



## Short communication

# Fabrication of nano-crystalline cellulose with phosphoric acid and its full application in a modified polyurethane foam



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## ABSTRACT

Nano-crystalline cellulose was fabricated in an anhydrous phosphoric acid system with medical absorbent cotton as its raw material. After ammonia neutralization, the whole system with produced phosphates and hydrolyzed saccharides was used as a modifier for preparing polyurethane foam (PUF). The NCC worked as a reinforce material, the phosphates served as flame-retardants, and the hydrolyzed saccharides partly replaced polyol. The addition of the modifier significantly improved mechanical property and flame-retardancy without an inferior thermal conductivity. When the dosage of modifier was 6% of the whole polyol, compressive strength increased 4.29 times, heat release rate dropped to 50.7%, and time to ignition extended to 2.6 times of those of the neat PUF. XRD and TEM analyses proved that the NCC in the modifier was rod-shape cellulose II with diameter of 10 nm or so. FTIR analysis confirmed that the modifier well reacted with isocyanate, and SEM results revealed that the flame-retardant PUF had more uniform cells and more regular skeleton structure than the neat PUF.

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## 1. Introduction

Nano-crystalline cellulose (NCC) has been focused by the scientific community due to its renewable nature, abundance, exceptional strength and physicochemical properties, and has been used for the preparation of many composites as a reinforced material [4,5,11]. Over the past decade, a large number of studies have been reported on isolation of NCC and its application. However, isolation of NCC still suffers from serious problems such as separation of products from catalysts and hydrolyzed water-soluble oligosaccharides with acid methods [1,6,10,12], or expensive solvents with ionic liquid methods [19,23], or very high cost in time and energy with mechanical methods [17,22]. Acid methods were used very common for NCC isolation. Usually, the catalyst (mostly sulfuric acid) and the oligosaccharide from hydrolyzed cellulose had to be fully removed from NCC suspension by repeated centrifugation and extensive dialysis [3], which are very time-consuming and the discharges might damage the environment. If it is not necessary to separate the NCC product from acid catalysts

and hydrolyzed oligosaccharides, NCC will be much easier to be commercialized and used for reinforcement.

Polyurethane foams (PUF) are widely used in many applications, which is prepared from polyol and isocyanate. Commercially, polyols used for manufacturing PUF are predominantly derived from petroleum based resources. With the increasing concern on fossil fuel depletion and environmental footprint, there is a strong global interest to explore renewable resources as alternative feedstock for making PUF [28]. Literature has shown that bark, starch, wood bagasse, and other lignocellulosic agricultural residues could be liquefied with acid catalysts and used as renewable polyols for preparing PUF [7–9,15,27]. Basically, the polyol substitute is mainly hydrolyzed carbohydrates. In addition, usual PUF was widely used almost all commercial applications both in industry and in daily life, but its great flammability could increase fire hazard, which limits its use in stringent fire situation [26]. Thus, it is necessary to develop flame-retardant PUF.

Considering those mentioned above, nano-cellulose was prepared with phosphoric acid and fully used to modify PUF, flame-retardant reinforced PUF. The NCC was used as a reinforcement material and the oligosaccharides from the hydrolyzed cellulose partly replaced polyol. The phosphoric acid was neutralized with ammonia and the formed ammonium phosphates served as flame-

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retardants. The flame-retardant reinforced PUF was prepared without any discharges and its properties were investigated.

## 2. Materials and methods

### 2.1. Materials

Medical absorbent cotton was made by Yanggu JYG Hygiene & Health Materials Factory, Shandong, China. Silicone oil (AK8805) was purchased from Jiangsu Maysta Chemical Co., LTD. Methylene diphenyl diisocyanate (WANNATE PM-200, NCO% = 30.2–35) was from Yantai Wanhua Polyurethanes Co., LTD. All other chemicals were analytical grade reagents.

### 2.2. Fabrication of NCC

Oksman et al. [23] reported that swelling treatment of cellulose is helpful for isolation of NCC. Boerstoele et al. [2] found that anhydrous phosphoric acid is an excellent swelling agent for cellulose. Hence, anhydrous phosphoric acid was prepared in this work before the isolation of the nano-cellulose. Polyphosphoric acid and 85% phosphoric acid was mixed for 1.5 h at 48 °C to prepare anhydrous phosphoric acid system ( $P_2O_5$  content = 74%) and then cooled down to 1–3 °C. Medical absorbent cotton was immersed in the anhydrous phosphoric acid system in mass ratio of 1:5 with stirring for 2 h, then the mixture was neutralized with aqueous ammonia in an ice water bath until the pH value reached 7.5. Therefore, besides NCC, the mixture was very rich in phosphates, which could endow flame-retardancy to the PUF.

### 2.3. Preparation of PUF

In this work, PUF was prepared by one step method. After dehydration, the NCC system was directly mixed with polyhydric alcohol (polyethylene glycol PEG#400 and glycerin in mass ratio of 7:3) at dosage of 0, 4, 6, 8 and 10% (w/w) of the whole polyol without removing salts and hydrolyzed oligosaccharides. Then water (1–2% of the whole polyol) as a blowing agent, silicone oil (3–5% of the whole polyol) as a stabilizer, triethylene diamine (1.5% of the whole polyol) and dibutyltin dilaurate (1.5% of the whole polyol) as catalysts were added into the system and full stirred. Finally MDI (110–120% of the calculated value) was added in the system with full stirring and poured into a mould to foam and cured for 48 h.

### 2.4. Characterizations of NCC and PUF

After removing phosphates and other water soluble substances with multiple centrifuging, the microstructure of the NCC was examined with a Hitachi 7560 transmission electron microscope (TEM) at 100 KV and a D8 ADVANCE XRD in the range of 5°–80° with a step size of 0.02° at scan speed of 1° s<sup>-1</sup>.

The compressive strength of the PUF samples was determined on a Zwick/z 010 universal testing machine at a speed of 2 mm min<sup>-1</sup>. The coefficients of thermal conductivity were tested using the tc-2/a heat conduction coefficient detector. The flame-retardancy was analyzed on a FTTDual CONE calorimeter at the heat radiance of 25 kW m<sup>-2</sup>. Thermogravimetric analysis (TGA) was conducted using a Netzsch TG209F1 instrument under air environment at a heating rate of 20 °C min<sup>-1</sup> over a temperature range of 35–800 °C. The pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) analysis was performed to analyze the volatile compounds during pyrolysis. It was conducted using a combination of a CDS Pyroprobe 5200 and an Agilent 7890 gas chromatograph combined with an Agilent 5975 mass selective

detector. The pyrolysis temperature was 600 °C. The GC oven temperature was initially held at 50 °C for 10 min, and then was programmed to 280 °C at a heating rate of 10 °C/min. The temperature of the GC/MS interface was set at 280 °C. The FTIR measurement was carried out using a Nicolet Magna 560 spectrometer with ATR attachment having a spectra range of 4000–400 cm<sup>-1</sup>. The cellular morphology of the foams was examined using a FEI QUANTA200 scanning electron microscope (SEM). Samples were cut along the rising direction of the foam, and the fracture surface was sputter-coated with gold before scanning.

## 3. Results and discussion

### 3.1. Characterization of the NCC

According to the TEM micrograph, the insoluble part of the modifier was rod-shape nano-crystalline cellulose with diameter of 10 nm or so. In order to identify its crystal structure, XRD analysis was performed. In the XRD pattern, there were high peaks appearing at about 12.4°, 20.5° and 22.2°, in which 12.4° and 20.5° were due to the 101 side and 22.2° was due to the 002 side of cellulose. All the characteristic peaks show that cellulose crystals in the modifier were typical cellulose II, in good agreement with previous report [14,16].

### 3.2. Properties of the modified PUF

#### 3.2.1. Compress strength

The compress strength of the PUF products was illustrated in Table 1. As mentioned above, NCC is a great reinforce material. On the other hand, incorporation of filler into PUF causes inferior physical and mechanical properties [25]. In this work, the compress strength of the flame-retardant PUF increased to some extent with the addition of the modifier, which implies that the modifier, the NCC with phosphorous salts and hydrolyzed saccharides, is compatible with others. When the dosage of the modifier was 6%, the compress strength reached up the highest, 107.5 kPa, which is four times that of the neat PUF. However, when the dosage of the modifier was greater, the compress strength reduced.

#### 3.2.2. Thermal conductivity

Thermal conductivity is a vital property of PUF. It is mainly used as a heat insulator due to its low coefficient of thermal conductivity. In this work, the NCC, the hydrolyzed saccharides, and the phosphates were used to reinforce the PUF, to partly replace usual polyol, to serve as flame-retardants, respectively. These additives might increase the thermal conductivity of the PUF. However, the data in Table 1 shows that its low coefficient of thermal conductivity was not changed. When the dosage of the modifier was 6% or 8%, the coefficients were 0.0231 w/m K or 0.0230 w/m K, respectively. Both are not higher than that of the neat PUF, 0.0243 w/m K.

**Table 1**

Effect of different NCC modifier dosages on compress strength, thermal conductivity, and flame-retardancy of the modified PUF products.

Dosage (%)	Compress strength (KPa)	Thermal conductivity (w/m K)	Heat release rate (HRR) (KW/m <sup>2</sup> )	Peak of heat release rate (pkHRR) (KW/m <sup>2</sup> )	Time to ignition (TTI) (s)
0	25.04	0.0243	97	249	3
4	69.89	0.0236	61	242	5
6	107.5	0.0231	49	235	8
8	98.61	0.0230	52	230	8
10	74.18	0.0238	62	215	14

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