

Article

Urethane Diols through Non-Isocyanate Approach and Their Application in MF Coating

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Abstract: In this work, two urethane diols with different middle chain lengths were prepared by the non-isocyanate approach from 1,4-diaminobutane or 1,6-diaminohexane with ethylene cyclic carbonate at room temperature without the aid of a catalyst. Different weight percentages of hexa(methoxymethyl) melamine (HMMM) crosslinker was mixed with urethane diols then cured under elevated temperature to generate the melamine-formaldehyde (MF) coating films. Two different linear diols without urethane linkage were chosen to crosslink with HMMM as the control group. The mechanical properties of these MF coatings were investigated by tensile test, adhesion test, and conical mandrel bend test. It was found that coatings incorporated with urethane diols exhibited enhanced mechanical properties and flexibility. These properties were also influenced by the weight percentage of HMMM crosslinker. This study provided a facile non-isocyanate way to produce urethane diols and successfully applied them in MF coating.

Keywords: non-isocyanate; urethane diols; MF coating



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1. Introduction

High-solid coatings are widely used as topcoats in the thermoset system in various industries. Most properties of high-solid coatings are derived from highly cross-linked networks. Melamine-formaldehyde (MF) resin is a common thermoset resin synthesized from melamine and formaldehyde which can be applied in many fields including fireproof and waste-water processing [1–3]. MF can also act as the crosslinking agent to crosslink with hydroxyl or carboxyl groups [4]. The hardness and chemical resistance of the networks are provided by the heterocyclic ring of melamine resin, while the base resin also aids in flexibility. Methylated amine, known as hexa(methoxymethyl) melamine (HMMM), is a widely used crosslinker not only due to its high reactivity with hydroxyl and carboxylic acid groups but also the limited self-condensation [5]. HMMM can react with primary and secondary hydroxyl groups to form the three-dimensional thermoset polymer network [6]. The reaction of MF with polyols is shown in Figure 1 [7].

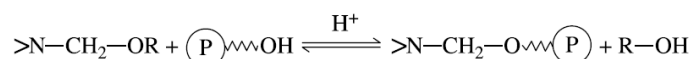


Figure 1. The reaction of MF resin with polyols.

Although melamine/polyol thermoset systems are widely used for many industrial coatings, there are drawbacks such as poor chemical resistance and the lack of flexibility in high solid applications. Therefore, there is motivation to investigate the approaches used to enhance the properties of melamine/polyol coating [4,8–10]. Many studies have investigated the effect of different polyols on the properties of melamine/polyol thermoset systems [11–14]. For example, Thomas et al. [14] investigate the effect of the functionality of vegetable-oil-based polyol on properties of MF coatings and compared with the commercial

polyols. Balgude et al. [15] modified the cardanol oil as bio-based polyols to improve the chemical resistance and the flexibility with the amount of HMMM crosslinker. Therefore, introducing urethane groups in polyols could be an effective modification to improve the properties of melamine/polyol coating, which needs full investigation.

The traditional pathway to synthesize urethane groups induces environmental concerns and safety issues. The raw material to produce urethanes is isocyanate, which is highly toxic and harmful to humans and the environment [16–19]. Some alternative and green methods have been explored to obtain urethane linkages, such as the reaction of cyclic carbonate and amines. This method has caught more attention due to the straightforward synthesis procedure and the formation of secondary hydroxyl groups from the ring-opening of cyclic carbonate which can be further functionalized or react with other materials such as MF [20,21]. Moreover, various cyclic carbonate and amines can be selected based on the goal of applications [22–26].

Herein, two urethane diols were obtained by a non-isocyanate process from cyclic carbonate and linear diamines with different chain lengths, then they were crosslinked with HMMM to get the coatings with different flexibilities and mechanical properties. The control group was also prepared from the linear diols with HMMM. The chemical structures of urethane diols were confirmed by Fourier transform infrared spectroscopy (FTIR) and ^1H nuclear magnetic resonance (NMR). The flexibility, adhesion, and tensile strength of MF coatings with various urethane diols and weight percentages of HMMM crosslinker were studied after the full curing of the coatings.

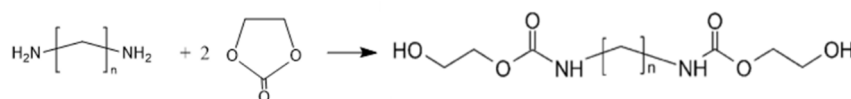
2. Experimental

2.1. Materials

Ethylene carbonate, 1,4-diaminobutane, 1,6-diaminohexane, 1,10-decanediol, 1,12-dodecanediol, ethanol, and methylene chloride were purchased from Sigma-Aldrich (St. Louis, MO, USA). HMMM was kindly supplied by Allnex (Wallingford, CT, USA) and para-toluenesulfonic acid (pTSA; K-cure 1040) was provided from King Industries (Norwalk, CT, USA). Steel substrates were purchased from Q-Lab (QD-36, $3 \times 6 \text{ in}^2$, Westlake, OH, USA). All the materials were used as received without further purification.

2.2. Synthesis of Urethane Diols

To synthesize 1,6-bishydroxyalkylcarbamates (BHC6), 26.3 g (0.30 mol) of ethylene carbonate, and 17.4 g (0.15 mol) of 1,6-diaminohexane were mixed well in the methylene chloride solution at room temperature, according to the previously published process [27]. The reaction is described in Scheme 1. Similarly, to synthesize 1,4-bishydroxyalkylcarbamates (BHC4), 26.3 g (0.30 mol) of ethylene carbonate and 13.2 g (0.15 mol) of 1,4-diaminobutane were added for the reaction following the same procedure to synthesize BHC6. The chemical structure of 1,6-diaminohexane and 1,4-diaminobutane is shown in Figure 2.



Scheme 1. Synthesis of urethane diols from ethylene cyclic carbonate and amines.

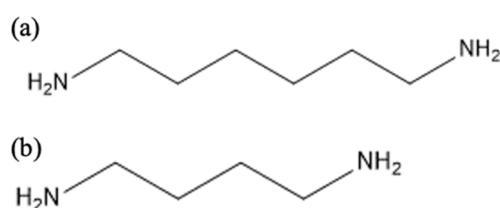


Figure 2. Chemical structure of (a) 1,6-diaminohexane and (b) 1,4-diaminobutane.

2.3. Preparation of MF Coating

The MF coatings were generated from urethane diols and the HMMM crosslinker. Firstly, urethane diols were dissolved into ethanol and then mixed well with the crosslinker. The mixture was coated on the steel panel by a film applicator and heated up to 120 °C for 2 h. Different weight percentages of HMMM crosslinker were chosen for the coating formation: 15 wt.%, 25 wt.%, and 35 wt.%. The linear diols without urethane groups were chosen as the control group in this study. The chemical structures of the linear diols are shown in Figure 3. They followed the same procedure as mentioned above to prepare the MF coatings. The formulation of the samples for the experimental group and the control group is summarized in Tables 1 and 2, respectively. The samples were named by the amount of HMMM crosslinker. For example, in the experimental group, BHC4-15% is the 1,4-bishydroxyalkylcarbamates with 15 wt.% of HMMM crosslinker. BHC6-15% is the 1,6-bishydroxyalkylcarbamates with 15 wt.% of HMMM crosslinker. Similarly, in the control group, BHC4C-15% is the 1,10-decanediol with 15 wt.% of HMMM crosslinker. BHC6C-15% is the 1,12-dodecanediol with 15 wt.% of HMMM crosslinker.

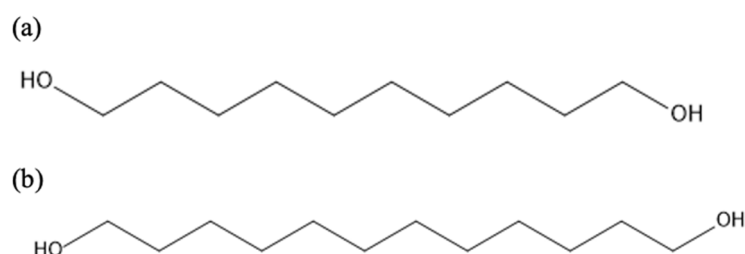


Figure 3. Chemical structure of (a) 1,10-decanediol and (b) 1,12-dodecanediol.

Table 1. Formulation of MF coatings for the experimental group (wt.%).

Experiment Group	Urethane Diols	HMMM	Curing Catalyst
BHC4-15%	82%	15%	3%
BHC6-15%	82%	15%	3%
BHC4-25%	72%	25%	3%
BHC6-25%	72%	25%	3%
BHC4-35%	62%	35%	3%
BHC6-35%	62%	35%	3%

Table 2. Formulation of MF coatings for the control group (wt.%).

Control Group	Linear Diols	HMMM	Curing Catalyst
BHC4C-15%	82%	15%	3%
BHC6C-15%	82%	15%	3%
BHC4C-25%	72%	25%	3%
BHC6C-25%	72%	25%	3%
BHC4C-35%	62%	35%	3%
BHC6C-35%	62%	35%	3%

2.4. Characterization Methods

The FTIR spectra were obtained by Nicolet iS10 FT-IR Spectrometer (resolution 4 cm⁻¹; scan number 64). The range of scanning wavenumber was from 4000 to 400 cm⁻¹. The FTIR testing was operated at room temperature. The ¹H NMR spectra were obtained by Varian INOVA 400 instrument in CDCl₃ at room temperature. The adhesion property was obtained by the cross-cut tape method according to ASTM D3359. The flexibility was evaluated by a conical mandrel tester based on ASTM D522. Mechanical properties of the coating films were measured by Instron 5567 tester. The samples were cut with a length of 20 ± 2 mm and a width of 10 ± 2 mm. The tests were carried out at room temperature

with a fixture moving speed of 5 mm min^{-1} . At least three available duplicates of each formulation were measured to obtain the average value of data. The viscoelastic properties of the MF coatings were obtained by a dynamic mechanical thermal analyzer (DMTA, Q800, TA instrument). The tension mode was applied with a constant frequency of 1 Hz. The samples were $15 \text{ mm} \times 10 \text{ mm}$ in size with a thickness of 0.1–0.2 mm.

3. Results and Discussion

3.1. Characterization of Urethane Diols

As mentioned in the Section 2, BHC6 was obtained in the reaction of ethylene carbonate with 1,6-diaminohexane at room temperature without any catalyst. After the reaction was completed, the final product was precipitated as a white powder. From the FTIR spectrum, as shown in Figure 4a, there was no absorption band characteristic for a carbonyl group of five-membered cyclic carbonate at 1800 cm^{-1} . Similar to BHC6, no catalyst was needed to synthesize BHC4, and the final product of BHC4 was also a white powder. In Figure 4b, the disappearance of the peak at 1800 cm^{-1} indicated that the reaction of ethylene carbonate with 1,4-diaminobutane was completed.

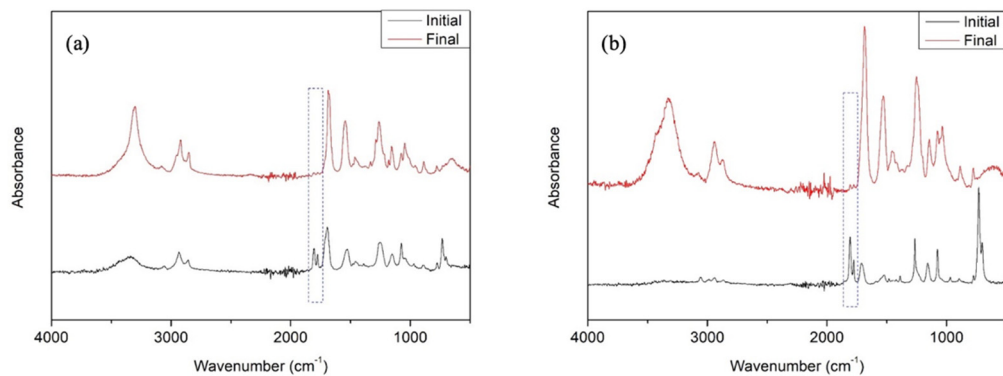


Figure 4. FTIR spectra of the initial reactants (top) and the final product (bottom) in the reaction for (a) BHC6 and (b) BHC4.

The BHC4 and BHC6 were also characterized by ^1H NMR as shown in Figure 5. Two signals of NH groups are found at 7.08 ppm and 6.72 ppm with an intensity ratio around 8 to 2. This is consistent with the previously reported work by Neffgen et al. [28] The BHC6 had one more peak at 1.2 ppm due to the additional carbon atom in the middle chain comparing to BHC4.

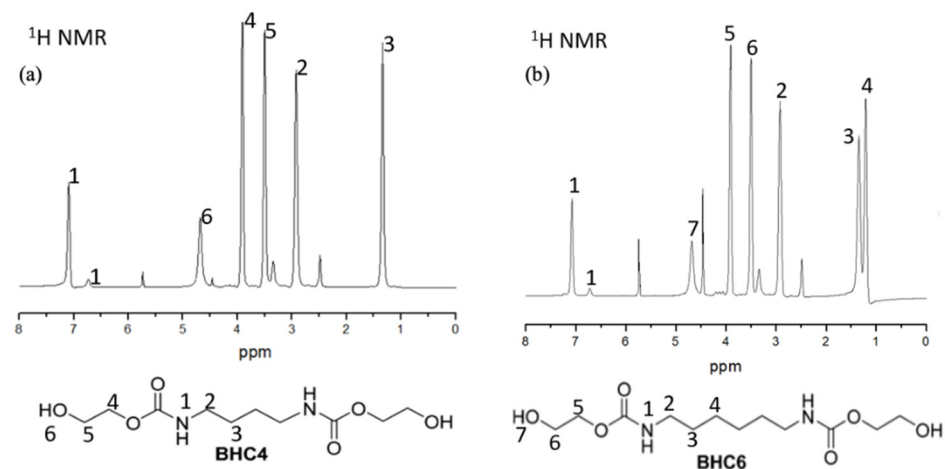


Figure 5. ^1H spectra of (a) BHC4 and (b) BHC6.

3.2. Mechanical Properties

Figure 6 is the comparison of tensile strength between the samples of the experimental group and the control group with different weight percentages of HMMM crosslinker. In the experimental group, by comparing the samples with different middle chain lengths, BHC4 samples showed higher tensile strength than BHC6 samples with the same weight percentage of the crosslinker. This is because the short middle chain of the urethane diols can strengthen the hydrogen bonding from urethane linkages. By comparing the same middle chain length with different weight percentages of the crosslinker, the tensile strength was enhanced with the increase in the percentage of the crosslinker both for BHC4 samples and BHC6 samples. This is caused by the increased crosslinking due to the increased amount of the crosslinker.

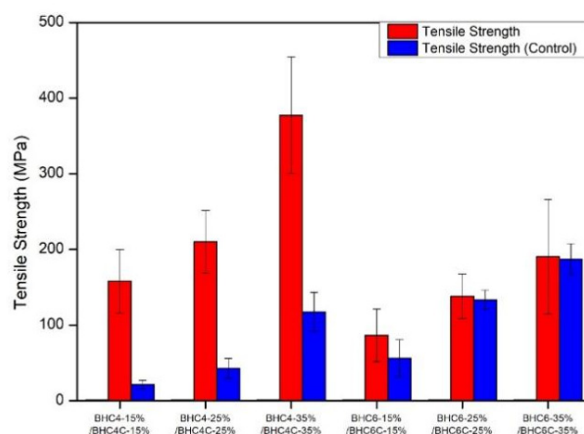


Figure 6. Tensile strength of samples from the experimental group and the control group. The experimental group refers to the formulation in Table 1; the control group refers to the formulation in Table 2.

In the control group, BHC6C samples had a similar tensile strength to the BHC4C samples. It suggests that the middle chain length in the linear diols has a tiny impact on the tensile strength. By comparing the same middle chain length with different weight percentages of the crosslinker, the tensile strength raised with the increase in the percentage of HMMM crosslinker. It is the same reason that HMMM can increase the amount of crosslinking to make a more rigid polymer structure.

As expected, the experimental group by urethane diols showed a significantly higher result in tensile strength, compared with the control group. Therefore, adding urethane groups to the diols is an effective way to improve the tensile strength of MF coatings. The effect of the HMMM crosslinker on the tensile strength is the same for the experimental group and the control group.

Figure 7 shows the elongation-at-break of the experimental group and the control group from the tensile test. In the experimental group, BHC6 samples showed a similar elongation-at-break to BHC4 samples with the same weight percentage of HMMM crosslinker. This indicates that the middle chain length had a slight impact on the flexibility. The elongation-at-break decreased along with the increase in the weight percentage of the HMMM crosslinker at the same middle chain length. This is because the structure of the crosslinked film became more rigid with a higher percentage of the crosslinker. More rigid structure and the hydrogen bonding from urethane groups could make the polymer films lose their flexibility. It shows that the excess of the HMMM could lead to the polymer network too rigid to elongate both for BHC4 samples and BHC6 samples.

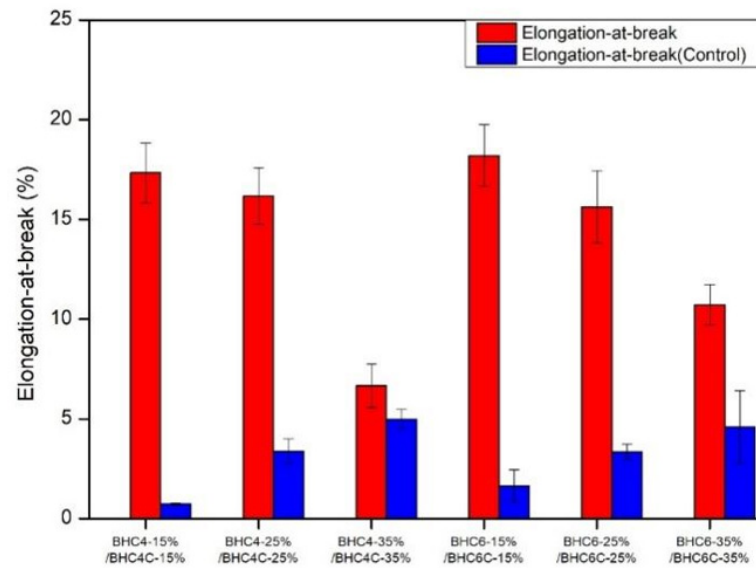


Figure 7. Elongation-at-break of samples from the experimental group and the control group. The experimental group refers to the formulation in Table 1; The control group refers to the formulation in Table 2.

However, for the control group, it finds out that the elongation-at-break is positively proportional to the weight percentage of the crosslinker. Moreover, the elongation-at-break of BHC4C samples and BHC6C samples performed similarly with the same weight percentage of the crosslinker, which demonstrates the middle chain length has a slight impact on the elongation. This is because there is only carbon-carbon bonding in the linear diols of the control group.

Compared to the experimental group with the control group, it is obvious that adding urethane groups into diols can provide the malleability of the polymer structure to improve its elongation with the proper amount of the crosslinker. The middle chain length influences slightly the flexibility of the experimental group and the control group.

3.3. Crosslinking of MF Coatings

To understand the different mechanical properties of the MF coatings, the crosslink density was obtained by DMTA measurement. The crosslink density can be calculated from Equation (1) [29–31]

$$v_e = E' / 3RT \quad (1)$$

where v_e is the number of moles of elastically effective network chains per volume of a film; E' is the storage modulus in the rubbery plateau region at $T_g + 50$ °C; R is the universal gas constant, and T is the absolute temperature corresponding to the storage modulus value in °K.

In Tables 3 and 4, the crosslink density of the experimental group is higher than that of the control group comparing the MF coatings with the middle chain length and the same percentage of the crosslinker. It demonstrates that the experimental group has a more rigid polymer network than the control group. It is because the internal hydrogen bonding is generated among urethane groups in the experimental samples while a carbon-carbon linear network is formed in the control samples. Generally, a higher crosslink density is achieved at a higher percentage of HMMM crosslinker in the experimental group. That is why the elongation-at-break decreased and tensile strength increased along with the increase in HMMM crosslinker in the experimental group. However, the trend in the control group is not obvious. The highest crosslink density is from the BHC4C-15% sample in the control group which shows the lowest elongation-at-break. The 25% HMMM and 35% HMMM samples with the same middle chain length do not show a significant difference in the crosslink density, which demonstrates the elongation-at-break of these samples are not

much different. Overall, the mechanical properties of MF coatings have been enhanced by using the urethane diols to increase their crosslink density.

Table 3. Viscoelastic properties of MF coating films for the experimental group.

Experimental Group	T _g (°C)	E' at T _g + 50 °C (MPa)	v _e (mol/m ³)
BHC4-15%	60.74	6.05	632.12
BHC6-15%	65.68	8.70	897.84
BHC4-25%	49.07	4.90	527.91
BHC6-25%	44.08	14.91	1628.58
BHC4-35%	94.11	6.69	642.91
BHC6-35%	66.87	34.68	3565.60

Table 4. Viscoelastic properties of MF coating films for the control group.

Control Group	T _g (°C)	E' at T _g + 50 °C (MPa)	v _e (mol/m ³)
BHC4C-15%	54.11	8.72	927.15
BHC6C-15%	59.73	4.65	487.78
BHC4C-25%	42.36	1.64	180.71
BHC6C-25%	59.36	6.03	632.80
BHC4C-35%	57.60	1.70	179.64
BHC6C-35%	29.81	5.84	663.35

3.4. General Coating Properties

All the adhesion results are summarized in Table 5. Generally, the experimental group presents better adhesion than the control group. This is because the urethane linkages in the experimental group increased the bonding of the coating to the substrate, while the control group only had hydroxyl groups bonding to the substrate. The BHC4 samples and BHC6 samples show similar adhesion results. It implies that the difference in middle chain length does not affect the adhesion of the coating in the experimental group. The dry adhesion has a significant increase as increasing the amount of HMMM crosslinker in the control group. Overall, adding urethane diols can enhance the adhesion of the MF coatings.

Table 5. Dry adhesion of MF coatings based on ASTM D3359.

Experimental Group	Dry Adhesion	Control Group	Dry Adhesion
BHC4-15%	5B	BHC4C-15%	1B
BHC6-15%	5B	BHC6C-15%	1B
BHC4-25%	4B~5B	BHC4C-25%	1B
BHC6-25%	5B	BHC6C-25%	2B
BHC4-35%	5B	BHC4C-35%	3B
BHC6-35%	5B	BHC6C-35%	3B~4B

As shown in Table 6 for the conical mandrel bend test, all the samples in the experimental group passed the test, no matter the amount of the crosslinker or middle chain length of diols. However, only two samples in the control group passed the test. This is because the control group only had hydroxyl groups that were brittle and easy to be broken. This conical mandrel bend test suggests that urethane diols can provide enough force to ensure the structure of the network that improves the flexibility of the MF coatings.

Table 6. Conical mandrel bend test results based on ASTM D552.

Experimental Group	Results	Control Group	Results *
BHC4-15%	Pass	BHC4C-15%	Pass
BHC6-15%	Pass	BHC6C-15%	Fail
BHC4-25%	Pass	BHC4C-25%	Fail
BHC6-25%	Pass	BHC6C-25%	Pass
BHC4-35%	Pass	BHC4C-35%	Fail
BHC6-35%	Pass	BHC6C-35%	Fail

* Pass: No cracking was on the coating surface and the coating film was attached to the substrate; Fail: Cracking appeared on the coating surface and the coating film was detached from the substrate.

4. Conclusions

Different urethane diols were synthesized and crosslinked with different weight percentages of HMMM crosslinkers. Characterization results showed that diols with urethane groups in MF coatings can bring better mechanical properties compared to those from the linear diols. The middle chain length is an important parameter in the tensile strength of MF coatings from urethane diols. In addition, the weight percentage of the crosslinker also influences the tensile strength and the elongation-at-break of MF coatings from urethane diols. Shorter carbon middle chain in urethane diols could make the structure of the polymer network rigid to enhance the tensile strength. On the other hand, the influence of middle chain length is not significant in MF coatings from the linear diols. Although the MF coatings from urethane diols showed enhanced property in the flexibility and tensile strength, excess of the HMMM crosslinker could diminish the elongation of the MF coatings. Based on all the results, urethane diols with 25 wt.% HMMM is an optimized option for the appropriate flexibility and tensile strength of the MF coating. This work provides a non-isocyanate approach to synthesize urethane diols which were successfully used in MF coatings to improve the mechanical properties of MF coatings.

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Conflicts of Interest: The authors declare no conflict of interest.

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