Preparation of waterborne polyurethane based on the organic solvent-free process

Yao Xiao, Xiaowei Fu, Yanyan Zhang, Zhimeng Liu, Liang Jiang, Jingxin Lei*

State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

(Corresponding author: Jingxin Lei, Tel: +86-28-85401152, Fax: +86-28-85404920, Email: ployscu@yeah.net)

A green waterborne polyurethane (WPU) was prepared based on an organic solvent-free process, using sodium 2,4-diaminobenzenesulfonate (SDBS) as chain extender. Water was only used to dissolve the solid reactants and reduce the viscosity, obtaining homogenized reaction mixture. Characterization results showed that this green WPU presented similar mechanical properties and water resistance with conventional WPU whose synthesis process involved organic solvents. In addition, the use of SDBS eliminated the employment of catalysts and reduced the reaction time and temperature of the chain extension step, showing the merit of energy saving.

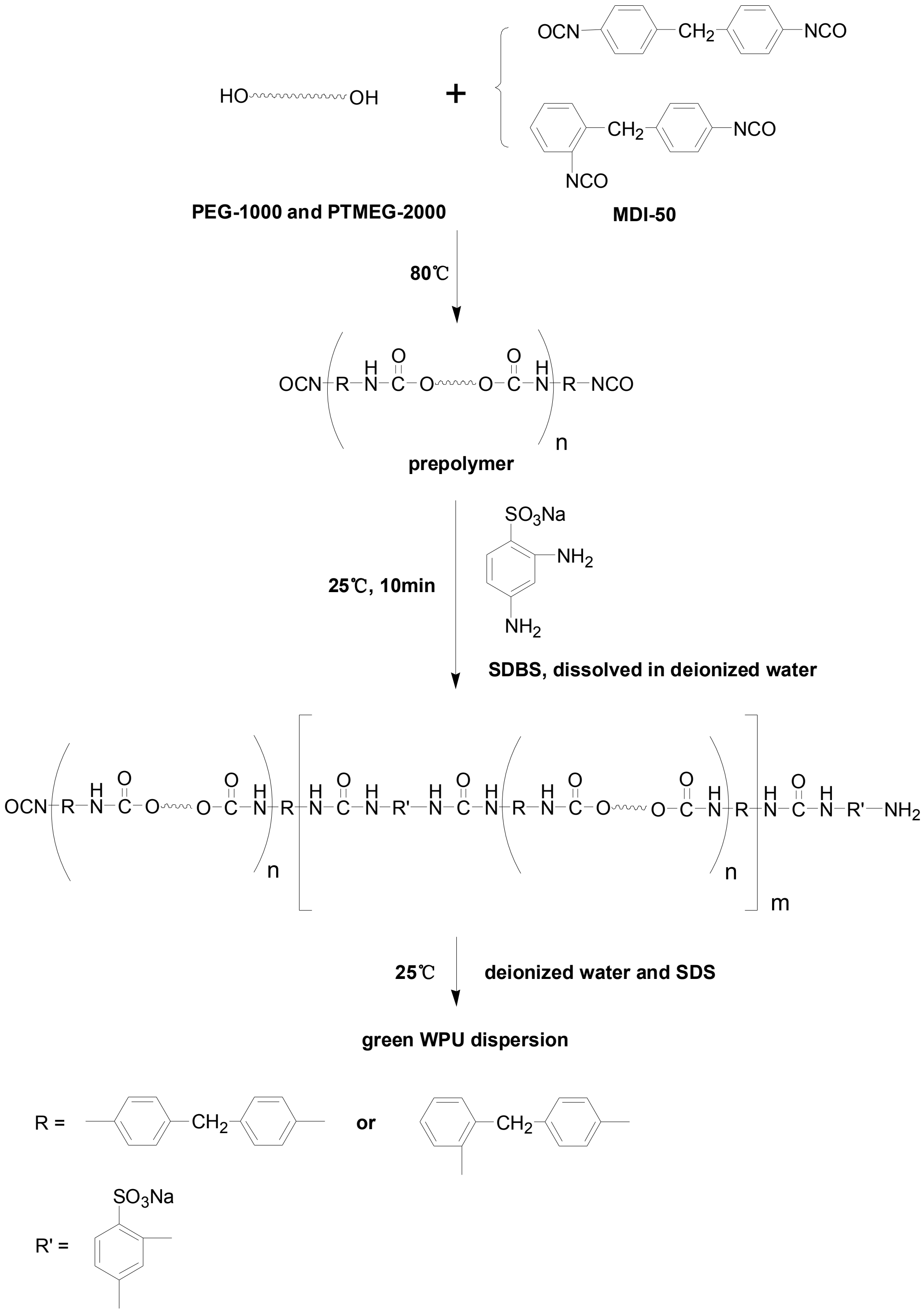
Waterborne polyurethanes (WPUs) have many advantages as same as solventborne polyurethanes (SPUs)，such as high tensile strength, high abrasion resistance, high flexibility, good adhesion ability and good low-temperature resistance.[1-5] Moreover, production and employment of WPUs don't cause the release of considerable volatile organic compounds (VOCs), which is an inevitable problem in the production and employment of SPUs.[6-10] As owning so many benefits, WPUs have drawn increasing attention and been widely used in many fields such as coatings, adhesives and leather finishings.[11-15]

The synthesis methods of WPUs mainly include prepolymer mixing process, acetone process, hot melt process and ketimine-ketazine process.[16,17] The first two methods are most widely adopted in industry. In the prepolymer mixing process, long-chain diols, dihydroxyl compounds with hydrophilic groups and organic solvents (typically N-methyl-2-pyrrolidone (NMP) and dimethyl formamide (DMF)) are added to get a homogenized mixture. Then excess diisocyanates and catalysts (if necessary) such as dibutyltin dilaurate (DBTDL) are added to react with the mixture, obtaining NCO-terminated prepolymer. This hydrophilically modified prepolymer mixture is directly dispersed in water. A small amount of organic solvents such as NMP or DMF can be added before the dispersion step if the viscosity of the prepolymer mixture is too high. Chain extenders such as di- or polyamines are added to the water-based prepolymer dispersion, consequently obtaining WPU dispersions.[16-20] In the reports of S.A. Madbouly et al. and S.M. Cakić et al., 14-30wt% of organic solvents like NMP or DMF based on the total feed were employed in the prepolymer mixing processes.[16,21] In the acetone process, long-chain diols react with excess diisocyanates (catalysts are used if necessary) to obtain NCO-terminated prepolymer, then chain extension is accomplished by the addition of dihydroxyl compounds with hydrophilic groups (dissolved by a small amount of NMP or DMF) and short-chain diols and/or diamines to the prepolymer. Acetone is added to reduce the viscosity of the reaction mixture. And then water is added to the acetone solution, obtaining WPU dispersions. Finally, acetone is removed from the WPU dispersions by vacuum distillation.[16,17,22-24] In the report of S.A. Madbouly et al., 85g acetone was applied to obtain a homogenized mixture in an acetone process.[16] It can be seen that the WPU dispersions prepared in industry are not absolutely waterborne dispersions, organic solvents are employed to reduce the viscosity of the reaction mixture or dissolve some solid reactants. The production and employment of these conventional WPU dispersions involve the release of VOCs more or less.

There were some researches about WPUs whose synthesis processes did not involve organic solvents. However, some properties of these WPUs such as mechanical strength and water resistance could not meet the industrial application requirements, or many of these WPUs needed to be prepared under harsh conditions. J. Jiang et al. prepared a WPU by an organic solvent-free process, using polyethylene glycol-1000 (PEG-1000) as long-chain diol.[25] This WPU showed low water resistance as PEG-1000 segments could totally dissolve in water, resulting in high water absorption ratio of WPU. L. Liu et al. reported a WPU prepared by a hot melt process without using organic solvents. This synthesis process needed high-power device, and obtained a low-molecule WPU with branching structure.[26] Many other researches of organic solvent-free WPUs were all based on the similar method as follows.[27-29] Long-chain diols and dihydroxyl compounds with hydrophilic groups reacted with excess diisocyanates, obtaining the hydrophilically modified prepolymers with low molecular weight, which could directly disperse in water under high-speed agitation. Chain extension was accomplished by the addition of short-chain diamines to the water-based prepolymer dispersions. The prepolymers of these organic solvent-free processes were not a homogenized mixture without the help of organic solvents; and the WPU dispersions exhibited broad particle size distribution as long-chain diols and dihydroxyl compounds had different activity towards diisocyanates, according to the study of S. Peng et al.[22] Heterogeneity of prepolymers and broad particle size distribution resulted in the instability of the WPU dispersions and relatively low mechanical strength of WPU films. In a word, there were few WPUs whose synthesis processes did not involve organic solvents and qualified for industrial production and employment. Design and preparation of green WPU with competent performance are still significant and urgent.

In order to prepare WPU without using organic solvents, water should completely replace organic solvents for reducing the viscosity of the reaction mixture and dissolving the solid reactants. Long-chain diols react with diisocyantes first to obtain NCO-terminated prepolymers, and then this prepolymer react with water-soluble chain extenders, which have much higher reactivity towards NCO groups compared to water, finishing the chain extension in a short time. Meanwhile, the water used to dissolve the chain extenders plays the important role to reduce the viscosity of reaction mixture in the chain extension step.

In this study, water-soluble sodium 2,4-diaminobenzenesulfonate (SDBS) was used to prepare green WPU as chain extender with much higher reactivity towards NCO groups than water. According to the technical information from the supplier, SDBS has a lower toxicity than hexamethylene diamine which is a common material for producing polyurethanes. As a solid reagent without volatilization, SDBS has limited and controllable harm. Additionally, with the reaction of NCO groups the rate constant of aromatic primary amino is lower than that of aliphatic primary amino, the reaction between the prepolymer and SDBS can be finished in a moderate and controlled way. Besides SDBS, diphenylmethane diisocyanate-50 (MDI-50), polyethylene glycol-1000 (PEG-1000) and polytetramethylene ether glycol-2000 (PTMEG-2000) were used to prepare green WPU as illustrated in Scheme 1. PEG-1000 and PTMEG-2000 were dried at 120℃ under vacuum for 3h before use. 4.0g (0.004mol) of PEG-1000, 56.0g (0.028mol) of PTMEG-2000 and 16.02g (0.064mol) of MDI-50 were added into a three-neck flask equipped with a mechanical stirrer and a thermometer, and reacted at 80℃ for 2h under continuous stirring (200 rpm), obtaining completely NCO-terminated prepolymer. The theoretical molecular weight of the prepolymer was 2406.75g/mol. Due to its low molecular weight and hydrophilic PEG segments, this preploymer could be easily dispersed in water. And the viscosity of the reaction mixture could be reduced by water. Then the prepolymer was cooled down to 25℃, and 6.73g (0.032mol) of SDBS (dissolved in 60g deionized water) was added to react with the prepolymer to accomplish the chain extension at 25℃ for 10min under continuous stirring (200 rpm). At last, 80g deionized water and 3.3g sodium dodecyl sulfate (SDS) as emulsifier were added to obtain green WPU dispersion under high-speed agitation (2000 rpm) at 25℃ for 20min.



Scheme 1. Synthetic route of green WPU

A conventional WPU was prepared for comparison. PEG-1000 and PTMEG-2000 were dried at 120℃ under vacuum for 3h before use. 1.0g (0.001mol) of PEG-1000, 62.0g (0.031mol) of PTMEG-2000 and 16.02g (0.064mol) of MDI-50 were added into a three-neck flask equipped with a mechanical stirrer and a thermometer, and reacted at 80℃ for 2h under continuous stirring (200 rpm), obtaining completely NCO-terminated prepolymer. Then the prepolymer was cooled down to 75℃, 5.7g (0.032mol) of sodium 1,2-dihydroxypropanesulfonate (dissolved in NMP) and 0.03wt% DBTDL (based on the total feed) were added to react with the prepolymer to accomplish the chain extension at 75℃ for 1.5h under continuous stirring (200 rpm). In the whole process, acetone was added to reduce the viscosity of the reaction mixture if necessary. 140g deionized water and 3.3g SDS as emulsifier were added to obtain conventional WPU dispersion under high-speed agitation (2000 rpm) at 25℃ for 20min. Acetone was removed from the conventional WPU dispersion by vacuum distillation. In the whole process, 35g acetone and 20g NMP were used as the total feed was 84.72g. Compared to this process, the synthesis process of green WPU eliminated the employment of catalysts and reduced the reaction time and temperature of the chain extension step, showing the merit of energy saving.

Mechanical properties and water absorption ratio of green and conventional WPU films are displayed in Table 1. There's no obvious difference of mechanical properties and water absorption ratio between the green and conventional WPU films. It's believed that the organic solvent-free process imparts green WPU films similar mechanical properties and water resistance with conventional WPU films.

Table 1. Comparison on mechanical properties and water absorption ratio

	green WPU films	conventional WPU films
tensile strength (MPa)	18.1	16.9
elongation at break (%)	653	671
Shore A hardness	84	83
water absorption ratio (%)	13.5	12.4

The formation of green WPU is revealed by Fourier transform infrared (FTIR) spectroscopy as shown in Fig.1. The urethane structures are confirmed by the characteristic peak at 3297 cm^{-1} ascribed to N-H stretching vibration. The absorption peaks at 2941 cm^{-1} and 2859 cm^{-1} are attributed to C-H stretching vibration of CH_2 from PEG and PTMEG segments. C=O stretching vibration of urethane structures displays an absorption peak at 1732 cm^{-1}. The absorption peaks at 1652 cm^{-1}, 1597 cm^{-1} and 1537 cm^{-1} are all connected to skeleton vibration of phenyls. C-N stretching vibration of SDBS segments shows an absorption peak at 1311 cm^{-1}. The absorption peak at 1221 cm^{-1} belongs to C-O stretching vibration of urethane groups. C-O-C stretching vibration from PEG and PTMEG segments displays an absorption peak at 1109 cm^{-1}. C-H bending vibration of phenyls presents an absorption peak at 752 cm^{-1}. There is no characteristic peak at 2270 cm^{-1} belongs to free –NCO groups, which completely reacted with OH or NH_2 groups.

Fig.2 exhibits the green WPU dispersion with 1-month storage and its particle size distribution and Scanning electronic microscopy (SEM) morphology. The green WPU dispersion still has good stability after 1 month. The measurement of Laser particle size analyzer (LPSA) shows that the green WPU dispersion has single and narrow particle size distribution and the average particles size is 12.1μm. SEM picture reveals that the morphology of the particles of the green WPU dispersion is spherules with a diameter of about 0.6-2.5μm. This difference of particle size between LPSA measurement and SEM picture is ascribed to the different status of particles as illustrated in Fig.3. When measured by LPSA, the particles of green WPU dispersion swell in water due to their molecular structures. PEG segments of green WPU molecules form hydrogen bonds with water; and sulfonates of green WPU molecules ionize in water and absorb water by salvation interaction. Moreover, molecular chains of green WPU stretch in water because of the repulsion force from sulfonic groups with same charge. This force not only exists between molecular chains but also inside in every single molecular chain. When detected by SEM, the particles collapse as water vaporizes, exhibiting smaller size.

Fig.4 shows the Dynamic mechanical analysis (DMA) and Differential scanning calorimetry (DSC) information of green WPU films. According to DMA, green WPU films have only one glass transition temperature (-57.7℃) which belongs to soft segments. It's concluded that there's no distinct phase separation between soft and hard segments of green WPU films. DSC demonstrates that these green WPU films have crystallization in the soft segments with a melting point of 16.7℃, which is lower than that of raw PEG-1000 or PTMEG-2000. The chemical linkages between soft and hard segments weaken the crystallization in the soft segments, decreasing the melting point of crystallization domain; and also restrict the movement of the molecular chains in the crystallization domain even at the temperature above the melting point, giving the green WPU films an elastomer state at ambient temperature.

The green WPU dispersion was used for the measurement of LPSA. The dispersion was diluted to 0.5wt%, and dried at ambient temperature for 3d, then observed by SEM. The WPU films were used for the characterizations of mechanical properties, water absorption ratio, FTIR, DSC and DMA. Films were obtained by casting the WPU dispersion onto a baffle plate to dry at ambient temperature for 7d then at 40℃ in a vacuum oven for 24h.

Conclusions

Green WPU was successfully prepared based on an organic solvent-free process by using SDBS as chain extender. The reaction time and temperature of the chain extension step reduced to 10 minutes and 25℃, respectively; and no catalysts were applied in this step. In the meantime, this green WPU had good mechanical properties and water resistance similar with conventional WPU. Optimization of this green WPU is under investigation in our lab.

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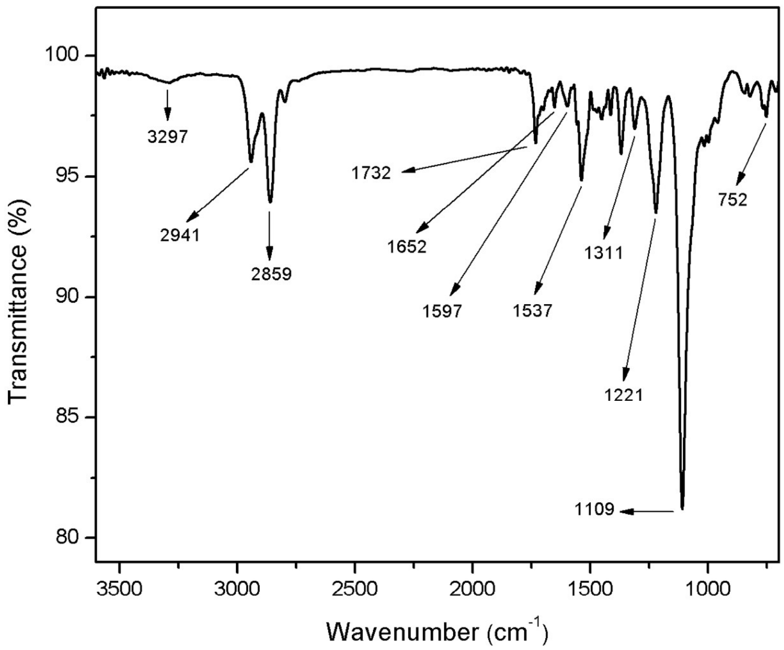


Fig.1. FTIR spectrum of green WPU films
215x166mm (300 x 300 DPI)

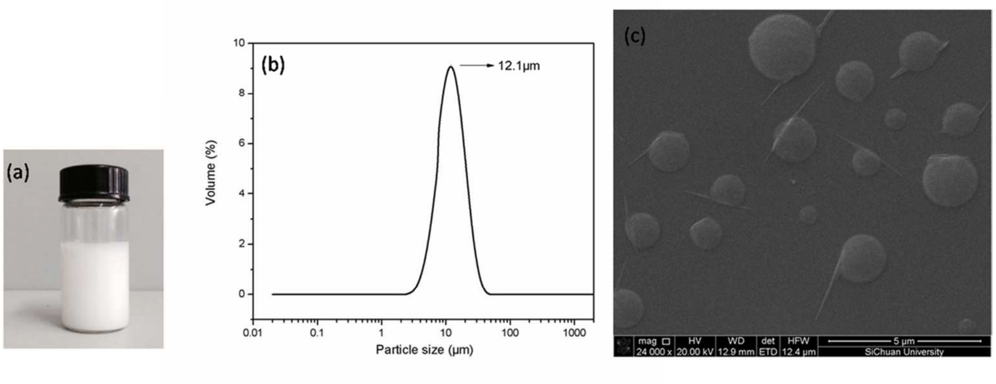


Fig.2. (a).Green WPU dispersion, (b).its particle size distribution, (c).its SEM morphology
99x38mm (300 x 300 DPI)

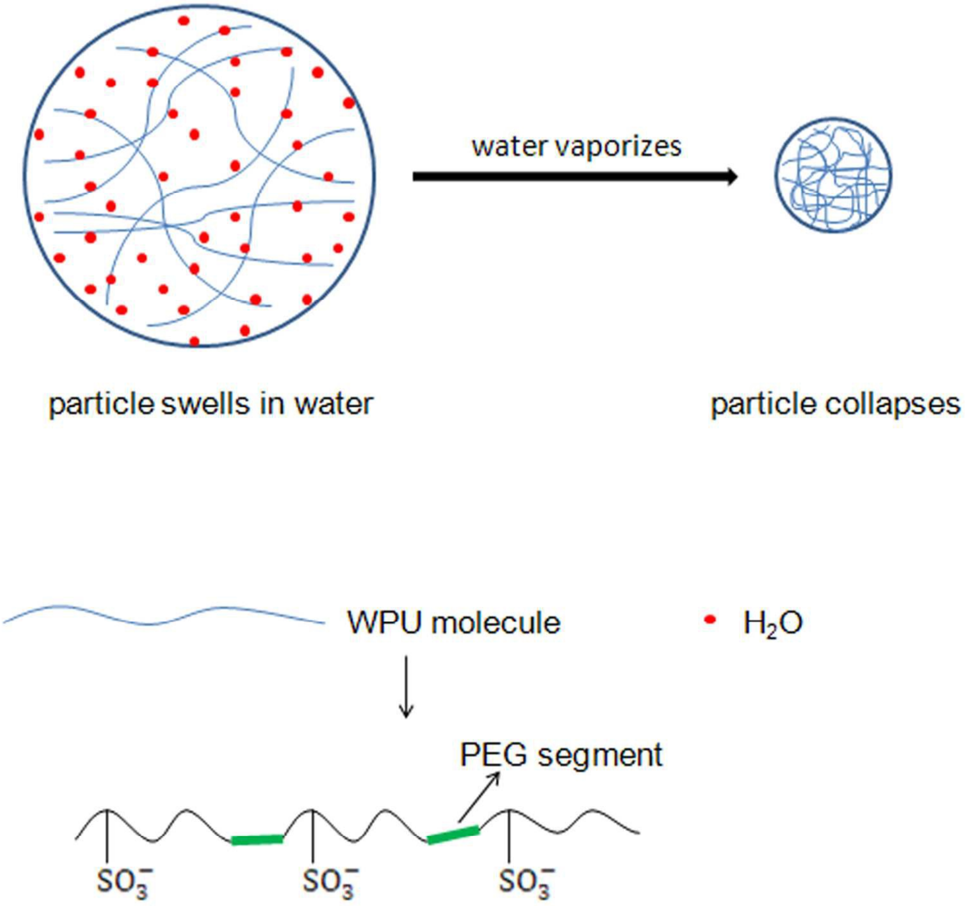


Fig.3. Scheme of particles of green WPU dispersion from swollen to collapsed status
175x168mm (300 x 300 DPI)

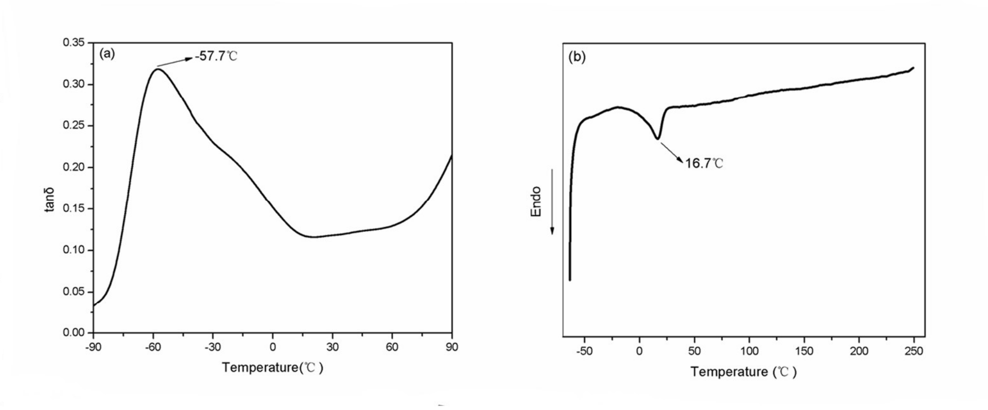
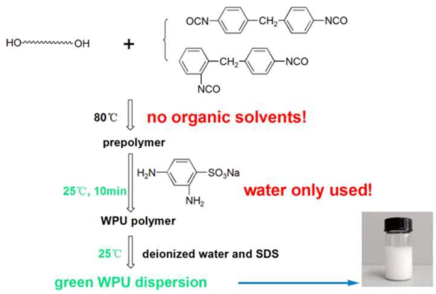


Fig.4. (a). DMA of green WPU films; (b). DSC curve of green WPU films
164x67mm (300 x 300 DPI)



Green WPU was prepared based on the organic solvent-free process, where water was only used to dissolve the solid reactants and reduce the viscosity.