination of gloss value at 20 degrees, 60 degrees and 85 degrees >.

Isocyanate content was tested according to DIN EN ISO 11909-2007 < Binders for paints and varnishes -- Polyisocyanate resins – General methods of test >.

SEM photos of polyurethane coatings were taken by a Hitachi TM3000 SEM, magnification ratio s were 100, 1000, 9000.

III. RESULTS AND DISCUSSION

A. *Material selection*

Materials of self-emulsifying waterborne polyurethane dispersions mainly include isocyanates, oligomer polyols, chain extenders, neutralizing agents, catalysts and solvents. Depending on the type of hydrophilic group in the molecular chain, polyurethanes can be divided into anionic, cationic, amphoteric and nonionic.

Oligomer polyols generally include polyether polyols and polyester polyols. PDMS backbone is composed of highly flexible silicon-oxygen bond, has low surface energy, good hydrophobility, oxidation resistance and thermal stability. Coatings have excellent and unique surface properties. PEG chain segment contains a large number of ether bonds, and has good crystallinity and hydrophilicity. Polyether segments may provide good emulsion stability, to constitute non-ionic self-emulsifying polyurethane. PEG segments and PDMS segments will interact in the polyurethane surface to form micro rough structure, resulting in matting effect, so we choose PDMS and PEG as the polyol component.

Isocyanates mainly include aromatic isocyanates, aliphatic isocyanates, and alicyclic isocyanates. The aromatic isocyanates have generally higher reaction activity, which will help reacting with the low-reactivity PDMS, so we choose TDI as material.

Commonly used DMPA is chosen as hydrophilic chain extender, which may help constitute the anionic self-emulsifying waterborne polyurethane and increase the molecular weight of the polyurethane.

DBTDL is chosen as catalyst, to accelerate the reaction rate.

TEA is chosen as neutralizer, to form hydrophilic structure with DMPA carboxy.

THF is chosen as solvent, of which boiling point range fit the reaction temperature. Series of experiments showed that commonly used acetone, methyl ethyl ketone as a solvent can cause precipitation of prepolymer at the end of reaction.

B. *Confirmation of synthesis conditions*

Terminal hydroxyls of PDMS react slower than normal polyols with TDI. Reactions were carried at different temperatures, to confirm reaction reaches end, content of isocyanates in prepolymer were measured over time.

Fig. 1 showed remaining content of isocyantes of prepolymerization at different temperatures. At 70℃ or 80℃, there were more isocyantes remaining than 90℃ after 4h. At 90℃, isocyantes content reached theoretical value after 4h. At higher temperature, more side reactions were initiated and caused yellowing of prepolymer. Therefore, prepolymerazation should be held at 90℃ for 4h. Chain extender DMPA reacted too fast with isocyantes at high temperature, so before adding DMPA, prepolymer should be cooled to 50℃ and diluted with solvents to avoid crosslinking. After this, heat prepolymer to 70℃ for 2h for reaction.

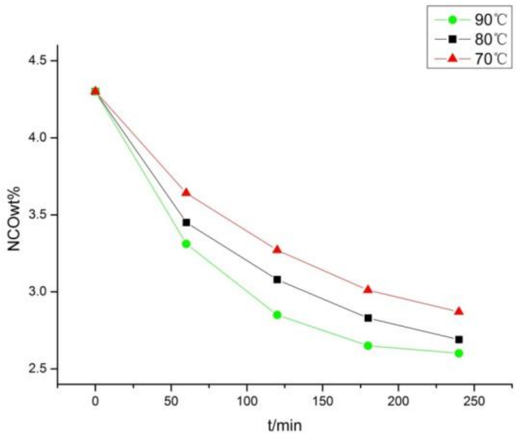

Figure 1. Remaining content of isocyantes of prepolymerization at different temperatures

DMPA content in PU has great influence on hydrophilicity of WPU and stability of dispersions. TABLE 1 showed influence of DMPA on WPU properties. When DMPAwt% is ≤5%, PU dispersions layer is formed due to lack of hydrophilicity. When DMPAwt% is ≥6%, PU dispersions are sTABLE. However, as DMPAwt% increases, matting effect of PU coatings dropped significantly. When DMPAwt% increases, length of PDMS segments and PEG segments between carbamates in polymer chain will become shorter, so it is harder for PEG and PDMS to interact on the surface. Distribution density of micro rough structures decreases and matting effect is worse. Therefore, DMPAwt% should be 6%.

R value is ratio of isocyantes to hydroxyl/amino in reaction. In this article, R of prepolymer is above 1.0, so there will be some isocyantes left when emulsifying. R value influences molecular weight of PU, and the amount of water molecules reacting with isocyantes when emulsifying, thus forms uramidos in PU chain. When R value is high, molecular weight of prepolymers is small, product has more uramidos and coatings are harder. TABLE 2 showed influence of R value on WPU properties. In this article, when R=1.2, ratio of hard segments to soft segments was appropriate, stability of dispersions was good. No significant influence on matting effect was observed when R value changed.

Compatibility of PEG and PDMS is poor. After copolymerization, interaction of segments formed micro rough structures on the surface of coatings. As the ratio of PDMS rises, the quantities of rough structures on the surface increase. The distribution density of rough structures also increases, and t has improved the matting effect.

TABLE I. INFLUENCE OF DMPA ON WPU PROPERTIES

DMPA weight percentage/%	Stability of dispersions	Gloss of Coatings
5	Layered	5.8
6	STABLE	3.3
7	STABLE	12.6
8	STABLE	42.6
9	STABLE	43.2

TABLE II. INFLUENCE OF R VALUE ON WPU PROPERTIES

R value	Stability of dispersions	Gloss of coatings
1.0	Sediment	2.6
1.1	Sediment	2.4
1.2	STABLE	3.3
1.3	STABLE	3.3

When PEG content is zero, micro rough structures cannot form on the surface of coatings. This will lower the matting effect of the coating. Moreover, PEG segments are hydrophilic, they can improve the stability of dispersions. TABLE 3 showed the influence of PEG/PDMS molar ratio on WPU properties. In this article, when PEG/PDMS=1:3, WPU dispersion stability and coating matting effect both have good performances.

TABLE III. INFLUENCE OF PEG/PDMS MOLAR RATIO ON WPU PROPERTIES

PEG/PDMS	Stability of dispersions	Gloss of coatings
1:2	STABLE	17.9
1:3	STABLE	3.3
1:4	STABLE	3.3

Interactions of PEG and PDMS segments are significantly related to segment length. Difference of segment length of PEG and PDMS will influence the distribution of hydrogen bonds formed near the surface, thus influence crystallization and distribution density of micro rough structures.

TABLE 4 showed influence of PEG molecular weight on WPU properties. In this article, PDMS molecular weight is 2000, when PEG molecular weight is 1000, coating matting effect is significantly better than group of 400, 600 and 2000.

TABLE IV. INFLUENCE OF PEG MOLECULAR WEIGHT ON WPU PROPERTIES

PEG molecular weight	Stability ofdispersions	Gloss of coatings
400	STABLE	46.6
600	STABLE	17.9
1000	STABLE	2.7
2000	STABLE	12.4

C. Characterization

FTIR spectra in Fig. 2 showed that the absorption peak of the -NCO group did not appear around 2270 cm^{-1}, this meant all isocyanates had reacted with hydroxyl groups. The absorption peak of the N-H group appeared at 3300 cm^{-1}, the absorption peak of the C=O group appeared at 1727 cm^{-1}, this meant the coating contain carbamates that indicated polyurethane existed. The deformation vibration peak of the C-H groups appeared at 1260 cm^{-1}, and stretching vibration absorption peak at 2850-2960 cm^{-1}. The stretching vibration peak of the Si-O-Si groups appeared at 1097 cm^{-1}, the stretching vibration peak of the Si-C group appeared at 800 cm^{-1}. This meant PDMS segments existed in the PU molecular chain. Peaks above proved that target product had been synthesized.

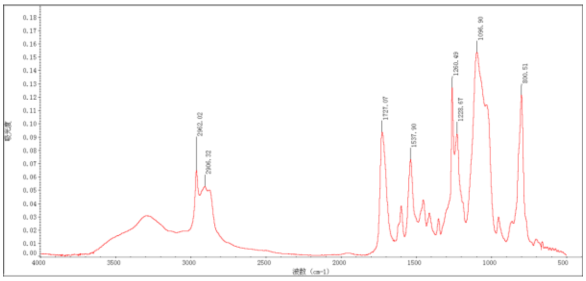

Figure 2. FTIR spectra of copolymerized matting WPU

Fig. 3(A) showed the micro rough structures on the coating surface. Cracks of micrometer can be observed on every coating sample that had matting effect. Micrometer rough structures can scatter incident light well and were a source of matting effect. As the cracks on the surface increases, the matting effect of the coating is better.

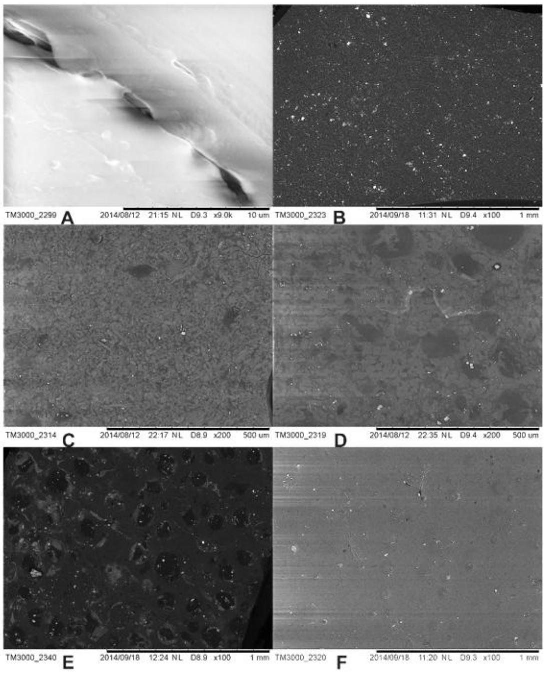

Figure 3. (A) micro rough structures on the coating surface; (B)-(F)PEG/PDMS=1:1-1:5 SEM photos of the coating surface.

When R=1.2, DMPAwt%=6%, PEG molecular weight=1000, PEG/PDMS=1:1, we could distinguish dark area from light area on the coating surface. Dark area and light area equals in area. When PEG/PDMS=1:2, the dark area declined and the light area grew. The dark area formed irregular strip structures in the light area. When

PEG/PDMS=1:3, the dark area declined and began to gather. When PEG/PDMS=1:4, the dark area declined continuously and the dark area was surrounded with the light area, forming sea-island structures. When PEG/PDMS=1:5, the dark area declined and it was hard to observe. Numbers of dark pixels and light pixels were calculated by image processing software, TABLE 5 showed dark area/ light area of SEM photos as PEG/PDMS changed. We found that PEG/PDMS was relevant to dark area/ light area. We could infer that dark area presented PEG aggregation phase and light area presented PDMS aggregation phase. This indicated that PDMS segments and PEG segments had macroscopic phase separation on the coating surface.

TABLE V. DARK AREA/ LIGHT AREA OF SEM PHOTOS AS PEG/PDMS CHANGED

PEG/PDMS	Dark area/Pixels	Light area/Pixels	Dark/Light area
1:1	147824	156236	1:1.057
1:2	105132	200788	1:1.908
1:3	81896	220184	1:2.688
1:4	61151	247830	1:4.049
1:5	49376	253984	1:5.155

IV. CONCLUSIONS

WPU matting dispersions were prepared by prepolymer method. The PU coating molecular structure was characterized with FTIR, the surface topography was characterized with SEM. Large quantities of micro rough structures were observed, indicating the coatings prepared coincided with the matting principle.

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