Fabrication of Crosslinked Waterborne Polyurethane with Low-Gloss and Micro Roughness for Matting Application

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Abstract. A groups of cross-linked waterborne polyurethane (CPU) coatings were successfully synthesized and characterized. The CPU emulsions could achieve low gloss effect without addition of any matting agents by the formation of self-roughed surface. Rheological research shows that the emulsions comply with the Herschel-Bulkley pseudoplastic fluid model with a yield stress, and exhibited the same behaviors as the gel. SEM and AFM illustrated the rough surface morphology of the films, and a series of roughness parameters were calculated. In general, the resulted CPU emulsions can provide moderate roughness levels, good hardness and adhesive strengths after film-forming, which were very appropriate for use as matt coating.

Keywords. Cross-linked waterborne polyurethane, micro-rough surface, low-gloss, coating.

1. Introduction

With the development of society and the improvement of people's living standards, there is a great demand for a series of waterborne polyurethane (WPU) coatings having low gloss surfaces, which are greatly different from the traditional high glossy WPU. Therefore, plenty of efforts have been devoted to develop techniques for preparing low-gloss WPU coatings. Adding a variety of matting agents (including clays, diatomaceous earth, zeolites, silicate, silica, silane, wax treated silica, etc.) into the WPU is the commonly used method in the past many years [1-7]. After-treatment, like etching or polishing the WPU coating surfaces with tools, is another method to decrease the gloss [8-10]. Recently, a new developed approach to fabricate matt coatings applied a two-step UV curing process [11-16]. Yet, very complex physical processes and the need for specific instruments and photosensitizing reagents have limited their widespread application.

In this conference paper, a facile approach was used to develop a low gloss and micro-rough surface. It was achieved by making the most of skin-formation phenomenon. We designed a novel cross-linked waterborne polyurethane (CPU) with high cross-linking density and strong gel-like behavior through introduction of the reactive bisphenol-A epoxy E-44 or E-51 resin and castor oil onto the WPU backbone structure. The resulted CPU resin also demonstrated a high apparent viscosity with no shear stress exerting even at the low solid content. The binding effect of the high apparent viscosity and the high cross-linking density of the CPU resin make it possible that the water evaporation rate was faster than the CPU particle diffusion rate and meanwhile was similar or slower than the CPU particle coalescence rate. The CPU resin formed a polymer skin at the film-air interface while the interior of the CPU film
was still in liquid. With the time goes by, the underlayer of the CPU film became come to dry. Hence, the mechanical mismatch between the surface layer and the underlayer of the CPU film, and the large volume shrinkage of the interior part introduced by plenty of water evaporation resulted in the formation of micro-rough surface.

2. Experimental

2.1. Materials
Isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), dimethylol propionic acid (DMPA), ethylene diamine (EDA), triethyl amine (TEA), castor oil (CP, 170-180 mg KOH g⁻¹). Poly (propylene glycol) (PPG, Mₐ = 2000 g mol⁻¹) was vacuumed at 50 °C for 10 h to remove residual water. Bisphenol-A epoxy E-51 and Bisphenol-A epoxy E-44 resin (epoxy value 0.51 and 0.44, respectively, Star Chemical New Material Co., Ltd).

2.2. Synthesis of CPU with Low Gloss and Micro-Roughness
Castor oil and PPG were first injected into a flask and heated to 80 °C for 30 min. Prepolymerization process was implemented at 80-90 °C by the addition of the IPDI under N₂ atmosphere for 2 h at the presence of DBTDL as the catalyst. Next, DMPA and bisphenol-A epoxy resin (E-44 or E-51) was added to the flask and continued to reaction for 2 h. The carboxylic groups of DMPA was neutralized with adding TEA at 50 °C for 30 min. Lastly, the above prepolymer product was dropwise added into a new flask filled with EDA and a lot of deionized water under high speed stirring. The molar ratio of PPG/IPDI/DMPA/TEA/EDA was 1:3,95:1:43:1:43:1.35. The recipes of the CPU samples with low gloss and micro-roughness can be seen in table 1. The resulted CPU emulsions were poured into a 10×10 cm Teflon plate and kept dry at ambient temperature for 48 h. The prepared Films were taken off from the plate and layed in a vacuumed desiccator for testing.

| Table 1. Recipes of the CPU with low gloss and micro-rough surface. |
|------------------------|--------|--------|--------|
| Composition | Castor oil (wt%) | E-44 (wt%) | E-51 (wt%) |
| CPU1 | 1.72 | 9.23 | 0 |
| CPU2 | 3.44 | 9.23 | 0 |
| CPU3 | 5.16 | 9.23 | 0 |
| CPU4 | 3.44 | 0 | 0 |
| CPU5 | 1.72 | 0 | 7.96 |
| CPU6 | 3.44 | 0 | 7.96 |

2.3. Characterizations
Atomic force microscopy (AFM): the AFM analysis was conducted at room temperature by the use of a Bruker Multimode 8-HR atomic force microscope in a 100×100 μm scan size and a 10 μm vertical range. The AFM equipment was placed on an active isolation plate which was supported by a large iron table to eliminate external vibrations. All of the pictures were acquired under ScanAsyst mode with a pixel resolution of 512×512. The resulted pictures were further analyzed and processed with NanoScope Analysis 1.8 software. 𝑆_a is the Average Roughness calculated based on the whole 3D surface seen in equation (1):

\[
𝑆_a = \iint_{\Delta} |Z(x,y)| \, d(x)\,dy
\]  

\[S_a\] is the Root Mean Square roughness calculated based on the whole 3D surface seen in equation (2):

\[
𝑆_q = \iint_{\Delta} (Z(x,y))^2 \, d(x)\,dy
\]  

\[S_q\] is the Maximum Peak Height, which represents the height of the highest point.
$S_r$ is the Maximum Valley Depth, which represents the depth of the lowest point.  
$S_z$ is the Maximum Height of the 3D Surface; $S_z = S_r - S_r$.  
$S_{ku}$ means the Kurtosis of the whole 3D surface. A data graph of all measured point heights is established and the deviation from a regular distribution is expressed by $S_{ku}$ seen in equation (3):

$$S_{ku} = \frac{1}{S_q} \int_a (Z(x, y))^4 )d(x)dy$$

(3)

$S_{sk}$ means the Skewness of the whole 3D surface. A data graph of all measured point heights is established and the deviation from a regular distribution is expressed by $S_{sk}$ seen in equation (4):

$$S_{sk} = \frac{1}{S_q^3} \int_a (Z(x, y))^3 )d(x)dy$$

(4)

Scanning electron microscopy (SEM): Film surface topographies were obtained using a Hitachi S-3400N SEM at room temperature, and at a 15kV accelerating voltage in a vacuum. Before the SEM observation, the dried films were first sticked on a copper with conductive adhesive tape and then were sprayed with gold powder on their surfaces.

Properties of CPU: The various physical properties of CPU2, CPU4 and CPU6 samples were evaluated. The CPU2, CPU4 and CPU6 emulsion viscosities was measured by NDJ-95 digital viscometer equipment at room temperature. The hardness of the CPU films was tested by a SDI-TH200 shore A type durometer. The resulted data was the mean of five tests. The adhesion properties of the films were measured with commercial cello tape on the basis of the cross-cut adhesion test method (ASTM D3359). The grades of 0B and 5B represent for an extremely poor adhering performance and a very good adhering performance, respectively. The swelling ratio of the CPU2, CPU4 and CPU6 films was gained by the following equation (5):

$$\text{Swelling ratio(%) } = 100\% \times \frac{(W_w - W_d)}{W_d}$$

(5)

where $W_d$ represents the weight of the dry film, and $W_w$ refers to the weight of the swollen film which was soaked into the deionized water at room temperature for 24 h and got rid of the excessive surface water. A facile glossmeter (KGZ-60, Tianjin Yaxing) was applied to determine the specular gloss levels. The reported gloss value was an mean value of ten tests at 60° angle of incidence. The reported value was the average of three tests. In addition, the PH, solid content, touch-feeling and storage stability were also assessed.

3. Results and Discussion

3.1. Surface topography

It is obvious both in SEM and AFM analysis that there were many microscale wave-crests and wave-troughs on the film surfaces (seen in figure 1). The rough surfaces were self-generated during the curing process. Meanwhile, the micro-roughed degrees increased regularly with increasing the castor oil contents. This result indicates that owing to the increase of castor oil contents, the cross-linking and branching density of the CPU emulsions increased. However, the CPU4 film demonstrates a relatively flat and smooth surface. This indicates that due to the lack of further cross-linking reaction with the bisphenol-A epoxy E-51 or E-44 resin, the cross-linking density of the CPU4 was not too high, the gel-like behavior was not very strong. Through the calculation of AFM analysis software, the values of different types of roughness parameters including $S_d$, $S_q$, $S_p$, $S_r$, $S_{ku}$ and $S_{sk}$ were calculated in table 2. It reveals that the roughness degree of film surfaces was in micro-scale range, the wave-crest and wave-trough morphologies was very fine and can not be seen in unassisted eyes.
Figure 1. SEM and AFM images of CPU2, CPU4 and CPU6 films, respectively.

Table 2. Roughness parameters obtained from AFM software calculation.

| Composition | $S_a$ (μm) | $S_d$ (μm) | $S_p$ (μm) | $S_v$ (μm) | $S_z$ (μm) | $S_{ku}$ | $S_{sk}$ |
|-------------|------------|------------|------------|------------|------------|---------|---------|
| CPU2        | 0.68       | 0.88       | 1.14       | -1.06      | 2.20       | 3.39    | 0.06    |
| CPU4        | 0.15       | 0.20       | 0.35       | -0.23      | 0.58       | 2.74    | -0.07   |
| CPU6        | 0.65       | 0.83       | 1.00       | -1.14      | 2.14       | 3.70    | -0.06   |

3.2. Rheological Behavior

In figure 2a, all three samples showed a very high apparent viscosity with no shear stress exerting. Once a certain minimum stress was exerted, the emulsions displayed a great shear thinning behavior [17]. Therefore, the rheological characteristics of these emulsions complies with the Herschel-bulkley pseudoplastic fluid model with a yield stress. In figure 2b, it shows that both of dynamic moduli of the three emulsions were independent of the angular frequency over the entire angular frequency. This was caused by the further cross-linking reaction with the bisphenol-A epoxy E-51 or E-44 resin, leading to the formation of a more well-developed cross-linked network structure. Moreover, the $G'$ was always higher than $G''$ over the entire frequency range, which reveals that these emulsions were dominated by the elastic behavior [18].

Based on the study of rheological properties, it is known that these resulted CPU emulsions embraced a very high apparent viscosity even at solid content of 20%. Thus, it is possible that the water evaporation rate was high enough to make the velocity of the receding waterfront faster than the polyeurethane particle diffusion rate during the wet film. Moreover, the CPU emulsions embraced a high cross-linking density structure and a strong gel-like behavior, which make it possible that the coalescence rate of the polyeurethane particles was similar or faster than the velocity of the receding waterfront. The binding effect of the high apparent viscosity and the high cross-linking density of the CPU emulsions make it possible to fabricate a polymer skin at the film-air interface before the underlayer of the films became dry. As a result, the mechanical mismatch between the surface layer and the underlayer of the CPU film, and the large volume shrinkage of the interior part introduced by plenty of water evaporation resulted in the formation of micro-rough surface.
3.3. Physical Properties
The physical performance of the CPU2, CPU4 and CPU6 samples could be seen in Table 3. The CPU2 and CPU6 samples showed the higher viscosity compared with CPU4 sample, which were ascribed to the higher cross-linked molecular structures. There were a lot of branched chains and cross-linked networks penetrating in the polyurethane backbone structure as a result of the introduction of reactive bisphenol-A epoxy E-51 or E-44 resin. In terms of hardness and swelling ratio, the CPU2 and CPU6 films demonstrated the higher hardness and lower swelling ratio than CPU4 film. In short, the CPU2 and CPU4 films showed highly low gloss values, good hardness, superior adhesion strengths and excellent storage stabilities, as well as soft-touch feelings which could meet the industrial demands for low gloss coatings.

Table 3. The Physical properties of the CPU2, CPU4 and CPU6 samples.

| Physical property          | CPU2   | CPU4   | CPU6   |
|---------------------------|--------|--------|--------|
| Viscosity (mPa.s)         | 2500   | 1800   | 2300   |
| Solid content (%)         | 20     | 20     | 20     |
| Hardness (shore A)        | 70     | 52     | 65     |
| Adhesion strength         | 4B     | 5B     | 4B     |
| pH                        | 7.0    | 7.0    | 7.0    |
| Swelling ratio (%)        | 10.5   | 15.8   | 13.0   |
| Specular gloss (60°)      | 15.2   | 94.5   | 19.8   |
| Touch feeling             | Good   | Good   | Good   |
| Stability                 | More than 6 months | More than 6 months | More than 6 months |

4. Conclusions
A group of low-gloss WPU resins that can provide low gloss and micro-roughness were successfully synthesized. With an increase in the bisphenol-A epoxy E-51 or E-44 contents, the rough levels of film surfaces increased, and the specular glosses of film surfaces decreased markedly. The prepared CPU emulsions exhibited very high apparent viscosities and high cross-linking densities. Therefore, a polymer skin of CPU resin was fabricated at the surface layer before the underlayer of the film became dry. the mechanical mismatch between the surface layer and the underlayer of the CPU film, and the large volume shrinkage of the interior part introduced by plenty of water evaporation resulted in the formation of micro-rough surface. It was greatly suitable for matting application in artificial leather or leather finishes because it met the demands for low gloss and micro-roughness.
References

[1] Diakoumakos C D and Jones F N 2002 Surf. Coatings Technol. 150 37-49
[2] Zhu B, Wei W, Ma G, Zhuang Y and Li J 2015 J. Supercrit. Fluids 97 1-5
[3] Yang X F, Li J, Croll S G, Tallman D E and Bierwagen G P 2003 Polym. Degrad. Stab. 80 51-58
[4] Cawthorne J E, Joyce M and Fleming D 2003 J. Coatings Technol. 75 75-81
[5] Linares M T 2013 Coatingstech 10 34-40
[6] Ou J, Zhang M, Liu H, Zhang L and Pang H 2015 J. Appl. Polym. Sci. 132 1-8
[7] Yong Q, Nian F, Liao B, Huang L, Wang L and Pang H, RSC Adv. 5 (2015) 107413-107420
[8] Maskery S E 1973 Pigment Resin Technol. 2 11-19
[9] Hong J K, Park H S, Lee B D, Jin Y S, Sun H R, Kim S K and Yoo Y D 2016
[10] Kim B E, Jung J H, Heo J W, Park K S, Jung Y J and Jin Y S 2015
[11] Bauer F, Decker U, Czihal K, Mehnert R, Riedel C, Riemschneider M, Schubert R and Buchmeiser M R 2009 Prog. Org. Coatings 64 474-481
[12] Bauer F, Decker U, Naumov S and Riedel C 2014 Prog. Org. Coatings 77 1085-1094
[13] Bahners T, Prager L, Kriehn S and Gutmann J S 2012 Appl. Surf. Sci. 259 847-852
[14] Scherzer T 2012 Macromol. Chem. Phys. 213 324-334
[15] Schubert R, Frost F, Hinkefuß M, Konieczny R, Marquardt B, Mehnert R and Buchmeiser M R 2009 Surf. Coatings Technol. 203 3734-3740
[16] R. Schubert, T. Scherzer, M. Hinkefuss, B. Marquardt, J. Vogel and M. R. Buchmeiser 2009 Surf. Coatings Technol. 203 1844-1849
[17] Jacquelot E, Galy J, Gérard J F, Roche A, Chevet E, Fouissac E and Verchère D 2009 Prog. Org. Coatings 66 86-92
[18] Zhang J, Li X, Shi X, Hua M, Zhou X and Wang X 2012 Prog. Nat. Sci. Mater. Int. 22 71-78