PREPARATION AND CHARACTERIZATION OF ROSIN-BASED WATERBORNE POLYURETHANE FROM MALEOPIMARIC ACID POLYESTER POLYOL

Xu Xu,[a] Shibin Shang,[a,b,]* Zhanqian Song,[a,b,]* Shuqin Cui,[a] Hongxiao Wang,[a] and Dan Wang [a,b]

Maleopimaric acid (MPA) can be used for polymer materials as a rosin derivative. In this study, rosin-based waterborne polyurethane (RWPU) was prepared with different content of maleopimaric acid polyester polyol (MAPP), which was synthesized from MPA. The properties of RWPU were studied by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Other properties including tensile strength, elongation at break, and water absorption were also determined. The onset decomposition temperature of RWPU with 30 wt% MAPP is improved from 170°C to 237°C, compared to the pure WPU. The tensile strength of the derivative was increased from 7.24 MPa to 23.24 MPa as well relative to the default polyurethane. The water absorption decreased significantly from 78.6% to 14.7%.

Keywords: Maleopimaric acid; Rosin; Polyester polyol; Waterborne polyurethane

*Contact information: a: Institute of Chemical Industry of Forestry Products, CAF; National Engineering Lab. for Biomass Chemical Utilization; Key Lab. on Forest Chemical Engineering, SFA, Key Lab. of Biomass Energy and Material, Jiangsu Province; Nanjing 210042, China; b: Institute of Forest New Technology, CAF, Beijing 100091, China ; *Corresponding author: lhssxly@hotmail.com, shangsb@hotmail.com*

INTRODUCTION

The decrease of petroleum has led to research and development activities worldwide for the use of alternative resource materials for polymers and petrochemicals (Satyanarayana et al. 2009; Belhassen et al. 2011). Being of an abundantly available natural origin, rosin is expected to be eco-friendly, biodegradable, and biocompatible (Liu et al. 2010; Satturwar et al. 2003; Fulzele et al. 2003). The hydrogenated phenanthrene ring structure of rosin acids is a rigid entity and could improve properties of polymer materials. For example, Arán-Aís et al. (2002, 2005) reported successful incorporation of a rosin acid as part of the chain extender in the synthesis of thermoplastic polyurethane elastomers (TPUs). However, rosin acids cannot be introduced in the main chains of polymer because of their monofunctionality. This attribute limits their application in polymer synthesis. The rosin derivatives may be increased in functionality through chemical modifications.

As one type of rosin derivative, maleopimaric acid (MPA) is the Diels-Alder adduct of rosin acids and maleic anhydride. Maleopimaric acid polyester polyol (MAPP) can be synthesized by MPA, and it could be a good alternative to current polymer materials.

Waterborne polyurethane (WPU) is a rapidly growing segment of the polyurethane industry in many applications such as coatings, adhesives, and thermoplastic elastomers (Zhang et al. 2011; Madbouly and Otaigbe 2009; Athawale and Nimbalkar 2010). To reduce environmentally undesirable emissions of volatile organic compounds (VOCs), WPU has grown commercially over the last three years (Kim et al. 2010; Hsu et al. 2010; Sardon et al. 2010).

In recent years, various bio-resources have also received attention in WPU synthesis including starch (Lu et al. 2005; Cao et al. 2008), vegetable oil (Patel 2010; Kumar et al. 2008), and cellulose (Hatakeyama et al. 1995; Wang et al. 2010; Cao et al. 2009). But little research has focused on WPU modified with rosin derivatives.

In this work, MAPP was introduced in the main chain of WPU to synthesize rosin-based WPU (RWPU). The preparation and properties including mechanical property, thermal stability, and water resistance of RWPU were investigated.

EXPERIMENTAL

Materials

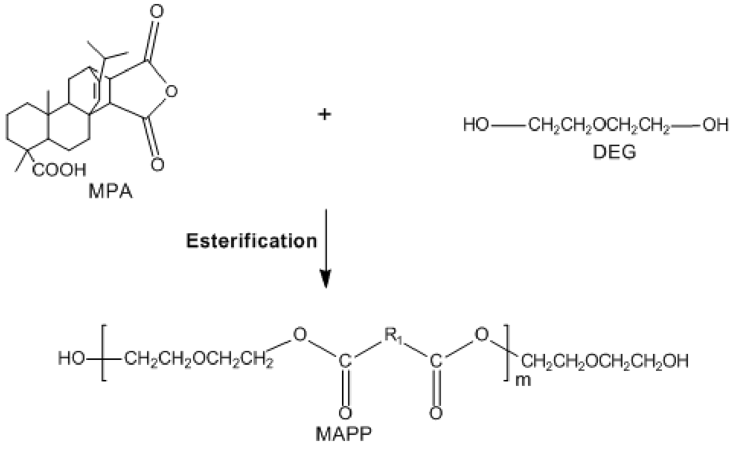
Rosin was supplied by Wuzhou Pine Chemicals Ltd. (Guangxi, China). Polyether glycol N-210 (average molecular weight 1000) was obtained from Sinopharm Chemical Reagent Co. Ltd. 2,4-Toluene diisocyanate (TDI) was purchased from Jiangbei Chemical Reagents Factory (Wuhan, China), and redistilled before use. Dimethylol propionic acid (DMPA) and dibutyl tin dilaurate of synthetic grade were purchased from First Chemicals of Tianjin (Tianjin, China). Triethylamine (TEA), acetone and diethylene glycol (DEG) were from Lingfeng Chemicals of Shanghai (Shanghai, China). TEA and acetone were treated with 3A molecular sieves to dehydrate. The polyol, DMPA and DEG were dehydrated at 100°C in vacuum for 24 h before use.

Methods

Synthesis of maleopimaric acid polyester polyol (MAPP)

Maleopimaric acid (MPA; 382) was purified from the Diels-Alder adduct of rosin and maleic anhydride.

The synthetic process is indicated in Scheme 1. In a four-necked round bottom flask equipped with mechanical stirrer, Dean Stark assembly, thermometer and nitrogen gas inlet, predetermined quantities of MAPP and DEG were charged as per the formulations. The temperature was initially raised to 120°C and thereafter increased with small increments of 20°C per hour until it finally settled at 240°C, where the reactions were continued until the desired acid values (<10 mg KOH/g) (ASTM D 16392-90) and hydroxyl values (ASTM D 1957-286) were obtained (8 h) (Athawale and Kulkarni 2010). Polyesterification was carried out in the presence of catalyst, under a slow stream of N_2 to provide an inert atmosphere and to avoid oxidation due to atmospheric oxygen. The progress of reaction was solely monitored from the acid value and the quantity of water of esterification accumulated during the course of reaction. Finally, the polyester polyols thus produced were discharged into glass stopper bottles and were placed in vacuum desiccator before the onset of further reactions.



Where R_1=MPA

Scheme 1. Polymerisation process for MAPP

Synthesis of RWPU

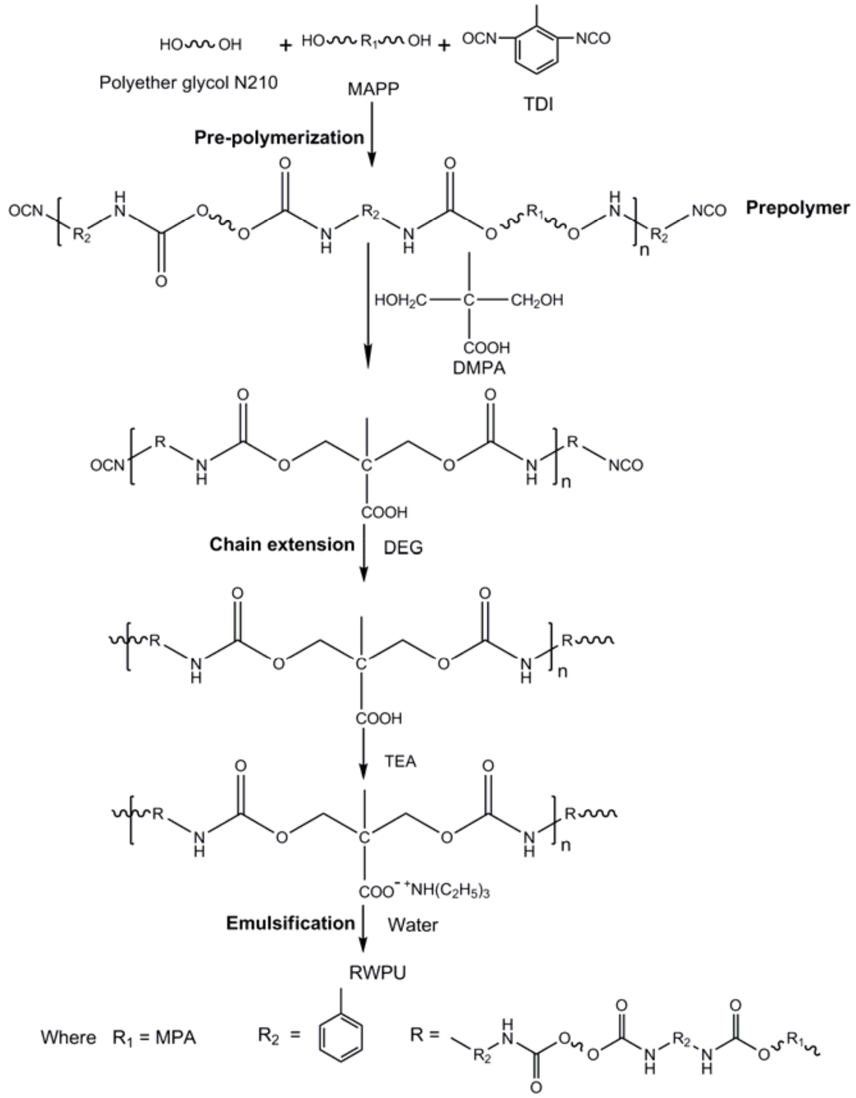
RWPUs were prepared by using the acetone process, having hard to soft segments molar ratios (NCO/OH 1.3). The DMPA content was set to 5.0 wt% and that of DEG was set to 1.5 wt% (with respect to the prepolymer weight).

The main steps of the synthetic route are indicated in Scheme 2. MAPP and polyether glycol N-210 were charged into a glass-jacketed reactor fitted with a mechanical stirrer, thermometer, reflux condenser, and nitrogen inlet. Reaction was carried out at 110°C for 3 h at reduced pressure to remove water. The resulting reactant was cooled to 80°C, and then TDI was added to the flask. The mixture was allowed to react at 80°C for 3 h. The prepolymer was extended by addition of DEG and DMPA, and allowed to react at 60°C for 3 h, and acetone was slowly added to obtain a homogeneous mixture. The mixture was then neutralised by addition of TEA under stirring at 30°C for 30 min. Dispersion was accomplished by slowly adding water (100.8 g) to the neutralised PU solution with vigorous stirring. After removing the acetone (by evaporation at 35°C in a rotary evaporator under reduced pressure), RWPU with about 35 wt% solids content was obtained.

Films of RWPU for testing were prepared by casting the emulsion onto a Teflon disk and drying under ambient conditions for one week.

Characterisation of RWPU

The average particle sizes of RWPU dispersions were obtained from Mastersizer APA2000 (Malvern Co., UK). The films were analysed by recording FT-IR spectra, using a Nicolet Magna IR 560 FT-IR spectrometer, from 4000 to 600 cm^{-1} for each sample 256 scans were obtained at 4 cm^{-1} resolution.



Scheme 2. Polymerisation process for RWPU composites

Mechanical properties of the RWPUs were measured by simple extension on dumbbell specimens with a Tinius Olsen (United States) 1000 tensile tester at crosshead speed 50 mm/min according to the ASTM D 412 standard. The quoted values were averages of the results for at least five specimens. Thermogravimetric analysis was carried out with a TAQ50 system from 40 to 800°C at heating rate 10°C/min in nitrogen. Water absorption measurements were conducted at 25°C. The composite specimens were weighed before being immersed in distilled water. After immersion for 24 h, excess water was removed from the specimens using filter paper, and the specimens were weighed to ±0.001 g. Differential scanning calorimetry (DSC) of the films was carried out with a DSC200 PC apparatus (Netzsch Co., Germany) under a nitrogen atmosphere. Each sample was subjected to heating/cooling cycles between -60 and 110°C to obtain reproducible glass transition temperature (T_g) values. The heating rate was 10°C/min.

RESULTS AND DISCUSSION

Average Particle Size of the WPU Dispersion

Figure 1 shows the average particle sizes of the aqueous polyurethane dispersions with varying MAPP content. As the MAPP content increased, bigger particles (from 142 to 204 nm) can be obtained during the synthesis of the dispersion. Our results follow this tendency, suggesting that the increase in the average particle size is due to the presence of a higher content of hydrophenanthrene ring groups from MAPP, considerably affecting the particle size.

MAPP with the structure of hydrophenanthrene groups is a polyfunctional compound, which can make molecule chains of WPU crosslink partly. That's why the particle size of RWPU increased with the increase of MAPP.

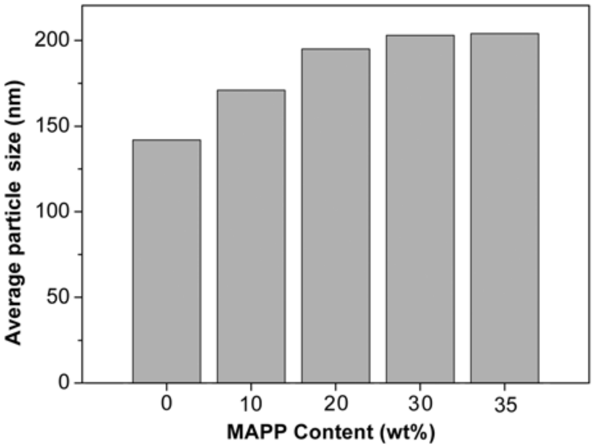


Fig. 1. Average particle size of RWPUs with varying MAPP content

FT-IR Analysis

FT-IR spectra of MAPP, RWPU, and WPU are presented in Fig. 2. The characteristic peaks in Fig. 2a show the presence of hydroxyl group (-OH, 3398 cm^{-1}), and carbonate group of anhydride ring (O=C-O-C=O, 1776 and 1710 cm^{-1}) absorbed in the MAPP.

It can be clearly seen (in Fig. 2b and c) that the spectra of RWPU and WPU reveal new bands compared to the unmodified MAPP, with maxima at 3296, 2970, 1600, 1533, 1221, and 1062 cm^{-1}. The newly formed bands at 3296 and 1600 cm^{-1} can be assigned to the stretching vibration and bending vibration of N-H bonds, from the hydrogen bonds to carbonyl oxygen, which were formed by interaction of the -NCO group of TDI with -OH group on MAPP and polyether glycol N-210 surfaces. The bands at 2970 cm^{-1} may be respectively ascribed to the C-H symmetric absorptions of the -CH$_3$ and -CH$_2$ groups attached to the surface of RWPU. The peaks at 1533, 1221, and 1062 cm^{-1} that appear clearly in the spectrum of the functionalised C=O were assigned to the stretching and deforming bands, respectively, of urethane. There is no peak near 2270 cm^{-1}, which indicates that no free -NCO groups were present in the RWPU.

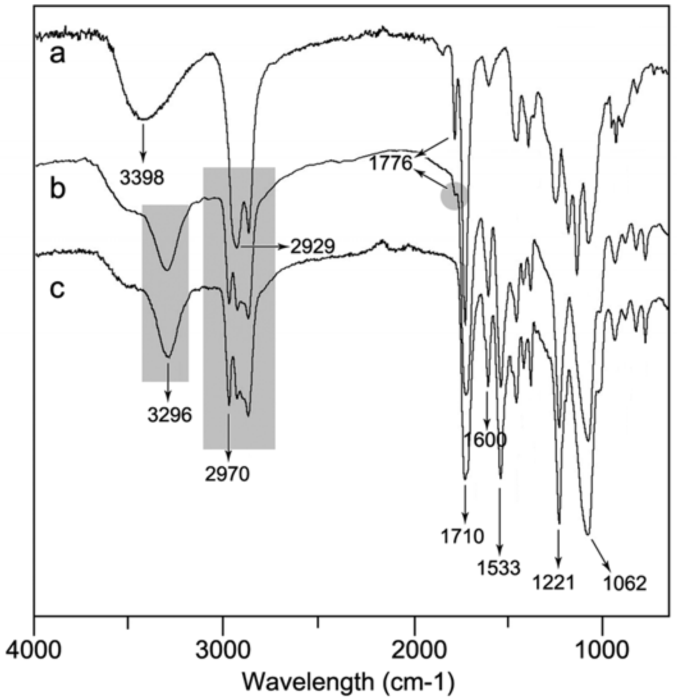


Fig. 2. FT-IR spectra of (a) MAPP, (b) RWPU and (c) WPU.

TGA Analysis

The TGA curves of WPU and RWPUs are shown in Fig. 3. The RWPUs displayed a weight loss at temperatures from 40 to 800°C. The onset decomposition temperatures (TOD) of the pure WPU (a) and the RWPU with 30 wt% MAPP (c) were 170 and 237°C, respectively. The delay in the TOD of the RWPU showed that its thermal stability was improved with increase of MAPP content, which may be attributed to the excellent thermal stability of the rigid structure from rosin acid (Artaki et al. 1992).

For the RWPU and the bare WPU sample, the degradation in the range of 200-300°C can be attributed to decomposition of the urethane bonds, which takes place through the dissociation to isocyanate and alcohol, the formation of primary amines and olefins, or the formation of secondary amines.

The degradation processes in the temperature range of 300-400°C are attributed to soft segments of polymer chains scission. The last steps in the weight loss rate centered at a temperature of 400°C, which is attributed to thermo-oxidative degradation of the WPU films (Patel et al. 2010). The slopes of these curves above 500°C were approximately equal.

It was observed that the 5% weight loss temperature of WPU was 183°C, and the temperatures of RWPU with varying MAPP loading level 10-30 wt% were from 223 to 259°C, respectively. The RWPU had higher decomposition temperature in comparison to the bare WPU because of the addition of MAPP, which results in more crosslink density to increase cohesive energy.

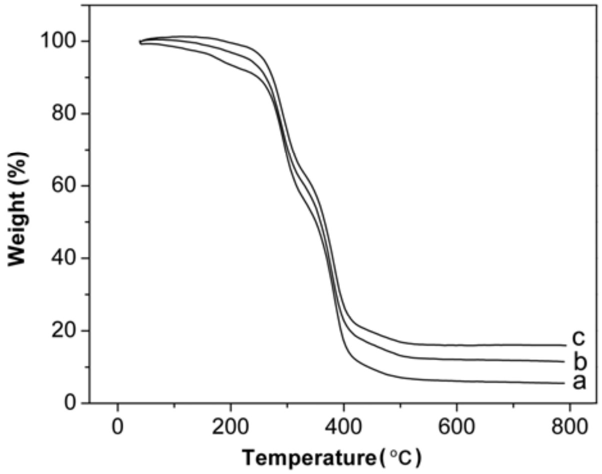


Fig. 3. TGA thermograms of (a) 0, (b) 10 and (c) 30 wt % MAPP.

DSC Study

Figure 4 shows DSC scans of WPU and RWPUs with different MAPP contents. In all of the scans a specific heat increment was observed at about -60°C, corresponding to the glass-rubber transition of the soft segments of the WPU matrix, and the half ΔC_p extrapolated temperature was taken as the glass transition temperature (T_g). The values of T_g and the heat capacity change (ΔC_p) are shown in Table 1. It was found that with increase in the proportion of MAPP, T_g (from -12.7 to 0.7 °C) increased compared to the value for neat WPU, and ΔC_p decreased from 0.58 to 0.49 J/g·K. The presence of MAPP can influence the magnitude of T_g in the following way. The rigid structure of MAPP can induce restricted mobility of WPU chains by steric hindrance in the interfacial area, resulting in a shift of T_g toward higher temperature. Thus the upward trend of T_g can be attributed to decreased degrees of freedom for the soft segment in WPU, as a result of decreased microphase separation between soft and hard segments. This is in good agreement with the result from TGA.

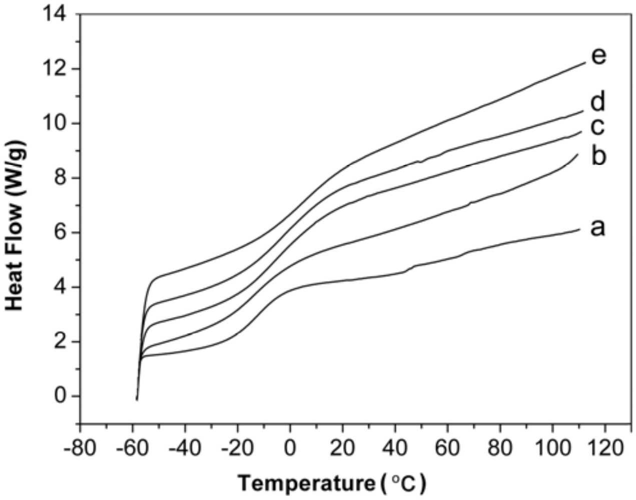


Fig. 4. DSC scans of WPU and RWPUs with varying MAPP content. (a) 0, (b) 10, (c) 20, (d) 30 and (e) 35 wt % MAPP

Table 1. Data Showing for WPU and RWPU with Varying MAPP Content: Glass transition temperature (T_g), Heat capacity change (ΔC_p), Tensile strength (σ_B), Elongation at break (ε), and Water absorption (W_a)

Sample	T_g (°C)	ΔC_p (J/g·K)	σ_B (MPa)	ε (%)	W_a (%)
WPU	-12.7	0.58	7.24	1003.26	78.6
RWPU (10 wt% MAPP)	-11.0	0.54	12.69	733.19	30.8
RWPU (20 wt% MAPP)	-9.1	0.53	15.62	613.55	23.4
RWPU (30 wt% MAPP)	-4.3	0.51	23.24	592.1	14.7
RWPU (35 wt% MAPP)	0.7	0.49	23.52	568.54	14.2

Mechanical Properties Study

The tensile strength (σ_B) and the elongation at break (ε) of films of the pure WPU and RWPU, shown in Fig. 5 and Table 1, demonstrate that the tensile strength of RWPU with 30 wt% MAPP content increased to 23.24 MPa by about 220%, compared with pure WPU (7.24 MPa). Clearly the amount of rigid structure from rosin increased with increasing MAPP content, thus enhancing the crosslink density. Hence more chemical interactions resulted in a greater degree of networking within the composites. It is well known that a network structure is favourable for enhancing mechanical strength. However, as the loading level of MAPP increased to 35 wt%, the tensile strength of the RWPU increased little but its stability decreased, which indicates that too much MAPP network can be the site of stress, causing decreased stability of the polymer matrix.

The elongation at break of the RWPU films decreased significantly with increasing MAPP loading levels up to 30 wt%, and reached a constant value at higher loading levels. Higher MAPP loading level results in increased crosslink density, which decreases the flexibility of molecular chains. Thus mobility of chain segments is reduced. According to Lu (2005) and Patel (2010), elongation is a property that is greatly influenced by mobility of chain segments. The reduced elongation is caused by lower mobility of chain segments.

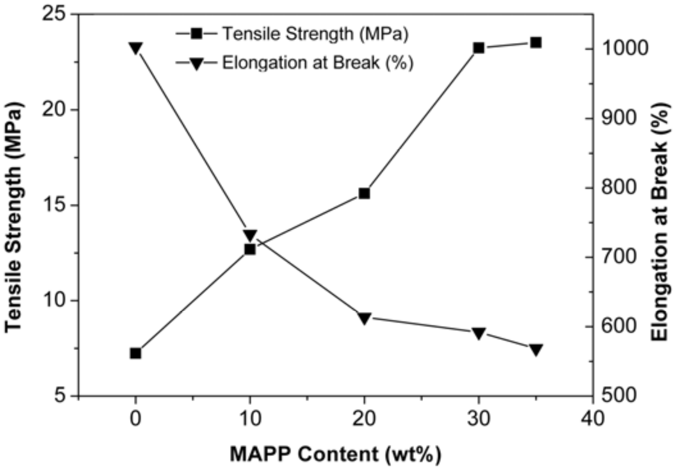


Fig. 5. Tensile strength and elongation at break of RWPU with varying MAPP content.\

Water Absorption Study

The water absorption of any polymeric material, whether filled or not, is of great importance for applications. Water absorption (W_a) was evaluated according to the following equation,

$$W_a=[(W_s-W_i)/W_i]\times 100\% \quad (1)$$

where W_i is the initial weight of the sample, and W_s is the sample weight after a specified time of immersion. Each water absorption experiment was repeated three times, and the average value was taken to ensure reliability of the results. The water absorption decreased significantly from 10 to 35 wt% MAPP (Fig. 6). The rigid structure of RWPU composite is favourable for reducing water absorption, so the incorporation of MAPP decreased water absorption (that is, increased water resistance). This is because rosin acids have a hydrophobic skeleton in combination with hydrophilic carboxyl groups. RWPU with MAPP can attain a hydrophobic skeleton in combination with hydrophilic carboxy groups to a greater extent than WPU (Atta et al. 2006), and consequently provide more barriers to the migration of water, giving much better water resistance.

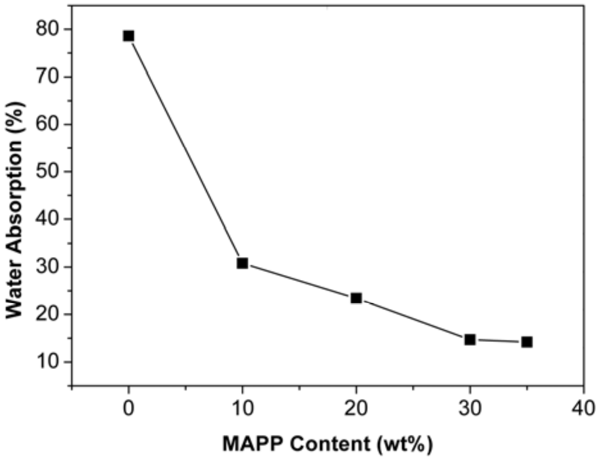


Fig. 6. Water absorption of RWPU with varying MAPP content

CONCLUSIONS

1. A derivatized rosin-based waterborne polyurethane (RWPU) was prepared with maleopimaric acid polyester polyol (MAPP), and its properties were found to be improved relative to the control waterborne polyurethane (WPU). Compared to pure WPU, the thermal stability of RWPU was enhanced, according to TGA and DSC results. The TOD and T_g of RWPU with 30 wt% MAPP were 67°C and 12°C higher than that of pure WPU, respectively. The delay in the TOD and T_g of the RWPU showed that its thermal stability were improved, which may be attributed to the excellent thermal stability of the rigid structure from MAPP.

2. The mechanical strength of RWPU also was enhanced. The tensile strength of RWPU with 30 wt% MAPP was significantly improved to 23.24 MPa as a result of crosslinking by MAPP.
3. Furthermore, it was observed that water absorption decreased from 78.6 % to 14.2 % for RWPU.
4. The improved mechanical property, thermal stability, and water resistance of the RWPU will certainly broaden the practical applications. The use of a rosin derivative is an interesting approach for increasing the usage of environmentally friendly and renewable resources.

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