

# Study on Preparation and Performance of Polyurethane Hot Melt Adhesive Films

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**Abstract.** Polyurethane hot melt adhesive films (PHMAFs) are green adhesives without any solvent. In this study, a series of polyurethane hot melt adhesive films with different crosslinking agent content were successfully synthesized. The melting temperature, water absorption, mechanical properties, and adhesion properties were studied. The results illustrate that the introduction of crosslinking agent could endow PHMAFs with better final adhesion strengths and water resistance ability, but also lead to decrease of tensile stress at break and elongation at break. The final T-peel strength of the films was in the range of 76.54-114.53 N/cm, which could meet the requirements of the industrial gluing in footwear.

**Keywords:** polyurethane; green adhesives; T-peel strength; water absorption.

## 1. Introduction

Polyurethane is a polymer containing carbamate groups in the macromolecular backbone, which is called polyurethane, or PU for short. In recent decade, environmental protection has garnered more and more attention and the environmental protection efforts are constantly strengthened. The traditional solvent-based polyurethane adhesives are gradually withdrawn from the market, because it will release toxic volatile organic compounds (VOCs) during usage. So the environment-friendly adhesives become an important development direction in adhesive field [1-3].

Polyurethane hot melt adhesives are favored for solvent-free, simple sizing, easy to store and transport [4-5]. In the process of polyurethane synthesis, the use of cross-linking agent will promote the formation of network structure, and different cross-linking degree will affect the water resistance and adhesive strength of the adhesive. Lei et al presented that intrinsic cross-linked waterborne polyurethane (CWPU), using castor oil (CO) as cross-linking agent, is prepared by condensation polymerization in the absence of any organic solvent. The prepared cross-linked CWPU films have good stability and outstanding mechanical strength [6]. Zhu et al reported that the adhesion, water resistance and anti-adhesion of the cross-linked network water-based ink with trimethylolpropane (TMP) were better than those of the linear water-based ink without TMP in application on polyethylene terephthalate (PET) substrate [7]. Yu et al prepared a series of crosslinked WPU films containing both fluorine and siloxane using trimethylolpropane-tris-( $\beta$ -N-aziridiny) propionate (XR-100) as a crosslinking agent. The introduction of XR-100 effectively improved the hardness, viscosity, tensile strength and solvent resistance of WPU films [8].

In this study, a series of polyurethane hot melt adhesive films were synthesized by polyester polyol, isocyanate, chain extender and trimethylolpropane as crosslinking agent. The effect of TMP content in PHMAFs on the melting temperature, water absorption, mechanical properties, and adhesion properties was studied.

## 2. Experimental

### 2.1 Materials

Polyethylene adipate diethylene glycol diol with a molecular weight of 3000 (PDA3000), isophorone diisocyanate (IPDI), dibutyltin dilaurate (DBTDL), 1-methyl-2 pyrrolidone (NMP), and acetone were obtained from Guangdong Yutian Bali Technology Co., Ltd. (Zhuhai, China); 1,4-butanediol (BDO), 2,2-bis(hydroxymethyl)propionic acid (DMPA), and 1,1,1-tris(hydroxymethyl)propane (TMP) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China); Triethylamine (TEA) was obtained from Guangdong Guanghua Sci-Tech Co. Ltd. (Guangzhou, China); tetrahydrofuran (THF) was purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

### 2.2 Preparation of the PU Prepolymer

PDA was put in a 250 mL four-necked flask and heated at 105°C under vacuum for 6 h to remove moisture. After the reactor was cooled to 70°C, IPDI and DBTDL were added into the polyol. The reaction was performed at 70~80°C for 1 h with a stirring speed of 400 rpm under nitrogen protection. After that, BDO, DMPA (soluble in NMP), and TMP were added into the reactor in turn as the chain extenders and the mixture was further operated for 5 h. Then the mixture was cooled to 40°C and TEA was added to neutralize the carboxylic acid for 1 h to obtain the PU Prepolymer.

### 2.3 Preparation of the PHMAF

The PU Prepolymer was transferred to a Teflon-coated mold and placed at 25°C and 50% relative humidity for 24 h. PHMAFs with 0.2 mm thickness were obtained for further test. The main compositions of the PHMAFs were summarized in Table 1.

Table 1. Main compositions of PHMAFs

Samples	PDA3000 (g)	IPDI (g)	BDO (g)	DMPA (g)	TMP (g)
PHMAF0	75.00	19.00	4.00	1.00	0.00
PHMAF1	75.00	19.00	3.30	1.00	0.75
PHMAF2	75.00	19.00	2.50	1.00	1.50
PHMAF3	75.00	19.00	1.80	1.00	2.25

### 2.4 Measurements

#### 2.4.1 Fourier Transform Infrared Spectroscopy

Fourier Transform infrared (FTIR) spectra of PHMAFs were determined with spectrometer (Shimadzu, IR Prestige-21, Kyoto, Japan). The samples were dissolve in THF and tested by coating method. The spectra were collected by 20 scans at a resolution of 2 cm<sup>-1</sup> from 400 to 4000 cm<sup>-1</sup>.

#### 2.4.2 Melting Temperature

Melting temperature of the PHMAFs was tested on X-4 digital display micro-melting temperature measuring instrument. The sample was put on the glass plate and observed the melting temperature by the micrometer.

#### 2.4.3 Water absorption

The films were cut into 6 cm×6 cm squares and dried at 40°C under vacuum for 3 h. Then the films were placed in a 25°C water bath for 24h. After that, the water on the surface of the film was removed before weighing. The percent water absorption was calculated by the following equation,

$$\text{Water absorption (\%)} = (M1 - M0) / M0 \times 100$$

where the M0 is the mass of dried sample and M1 is the mass of swollen samples.

#### 2.4.4 Mechanical properties

The films were cut into squares with a thickness of 1 mm, a width of 20 mm and a gauge length of 50 mm according to China national standard GB\_T 1040.3-2006 (Plastics - Determination of tensile properties - Part 3: Test conditions for films and sheets). Tensile tests were performed on a universal testing machine (Gotech Testing Machines Co., Ltd, AI-7000S) at a tensile speed of 50 mm/min.

#### 2.4.5 T-Peel Adhesion Strength

A certain size of the PHMAFs were applied to rubber strips (100 mm×25 mm×4 mm) treated with rubber treatment agent. Then the films completely melted at 90°C for 5 min. After that, the strips were fixed in contact and pressed at 6 MPa for 30 s. After curing at 25°C and 50% relative humidity for 24 h, the final T-peel strength tests were performed on a material tensile machine HD-615A-S instrument at a peel rate of 100 mm/min.

### 3. Results and discussion

#### 3.1 FTIR Analysis

The structures of the PHMAFs were confirmed by FTIR spectra (Figure 1). The stretching vibration of C=O groups at 1733 cm<sup>-1</sup> and the -NH groups at 3361 cm<sup>-1</sup> confirmed the presence of the urethane. The deformation vibration of N-H groups were at 1532 cm<sup>-1</sup>. The peaks at 2956 cm<sup>-1</sup> and 2896 cm<sup>-1</sup> were attributed to the stretching vibration of -CH<sub>2</sub> and -CH<sub>3</sub> groups. The peaks at 1069 cm<sup>-1</sup> can be assigned to the stretching vibration of C-O-C groups. The absence of absorption at 2260-2280 cm<sup>-1</sup> confirmed the absence of free -NCO groups in the polymer structure, which indicated the complete curing of PHMAFs. The above characters confirm that the PHMAFs have been successfully synthesized.

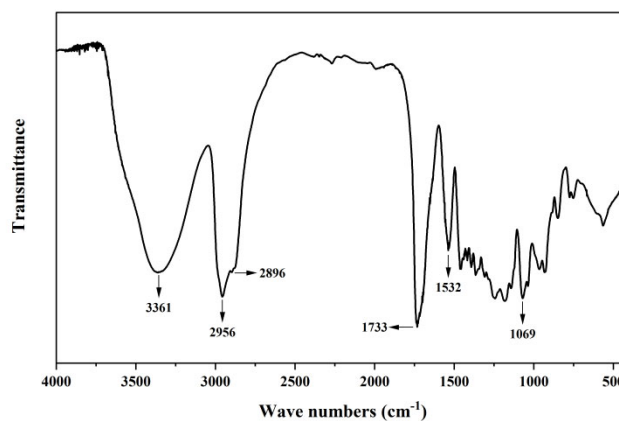


Figure 1. FTIR spectra of PHMAF.

#### 3.2 Melting temperature and water absorption

The melting temperature and water absorption of the PHMAFs are shown in Table 2. It can be seen that the initial and final melting temperature of PHMAFs gradually increased with the increase of TMP content. The water absorption of the PHMAFs decreased with the increase of TMP content.

These results represent that the introduction of TMP is beneficial to the formation of cross-linked network of PHMAFs. The denser cross-linked network improves the heat resistance of the films and the ability to limit the permeation of water molecules.

Table 2. The melting temperature and water absorption of PHMAFs

Samples	Initial melting temperature (°C)	Final melting temperature (°C)	Water absorption (%)
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PHMAF0	45	49	3.84
PHMAF1	46	49	1.42
PHMAF2	48	50	0.96
PHMAF3	50	53	0.41

### 3.3 Mechanical properties

The stress-strain curves of PHMAFs are shown in Figure 2. It can be seen from Table 3, the tensile strength ( $\sigma_m$ ) increased a little from PHMAF0 to PHMAF2, but the  $\sigma_m$  of all the other samples with TMP decreased comparing with PHMAF0. The tensile stress ( $\sigma_b$ ) at break and elongation at break ( $\varepsilon_b$ ) of PHMAF0 were the highest among the samples. The  $\sigma_b$  and  $\varepsilon_b$  of PHMAF2 were higher than the other samples with TMP. These might be ascribed to that the introduction of a low content or high content of TMP would both cause the uneven distribution of the cross-linked network in polyurethane, resulting in low tensile strength and elongation at break.

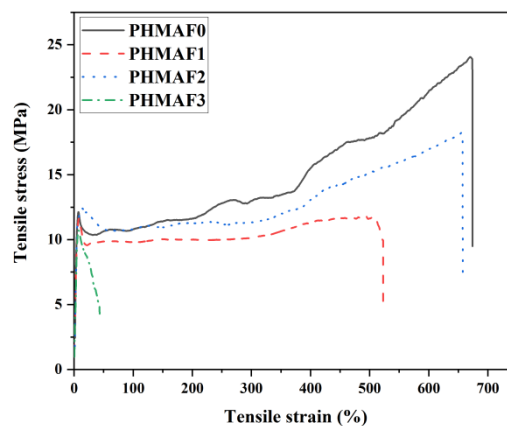


Figure 2. The stress-strain curves of PHMAFs.

Table 3. Mechanical properties of PHMAFs

Samples	Tensile strength (MPa)	Tensile stress at break (MPa)	Elongation at break (%)
PHMAF0	12.14	23.89	674
PHMAF1	11.66	9.95	523
PHMAF2	12.40	18.21	657
PHMAF3	10.71	4.28	43

### 3.4 Adhesion properties

The final T-peel strength of the PHMAFs are shown in Figure 3. With the introduction of TMP, the final strength increased from 76.54 N/cm to 85.12-114.53 N/cm. The cross-linked network improves the cohesion of the films which increase the resistance to cohesive failure in bond failure. All the PHMAFs met successfully the quality requirements of footwear, marked with a dashed line, indicating the considerable potential of PHMAFs for hot melt adhesive applications.

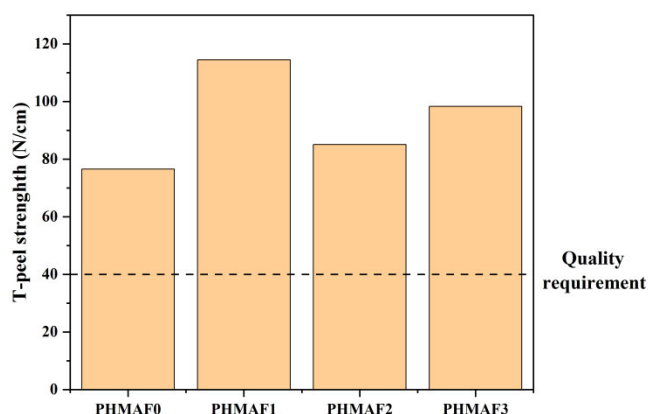


Figure 3. The final T-peel strength of PHMAFs.

#### 4. Conclusions

A series of polyurethane hot melt adhesive films were successfully synthesized. The introduction of TMP would lead to increase of melting temperature and final T-peel strength, but obvious decrease of tensile stress at break and elongation at break. The mechanical properties of PHMAF2 were the best among the samples with TMP. Increasing content of TMP would lead to significant decrease of water absorption, which improved the water resistance ability of the films. The final T-peel strength of all the PHMAFs were much higher than the footwear industrial quality requirements, showing the application prospect in industrial gluing.

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