

Green synthesis process and properties of polyurethane completely using ethanol as solvent

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Abstract It is a challenge to simultaneously retain high performance and green synthesis process of polyurethane (PU). Here, a PU was synthesized completely using ethanol as solvent based on the chain extender, hexanediamine (HMD), with higher reactivity towards isocyanate groups than ethanol. Chemical components in PU prepared by a green process (GPU) were characterized by Fourier Transform Infrared Spectroscopy (FTIR). Molecular weight and its distribution of GPU were characterized by Gel Permeation Chromatography (GPC). Mechanical properties and thermal-mechanical properties of GPU were characterized by Electronic Tensile Testing Machine and Dynamic Thermomechanical Analysis (DMA) separately. The glass transition temperature (T_g) and thermal stability of GPU were characterized by Differential Scanning Calorimeter (DSC) and Thermogravimetric Analysis (TGA). Results showed that this GPU presented superior mechanical properties of 61.4 MPa and low saturated water absorption of 6.6% compared with conventional solvent-based PU and waterborne PU whose synthesis process contained some toxic organic solvent.

Keywords Polyurethane · Green synthesis process · Ethanol · Chain extender

Introduction

Polyurethane (PU) as one of the most versatile synthetic materials has attracted great attentions because of a variety of applications such as elastomers, coating, smart actuators, and wearable electronics [1–4]. During the past few decades, environmental problems have driven the PU technologist to explore newer approaches to decrease the usage of toxic organic solvent. The waterborne PU has many excellent properties, such as high tensile strength, high abrasion resistance, and good weatherability [5, 6]. Therefore, waterborne PU is one of the most rapidly growing fields of PU chemistry, and is widely used as adhesives, coatings and printing inks [7]. However, the conventional waterborne PU has its inherent disadvantages of high water absorption, large particle sizes, poor film-forming property and the use of toxic solvent, such as N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), toluene, acetone and so on, which limit its application [8, 9]. Moreover, the hydrolysis of the ester linkages in aquatic environment decreases the molecular weight and deteriorates the physical and mechanical properties. Therefore, the improvement of these properties of conventional waterborne PU and synthesis of PU prepared by a green process (GPU) has been the subject of continued research.

Zhang et al. [8] reported the liquid polysulfide-modified waterborne PU. In that study, the water absorption decreases from 6.2% to 3.4% as the liquid polysulfide content increases from 0 to 20%, while the tensile strength and thermal stability decreased and the toxic NMP and acetone were added in order to dissolve the hydrophilic monomers and reduce the viscosity of the system. Jiang et al. [10] synthesized a waterborne PU by non-solvent process using polyethylene glycol (PEG) and dimethylol propionic acid (DMPA) as long-chain diol without addition of diol or diamine as chain extender. To the best of our knowledge, the waterborne PU prepared by this method

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would show low molecular weight and totally dissolve in water which obviously couldn't meet the requirement of industry application. Xiao et al. [6] reported a waterborne PU based on the organic solvent-free process and the water absorption as high as 13.5% due to the anionic hydrophilic extender. Moreover, the PU latex particle size of 12.1 μm will lead to bad leveling property, glossiness, adhesion, and storage stability.

Since the waterborne PU has so many inherent disadvantages that it cannot totally meet industrial application requirements so far. In fact, more solvent-based PUs was used. Yadav and Cai et al. reported a DMF-solventborne PU with poly(ϵ -caprolactone) (PCL), 4, 4-methylene bis(phenylisocyanate) (MDI) and 1, 4-butanediol (1, 4-BD) [1, 11]. Gite et al. [12] reported a modification of the PU based on the reaction of acrylic polyols and isophorone diisocyanate (IPDI) with xylene and tetrahydrofuran (THF) as solvent. Chen et al. [4] reported a PU using MDI, polytetramethylene ether glycol (PTMEG), and 1, 4-BD as chain extender with a solvent of DMF. In summary, there were few waterborne PU and solvent-based PU which did not contain toxic organic solvent in the synthesis process or retain the high performance which meets the industrial application requirements [1]. In addition, the chain extension reaction of conventional solvent-based PU was almost accomplished by diol which mostly leads to low molecular weight of PU due to the absorption of water in diol and solvent. Therefore, the design and synthesis of novel GPU totally satisfying all the industrial production, environmental requirements and retaining the high performance are still significant and urgent.

Now that the non-organic waterborne PU has its inherent disadvantages that it could not be widely used in industry. Solvent-based PU with the excellent property was widely used in industry. To the best of our knowledge, ethanol is an environmental friendly organic solvent and preparation of a PU completely using ethanol as solvent has not been explored so far [13]. In order to synthesize PU completely using green ethanol as solvent, the decreasing viscosity of the mixture and the dissolving of the solid reactant should be fulfilled by ethanol. The diols react with diisocyanates first to form isocyanate-terminated prepolymer, and the prepolymer react with ethanol-soluble chain extenders. In this chain extension process, the chain extender must have high enough reactivity towards diisocyanates group compared with ethanol, accomplishing the extension process in a short time.

In this research, ethanol-soluble hexanediamine (HMD) was used to synthesis GPU due to the higher reactivity of amino group towards diisocyanates group than hydroxyl group. As the activity of diisocyanates group in IPDI is lower than that of MDI, the reaction between the prepolymer and HMD can be performed in a moderate and controlled method. Besides, the phosphoric acid was used to reduce the rate of chain extension reaction. The GPU were tested by Fourier

Transform Infrared Spectroscopy (FTIR), Gel Permeation Chromatography (GPC), Dynamic Thermomechanical Analysis (DMA), Differential Scanning Calorimeter (DSC) and Thermogravimetric Analysis (TGA) measurement.

Experimental

Materials

The content of more than 99.5% of isophorone diisocyanate (IPDI) was obtained from Bayer Co., Ltd. Polytetramethylene ether glycol (PTMEG, $M_w = 1000$, Korea PTG Co., Ltd) and CP-2110 ($M_w = 1000$, a polyester glycol prepared from phthalic acid and propylene glycol) were dried at 105 °C under vacuum for 90 min before use. Dibutyltin dilaurate (DBDTL) was purchased from Aladdin Reagents Co., Ltd. Hexanediamine (HMD), phosphoric acid and anhydrous ethanol were purchased from Kelong Chemical Reagent Co., Ltd.

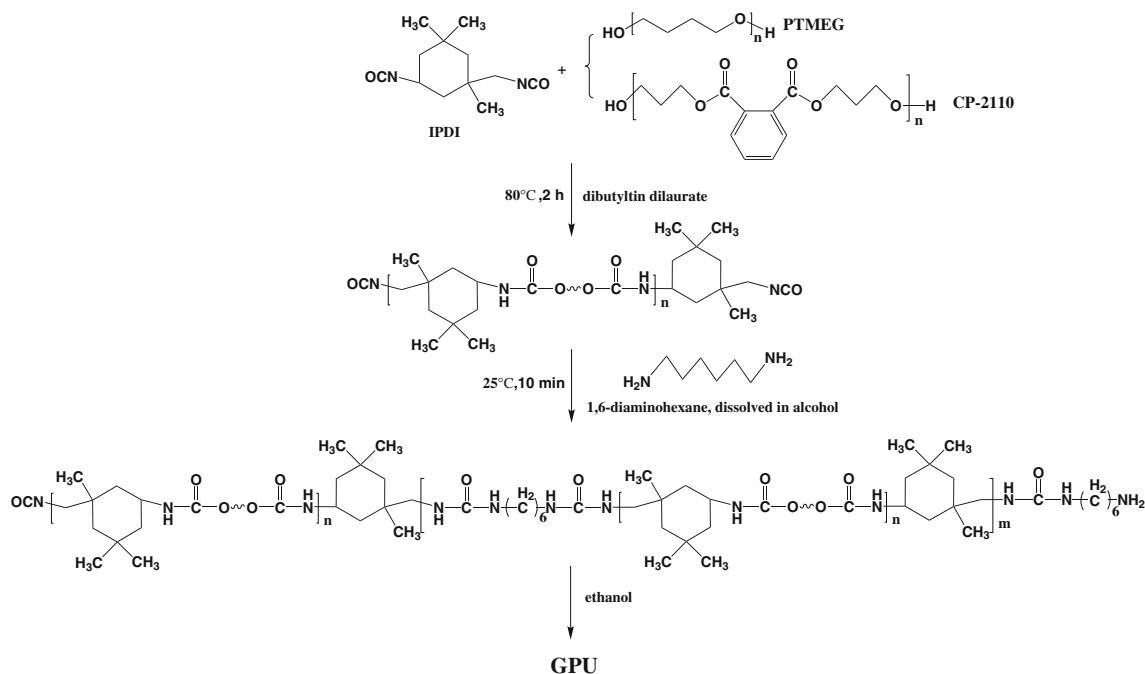
Synthesis of PU prepared by a green process (GPU)

The IPDI, PTMEG, CP-2110 and HMD were used to synthesis GPU as illustrated in Scheme 1. 10 g (0.010 mol) of CP-2110 and 23.3 g (0.023 mol) of PTMEG were added into a three-neck flask equipped with a mechanical stirrer and a thermometer, and dried at 105 °C under vacuum for 90 min before use. Then 14.8 g (0.067 mol) of IPDI and about 0.01 g of dibutyltin dilaurate was added into this system orderly when the temperature of this mixture cooled to ambient temperature, and reacted at 80 °C for 2 h under continuous stirring of 180 rpm to obtain an isocyanate-terminated prepolymer. 0.2 g of phosphoric acid was added into this flask when the pre-polymerization was completely finished. Then the reactant was cooled down to 25 °C, 10 g of ethanol was added into this mixture to decrease the viscosity of the mixture, and 3.87 g (0.033 mol) of HMD (dissolved in 10 g ethanol) was added dropwise to react with the prepolymer to accomplish the chain extension process at 25 °C for 10 min under continuous stirring of 300 rpm. In the whole process, ethanol was added dropwise to decrease the system viscosity. Finally, the prepared GPU was stirred at ambient temperature for 60 min. The obtained GPU with about 25 wt.% of solid content was formed. The optical image of green PU is shown in Fig. 1.

Characterization

The chemical components of GPU were recorded with a Thermo Scientific Nicolet iS10 Fourier Transform Infrared Spectroscopy (FT-IR) spectrometer. The sample was scanned from 4000 to 400 cm^{-1} with a resolution setting of 4 cm^{-1} .

The molecular weight and its distribution of GPU was measured with Gel Permeation Chromatography (GPC) on



Scheme 1 Schematic illustration of the preparation process for the GPU

an Agilent 1100 column using dimethyl formamide as the eluent and polystyrene standards for calibration.

The mechanical property of GPU was measured at room temperature using an Instron-4302 material testing machine. A dumbbell specimen (4 mm in diameter and 75 mm in gage length) was fabricated for the evaluation of the mechanical properties. A cross-head speed of 100 mm/min was used to determine the ultimate tensile strength and elongation at break.

The water resistance of GPU was evaluated by the measurement of water sorption of the different samples. Each sample was cut into $12 \times 12 \times 4 \text{ mm}^3$. The samples were immersed in water for 12 h, 24 h, 36 h, 48 h and 60 h at ambient temperature respectively. The water absorption of the different film samples was calculated with the following equation:

$$\text{Water absorption}(\%) = \frac{w_1 - w_0}{w_0} \times 100\%$$



Fig. 1 Optical image of GPU

Where w_0 is the weight of the dried film and w_1 is the weight of the film at equilibrium absorption. At least five specimens were tested and the average results are recorded.

The glass transition temperature and melting point of GPU was carried out on a Differential Scanning Calorimeter (DSC) 204 Instruments apparatus from $-70 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ under nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$.

The thermostability of GPU was performed on a Thermo Gravimetric Analysis (TGA) SDT-Q600 Thermogravimetric Analyzer. Each sample was scanned from $25 \text{ }^\circ\text{C}$ to $600 \text{ }^\circ\text{C}$ under a nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$.

The dynamic mechanical properties of the GPU was examined using Dynamic Mechanical Analysis (DMA) Q800, TA Instrument, under a nitrogen atmosphere, at a frequency of 1 Hz and a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$.

Results and discussion

FTIR spectroscopy of PU prepared by a green process (GPU)

Fig 2 shows the Fourier Transform Infrared Spectroscopy (FTIR) of the prepared GPU. The infrared band at 3330 cm^{-1} is due to the hydrogen-bonded N-H stretching vibration which conforms to the forming of urethane structure. The band at 1717 cm^{-1} is associated with the hydrogen-bonded carbonyls. There were no obvious band appeared at 3480 cm^{-1} and 1733 cm^{-1} , indicating that the N-H and C = O groups in the GPU film were nearly completely hydrogen-

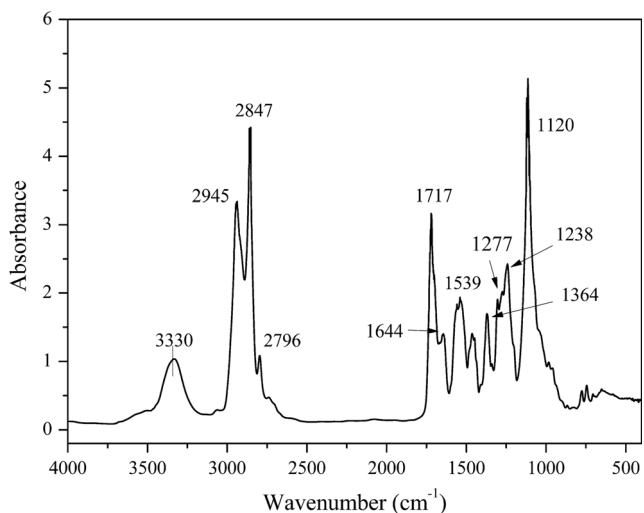


Fig. 2 FTIR spectroscopy of GPU

bonded [14]. The absorption peaks at 2945 cm^{-1} and 2847 cm^{-1} are due to the C-H stretching vibration from CP-2110 and PTMEG segments [15]. The disappearance of characteristic peak at 2255 cm^{-1} which was ascribed to diisocyanates group indicates that all of the diisocyanates groups react with amino group or hydroxyl group and the GPU was successfully synthesized.

GPC characterization of GPU

To get further information regarding the molecular weight and its distribution of this GPU, the film was measured by Gel Permeation Chromatography (GPC). The elution volume with different time is shown in Fig. 3. From Fig. 3 it can be seen that the elution volume shows a unimodal distribution with increasing of time. According to the principle of GPC measurement, the molecular weight of green PU also shows a unimodal distribution with increasing of molecular weight, and the weight-average molecular weight of this GPU is

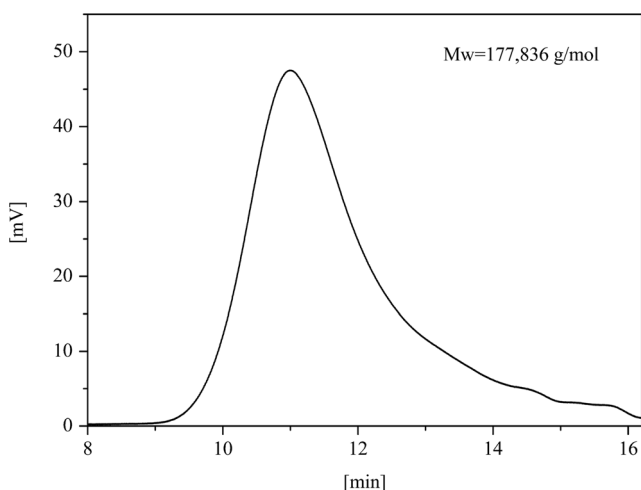


Fig. 3 GPC result of GPU

$177,836\text{ g/mol}$ and the molecular weight distribution is 2.558 (M_w/M_n) which indicates that the chain-extension reaction has been completed as expected.

Mechanical properties and water absorption

The mechanical properties and water absorption of the prepared GPU are displayed in Fig. 4 a and b. The detailed comparison data of mechanical properties and water absorption of GPU, conventional solvent-based PU and waterborne PU are shown in Table 1. The results show that the prepared GPU exhibits good mechanical properties compared with conventional solvent-based PU and waterborne PU considering the elongation at break in these references was calculated based the elastic length of 25 mm instead of 45 mm (in our research). The water absorption of this GPU is only 6.6% (saturated water absorption) compared with the 13.5% (just 24 h) of waterborne PU. It's believed that this GPU using ethanol as solvent shows good mechanical properties and low water

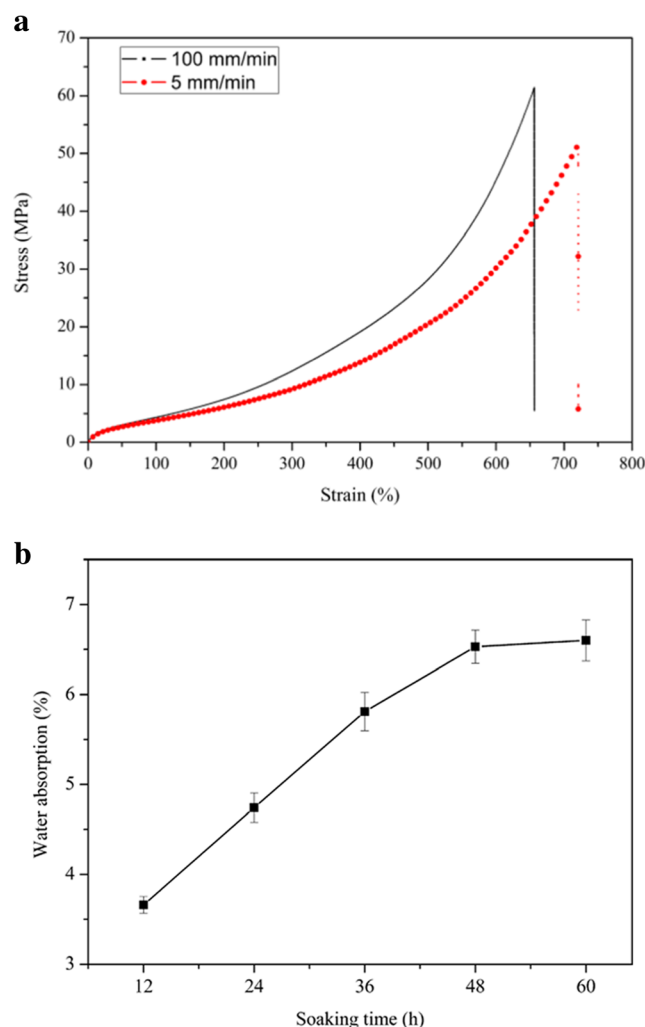


Fig. 4 Mechanical properties **a** and water absorption **b** of GPU

Table 1 Comparison of mechanical properties and water absorption of the PU films

| | GPU films 100 mm/min 5 mm/min | | Solvent-based PU films | Waterborne PU films |
|---------------------------|-------------------------------------|------|---------------------------|------------------------|
| Tensile strength (MPa) | 61.4 | 51.6 | 47.3 | 18.1 |
| Elongation at break (%) | 656 | 720 | 775 | 653 |
| Modulus (MPa) | 30.5 | 21.4 | 18.3 | — |
| Water absorption rate (%) | 6.6 (saturated) | | — | 13.5 (24 h) |
| References | Our study | | Tijing et al. [16] | Xiao et al. [6] |

absorption compared with conventional solvent-based and waterborne PU.

DMA and DSC analysis of GPU

Fig. 5 a and b show the Dynamic Mechanical Analysis (DMA) and Differential Scanning Calorimetry (DSC) curves of GPU samples. From Fig. 5a, it can be seen that this GPU

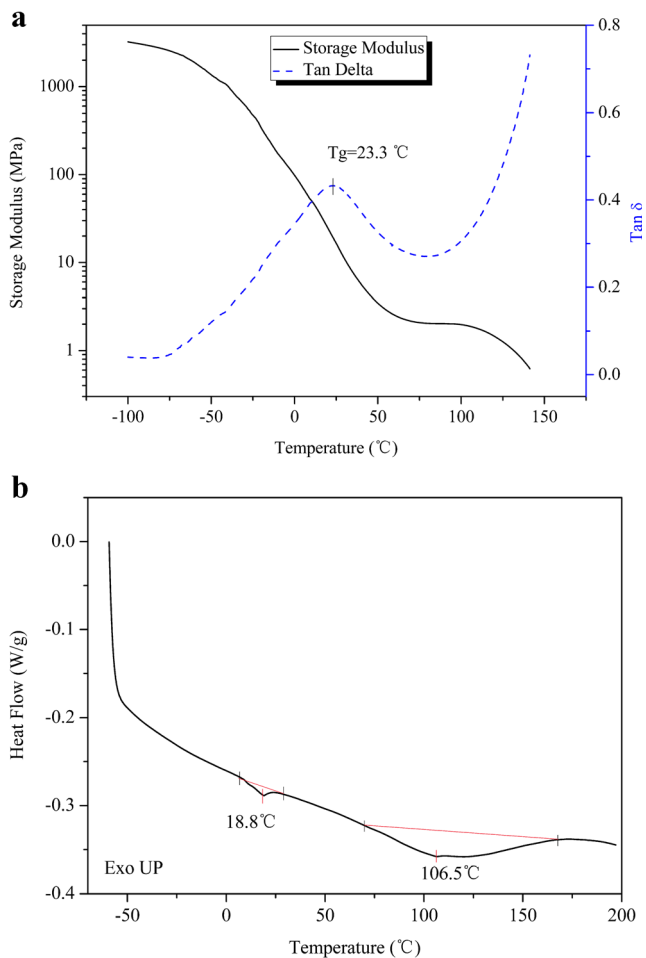


Fig. 5 DMA a and DSC b result of GPU

only shows one glass transition temperature (T_g) of 23.3 °C and a higher deformation temperature of 100 °C at least. It can be concluded that this GPU shows no distinct phase separation and it could be used in a wide temperature range. DSC curve show that this GPU has weak crystals in the soft segment with a melting point of 18.8 °C which was due to the crystallization of PTMEG-1000. A higher melting temperature of 106.5 °C was ascribed to the melting of hard segments containing diisocyanates group and chain extender.

TGA analysis of GPU

Thermal stability of the GPU film was assessed using a Thermogravimetric Analysis (TGA) technique. According to the degradation mechanism of PU, the decomposition reaction occurs around 180°C which was ascribed to the breakdown of urethane bonds. Then, the polyols and polyisocyanates start to decompose respectively [17]. The TGA curve in Fig. 6 displays that the GPU has a high initial decomposition temperature of 265.1 °C which guaranteed its usage in the surrounding of higher temperature. The derivative thermogram curve clearly indicates a two-step degradation profile with an initial decomposition temperature around 265.1 °C which was ascribed to the decomposition of carbamido synthesized by diisocyanates group and amino group. The first-weight loss stage, in the temperature range of about 260–330 °C, was attributed to the dissociation of the hard segment [18]. The second weight loss stage, in the temperature range of about 330–380 °C, was due to the dissociation of the soft segment [19]. The final decomposition temperature exceed 380 °C. It can be seen that the GPU exhibits good thermal stability.

Conclusions

A GPU was synthesized successfully completely using ethanol as solvent based on the HMD chain extender, with higher

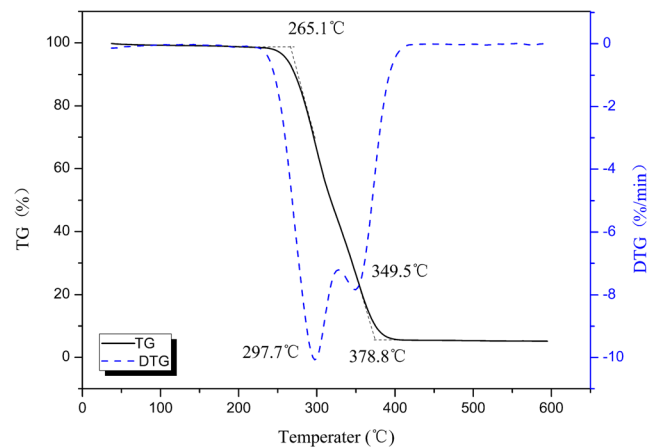


Fig. 6 TG curve of green PU

reactivity towards isocyanate groups than ethanol. The reaction between the prepolymer and HMD can be performed in a moderate and controlled method. The prepared GPU shows excellent mechanical properties of 61.4 MPa and low saturated water absorption rate of 6.6% compared with conventional solvent-based PU and waterborne PU. The good comprehensive properties indicate that this novel GPU has great potential application such as, elastomers, textiles, medical devices, and wearable electronics, however more evaluation and testing needs to be performed.

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