Preparation and Performance Research of WPU Modified by Nanopolyphosphazenes

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Abstract: It is reported in this paper that waterborne polyurethane (WPU) can be modified by nanopolyphosphazenes fibers, which had been prepared containing hydroxyl groups, followed by reaction with WPU. At the same time, physical blends had also been carried out in the experiments. The results showed that the tensile strength of the WPU films through chemical modification containing 0.5 wt% fibers is, 1.22 MPa, and that the elongation at break is 1294.50%. This data has significantly increased when compared against WPU, in which the elongation at break is only 785.50%. The thermal decomposition temperature of the WPU modified by nanopolyphosphazenes is 50 % higher than that of regular WPU. At the same time, its preparation method had some influences on the mechanical properties of the composite materials.

Keywords: Modification, nanopolyphosphazenes, preparation, waterborne polyurethane.

1. INTRODUCTION

Waterborne resins forming a non-sticking surface have been investigated because of their maintenance-free material demands, as well as emphasis on the reduction of solvent emissions. Waterborne polyurethane, which the organic solvent is replaced by water as a dispersion medium, has been used in textile, leather, paper and the other fields. WPU has excellent dispersion stability and good film-forming properties. However, there are still some inevitable defects of WPU, its modification also become a hot research topic [1-3]. The improvement methods of WPU have been widely reported [4-9]. Polyphosphazenes are phosphorus and nitrogen's compounds with alternating single and double bonds [10]. Therefore, the main chain of polyphosphazenes is very soft and is mainly used in biological medicine, aerospace materials, flame retardants and so on [11]. So, WPU modified by nanopolyphosphazenes fibers are investigated in this paper.

2. EXPERIMENTAL

2.1. Materials

Hexachloro cyclotriphosphazene (HCCP, 99%), 4,4'-nanomaterials dihydroxy diphenyl sulfone (BPS, 99%) and 2, 2 - (hydroxymethyl) propionic acid (DMPA, 98%) were supplied by Shanghai Jichun reagent Co., Ltd.; acetone (A.R) was supplied by Shanghai Runjie chemical reagent Co., Ltd.; tetrahydrofuran (A.R) was supplied by Tianjin Bodi chemical reagent Co., Ltd.; polyether glycol (PPG2000, Mn=2000) was supplied by Sangsu Haian Petroleum chemical Plant; and isophorone diisocyanate (IPDI, 99%) was supplied by Shanghai Hansi chemical reagent Co., Ltd.

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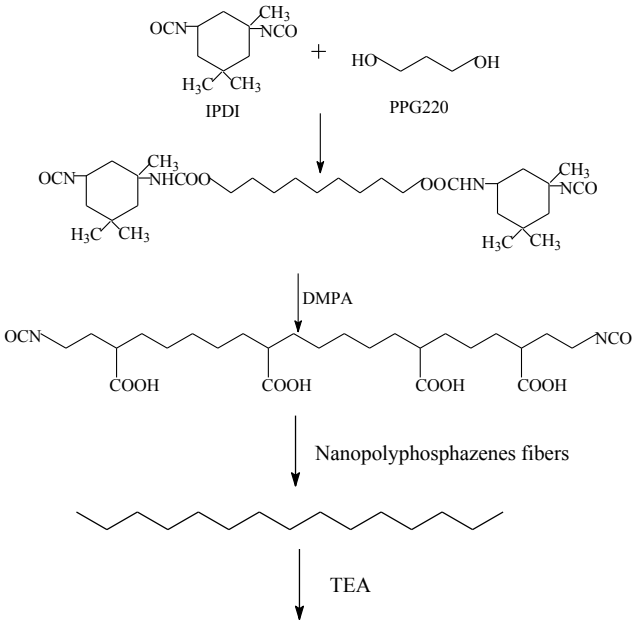
2.2. General Procedure



Synthetic route of WPU modified by nanopolyphosphazenes.

2.3. The Synthesis of Nanomaterials Polyphosphazenes

According to the raw material mole ratio (HCCP: BPS: TEA = 1:3:9), the concentration of the HCCP is about 4.5 to 5.5 g/L, of which acetone was selected as solvent, and then polyphosphazenes had been prepared by ultrasonic cleaning machine, and the reaction temperature is about 10°C, and the power transferred is about 40-50 KHZ. At the end, some nanofiber samples of polyphosphazenes can be obtained, which is the white powder solid.

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2.4. WPU Modified by Nanopolyphosphazenes

As shown in Section 2.2, according to Mole ratio of IPDI:PPG2000: DMPA=2.5: 1: 1, the composite materials of WPU modified nanopolyphosphazenes had been prepared by chemical reaction, which the nanopolyphosphazenes had been added with 0.5% and 1% of the content of the WPU mass. At the same time, the pure WPU had also been prepared, and blended physically with the nanopolyphosphazenes.

2.5. Detection Method

WPU had been put into the glassware, and then it would be put into the constant temperature vacuum drying oven for 12 h after room temperature drying. After cooling the WPU films would be removed into the oven at room temperature. The films of WPU modified nanopolyphosphazenes by chemical reaction and blended physically had also been prepared. Nanopolyphosphazenes had been analyzed by the fourier transform infrared spectrometer (NEXUS-870, Thermo Nicolet, USA) at room temperature, with scanning wave number range 500-4000 cm^{-1}, and scanning interval 44 cm^{-1}. The morphology of the nanopolyphosphazenes had been observed by scanning electron microscope (S4800 type, HITACHI, Japan), and the samples had been sprayed by gold. The thermostability of films had been tested by the thermogravimetric analyzer (HTG – type, Beijing Henjiu scientific instrument, China) at room temperature. The temperature range is 0-900°C, and the heating rate is 20°C/min. Mechanical properties were investigated by a universal testing machine that is DELL-20000 tensile tester supplied by Shanghai Dengjie Machine Co., Ltd according to GB/T528—2009. Experiments were conducted in laboratory air at room temperature and relative humidity of about 50±10%, the tensile speed of 5 mm/min; dumbbell specimens were prepared by omnipotent sample maker.

3. RESULTS AND DISCUSSION

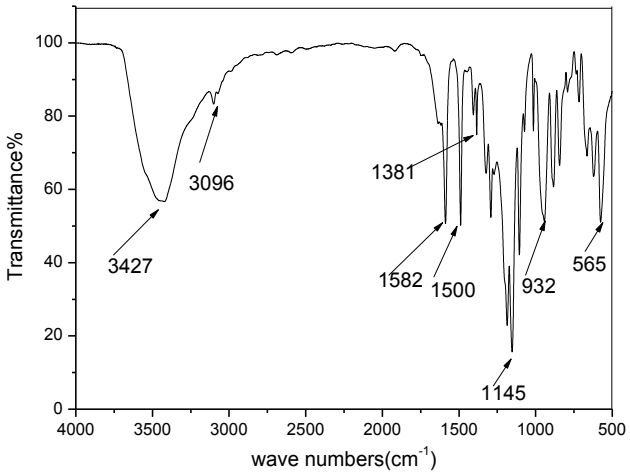
3.1. FTIR Analysis

As shown in Fig. (**1**), the vibration absorption peak of -OH and -P=N- can be observed in (a), which are -3427 cm^{-1} and 1381 cm^{-1} respectively, the vibration absorption peak of -NHCOO-, -C-O-C- and -C-N can be observed in (b), which are 1631 cm^{-1}, 1383 cm^{-1} and 1119 cm^{-1} respectively. FTIR of WPU modified by nanopolyphosphazenes fibers can be seen in Fig. (**1c**), the vibration absorption peak of –NCO cannot be found. It could be inferred from the fact that there is a chemical reaction between waterborne polyurethane and nanopolyphosphazenes through –NCO and –OH.

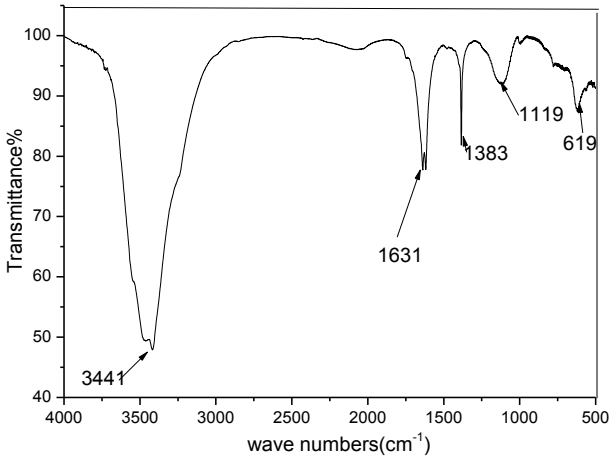
3.2. Morphology Analysis of Nanopolyphosphazenes

As shown in Fig. (**2**), it can be seen that there is a large number of irregular silk fibers with tangles, in which the diameter of those fibers is about 50-200 nm. It could therefore, be inferred that nanopolyphosphazenes in the synthetic process had some influence by ultrasonic separation, which resulted in the small size of nanopolyphosphazenes that helped progress the polymerization at a continued pace.

(**a**) Nanopolyphosphazenes fibers



(**b**) WPU



(**c**) WPU modified by nanopolyphosphazenes fibers (1.0wt %)

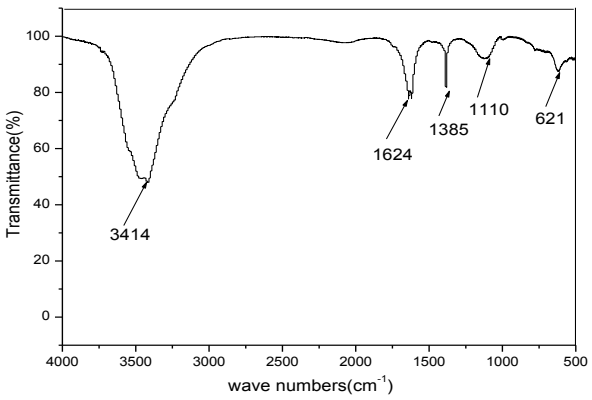


Fig. (1). FTIR of nanopolyphosphazenes and WPU modified by nanopolyphosphazenes fibers.

3.3. Thermostability

As shown in Fig. (**3**), the films of WPU and WPU modified by nanopolyphosphazenes fibers had been analyzed by thermogravimetry. It can be observed that: (a) when the

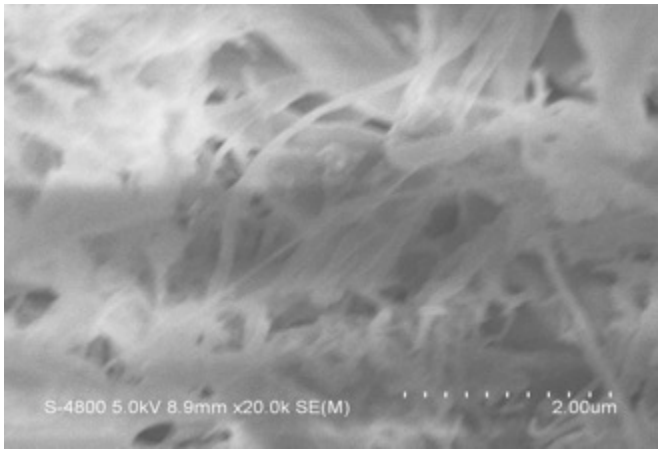
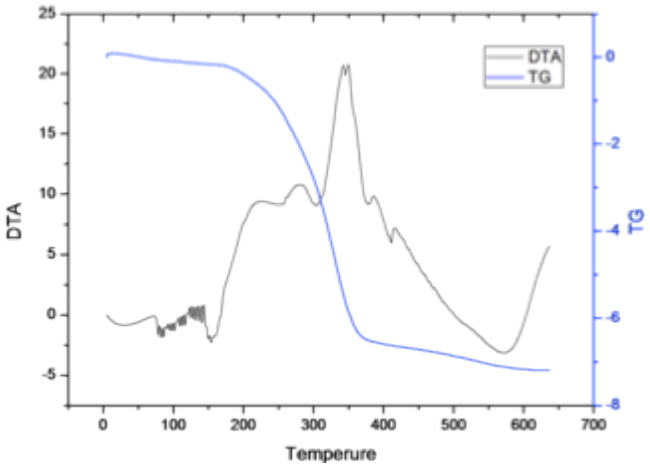


Fig. (2). SEM of nanopolyphosphazenes fibers.

(**a**) WPU



(**b**) WPU modified by nanopolyphosphazenes fibers

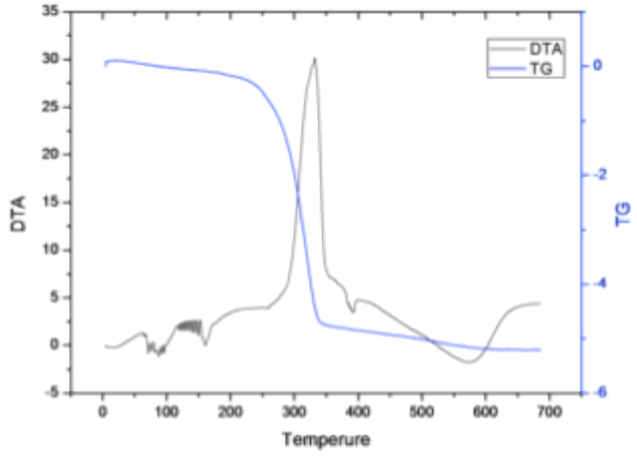


Fig. (3). TGA curves of WPU and WPU modified by nanopolyphosphazenes fibers (1.0wt %).

thermal decomposition temperature of WPU is about 200°C. With the rise of temperature, the thermal pyrolysis is obvious compared to before the decomposition temperature, of which the first thermal pyrolysis is about 155°C; (b) when the thermal decomposition temperature of WPU modified by nanopolyphosphazenes fibers is about 250°C. With the rise of temperature, the thermal pyrolysis almost did not exist compared to before the decomposition temperature. Therefore, it can be inferred that thermostability of the composite materials of WPU modified by nanopolyphosphazenes could be much improved compared to that of WPU.

3.4. Mechanical Properties

Table **1** shows the data tensile strength versus elongation at break of WPU and WPU modified by different contents of nanopolyphosphazene fibers. The tensile strengths respectively 0.5 wt% and 1 wt% of nanopolyphosphazenes fibers/WPU are all 1.22 MPa, in which the tensile strength of modified WPU is less than that of WPU. But the elongation at break had been improved obviously by modification, which has achieved a value up to 1294.50%. With the increase of nanopolyphosphazene fibers, the elongation at break of WPU modified by nanopolyphosphazenes fibers decreased, which shows that the toughness of WPU can be improved by adding an appropriate amount of nanopolyphosphazene fibers. So the waterborne polyurethane material modified by nanopolyphosphazenes is more suitable for applications in manufacturing high elastic film products.

In order to study the composite methods, nanopolyphosphazenes fibers and WPU had been blended physically, and the tensile strengths of 1.0 wt% and 1.5 wt% nanopolyphosphazene fibers/WPU are about 1/6 of that of WPU, which is also lower than that after the chemical modification. However, the elongation at break obviously increased. Therefore, it is concluded that the composite methods of WPU and nanopolyphosphazenes would influence the mechanical properties.

CONCLUSION

The nanopolyphosphazene fibers and the composite materials of WPU modified by fibers had been prepared in the experiments; the size of nanopolyphosphazene fibers is about 50-200 nm.

The thermal decomposition temperature of WPU modified by nanopolyphosphazenes fibers is about 250°C, which is higher than that of WPU.

The toughness of WPU can be improved through modification. The elongation at break of WPU modified by nanopolyphosphazenes fibers is up to 1294.50%. At the same time, the composite methods of WPU and nanopolyphosphazenes would influence the mechanical properties.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

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Table 1. Mechanical parameters of WPU and WPU modified by nanopolyphosphazenes.

Samples	Tensile Strength (MPa)	Elongation at Break (%)
WPU	2.40	785.50
0.5 wt% nanopolyphosphazenes fibers/WPU (reaction)	1.22	1294.50
1.0 wt% nanopolyphosphazenes fibers/WPU (reaction)	1.22	1194.42
1.0 wt% nanopolyphosphazenes fibers/WPU (blend)	0.41	1534.60
1.5 wt% nanopolyphosphazenes fibers/WPU (blend)	0.40	1540.70

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