# Preparation and Properties of Matting Waterborne Polyurethane with Polybutadiene

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**Summary**

A matting waterborne polyurethane (MWPU) emulsion was prepared using polybutadiene diol (HTPB), polybutylene adipate diol (PBA) and isophorone diisocyanate (IPDI) as the main raw materials, dimethylolpropionic acid (DMPA) as a hydrophilic chain extender and ethylene diamine as a post chain extender, this was applied to the surface treatment of the leather. The surface microstructure of the MWPU film was studied by SEM. The results showed that when the content of HTPB increased, the particle size of MWPU emulsion increased, the stability decreased, the mechanical properties and surface roughness of MWPU film increased, the elongation at break, water absorption and light transmittance decreased. Combined with the matting effect, the gloss of the MWPU film was as low as 23GU, and the surface particles of the film were more obvious. The folding fastness was free from cracking, and the abrasion resistance could reach 154 circles [rubs], which meets the testing standard of leather.

## INTRODUCTION

Due to the development of the economy and the rising awareness of environmental protection, waterborne polyurethane (WPU) coatings with non-toxicity and good physical and mechanical properties have not only attracted the attention of academic and industrial circles,[1] but also contributes to the application of WPU in various fields, such as leather surface treatment agent, giving it soft lustre and good durability.[2]

The main traditional production method of matting waterborne polyurethane surface treatment is to add $SiO_2$ matting powder and various additives to the aqueous polyurethane dispersion, so that the polyurethane film is dried to form a rough surface to achieve the matting effect.[3,4] However, the use of $SiO_2$ matting powder will reduce the performance of the polyurethane film, giving such as decreased storage stability, scratch resistance and bending resistance.[5-7] In recent years, matting waterborne polyurethane surface treatment has become a hotspot and been widely investigated by domestic and foreign scholars. They adopted different methods to prepare matting waterborne polyurethane.[8-11] Zheng Wen, Zeng Wenbo, Li Jianjun *et al*.[8] prepared matting waterborne polyurethane without any matting powder by using PTMEG, IPDI and DMPA as pre-polymer reaction monomers, sodium sulfamate aqueous solution (A95) and hydrazine hydrate as secondary chain extender. The structure of the surface of the films were observed by SEM and AFM, which showed that the microstructure of the surface of the WPU film conforms to the extinction mechanism. The WPU film showed the best matting performance with the amount of 45% hydrazine hydrate, 2.6% DMPA and 0.084% A95.

In this study, IPDI, PBA and HTPB are used as the main raw materials to prepare matting waterborne polyurethane (MWPU) through prepolymer dispersion by introducing a poorly compatible component hydroxylated polybutadiene diol (HTPB). Due to the difference in film formation speed and compatibility of each component, MWPU exhibits a good matte effect because it forms a rough surface. In addition, MWPU modified by HTPB shows better water resistance and mechanical properties, so it has a wide scope of applications in a film-forming substance for matte leather aqueous surface treatment.

## EXPERIMENTAL PROCEDURE

### 1.1 Experimental materials and instruments

Isophorone diisocyanate (IPDI) was provided by Wanhua Chemical Group Co. Ltd. (Yantai, China). Poly(1,4-butylene adipate) (PBA, Mn=1000) was purchased from Taizhou Hongdeli Co. Ltd. (Taizhou, China). Hydroxyl-terminated polybutadiene (HTPB) was provided by Yunlong Chemical Materials Co. Ltd. (Weihai, China). N-Methyl pyrrolidone (NMP) was provided by Tianjin Yongsheng Fine Chemical Co. Ltd. (Tianjin, China). Dibutyltin dilaurate (DBTDL), dimethylol propionic acid (DMPA), triethylamine (TEA), ethylenediamine, thickener, defoamer and levelling agent were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China).

A Fourier transform infrared spectroscope (FTIR) image of the sample was taken using a Perkin-Elmer spectrum 22000; provided by American Perkin Elmer Co. Ltd. The thermogravimetric analysis was performed using a thermogravimetric analyser – a

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differential scanning calorimeter (TGA-DSC, STA449F3-1053-M provided by Bruker, Germany). The maximum tensile strength and elongation at break of the samples were measured with a tensile tester according to QBT 2710-2005 (electronic stretching machine LDW-1; provided by Jinan Dongfang Testing Instrument Co. Ltd.). The gloss test was carried out with a gloss tester (ETB-0686; provided by Sitong Electronic Instrument Co. Ltd.). Particle size was measured using a nanoparticle size surface potential analyser (NANO-ZS90; provided by English Malvern Co. Ltd.). UV-vis absorption and transmittance spectra were taken from a UV-vis spectrophotometer (TU-1901, Pgeneral Instrument Inc., China). The surface topography of the sample was obtained under a scanning electron microscope (SEM, S4800, Hitachi). Colour fastness to rubbing was performed using a rubbing fastness tester (Y571B; Wenzhou Fangyuan Testing Instrument Co. Ltd.). Wear resistance was performed using a fabric wear resistance tester (YG522; Wenzhou Fangyuan Testing Instrument Co. Ltd.).

### 1.2 Preparation of MWPU emulsion

The preparation was as follows: (1) Specified amounts of PBA, HTPB and IPDI, after vacuum dehydration, were placed in a three-necked flask according to a specific charging ratio, and the system temperature was gradually raised to 85°C; (2) Hydrophilic chain extender DMPA was added to the reactants and the reaction continued for nearly 30 minutes until the remaining isocyanate group (-NCO) reached a theoretical value (the NCO content was ascertained using the standard titration method ASTM D 2572-87); (3) The temperature of the above reactant was lowered to 30°C, and the reaction is neutralised by adding triethylamine for 30 minutes. An appropriate amount of NMP can be added according to the viscosity to reduce the viscosity during the reaction; (4) An appropriate amount of water containing ethylenediamine was added under strong stirring, and the mixture was emulsified at 350r/min for 1 hour to produce a matt MWPU emulsion with a solid content of 30%. The synthetic route is shown in Fig. 1.

### 1.3 Preparation of MWPU film

MWPU film was prepared by placing about 100 mL of mixed emulsion in a PTFE mould and allowing drying at ambient temperature for 2 days. The polyurethane films obtained were baked in an oven at 150°C for 10 minutes to ensure the full removal of water in the film. The final films were incubated in a desiccant at ambient temperature.

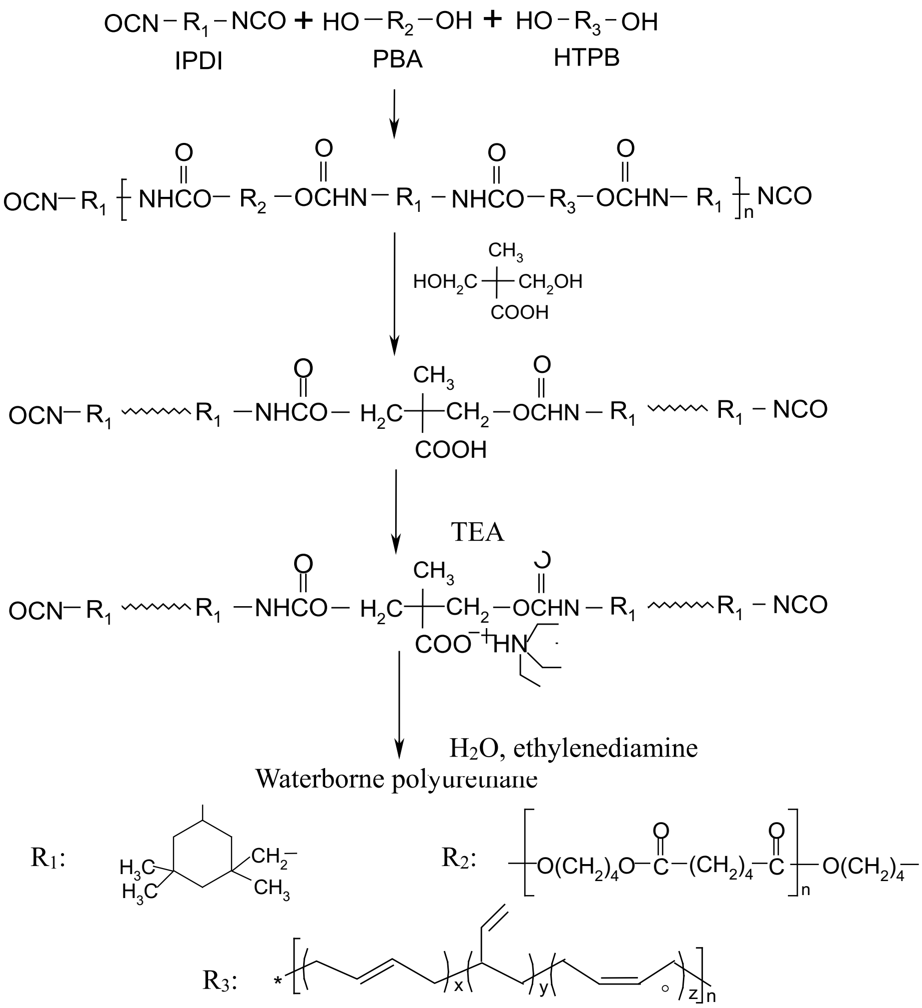



**Figure 1**. Synthetic route to waterborne polyurethane.

### 1.4 Effect of HTPB content on MWPU performance

A series of MWPU emulsions with different HTPB contents were synthesized under the condition that DMPA content was 4% and R value was 1.6. The appearance and stability of the emulsion were observed, and the effect of HTPB content on the properties of MWPU film was studied.

### 1.5 Preparation of matting waterborne surface treatment agent

TABLE I
The formula of matting waterborne surface treatment agent

| | |
|---|---|
| MWPU emulsion | 100 |
| Thickener | 1 |
| Defoaming agent | Moderate amount |
| Leveling agent | Moderate amount |

MWPU emulsion and various additives were poured into a beaker according to the formula of Table I and stirred evenly. The prepared matting aqueous surface treatment agent was evenly coated on the surface of leather sample by using a 20μ coating roller, and then we placed the leather sample in an oven at 120°C for drying and then taken out for performance testing.

### 1.6 Characterisation and test methods

*1.6.1 Gloss test of MWPU film*

The test was carried out using an ETB-0686 Gloss Tester with an incident angle of 60°. Multiple parallel tests were made on the leather samples, and then the average gloss was taken to determine the gloss of the polyurethane film. Extinction rate = $(Z_1-Z_2) / Z_1 \times 100\%$. Where $Z_1$ is the gloss of the substrate and $Z_2$ is the gloss of the substrate after matting.

*1.6.2 Determination of fastness to folding of MWPU film*

The test was carried out in accordance with QB/T 2714-2005. The test results include the following: whether the colour of the film changes without damage to the surface film; the number of cracks in the film; any abnormal change of the film adhesion; whether cracks, powders or flakes appear on the film surface. Three sets of parallel tests were performed, and the lowest level of the sample was judged as the test result.

*1.6.3 Wear resistance test of MWPU film*

The test was carried out in accordance with QB/T2726-2005. Based on the exposure of the substrate on the leather surface, the number of revolutions was recorded, and three groups of parallel tests were carried out. The minimum number of turns of the sample was taken as the test result.

## RESULTS AND DISCUSSIONS

### 2.1 Effect of HTPB content on the appearance and stability of MWPU emulsion

The effect of HTPB content on the appearance and stability of MWPU emulsion is shown in Table II.

It can be seen from Table II that with the increase of HTPB content, the stability of MWPU emulsion became worse, the tensile strength of MWPU film increases, and the elongation at break decreases. This is mainly because the PBA molecule has the regular segmentation and is easy to crystallize, and the PBA macromolecular segment slides with difficulty during stretching. When the HTPB segment is introduced into the soft segment, the PBA-HTPB mixed soft segment increases the degree of disorder of the soft segment, which makes the phase separation of the soft segment and hard segment of the MWPU more obvious, and also reduces the stability of the MWPU emulsion. When the HTPB content is less than 30%, a stable MWPU emulsion can be obtained, and when the HTPB content exceeds 30%, the stability of the MWPU emulsion is deteriorated and cannot be stored for 6 months. In addition, due to the poor regularity of HTPB structure, decreases the crystallinity of soft segment and the flexibility between MWPU macromolecular chains is improved, the elasticity of MWPU film decreases, and the elongation at break of MWPU film decreases. When HTPB segment is added to the soft segment, the C=C double bond contained in HTPB can increase the

TABLE II
Effect of HTPB content on the appearance and stability of MWPU emulsion

| HTPB content /% | 0 | 10 | 20 | 30 | 40 | 50 |
|---|---|---|---|---|---|---|
| Appearance of MWPU emulsions | Semi-transparent light blue | Semi-transparent milk white | Non-transparent creamy yellow | Non-transparent creamy yellow | Non-transparent creamy yellow | Non-transparent creamy yellow |
| Stability of MWPU emulsions | stable | stable | stable | stable | large particles appear after 3 months | large particles appear after 1 month |
| The tensile strength/Mpa | 10 | 15 | 19.2 | 30 | 31.7 | 33 |
| Elongation at break /% | 700 | 600 | 561 | 500 | 499 | 483 |

cross-linking degree, and increase the mechanical properties of the MWPU film.

The effect of HTPB content on the gloss of MWPU film is shown in Table III.

**TABLE III**
**Effect of HTPB content on gloss of MWPU films**

| HTPB content/% | 0 | 10 | 20 | 30 | 40 | 50 |
|---|---|---|---|---|---|---|
| Gloss of MWPU film/GU | 127 | 88 | 50 | 23 | 35 | 45 |

As can be seen from Table III, with the rise in HTPB content, the gloss of the film first decreased and then increased. The surface of the MWPU film without HTPB is very smooth and has a high gloss. With the HTPB content increases, the gloss decreases. This is because the compatibility of HTPB and PBA segments is poor, and the soft segment separation microdomain of HTPB appears. As the amount of HTPB added increases, the number of protrusions formed by the aggregation of HTPB segments during film formation increases, and the surface roughness of the film decreases, so the gloss is lowered. However, when the HTPB content is 40%, the dispersion of HTPB segment and PBA segment in the MWPU molecular becomes uniform, and it is difficult to form protrusions and the gloss is increased. When the HTPB content reaches 50%, the hydrophilicity of the MWPU macromolecular segment is greatly reduced, the emulsion stability is deteriorated. Therefore, considering the matting effect, the gloss of the MWPU film is at least 23GU, and the film surface particles of the MWPU film are more pronounced. It can be used as a matt waterborne surface treatment agent.

## 2.2 Effect of HTPB content on water absorption rate of MWPU film

The effect of HTPB content on the water absorption of MWPU membrane is shown in Fig. 2.

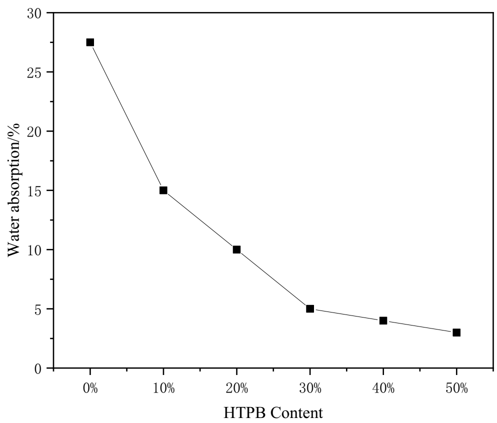



**Figure 2**. Effect of HTPB content on water absorption of MWPU film.

It can be seen from Fig. 2 that when the amount of the hydrophilic group is unchanged, the water absorption of the MWPU film decreases, ranging from 27% to 2.5% . This is mainly because the introduction of HTPB increases the hydrophobicity of the MWPU segment. The higher the HTPB content, the higher the water resistance of MWPU film. At the same time, because the HTPB segment contains the C=C double bond, and can occur the self-crosslinking reaction, and it can increase the cross-linking density of the MWPU film, thereby improving the water resistance of the MWPU film.

## 2.3 Effect of HTPB content on particle size of MWPU emulsion

The effect of HTPB content on the particle size distribution of MWPU emulsion is shown in Figs. 3 and Fig. 4.

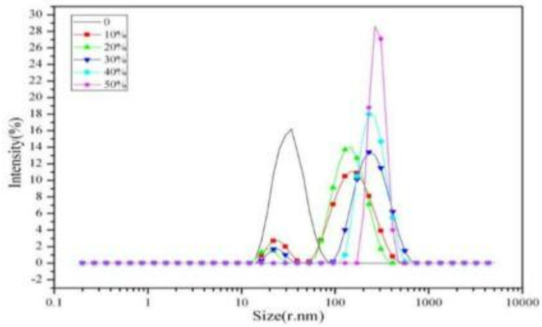



**Figure 3**. Effect of HTPB content on the particle size distribution of MWPU emulsion.

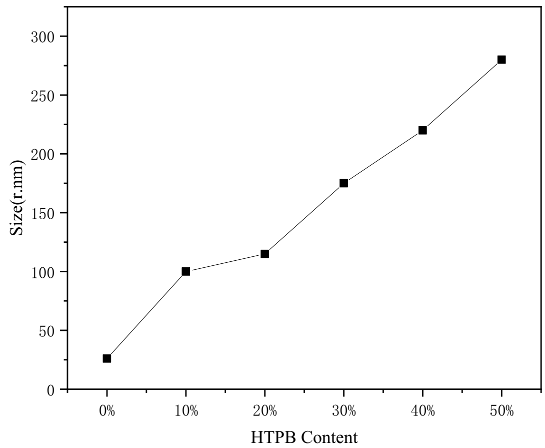



**Figure 4**. Effect of HTPB content on the diameter of MWPU emulsion.

It can be seen from Figs. 3 and Fig. 4 that with the increase of HTPB content, the particle size of MWPU emulsion gradually increases, the particle size distribution becomes wider, and it changes from single peak to double peak, which is mainly because the HTPB segment is strongly hydrophobic and contains colloidal particles of the HTPB segment which require more hydrophilic groups to form a dispersion, resulting in an increase in particle size. Another reason may be that the structure of the HTPB molecular segment is irregular, and the C=C in the repeating structural unit includes three kinds, which are 1,4 cis structure, 1,4 trans structure, and vinyl structure. During the emulsification of MWPU prepolymer, the irregular HTPB segment hinders the free movement of the MWPU molecular chain, making the MWPU macromolecules unable to be closely arranged, thereby increasing the particle size. However, when the HTPB content reaches 40%, the particle size distribution of the MWPU emulsion becomes a single peak and the particle size increases. Mainly because the content of PBA and HTPB is basically the same, the hydrophobicity of the segment is increasing, and basically all the rubber particles contain HTPB segments, so the particle size distribution becomes uniform.

### 2.4 Effect of HTPB content on light transmittance of MWPU film

The effect of HTPB content on the light transmittance of MWPU film is shown in Fig. 5.

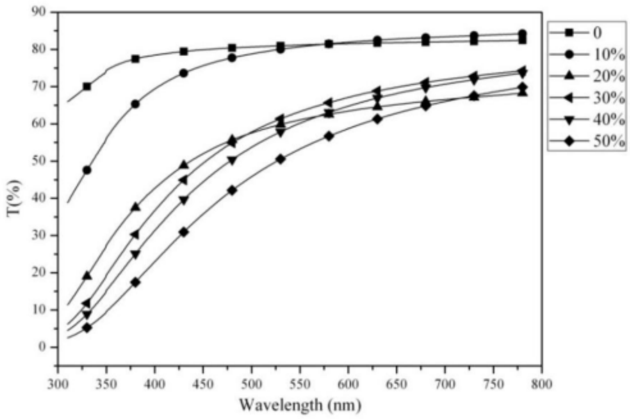



**Figure 5.** Effect of HTPB content on the light transmittance of MWPU film.

It can be seen from Fig. 5 that as the HTPB content increases, the light transmittance of the MWPU film gradually decreases. The MWPU film without HTPB has a high light transmittance and is almost transparent. After the addition of HTPB, due to the incompatibility between HTPB and PBA, the soft segment separation microdomain of HTPB appeared during the film formation process, the transparency of MWPU film decreased, and the light transmittance decreased. The MWPU film had an average light transmittance of 35% at a HTPB content of 30%.

### 2.5 SEM analysis

The effect of HTPB content on the surface microstructure of MWPU film is shown in Fig. 6.

It can be seen from Fig. 6 that with the increase of HTPB content, many convex particles are formed on the surface of MWPU film, and the surface roughness increases because HTPB and PBA have large polarities and are incompatible with each other. The soft segment separation microdomain of HTPB appears during film formation, and the protrusion formed by the aggregation of HTPB segments increases the surface roughness of the film to achieve the matting effect.

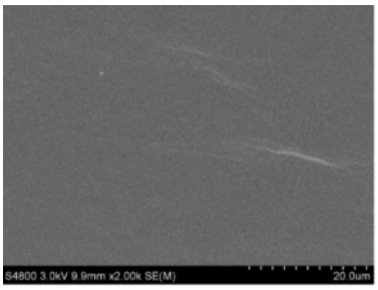
### 2.6 Surface treatment test results of MWPU film on leather

The surface treatment test results of the MWPU film on leather are shown in Table IV.

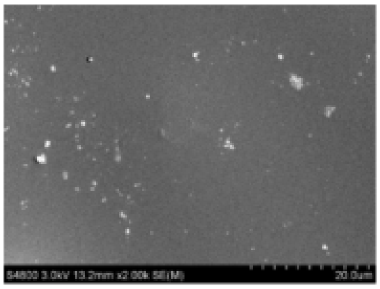
**TABLE IV**
**Test results of the surface treatment**

| | Leather | |
|---|---|---|
| | Folding fastness | Wear resistance |
| MWPU film | No cracks | 154 circles |

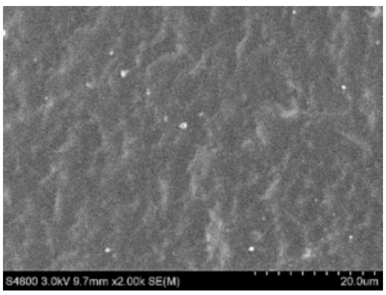
The folding fastness test of the MWPU film shows that it has no cracks, the wear resistance of the MWPU surface treatment agent on leather can reach 154 circles [rubs]. the surface roughness is caused by the incompatible components of MWPU itself, and has no effect on the strength of the MWPU film, the addition of HTPB increases the strength of the MWPU, making the



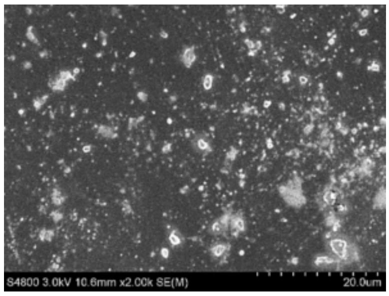
**a**) SEM of MWPU film when HTPB content is 0%



**b**) SEM of MWPU film when HTPB content is 20%



**c**) SEM of MWPU film when HTPB content is 40%



**d**) SEM of MWPU film when HTPB content is 50%

**Figure 6.** Effect of HTPB content on microstructure of MWPU films surface.

MWPU film less susceptible to wear, so the folding fastness and wear resistance can meet the requirements of leather.

## CONCLUSIONS

(1) With the increase of HTPB content, the appearance of MWPU emulsion changes from semi-transparent to un-transparent, the particle size increases, the stability decreases, the mechanical properties of MWPU film increase, the elongation at break, water absorption and light transmittance decrease. Considering the matting effect, the gloss of the MWPU film is as low as 23GU, and the particle surface is more obvious.

(2) The MWPU film shows no cracking on the leather, and the wear resistance can reach 154 circles [rubs], which meets the testing standards of leather.

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