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Catalytic degradation of thermosetting unsaturated polyester via a green coupled acid catalytic system

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Materials

Thermosetting unsaturated polyester resin (TUPR) was obtained by cross-linking unsaturated polyester with styrene.[1] Glacial acetic acid (HAc), ethylene glycol (EG), alcohol (EtOH) and tetrahydrofuran (THF) were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (China). Phosphotungstic acid hydrate (HPWH), p-Toluenesulfonic acid (p-TSA), benzenesulfonic acid (BSA), ethanesulfonic acid (ACES) and dodecyl benzene sulphonic acid (DBSA) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All the materials were used without purification.

Degradation of TUPR

Typically, TUPR (1 g, 40-60 mesh) was dispersed in 15 mL of the mixture of glacial acetic acid containing certain concentration of acid catalyst. Then, the mixture was heated to 100-160°C for 8 h in a hydrothermal reactor. After the reaction was terminated, the solid product was separated via vacuum suction filtration and washed with glacial acetic acid and water. Then, the gel product was obtained by alkalization treatment of the solid product. The filtrate was subjected to rotary distillation to remove HAc and then added 15 mL water to dissolve HPW, the product insoluble in water was collected by centrifugation, washed with water and dried at 80°C. The degradation rate (D) of TUPR was measured by gravimetric method and the swelling ratio of gel product was calculated as the following equations:

$$D = 1 - \frac{m_1}{m_0} \times 10 \quad 0\% \qquad (1)$$

$$S_{gel} = \frac{(m_2 - m_1)}{m_1} \times 100\% \qquad (2)$$

Where m_0 (g), m_1 (g) and m_2 (g) are the weight of TUPR, dried solid product and swollen gel, respectively.

Swelling process of TUPR

TUPR (1 g, 40-60 mesh) was dispersed in 15 mL of glacial acetic acid containing certain concentration of phosphotungstic acid hydrate (0%, 1.9% and 4.8%). To reduce the effect of TUPR degradation in the presence of HPWH, the mixture was heated to 80^{o}C for 1-8 h in a hydrothermal reactor. After the swelling was terminated, the TUPR was separated via filtration with filtration fabric (200 mesh) and quickly removed the free solvent on the resin surface with absorbent paper. In addition, the influence of temperature on the swelling of TUPR without phosphotungstic acid hydrate was also investigated as described in the previous steps. The swelling ratio of TUPR was calculated as the following equations:

$$S_{TUPR} = \frac{(m_3 - m_0)}{m_0} \times 100\% \quad (3)$$

Where m_0 (g) and m_3 (g) are the weight of TUPR and swollen TUPR.

Characterization

The microstructures of the gel products were observed by environmental scanning electron microscope (ESEM, FEI Prisma E). The morphologies were analyzed with scanning electron microscope (SEM, Carl Zeiss SUPRA55). Fourier transform infrared spectra (FTIR) of the samples were performed using Carl Zeiss SUPRA55 spectrometer over a wave number range from 400 cm^{-1} to 4000 cm^{-1}. Solid-state NMR spectra of all samples was recorded on a Bruker AVANCE 600MHz spectrometer operating at 600 M. Thermogravimetric analysis was carried on NETZSCH STA 449F5 at a heating rate of 5/10^{o}C·min^{-1} under an nitrogen atmosphere. The UV-Vis absorption spectra of the samples were measured by using a TU-1810 spectrophotometer.

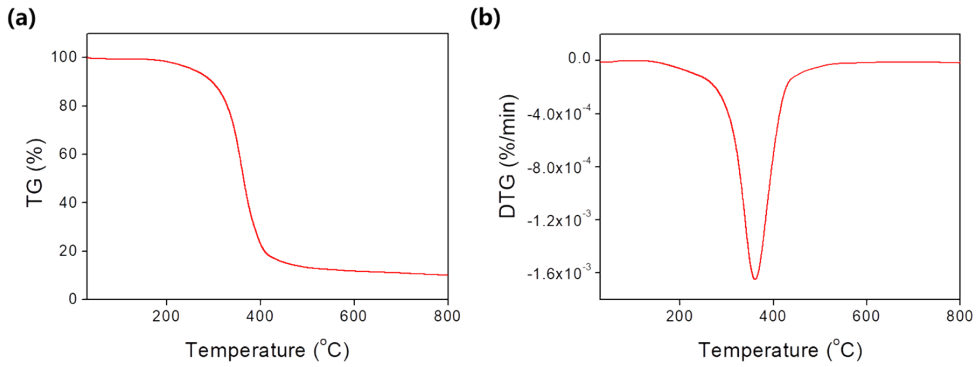

Figure S1 The TG (a) and DTG (b) curves of TUPR in nitrogen atmosphere.

The thermal stability of TUPR in nitrogen was evaluated by TG and the results shown in Figure S1. The weight loss of TUPR was less than 1% before 170°C and the temperature of maximum weight loss reached to 361°C (Figure S1a and b), indicating the excellent thermal stability of TUPR.

The curing rate of TUPR was measured by soxhlet extraction method using tetrahydrofuran extraction for over 50 h, and the result shown that the curing rate of TUPR was more than 99%, exhibiting a high degree of cross-linking.

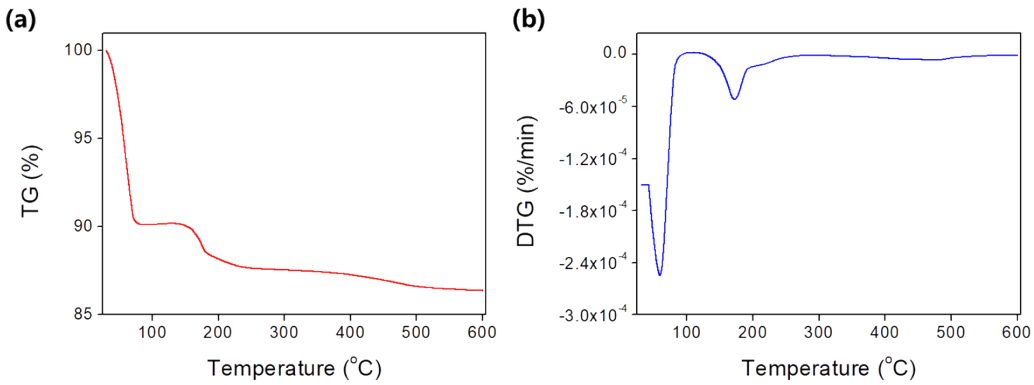

Figure S2 The TG (a) and DTG (b) curves of HPWH in nitrogen atmosphere.

Table S1 Determining content of crystal water in HPWH

adsorption drying	TG	adsorption drying	Heat drying
Detection value (%)	9.83	9.79	9.62

The content of crystal water in HPWH was determined with different methods, and the results shown in the table S1. The adsorption drying was carried out by putting about 10 g HPWH in a desiccator fitted with phosphorus pentoxide, experienced water vapor adsorption for 15 days and obtained the dehydrated HPW. The Heat drying method was succeeded by heating the 10 g HPWH in an oven at 120°C for 12 h removing the H_2O. The detection value by different methods was 9.83%, 9.79% and 9.62% respectively.

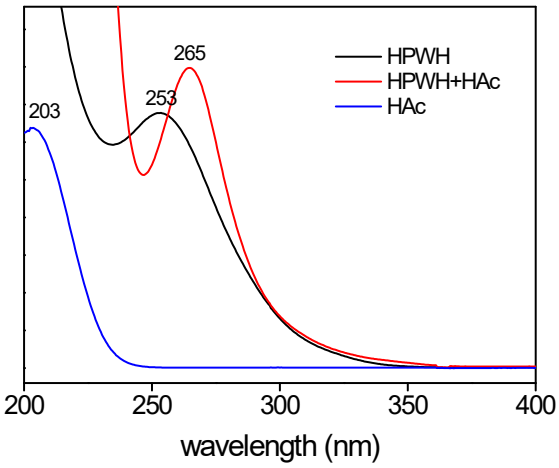

Figure S3 The UV-Vis absorption spectra of HPWH, HAc, and the mixture of HPWH and HAc in water.

The absorption of HPWH, HAc, and the mixture of HPWH and HAc in water, respectively, were observed before 350 nm. When the HAc was added to HPWH, the band of HPWH at 253 nm shifted to 265 nm, indicating that there might be interactions such as the hydrogen bonding effect between HPWH and HAc.

References

1. W. An, X.-L. Wang, Y. Yang, H. Xu, S. Xu and Y.-Z. Wang, *Green Chem.*, 2019, **21**, 3006-3012.