

Supporting information

Novel Amphoteric Polyurethane Dispersion with Postpolymerization Crosslinking Function Derived from Hydroxylated Tung Oil: Synthesis and Properties

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Experimental Section

Materials.

Hydroxylated tung oil (HTO, trade name is TG20C) was kindly provided by US A-line Co. It was synthesized by alcoholysis using trimethylolpropane (TMP). The hydroxyl number is 282 with functionality of 2. The HTO is mainly composed of two di-functional components (see Figure 1 in Results and discussion). It is clearly seen from its FTIR spectrum (Figure 1S) that there is a strong ν OH band at 3421cm^{-1} ; the band at 1739 cm^{-1} from the ester group and the band at 991 cm^{-1} from the conjugated double bond are very obvious. In addition, the band at 3012cm^{-1} also shows the characteristics of unsaturated hydrocarbon chain in HTO.

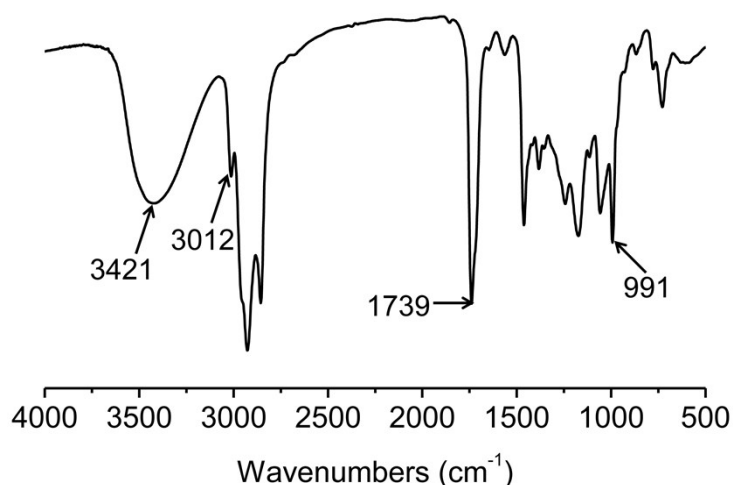


Figure 1S. FTIR spectrum of HTO

Polyethylene glycol with molecular weight of 800 (PEG-800, Dow Chemical) were dried by vacuum distillation at 110°C before use. Dimethylol propionic acid (DMPA, $\geq 99\%$, Hangzhou Tonghe Chemical) and N-methyldiethanolamine (MDEA, 99% , Shanghai Ziyi Reagent) and polypropylene glycol (PPG) with molecular weight of 400 (PPG-400, Shanghai Ziyi Reagent) were dried under vacuum at 60°C over

night before use. 4,4 methylene dicyclohexyl diisocyanate (HMDI, Wanhua Chemical) and glacial acetic acid (HAc) were used as received.

Synthesis of hydroxylated tung oil based amphoteric polyurethane dispersion (HTO-AmPUD)

The synthesis of HTO-AmPUD-1 (HTO weight content is 12.9%) was conducted in a four-neck round-bottom flask with stirrer, thermometer, feeding funnel and N₂ inlet. PEG-800 (3 moles) was first added into the reactor and dehydrated as mentioned above, then when the temperature cooled down, HMDI (11 moles) was added and the temperature was elevated to 90°C under stirring, then DMPA (3 moles) was added. The temperature was cooled down to 60°C when DMPA had dissolved. Then HTO (2 moles) and MDEA (3 moles) were added and the reaction temperature was slowly raised to 90°C and kept reacting for 2-3 hrs. During the reaction, a small amount of accessory solvent was added to adjust viscosity. When NCO residue reached to theoretical amount, the reaction temperature was cooled down to 85°C. Stoichiometric amount of 50% HAc (by weight) was added to conduct the neutralization for 20 minutes. And finally distilled water was added at 80°C for 30 minutes to finish the final emulsion preparation with solid content of 25% (by weight). HTO-AMPUDs with different HTO content and the control sample PPG-AmPUD (HTO-AmPUD-0) were prepared in the similar way. For each sample, the mole ratio among four raw materials having hydroxyl group can be seen in Table 1 in Results and Discussion. The equivalent of isocyanate group of HMDI is equal to the total hydroxyls.

Preparation of HTO-AmPUD film

The HTO-AmPUD was poured into a polytetrafluoroethylene disc and kept in vacuum oven at 60°C until the film weight remained unchanged. The HTO-AmPUD films thus prepared were the initial samples for further measurement.

Characterization

Fourier Transform Infrared Spectroscopy (FTIR) and Attenuated Total Reflectance (ATR)

The infrared spectra were obtained by using a SHIMADZU FTIR-8700 Spectrophotometer. The frequency range was from 4000 to 400 cm^{-1} with average of 32 scans at a resolution of 4 cm^{-1} . For the FTIR spectra of HTO-AmPUD, the emulsion was directly sprayed onto KRS-5 salt plate whereas for HTO-AmPUD film treated at different temperatures, ATR method was used since the films have been partially crosslinked and cannot be dissolved in solvent.

The comparative FTIR spectra (Figure S2, Supporting Information) between HTO-AmPUD and PPG-AmPUD show that both AmPUDs display the characteristic bands of polyurethanes, including the νNH bands at 3324 and 3339 cm^{-1} , the $\nu\text{C}=\text{O}$ bands at 1710 and 1719 cm^{-1} , as well as the amide II and III bands at 1532 and 1246 cm^{-1} , respectively. Differing from PPG-AmPUD, HTO-AmPUD has another band at 991 cm^{-1} representing the wagging vibration of the conjugated double bonds chain [7a], showing that the conjugated double bonds have been successfully introduced into the AmPUD.

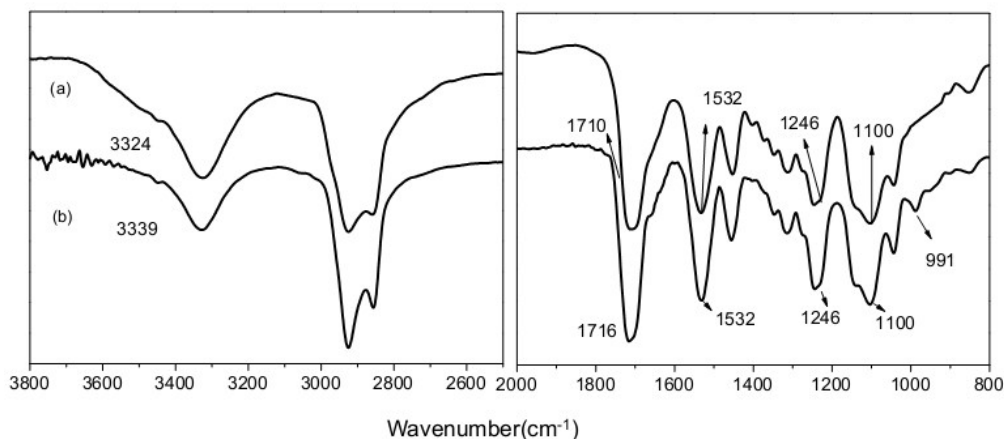


Figure S2. FTIR spectra of PPG-AmPUD and HTO-AmPUD
(a. PPG-AmPUD; b. HTO-AmPUD)

Proton and Carbon Nuclear Magnetic Resonance Spectroscopy (^1H NMR and ^{13}C NMR)

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III-400MHz superconducting NMR Spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C , respectively) using DMSO-d_6 as solvent. All spectra were recorded at room temperature (293°K). Chemical shifts (δ) were given in parts per million downfield from tetramethylsilane (TMS, 0.1%) as internal standard.

It is also seen from the comparative NMR spectra (Figure S3 and S4, Supporting Information) that a group of new resonances appear at δ_{H} 4.5-6.5 in ^1H NMR and δ_{C} 120-140 in ^{13}C NMR in addition to the polyurethane characteristic bands, which show the presence of the conjugated double bonds in HTO-AmPUD. Based on the similarity and difference between PPG-AmPUD and HTO-AmPUD, as well as the assignments for similar HTO in our previous work^[16-17], it is clear that the resonances around δ_{C} 174, 70 and 56 are the carbon from COOH in DMPA, $-\text{CH}_2\text{O}-$ in PEG, and $-\text{CH}_2\text{N}-$ in MEDA, respectively. These results show that all of the three

water borne components have been introduced to the polyurethane chain. The detailed assignments for HTO-AmPUD will be done elsewhere.

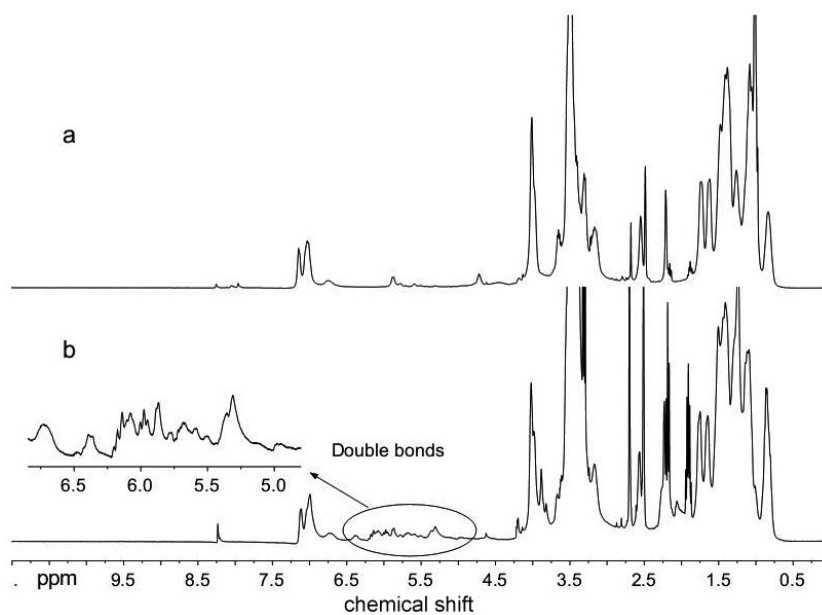


Figure 3S. ^1H NMR spectra of PPG-AmPUD (a) and HTO-AmPUD (b)

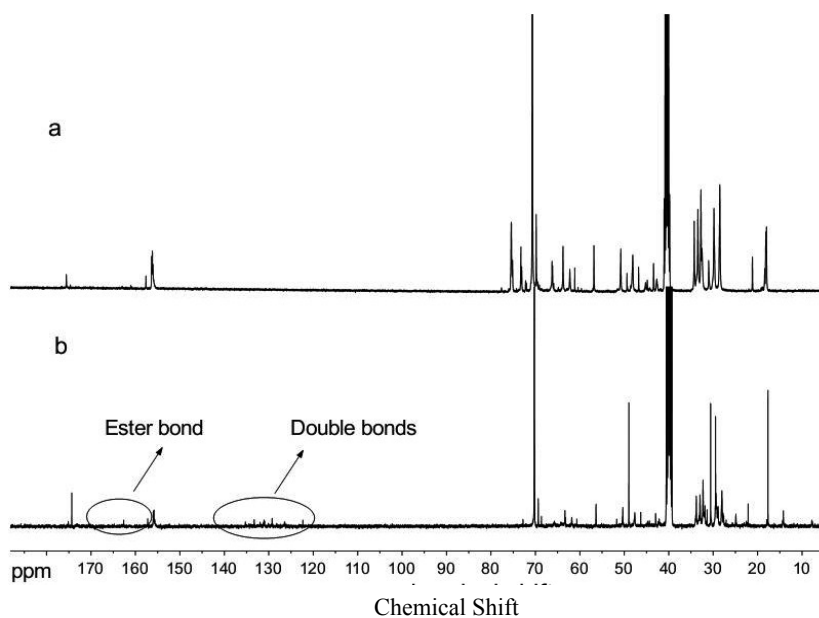


Figure 4S. ^{13}C NMR spectra of PPG-AmPUD (a) and HTO-AmPUD (b)

Gel Permeation Chromatography (GPC)

The molecular weight and its distribution (M_w/M_n) were determined by GPC at

25°C on a Waters 2695 using a series of monodisperse polystyrenes as standard and DMF as the fluent with a flow rate of 1.0 mL/min.

Isoelectric points (IEPs) and particle size vs pH

IEPs were determined according to the dependence of conductivity on the pH by conductometric titration method with DDS-11A conductometer and PHSJ-5 pH meter at 25°C. Malvern Zen 3690 Laser Particle Analyzer/Zeta Potential Meter was used to measure particle size. 0.1 mol/L of HCl solution was first used to adjust the pH of HTO-AmPUD to 1.5, then 0.1 mol/L of NaOH solution was used to titrate it to alkaline state. The conductivity value and particle size were recorded during the titration process. Every measurement was recorded after stirring for minutes to reach a stable state.

Table S1. Effect of acid and basic group ratio and HTO content on IEP and pH applicable range

Samples	IEP	Applicable pH scope
HTO-AmPUD-0	6.80	1.5-5.6 /8.5-12
HTO-AmPUD-1	6.70	1.5-5.6 /8.5-12
HTO-AmPUD-2	6.70	1.5-5.6 /8.5-12
HTO-AmPUD-3	6.40	1.5-5.6 /8.5-12
COOH/-N(CH ₃) _n =1/2	4.67	2-6.5

Critical aggregation concentration (CAC)

CACs were tested by both conductometric and surface tension methods using DDS-11A conductometer and Dataphysics DCAT21 Surface Tensiometer. When adopting the surface tension method, the HTO-AmPUD was first made into solid after being neutralized, then the solid sample was exactly weighed to prepare solutions

with different concentrations. The surface tension of HTO-AmPUD was measured at 25°C. The CAC is the value of the emulsion concentration when the tension has a sudden change; when adopting the conductivity method, the same concentrations of solution were used to measure the conductivity. The CAC is the emulsion concentration when the conductivity has a sudden change.

Mechanical properties

Stress-strain properties were tested in an RGM-3010 Universal Tester. Specimens of each sample were cut and tested at room temperature at 200 mm/min, according to the ASTM D638-94. At least, four specimens of each sample were used, and the average values are reported.

Dynamic Thermomechanical Analysis (DMA)

DMA were performed using Netzsch DMA242, in stretching mode with sample size of 20 mm × 4mm × 1mm. The frequency of the forced oscillations was fixed at 1 Hz and the heating rate was of 2°C/min during the heating process from 50~600°C.

Table 2S. Resistance to solvents for HTO-AmPUD casting films

Samples	T/°C	Solvents						
		toluene	xylene	ethyl acetate	ethanol	isopropano	acetone	NMP
HTO-AmPUD-0*	90	broken	broken	broken	broken	broken	broken	broken
	120	blur	blur	blur	blur	blur	blur	broken
	150	blur	blur	blur	blur	blur	blur	broken
HTO-AmPUD-1	90	--- **	---	---	blur	---	---	coarse
	120	---	---	---	---	---	---	---
	150	---	---	---	---	---	---	---

* without HTO

** no effect

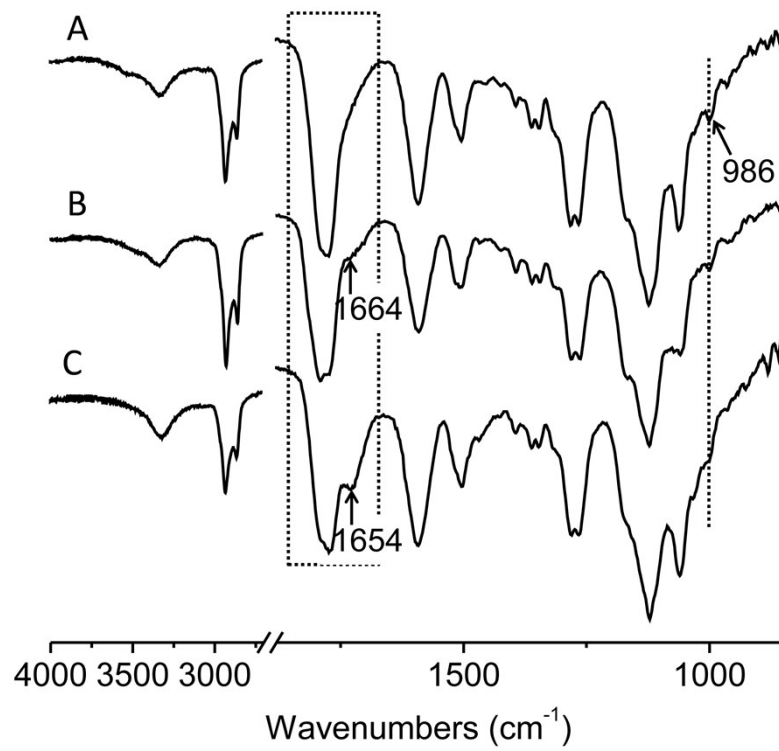


Figure 5S. ATR spectra of HTO-AmPUD-1 films after heat treatment at different temperatures (A: Initial film; B: 120°C; C: 150°C)