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From Castor Oil-Based Multifunctional Polyols to Waterborne Polyurethanes: Synthesis and Properties

Yuehong Zhang,* Zhenqiang Wu, Lei Shi, Langlang Dai, Ruijing Liu, Lei Zhang, Bin Lyu,* Shunhua Zhao, and Vijay Kumar Thakur*

A novel castor oil-based multifunctional polyol (CM) is fabricated through mild thiol-ene photo induced reactions using castor oil (CO) and 1-thioglycerol (MPD) as building blocks. The effect of the reaction time, molar ratio of thiol to carbon-carbon double bond, and the loadings of photo-initiator are optimized. The resulting CM is combined with CO and employed as cross-linkers to prepare castor oil-based water-borne polyurethane emulsion with desirable mechanical properties and water resistance. Owing to the incorporation of CM cross-linker with high hydroxyl value of 371 mg KOH/g (which is 2.27 times higher than that of the CO), the prepared castor oil-based waterborne polyurethane (CMWPU) possesses compacted 3D network structure with high cross-linking degree, leading to improved glass transition temperature (45 °C), tensile strength (10.8 MPa), water contact angle (87.4°), and decreased water absorption rate (16.12%) with 20% CM additions. Overall, this work illustrates the feasibility of introducing bio renewable CM combined with CO to develop castor oil-based WPU employing a sustainable development strategy.

1. Introduction

Polyurethanes (PUs) are one of the most widely used synthetic polymers due to their excellent chemical resistance, controllable mechanical properties, and flexibility.^[1-4] With the increasing environmental concerns, water-borne polyurethane (WPU), synthesized with isocyanates, polyols, emulsifiers, chain extenders and water, has become one of the research hotspots.^[5-7] However, most of the polyols employed are derived from nonrenewable petrochemical resources. Furthermore, during the preparation of WPU, multiple hydrophilic groups (hydroxyl, amino, carboxyl and sulfonic group) were introduced into the system, leading to the resultant WPU having poor water resistance, which is not conducive to the utilization of WPU in various fields.^[8-10] Therefore, developing environmentally friendly bio-based WPU

has attracted increasing attention due to its merits of sustainability and environmental friendliness.

An array of renewable feedstocks and their derivatives with reactive hydroxyl groups, such as cardanol,^[11] soy protein,^[12] polysaccharide,^[13,14] lignin,^[15,16] and vegetable oils (castor oil, linseed oil, soybean oil, etc.),^[17-20] have been employed to partially or completely substitute petroleum-based polyols in the preparation of WPU. Among them, vegetable oils offer the advantages of abundant resources, easy availability, low cost, and multiple modification strategies, which are potential promising building blocks to fabricate bio-based WPU.^[21] However, vegetable oil-based WPUs always exhibit undesirable water resistance and mechanical properties.^[22] In order to improve the water-resistance of the vegetable oil-based WPU, many strategies have been employed to tackle the problem, including decreasing the number of the hydrophilic group in the WPU material,^[23] increasing the cross-linking degree of the WPU material,^[24,25] introducing components (silicon and fluorine-containing chemicals) with low surface energy,^[26-28] and incorporating organic fillers (especially two-dimensional nanomaterials).^[29,30] Among them, introducing efficient cross-linkers to increase the cross-linking degree of the WPU system is one of the most effective and widely used strategies. Therefore, there is an urgent need to fabricate bio-derived polyol cross-linker.

Generally, the higher the number of hydroxyl groups in vegetable oils, the higher the cross-linking degree of the resultant

Y. Zhang, Z. Wu, L. Dai, R. Liu, L. Zhang, B. Lyu
College of Bioresources Chemical and Materials Engineering
Xi'an Key Laboratory of Green Chemicals and Functional Materials
Shaanxi University of Science and Technology
Xi'an 710021, China

E-mail: yuehong.zhang@sust.edu.cn; lvbin@sust.edu.cn

L. Shi, S. Zhao

Zhejiang Hexin Science and Technology Co., Ltd
Jiaxing 314003, China

V. K. Thakur

Biorefining and Advanced Materials Research Centre
Scotland's Rural College

Kings Buildings, Edinburgh EH9 3JG, UK


E-mail: vijay.thakur@sruc.ac.uk

V. K. Thakur

School of Engineering

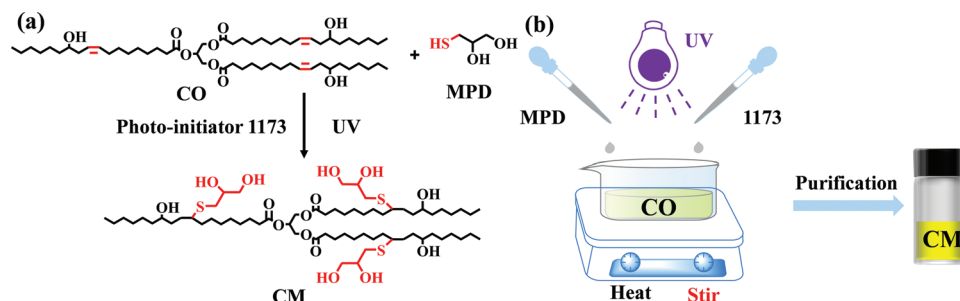
University of Petroleum & Energy Studies (UPES)

Dehradun, Uttarakhand 248007, India

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/mame.202200662>

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Scheme 1. a) Schematic and b) detailed preparation diagram of CM via thiol-ene photo click reaction.

WPU network and the better the water resistance of the WPU material. Therefore, during the past years, a series of vegetable oils (such as soybean oil, castor oil, linseed oil, etc.) have been modified utilizing transesterification,^[31] epoxy ring-opening reaction,^[32,33] and thiol-ene click reaction,^[34,35] to introduce more hydroxyl groups and employed as bio-derived polyol cross-linker to prepare vegetable oil-based WPU with improved water resistance. For example, Zhang et al. prepared bio-based polyols with different hydroxyl values by epoxidation and reduction of various vegetable oils (castor oil, epoxidized soybean oil, and epoxidized linseed oil) with LiAlH_4 .^[36] Castor oil, one of the inedible vegetable oils, inherently contains reactive hydroxyl groups and unsaturated carbon-carbon double bonds, which can be directly used as bio-based polyols to completely or partially replace petroleum-based polyols to prepare bio-based WPU. However, 1 mole of castor oil generally contains 2.7 moles of free secondary hydroxyl groups, leading to limited hydroxyl value and low reactivity.^[37,38] Hence, it is desirable to modify castor oils to improve their hydroxyl value and simultaneously employ them as cross-linkers of WPU.

The thiol-ene click reaction offered the merits of high yield, mild reaction conditions, short reaction time, and easy purification, which can be used to prepare multi-hydroxyl vegetable oil-based polyols.^[39–41] For example, Liang et al. prepared bio-based polyols through photo-initiated thiol-ene click reaction using olive oil, castor oil, corn oil, rape oil, rice bran oil, grape-seed oil, and linseed oil as raw materials, and 2-Mercaptoethanol was employed as sulfhydryl reagent.^[42] But 2-Mercaptoethanol is highly toxic (LD_{50} : 244 mg kg^{-1} (rat oral); 190 mg kg^{-1} (mice oral); 150 mg kg^{-1} (rabbit percutaneous)). Moreover, the hydroxyl group numbers of the vegetable oil-based polyols are still relatively low, leading to the limited cross-linking degree of the resultant WPU. Compared with 2-Mercaptoethanol, 1-Thioglycerol is non-toxic, and the hydroxyl group number of per mole of 1-Thioglycerol is twice as that of 2-Mercaptoethanol. Therefore, introducing 1-Thioglycerol to modify vegetable oil has great potential to increase the hydroxyl group number of vegetable oils and further increase the cross-linking degree of vegetable oil-based WPU.

In this paper, castor oil-based multifunctional polyol (CM) was prepared via facile thiol-ene click reaction with castor oil and 1-Thioglycerol (sulfhydryl agent) as raw material, and the reaction conditions were optimized. Then CM combined with CO was introduced into the castor oil-based waterborne polyurethane system and employed as cross-linking agents. The effect of the CM loading on the water absorption, thermal stability, and mechani-

cal properties of the WPU was explored, which provides an effective way to develop castor oil-based polyol and its corresponding WPU.

2. Experimental Section

2.1. Materials

Castor oil (CO, hydroxyl value: 167 mg KOH/g) was obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. 2-Hydroxy-2,2-dimethylacetophenone (1173) was purchased from Ryoji Organic Chemical Co., Ltd. Isophorone diisocyanate (IPDI) was supplied from Bayer Germany. 2,2-Dimethylolbutyric acid (DMBA) was bought from Shanghai Aladdin Biochemical Technology Co., Ltd. 1-Thioglycerol (MPD), dibutyltin dilaurate (DBTDL), and triethylamine (TEA) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All chemicals were used without further purification.

2.2. Synthesis of Castor Oil-Based Multifunctional Polyols (CM)

CO (5 g), different content of MPD (the molar ratios of thiol (MPD) to carbon-carbon double bond (CO) was varied from 3:1, (1.5:1 and 1:1) and photo-initiator 1173 (1%, 2%) were charged into a 50 mL beaker at 25 °C with continuous stirring. Then the beaker was placed under a 25 mW cm^{-2} UV-LED and irradiated for different times (0.5, 1, 1.5, and 3 h) at 25 °C. After that, the crude product was diluted with ethyl acetate, washed with saturated sodium chloride solution at least 3 times, dried over anhydrous magnesium sulfate, and filtered. Finally, ethyl acetate was removed with a rotary evaporator and dried with a vacuum oven to obtain CM. The schematic of the preparation of CM by thiol-ene click reaction is shown in **Scheme 1**.

2.3. Preparation of WPUs from CO and CM

The molar ratio of the raw material of castor oil-based WPU is summarized in **Table 1** (the OH/NCO molar ratio was maintained at 1:1.4). First, the hydroxyl groups within CO and CM with different molar ratios (100:0, 95:5, 90:10, 85:15, 80:20, 75:25) were charged into a three-necked flask and stirred uniformly at 25 °C. Then 11.11 g (0.05 mol) of IPDI and two drops of catalyst DBTDL were added into the flask and reacted at 78 °C for 3 h. Subsequently, 2.06 g of DMBA was added into the flask and reacted for 2 h; after that, the mixture was lowered to 40 °C, neutralized

Table 1. Composition of castor oil-based WPU.

Sample	Molar ratio			
	–NCO [IPDI]	–OH [Castor oil]	–OH [CM]	–OH [DMBA]
CMWPU-0	1.400	0.610	0.000	0.389
CMWPU-5	1.400	0.579	0.031	0.389
CMWPU-10	1.400	0.548	0.062	0.389
CMWPU-15	1.400	0.517	0.093	0.389
CMWPU-20	1.400	0.486	0.124	0.389
CMWPU-25	1.400	0.455	0.155	0.389

with TEA under stirring (1.0 equiv. relative to DMBA) for 0.5 h, and then cooled to room temperature. Finally, deionized water was added for emulsification for 1 h to obtain castor oil-based anionic WPU with a solid content of $\approx 30\%$. The castor oil-based WPU was cast into a Teflon mold, dried at room temperature for 48 h, 60 °C for 24 h, and 80 °C for 2 h to obtain castor oil-based WPU film, and the prepared WPU film was labeled as CMWPU-*x*, where *x* represents the percentage of hydroxyl group content in the CM to the hydroxyl group content in the whole polyol system. The preparation route of WPU from modified castor oil-based polyols is shown in **Scheme 2**.

2.4. Characterization

The prepared CM was analyzed using an AVANCE NEO 600 MHz proton nuclear magnetic resonance (^1H NMR) spectrometer from Bruker, and CDCl_3 was employed as a solvent.

Fourier transform infrared (FT-IR) spectra of CO and CM in the transmission mode with KBr and CMWPU in the total reflection mode were recorded using a VECTOR22 Fourier transform infrared spectrometer (Bruker, Germany), at a scanning range of 400–4000 cm^{-1} .

The viscosity of CO and CM was measured by a DHR-1 rheometer (TA Instruments) equipped with a 25 mm circular parallel plate, the test temperature was 25 °C, and the shear rate was in the range from 1 to 200 s^{-1} . Each sample was measured three times.

The hydroxyl value of the polyols was determined by the phthalic anhydride method:^[34] 25 mL of the phthalic anhydride-pyridine mixture (the mass ratio is 6.1:1) and 1.0 g (*m*, g) of CM or CO were added to a flask under continuous stirring. After the mixture reacted at 113–117 °C for 1 h, the product was titrated with 1 mol L^{-1} (c) NaOH solution with phenolphthalein as an indicator. A blank experiment was performed following a similar procedure.

$$Hv = \frac{(V_1 - V_2) \times c \times 56.1}{m} \quad (1)$$

where *Hv* (mg KOH/g) is the hydroxyl value of CO and CM, V_1 (mL) is the consumed volume of NaOH solution in the blank experiment, V_2 (mL) is the consumed volume of NaOH solution for the polyol CO or CM, *c* (mol L^{-1}) is the concentration of NaOH standard solution, and *m* (g) is the mass of the polyol CO or CM.

The particle size distribution and Zeta potential of the CMWPU emulsions were characterized by dynamic laser light

scattering (DLS) using a nanoparticle size surface potential analyzer (Malvern, UK). The CMWPU emulsion was diluted with distilled water into a 0.1% aqueous solution before measurement, and each sample was measured three times.

The solid content of the CMWPU emulsion was measured upon heating ≈ 2 g of sample in a 103 °C oven until the mass no longer changed.

The centrifugal stability of the CMWPU emulsion was evaluated by centrifuging the emulsion at 3000 r min^{-1} for 30 min on an H4-20K centrifuge (Hunan Kecheng Instrument Equipment Co., Ltd.). In addition, another batch of the CMWPU emulsion was stored in the dark at room temperature for 6 months before visual observation.

The hydrophobicity of the CMWPU film was measured using a contact angle goniometer (Biolin Attension Theta). The water contact angle of the CMWPU film was measured by the static drop method at room temperature.

The water resistance of the CMWPU films was evaluated by immersing the dried rectangular films (3 mm \times 3 mm) in water for 24 h according to the Chinese Standard GB/T 1034–2008 water absorption test.

The tensile property of the CMWPU film was tested using a GTS-2000-S servo system (Taiwan High-Speed Rail Technology Co., Ltd.) according to Chinese Standard GB/T 528–2009. Dumbbell-shaped specimens were employed for the test with a cross-head speed of 10 mm min^{-1} . At least three parallel samples were measured to obtain the final tensile strength and elongation at break.

The dynamic mechanical properties of the CMWPU film were performed on a Q800 dynamic mechanical analyzer (DMA, TA Instruments) using a tensile mode at 1 Hz, rectangular specimens with dimensions of 8 mm \times 6 mm were first cooled to -60 °C and held for 5 min, and then heated at a heating rate of 5 °C min^{-1} to 120 °C. According to the elastic theory of rubber,^[43] the cross-linking degree (*v*) of the CMWPU films was calculated:

$$v = \frac{E'}{3RT} \quad (2)$$

where *v* (mol m^{-3}) is the cross-linking degree, E' (MPa) is the rubber modulus at $T_g + 30$ °C, *T* (K) is the absolute temperature, and *R* is the gas constant (8.314 J mol^{-1} K^{-1}).

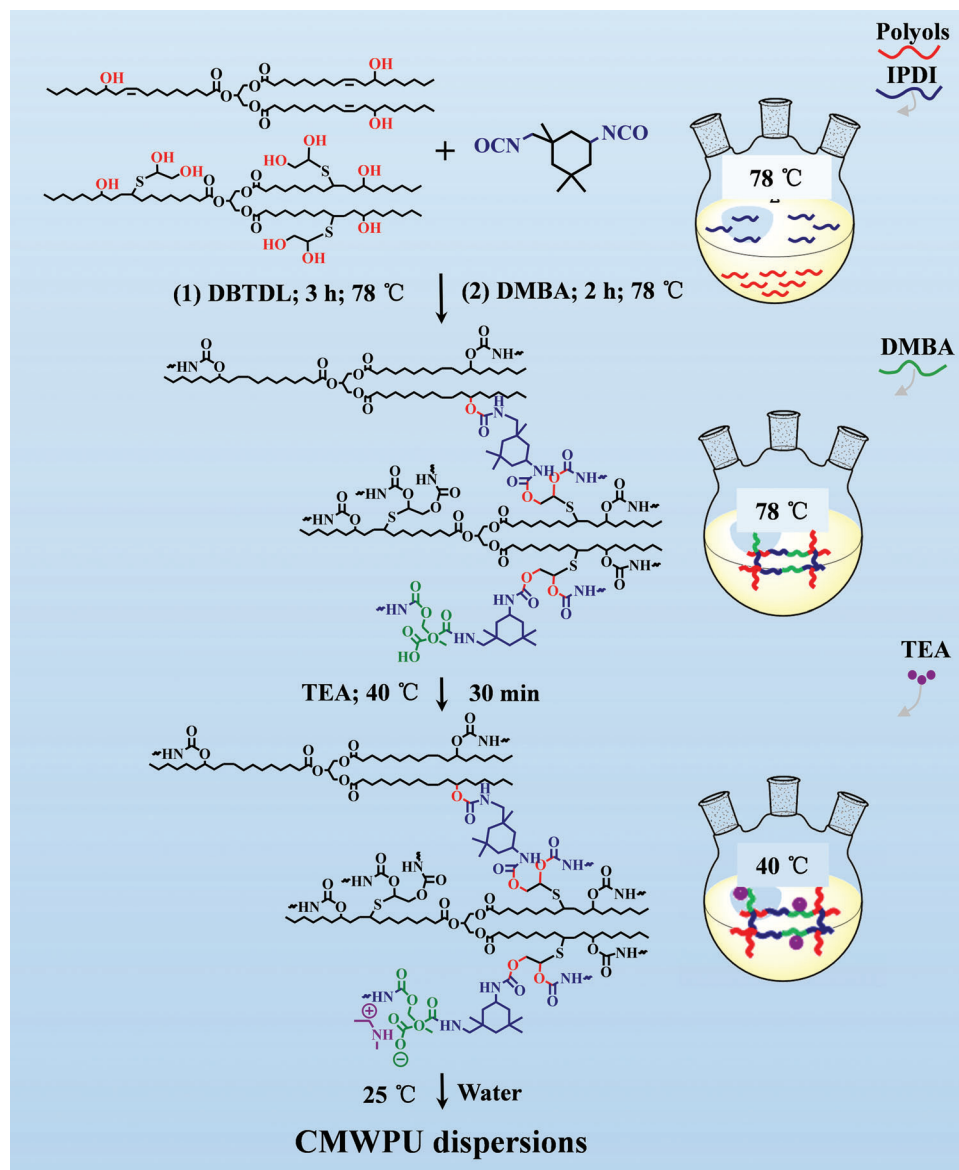
The thermal stability of the CMWPU film was evaluated by a Q500 thermal gravimetric analyzer (TGA, TA Instruments) at the temperature range from 30 to 650 °C at a heating rate of 10 °C min^{-1} under an N_2 atmosphere.

The chemical resistance of the CMWPU film was evaluated by immersing the rectangular sample (1 cm \times 1 cm) in acidic (1 M HCl) or alkaline (1 M NaOH) solution with continuous stirring at room temperature for 24 h, and the changes of the rectangular samples were observed and recorded.

3. Results and Discussion

3.1. Preparation and Characterization of Castor Oil-Based Polyol Cross-Linker (CM)

Castor oil-based polyol was prepared using castor oil and 1-Thioglycerol as raw material through facial and “green”



Scheme 2. Schematic of the preparation route of CMWPU from CO and CM.

UV-initiated thiol-ene click chemistry at room temperature (Scheme 1). Several key preparation parameters were optimized. The molar ratio of thiol (MPD) to carbon-carbon double bond (CO), the loading of photo-initiator 1173, and the reaction time on the structures of the resultant polyols is investigated and presented in Figures S1–S6 (Supporting Information) (^1H NMR and FT-IR). And the results showed that the optimal preparation conditions of CM were as follows: the molar ratio of thiol to double bond was 1.5:1, the reaction time was 1 h, and the loadings of photo-initiator 1173 was 2 wt.%.

The chemical structure of the CM prepared under optimal conditions is verified by ^1H -NMR and FT-IR and presented in Figure 1a,b. Compared with CO, after reacting with MPD, the chemical shift at 5.3–5.6 ppm corresponding to the carbon-carbon double bonds ($-\text{CH}=\text{CH}-$) completely disappeared for CM. Meanwhile, new resonance signals at 2.4–2.7, 2.8–3.2, and 3.7–3.9 ppm

attributed to the methylene ($-\text{CH}_2-$ and $-\text{CH}-$) and the tertiary carbon protons connecting to hydroxyl groups ($-\text{CH}-\text{OH}$) of the thioglycerol moiety appeared (Figure 1a), confirming the carbon-carbon double bonds were successfully converted to thioglycerol moiety to form CM. The hydroxyl value of the prepared CM reached $371 \text{ mg KOH g}^{-1}$ (Figure 1c), which was 2.27 times higher than that of native CO ($163 \text{ mg KOH g}^{-1}$). Furthermore, as shown in Figure 1b, the band at 3042 cm^{-1} , attributed to the $=\text{C}-\text{H}$ stretching vibration of CO, disappeared entirely in the CM spectra,^[44] and the intensity of the peak at 3527 cm^{-1} assigned to the hydroxyl group enhanced significantly in the spectrum of CM (the peak at 2900 cm^{-1} was used as internal standard), which was in good agreement with the ^1H NMR results.

Furthermore, as shown in Figure 1d, the color of CO is light yellow, while that of CM is yellow. Likewise, both CO and CM showed shear thinning behavior, this was mainly due to the

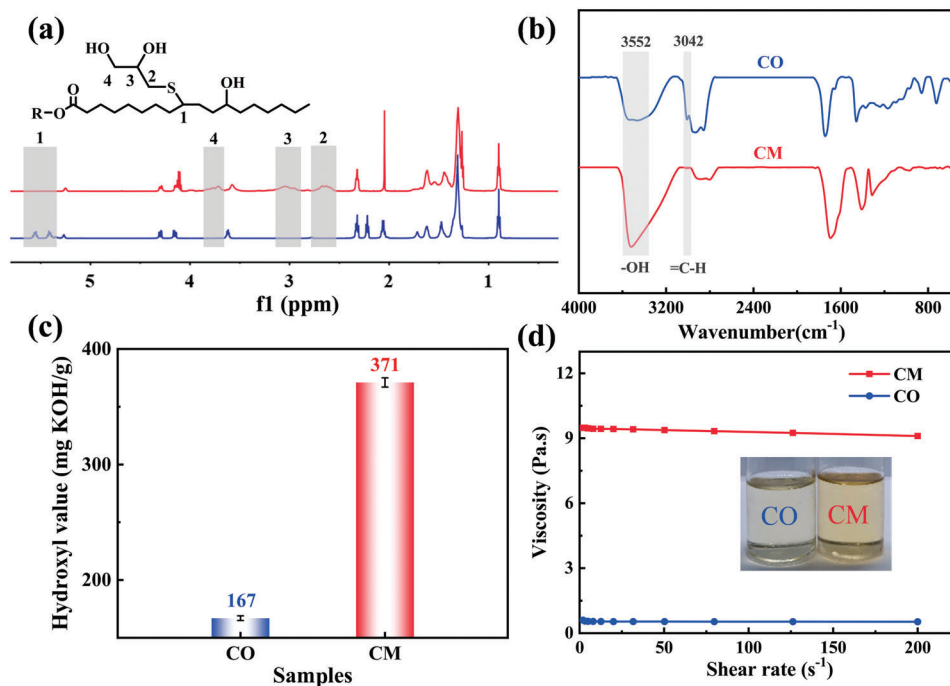


Figure 1. a) The $^1\text{H-NMR}$, b) FT-IR, c) viscosity, and d) hydroxyl value of CO and CM.

presence of van der Waals force and hydrogen bond interactions within CO and CM. Nevertheless, the viscosity of CO was 0.60 Pa.s at 25 °C (shear rate: 2 s^{-1}), while that of CM was 9.45 Pa.s, which was ≈ 15.75 times higher than that of CO. This was mainly due to CM owned long aliphatic chains and abundant hydroxyl groups (confirmed by the hydroxyl value of 371 mg KOH g^{-1}), which is not only prone to form entanglement of flexible molecular chain but also the hydroxyl groups within CM could form strong hydrogen bond interactions, and thus increasing the friction force of CM upon flowing.^[45] All these results confirmed the successful preparation of CM, and the yield of CM prepared under optimal conditions was 93.8%. The sustainability of CM was estimated by bio-based carbon content, and the bio-based carbon content was defined as the proportion of bio-based carbon to the total organic carbon content in a monomer, the bio-based carbon content of CM was calculated as 86.4%.

The prepared castor oil-based polyol CM combined with CO was employed as cross-linkers to prepare bio-based WPU. As CM contains 2.27 times more primary hydroxyl groups than CO, the more CM introduced into the WPU, the higher the cross-linking degree of the resultant WPU network. Therefore, with the loading of CM reached 25%, the reaction system of CMWPU-25 cross-linked to form a gel that cannot be emulsified. This was mainly due to the significantly increased cross-linking degree and molecular weight of the reaction system of CMWPU-25. Therefore, the maximum loading of CM is 20%.

3.2. Properties of Bio-Based CMWPU Emulsions

The storage stability of the CMWPU emulsion with different loadings of CM was investigated, and the results are shown in

Figure 2 and **Table 2**. As shown in Figure 2a,b, no precipitation and stratification were observed for the CMWPU emulsions with CM loadings ranging from 0% to 20% after storage for 6 months, implying excellent storage stability. This was also confirmed by the high-speed centrifugation test, as the CMWPU emulsion maintained excellent stability after centrifuging at 3000 r min^{-1} for 30 min. This was mainly due to the prepared CMWPU emulsions having relatively small and uniform particle size ranged from 115.4 to 216.6 nm with the introduction of CM from 0% to 20% (Figure 2c), the small particle size of the latex particles contributed to the stability of the emulsion. Furthermore, the latex particles of the CMWPU emulsion were negatively charged, and the absolute value of the zeta potential of CMWPU emulsion was all higher than 30 mv (Figure 2d), implying strong electrostatic repulsion interaction present between latex particles, which hindered the aggregation of latex particles, further confirming excellent stability of the CMWPU emulsion.

3.3. Properties of Cured CMWPU films

The prepared CMWPU emulsion was then cured to fabricate CMWPU films, and the FT-IR spectra of the CMWPU film are shown in **Figure 3**. The peak at 3306 cm^{-1} was assigned to the stretching vibration of the $-\text{NH}$ bond and the peaks at 3020 and 2786 cm^{-1} was attributed to the $-\text{CH}_2-$ and $-\text{CH}-$ bond of polyurethane. In addition, the peak at 1701 cm^{-1} was assigned to the $-\text{C}=\text{O}$ stretching vibrations, confirming the formation of the urethane group. The new peak at 649 cm^{-1} corresponding to the $\text{C}-\text{S}-\text{C}$ stretching vibrations was also observed, confirming the successful introduction of CM into the WPU. Meanwhile, no

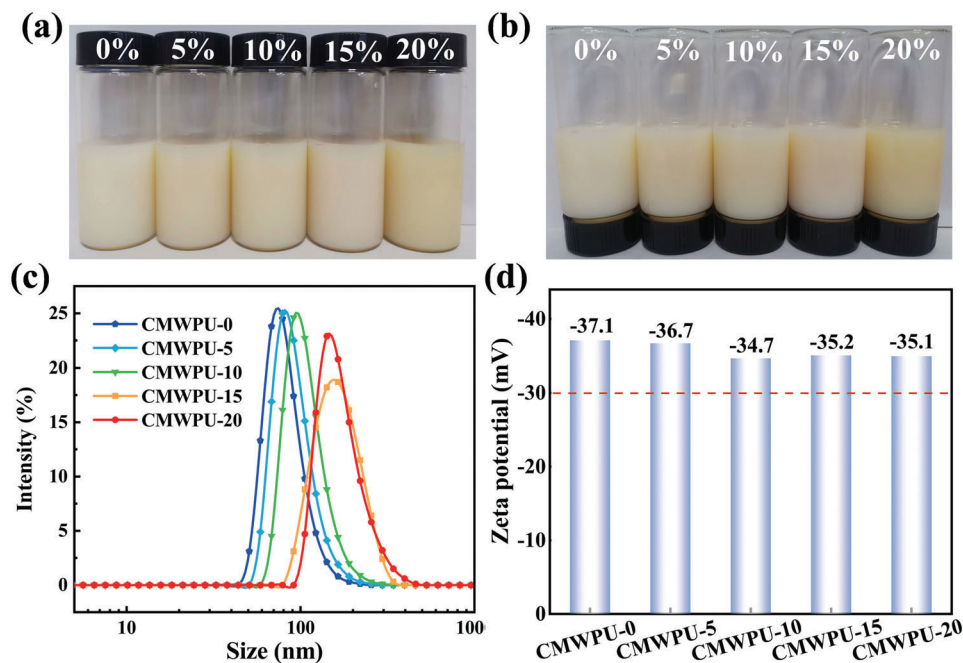


Figure 2. Photos of CMWPU emulsions after storage for a) 1 day and b) 6 months, c) particle size distribution and d) zeta potential of CMWPU emulsions.

Table 2. Appearance, storage stability, and viscosity of the CMWPU emulsions.

Samples	Appearance	Storage stability [months]	Viscosity [mPa s]
CMWPU-0	milky	>6	115.4
CMWPU-5	yellowish white	>6	130.4
CMWPU-10	yellowish white	>6	157.4
CMWPU-15	yellowish white	>6	161.6
CMWPU-20	yellowish white	>6	216.6

–NCO stretching peak (at $\approx 2260\text{ cm}^{-1}$) was observed, implying the –NCO within the system has been fully reacted.

The storage modulus (E') and $\tan \delta$ of the CMWPU films are shown in **Figure 4**, in the case of the prepared CMWPU film, with the CM loading increased from 0% to 20%, the storage modulus showed an increasing trend from 97.3 to 273.6 MPa (25 °C, **Table 3**), there is an improvement of 181.2%, this was mainly due to higher cross-linking degree of CMWPU-20 (157.7 mol m^{-3}) than that of CMWPU-0 (115.8 mol m^{-3}).

The glass transition temperatures (T_g) were obtained from the peak of $\tan \delta$ curves. All the CMWPU films exhibited only one single T_g peak, indicating excellent homogeneity of the cured CMWPU films. With the CM loading increased from 0% to 20%, the T_g of the CMWPU film increased from 35.3 to 45.0 °C, exhibiting an improvement of 27.48%. In general, the molecular chain's rigidity and the network system's cross-linking degree greatly influence the T_g . Although the introduction of CM has no significant effect on the rigidity of the CMWPU system (**Table 3**, the hard segment content of the CMWPU system ranged from 45.1% to 46.9%), while introducing CM cross-linker with abundant hydroxyl groups increased the cross-linking degree of the

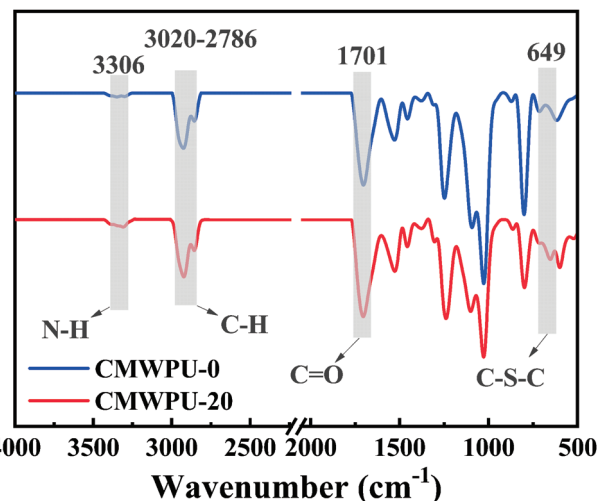


Figure 3. FT-IR spectra of the cured CMWPU films.

CMWPU film system, which limited the mobility of the molecular chains, thus contributing to densely cross-linking network structure and increased T_g .

The thermal stability of the CMWPU films with different loadings of CM is displayed in **Figure 5**. All the TGA curves (**Figure 5a**) of the CMWPU films exhibited basically similar decomposition behavior, implying a similar thermal decomposition mechanism of the CMWPU films. According to the derivative curves of the CMWPU films (**Figure 5b**), all the CMWPU films exhibited a two-stages of thermal decomposition. The first decomposition stage, ranging from 180 to 350 °C was derived from the cleavage of the labile urethane bonds ($-\text{COO}-\text{NH}-$),^[25] and the second decomposition stage at 350–450 °C was ascribed to the

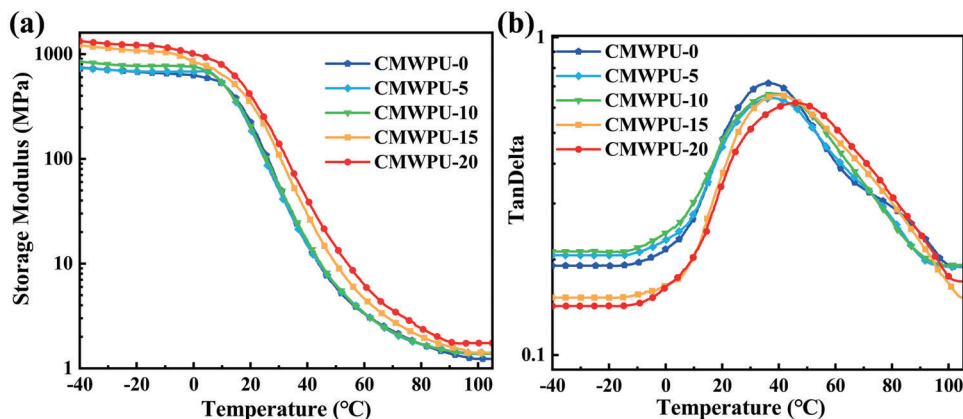


Figure 4. a) Storage modulus and b) loss factor of the CMWPU films with different CM loadings.

Table 3. DMA and TGA data of the CMWPU films with different loadings of CM.

Samples	V_e [mol m ⁻³]	DMA		TGA		
		T_g [°C]	E' at 25 °C [MPa]	T_5 [°C]	T_{50} [°C]	T_{max} [°C]
CMWPU-0	115.8	35.3	97.3	187.0	340.2	326.3
CMWPU-5	126.4	38.4	117.3	203.1	345.2	324.7
CMWPU-10	135.7	40.1	211.1	215.7	348.6	325.1
CMWPU-15	152.0	41.2	237.6	230.3	354.3	327.4
CMWPU-20	157.7	45.0	273.6	256.1	354.6	329.6

random decomposition of chain scission and network structure. Furthermore, with the CM loading increased from 0% to 20%, the temperature of 5% weight loss (T_5 , onset decomposition temperature), and 50% weight loss (T_{50}) of the cured CMWPU films increased from 187.0 to 256.1 °C and 340.2 to 354.6 °C, respectively, this was mainly due to the introducing of CM cross-linker increased the cross-linking degree of the CMWPU film, which has a great influence on the initial decomposition temperature of the cured CMWPU film.

The stress–strain curves of the CMWPU films are shown in **Figure 6**, and Young’s modulus, tensile strength, elongation at break and toughness of the CMWPU films are shown in **Table 4**. With the loading of CM increased from 0% to 20%, the tensile strength, Young’s modulus and toughness of the CMWPU films increased from 5.9 to 10.8 MPa, 51.5 to 138.4 MPa, and 4.1 to 6.6 MPa, respectively, and the corresponding increment reached 83.1%, 168.7%, and 61.0%, respectively. Meanwhile, the elongation at break decreased from 127.3% to 80.0%, exhibiting a decrease of 37.2%, this was mainly due to the cross-linking degree of the CMWPU film increased from 115.8 to 157.7 mol m⁻³ with the CM loading increased from 0% to 20%.

Furthermore, the water resistance of the CMWPU films was evaluated employing 24 h of water absorption test. It can be concluded that the more CM introduced into the CMWPU film system, the lower the water absorption rate of the CMWPU film, the water absorption rate of the CMWPU-0 film was 28.91%. In comparison, the water absorption rate of the CMWPU-20 film decreased to 16.12%, implying significantly improved water resistance of the CMWPU films. This was mainly due to the higher CM loading led to a compacted 3D network structure with high cross-linking degree, and thus preventing the water from penetrating into the interior of the films. Meanwhile, the loading of emulsifier DMBA remained constant, which had no significant

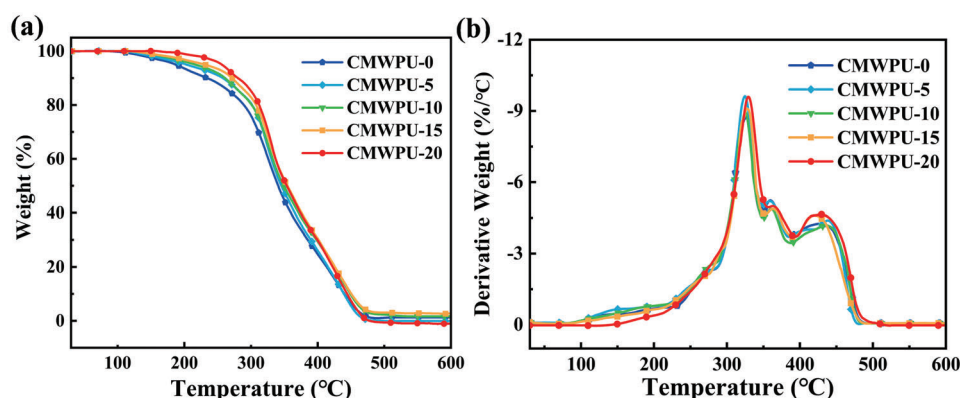


Figure 5. a) Thermogravimetric curves and b) their derivative curves of the CMWPU films with different loadings of CM.

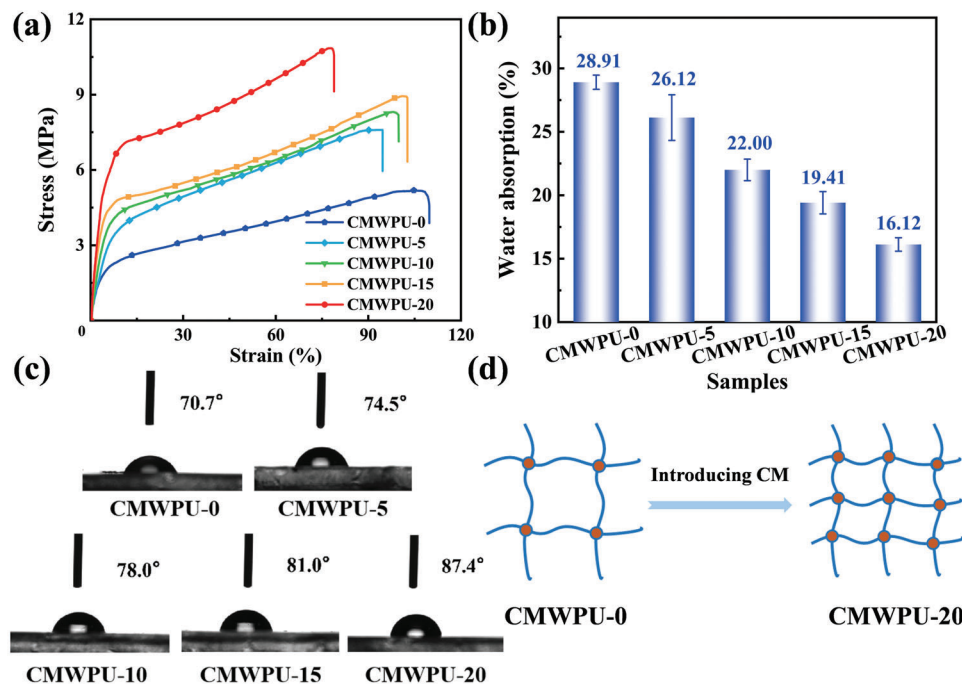


Figure 6. a) Stress–strain curve, b) water absorption rate, c) water contact angle images, d) structure of the change of the cured CMWPU films.

Table 4. Mechanical properties of the cured CMWPU films.

Samples	Hard segment content [wt.%]	Young's modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]	Toughness [MPa]
CMWPU-0	47.5	51.5	5.9 ± 0.7	127.3 ± 15.8	4.1
CMWPU-5	48.0	56.0	7.7 ± 0.2	105.0 ± 10.0	5.3
CMWPU-10	48.5	82.4	8.0 ± 0.3	101.5 ± 2.0	6.0
CMWPU-15	48.9	113.5	9.2 ± 0.5	98.8 ± 3.8	6.6
CMWPU-20	49.5	138.4	10.8 ± 0.2	80.0 ± 5.6	6.6

Note: hard segment content refers to the ratio of the mass of hard segments (IPDI, DMBA) in WPU to the total mass of polyurethane (IPDI, DMBA, CM, CO).

effect on the water absorption of the CMWPU films. The water contact angle was employed to assess the hydrophobicity of the surface of the CMWPU films, as shown in Figure 6c. With the introduction of CM cross-linker up to 20%, the prepared CMWPU films exhibited increased water contact angle from 70.7° to 87.4°, confirming improved hydrophobic of the CMWPU film, which can prevent water from infiltrating. This phenomenon could be explained by the formation of a dense cross-linking network structure with a high cross-linking degree due to the introduction of more CM cross-linkers. This result is consistent with the conclusion of DMA in Figure 4, tensile properties and water absorption rate in Figure 6.

The chemical resistance of the CMWPU films with different CM loadings was investigated in 1 mol L⁻¹ HCl, 1 mol L⁻¹ NaOH, and saturated NaCl solution (Figure 7), respectively. The swelling behavior was observed for all the CMWPU films in 1 mol L⁻¹ HCl, and saturated NaCl solution, but no chemical dissolution

was observed, and the weight loss of the CMWPU films was <1.5% after soaking at 25 °C for 24 h in 1 mol L⁻¹ HCl and saturated NaCl solution, implying excellent chemical stability of the CMWPU films in acidic and neutral environments, this was mainly attributed to the compacted cross-linking network structure prevented the acid and salt solutions from penetrating into films. While all the CMWPU films with different CM loadings took different time to dissolve in 1 mol L⁻¹ NaOH solution, this was mainly due to the urethane bonds (–COO–NH–) within the cross-linking network are prone to breakage in 1 mol L⁻¹ NaOH solution to form carboxylate segment with low molecular weight.^[46–48] With the CM loadings increased from 0% to 20%, the degradation time of the CMWPU films in an alkaline environment gradually increased. This was mainly due to the 3D network structure with a high cross-linking degree limiting the diffusion and penetration of NaOH solution into the interior of the CMWPU film, leading to prolonged degradation time.

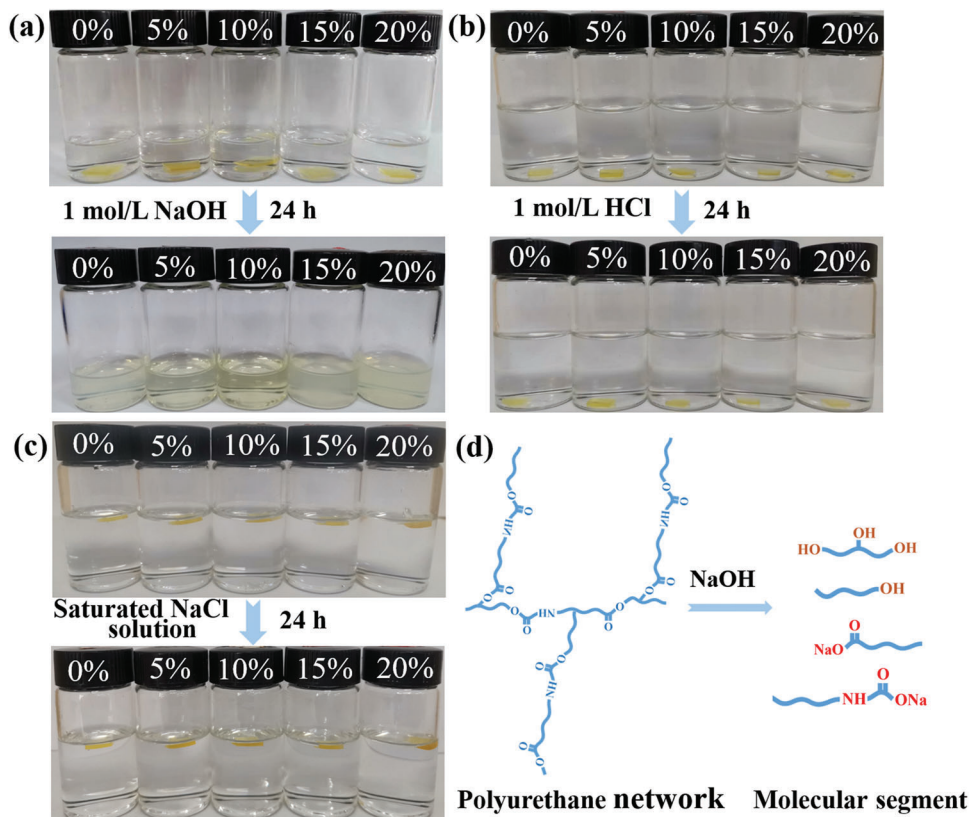


Figure 7. Chemical resistance of CMWPU films before and after degradation a) 1 mol L^{-1} NaOH solution; b) 1 mol L^{-1} HCl solution; c) saturated NaCl solution; d) schematic of degradation in alkaline solution.

4. Conclusion

A novel bio-based polyol CM with high hydroxyl value ($371 \text{ mg KOH g}^{-1}$) and high yield (93.8%) was obtained via the thiol-ene photoinduced reactions, and several key preparation parameters were optimized. The resulting CM combined with CO was employed as bio renewable cross-linkers to prepare castor oil-based CMWPU emulsion, all the CMWPU emulsions exhibited excellent storage stability when the loading of CM was $\leq 20\%$, and the particle size of the corresponding emulsions ranged from 115.4 to 216.6 nm with the introduction of CM from 0% to 20%. After being cured, the CMWPU films exhibited improved glass transition temperature ($45 \text{ }^\circ\text{C}$), tensile strength (10.8 MPa), water contact angle (87.4°), and decreased water absorption rate (16.12%) with 20% CM additions. In conclusion, this work provides an effective strategy to prepare castor oil-based WPU with desirable properties and high bio-based carbon content.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Author Contributions

Y.Z. conceptualized, supervised, and performed resources and project administration. Z.W. performed investigation and wrote original draft. L.S. performed methodology and data curation. L.D. performed methodology and formal analysis. R.L. performed investigation. L.Z. performed investigation and data curation. B.L. performed conceptualization and methodology. S.Z. performed data curation. V.K.T. performed validation, editing, and review writing.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

castor oil, polyol, polyurethane, thiol-ene click reaction, water resistance

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