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Flame retardancy and thermal degradation of cotton textiles based on UV-curable flame retardant coatings

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ABSTRACT

The flame retardant coatings were prepared through UV-curable technique using tri(acryloyloxyethyl) phosphate (TAEP) and triglycidyl isocyanurate acrylate (TGICA). Results from FTIR-ATR spectroscopy and scanning electron microscopy (SEM) showed that flame retardant coatings were successfully coated onto the surface of cotton fabrics. The flame retardancy of the treated fabrics was studied by Micro-scale Combustion Calorimeter (MCC) and limited oxygen index (LOI). The cottons coated flame retardant coatings had the lower peak heat release rate (PHRR), heat release capacity (HRC), total heat of combustion (THC) and higher LOI value compared with untreated cotton. The results from TGA test showed that the flame retardant coatings lowered the decomposition temperature of treated fabric. The thermal decomposition of cottons was monitored by real time FTIR analysis and thermogravimetric analysis/infrared spectrometry (TGA-IR). The enhanced flame retardant action might be caused by thermal decomposition of TAEP structure, producing acidic intermediates, which could react with fabrics to alter its thermal decomposition process.

1. Introduction

Currently, both synthetic and natural polymers have been widely used in textile and clothing products. Among various textile materials, cotton is one of the most commonly used materials for textiles and clothing. Compared with some synthetic polymer fibers, the main drawback of cotton fibers is its high flammability, and therefore it cannot be used for special textiles [1]. It is very important for public safety to find ways to render this material less flammable. Hence there have been a large number of studies to understand the combustion of cotton and ways to make it more flame resistant in the past.

Many people frequently use halogen-free phosphorus-compounds as flame retardants for cotton textiles. They are cheap to manufacture, are less volatile, have good thermal stability and promote char formation during the burning process. Some studies [2,3] have shown that, phosphorus-compounds can catalyze char formation and reduce the flammability of cotton textiles.

Phosphorus-based flame retardants impart flame retardancy to cotton by the following mechanism. Firstly, they release polyphosphoric acid on heating, which phosphorylates the C-6 hydroxyl group in the anhydro glucopyranose moiety and simultaneously they serve as an acidic catalyst for the dehydration. The first reaction could reduce formation of laevoglucose, which will further break down to flammable volatiles. This can increase the char yield by altering the chemical reactions yielding carbonaceous char rather than CO or CO_2. The acidic catalytic effect of the released polyacid could further accelerate the rate of this reaction [4].

Many of the phosphorus-based flame retardants which evoke these effects also contain nitrogen-based flame retardants. This observation has led to the proposal of a synergistic effect between phosphorus and nitrogen. Several studies [5–7] have demonstrated that the flame retardant containing phosphorus and nitrogen compounds are more efficient flame retardants due to the char formation increases.

As one of the easiest and most efficient ways, flame retardant coatings have been employed widely to protect a substrate against fire [8–10]. It can prevent heat from penetrating and flames from spreading [11,12].

As improvement of living standards and society for human, a novel flame-retardant coating, UV-curing coating, is gradually developing. UV-cured coatings have many advantages, such as very rapid curing, lower energy consumption, less environmental pollution, lower process costs, high chemical stability and lower VOCs

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[13,14]. This technology is satisfying new requirements for traditional or advanced applications, since it can offer a broad range of the changes in formulation and curing conditions.

In this paper, we introduce a method to prepare flame retardant cotton, UV-curable technology. This way is flame-retardant monomer polymerization on the surface of cotton textiles. To our knowledge, the study on flame retardancy and thermal degradation of cotton based on UV-curable flame retardant coatings has not been reported.

In the present work, we investigated the polymerization processes taking place on the surface of cotton textile through ATR spectroscopy and SEM. The flame retardant effect and thermal stability were investigated and discussed here. Furthermore, the changes of chemical structure for fabrics during the thermal degradation were monitored by real time FTIR analysis.

2. Experimental

2.1. Materials

Phosphorus oxychloride ($POCl_3$) and triethylamine (TEA) were distilled before use. 2-Hydroxylethyl acrylate (HEA), supplied from Dong-fang Chemical Co., Beijing, China, was distilled at reduced pressure and dried over 4 Å molecular sieves before use. Acetone, ethyl ether, dioxane and acrylic acid were purchased from Shanghai Chemical Reagents Company in China. Triglycidyl isocyanurate was purchased from Anhui Taida New Materials Co., Ltd. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur1173) was used as a photoinitiator. The ultrasonic treatment was carried out by a KS-900 ultrasonic generator (Ningbo Kesheng) at room temperature under air atmosphere. UV irradiation equipment was made by Lantian Co. in China (80 W cm^{-2}). Plain-weave cotton fabrics were from the market with an areal density of 156 g^{-2}. Cotton fabrics were pre-treated in the solution containing 18 wt% NaOH and rinsed with distilled water then air-dried at room temperature.

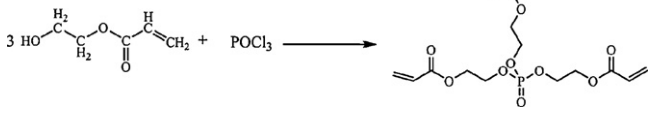
2.1.1. Preparation of tri(acryloyloxyethyl) phosphate (TAEP) [15]

HEA (17.75 g, 0.153 mol), TEA (18.05 g, 0.18 mol) and 60 mL ethyl ether were placed into a 250 mL round-bottomed flask with a calcium chloride drying tube. A mixture of 7.86 g $POCl_3$ (0.05 mol) and 20 mL of ethyl ether was slowly added into the above flask at 0 °C using an ice bath, and then kept at ambient temperature for 12 h. The triethylamine hydrochloride salt by-product was removed by filtration. The obtained filtrate was twice extracted by HCl (1 M), $NaHCO_3$ (10%) and NaCl (saturated) aqueous solution. After drying over sodium sulfate, the solvent was removed under vacuum, obtaining a colorless liquid product, named TAEP. The synthetic route of TAEP is shown in Scheme 1.

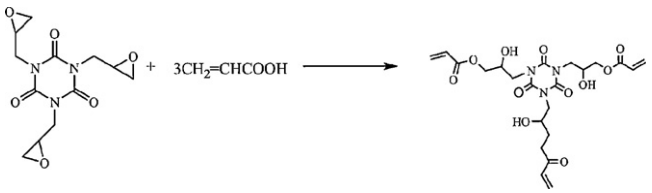
IR (KBr) (cm^{-1}): 1265 (—P═O); 1058 and 980 (—P—O—C); 1727 (—C═O); 1635; 1410; 810 (—C═C).

2.1.2. Preparation of triglycidyl isocyanurate acrylate (TAEP) [16]

TGIC (29.75 g, 0.1 mol), AA (21.6 g, 0.3 mol), and 100 mL dioxane were placed in a 250-mL four-necked round bottom flask, which was equipped with a mechanical stirrer, reflux condenser, and thermometer. And triethylamine (0.3 mL, as catalyst), 4-methoxyphenol (0.3 g, as polymerization inhibitor) were also added. And then, the temperature was raised to 105 °C, kept at this temperature for 3 h. After that, the solution was placed in a rotary evaporator to remove any unchanged reactants and solvent. A colorless sticky liquid product was obtained, named TGICA. The schematic process of the reaction was presented in Scheme 2.



Scheme 1. The synthetic route of TAEP.



Scheme 2. The synthetic route of TGICA.

IR (KBr) (cm^{-1}): 3448 (—OH); 1731 (C═O); 1061 (—C—O—C—); 1636; 1409; 810 (—C═C).

2.2. Preparation of flame retardant cotton

In the first step, pieces of bleached cotton fabrics were immersed in an acetone solution containing 50 g/L, 100 g/L and 200 g/L of the flame retardant monomers (as shown in Table 1) (FR (g)/acetone (L); FR: TAEP/TGICA = 1/1, by weight; 4% (w/w) of the photoinitiator (Darocur1173)) at room temperature for 30 min, respectively. Each mL of these solutions contains 0.05 g, 0.10 g, 0.20 g reactive compounds, respectively. And then ultrasonic treatment was carried out for 10 min. And finally, these impregnated fabrics were removed from the solution, placed onto glass plates and irradiated on both sides each 10 s under UV-source in an air atmosphere. (80 W cm^{-2}; the distance between the light source and the sample is 8 cm.). After radiation, the fabric was firstly washed with acetone, and then extracted by tetrahydrofuran for 48 h to remove the generated homopolymers. Finally, the fabric was dried in air, then under vacuum until no weight lost could be detected.

2.3. Measurements

2.3.1. ATR measurements

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry was performed using a Thermo Nicolet Avatar 6700 FTIR equipped with an attenuated total reflectance device.

2.3.2. Microscale Combustion Calorimeter (MCC)

GOVMARK MCC-2 Microscale Combustion Calorimeter was used to investigate the combustion of cotton fabrics. In this system, about 5 mg sample was heated to 700 °C at a heating rate of 1 °C s^{-1} in a stream of nitrogen flowing at 80 cm^3 min^{-1}. The volatile, anaerobic thermal degradation products in the nitrogen gas stream are mixed with a 20 cm^3/min stream of pure oxygen prior to entering a 900 °C combustion furnace. Measured during the test is the heat release rate dQ/dt (W) and sample temperature as a function of time at constant heating rate [17,18]. The specific heat release rate HRR (W/g) is obtained by dividing dQ/dt at each point in time by the initial sample mass. A derived quantity, the heat release capacity HRC (J/g K) is obtained by dividing the maximum value of the specific heat release rate by the heating rate in the test. The heat release capacity is a molecular level flammability parameter that is a good predictor of flame resistance and fire behavior when only research quantities are available for testing [19].