



Flame retarding and reinforcing modification of ramie/polybenzoxazine composites by surface treatment of ramie fabric



Nannan Li ^{a, b}, Hongqiang Yan ^a, Lei Xia ^a, Lebo Mao ^a, Zhengping Fang ^{a, b, *}, Yihu Song ^b, Hao Wang ^c

^a Laboratory of Polymer Materials and Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China

^b MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

^c Centre of Excellence in Engineered Fiber Composites, University of Southern Queensland, Toowoomba, Queensland 4350, Australia

ARTICLE INFO

Article history:

Received 2 April 2015

Received in revised form

11 June 2015

Accepted 23 July 2015

Available online 29 July 2015

Keywords:

Flame retardancy

Fabrics/textiles

Laminate

Surface treatments

Mechanical properties

ABSTRACT

Ramie fabrics were firstly treated with amino functional silane coupling agent. Then the layer-by-layer self-assemble technique was used to develop flame retardant coating on flexible and porous ramie fabrics through the electronegativity of ammonium polyphosphate (APP) and the electropositivity of polyethyleneimine (PEI). The content of the coating was measured to be 13.8 wt.%. The flame retardant ramie/polybenzoxazine composites were prepared with APP/PEI treated ramie fabrics as reinforcement. The self-assembly of the flame retardant coating on the fabric surface endowed the composites with self-extinguishing ability, and the treated composites can reach UL-94 V-0 rating during the vertical flame tests. Moreover, the interfacial adhesion of the treated composites has been enhanced. In consequence, its tensile and flexural properties have been improved and the treated composites show much higher strength and toughness compared with the untreated composites.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

As a kind of interesting natural cellulosic fiber, ramie has many advantages such as cheapness, low density and environmental friendliness. Especially, ramie has a higher tensile strength at 850–900 N/mm² than that of flax and jute, and the tensile strength of ramie is approximate to that of glass fiber [1]. It has been studied as the reinforcement for different polymers such as poly(lactic acid), polypropylene, epoxy and benzoxazine resin [2–5] etc. However, plant fibers would decompose rapidly at about 300–400 °C and the char at 600 °C is almost zero, indicating low thermostability [6]. Moreover, its limiting oxygen index (LOI) value is only about 19.0 [7], and once the fiber is ignited, the flame would spread rapidly. The low thermostability and the highly flammable nature limit the practical applications of ramie. The flame-retarding modifications of ramie fiber/fabric and their application in fiber-

reinforced composites have been studied widely [5,8–10]. Nevertheless, the adhesion between fibers and polymer matrices, which is crucial for the mechanical properties of the composites, is generally insufficient owing to the poor wettability and adsorbability towards polymers resulting from the hydrophilicity of ramie fibers. Thus, how to improve the thermal stability and flame retardancy of the natural fiber-reinforced composites without reducing the mechanical properties is one of the main focuses. Layer-by-layer (LBL) assembly technology [11], based on the alternating electrostatic attraction of oppositely charged polyelectrolytes, has attracted more and more interest to improve the flame retardancy of fibers in recent years [12–16]. Preparing flame retardant natural fiber enhanced composites without reducing the mechanical properties by LBL assembly technology is a meaningful subject.

Like traditional phenolic resins, polybenzoxazine has high heat resistance and good flame retardancy [17]. It also provides some superior properties, including high glass-transition temperature and modulus, low water absorption and dielectric constant, and near-zero shrinkage upon curing [18]. Hence, benzoxazine resins are generally used as matrix resin in high performance fiber-reinforced composites.

* Corresponding author. MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China.

E-mail address: zpfang@zju.edu.cn (Z. Fang).

This work aims to prepare ramie/polybenzoxazine resin laminates with both flame retardant properties and satisfactory mechanical properties. Ramie fabrics were pretreated with amino functional silane coupling agent firstly. Then LBL self-assemble technique was used to develop phosphorus-nitrogen intumescent flame-retardant coating on the flexible and porous ramie fabrics. The ramie/polybenzoxazine resin laminates were prepared using flame retardant treated ramie fabrics as reinforcement.

2. Experimental

2.1. Materials

Plain ramie fabrics (250 mm × 250 mm), purchased from Jiangxi Jingzhu Ramie Textile Co., Ltd. (China), were washed in deionized water for several times and dried under vacuum at 60 °C for 3 h before use. (3-aminopropyl) triethoxysilane (KH550) was purchased from Jiangsu Silane Coupling Agents Company (China). Benzoxazine (BZ, PX-PN 001) was provided by Shanghai Zhaoyu Chemical Materials Co., Ltd. (China). Polyethylenimine (PEI, branched, $M_w = 25,000$, $M_n = 10,000$) was acquired from Sigma–Aldrich. Ammonium polyphosphate (APP, JLS-APP104MF, P % = 28.0–30.0 wt.%) was received from Hangzhou JLS Flame Retardants Chemical Co., Ltd. (China). 4-toluenesulfonic acid methyl ester (98%) was obtained from Aladdin (China). Deionized water with a resistance of 18 M Ω was used for all the experiments. All other chemical agents were commercially available and used as received.

2.2. LBL self-assembly for the ramie fabrics

Ramie fabric was immersed in 0.5 wt.% KH550 solution for 3 h and dried at 70 °C to constant weight in blast drier. The pre-processed fabrics were alternately immersed in negatively (APP) and positively (PEI) charged baths. The fabrics were washed with deionized water to remove the excess ions after each immersion step. The immersion period for each layer was set at 10 min and the process was repeated until 20 bilayers were built on the fabric surface. The treated fabrics were kept at 70 °C in a blast drier to constant weight. The coating content was calculated to be 13.8 wt.%.

2.3. Preparation of ramie/polybenzoxazine laminates

4-Toluenesulfonic acid methyl ester was added in benzoxazine with the content of 5 wt.%. The mixture was homogeneously coated on the surfaces of pristine and treated fabrics. The benzoxazine coated ramie fabrics were pre-cured for 3 min at 130 °C. The prepreg was tiled layer-by-layer and pre-heated for 15 min at 130 °C under XLB 50-D Flat Vulcanizing Machine (Huzhou Xingli Plastic Machine Factory, China). After the pre-heated process, the pressure was kept at 6–8 MPa, and the prepreg was kept successively at 130 °C for another 15 min, and 140 °C, 150 °C, 160 °C, 170 °C for 30 min, respectively. The laminates were obtained after natural cooling to room temperature under pressure at 6–8 MPa. The resin content was kept at 30–35 wt.%. The laminate obtained by pristine ramie fabrics was marked as Laminate-1, and the laminate obtained by APP/PEI treated ramie fabrics was marked as Laminate-2. The resin content in the laminates is calculated by deducting the mass of the resin flowed out during the laminating process.

2.4. Measurements and characterizations

A Netzsch TG 209 F1 Thermogravimetric Analyzer (Germany) was used to study the thermal stability of the composites, with

5 mg of samples scanned from room temperature to 700 °C at a heating rate of 20 °C/min under nitrogen or air flow. The FT-IR spectra of the thermal decomposition products were recorded by a ThermoFisher Scientific Nicolet iS10 Infrared Spectrometer (USA). Microscale combustibility experiments were conducted on a Govmark MCC-2 Microscale Combustion Calorimeter (MCC). For this purpose, the samples (3–5 mg, in triplicate) were heated from 100 to 700 °C with a heating rate of 1 °C/sec in a mixed stream of oxygen (20 mL/min) and nitrogen (80 mL/min) flowing. The limiting oxygen index (LOI) values of the composites with the specimens cut to 120 mm × 6 mm × 3 mm were measured by JF-3 Oxygen Index Instrument (Chengde Dajia Instrument Co., Ltd., China) according to GB/T 2406.2-2009. Vertical flame tests were performed according to GB/T 2408-2008, using a vertical burning tester (CZF-3, Nanjing Jiangning Analytical Instrument Factory, China) with sample dimensions of 130 mm × 13 mm × 3 mm. Mechanical properties were tested on CMT4204 SANS electromechanical universal testing machine produced by MTS Industrial System (China) Co., Ltd. The tensile tests were according to GB/T 1040-92 with the dumbbell-shape specimen [19,20] dimensions of 150 mm × 20 mm × 4 mm and the flexural tests were according to GB/T 9341-2008 with the specimens of 80 mm × 15 mm × 4 mm. Five specimens for each test were measured to obtain the mechanical properties of the composites. The morphologies of the char residues after vertical burning tests and tensile fractured surfaces were investigated using Scanning Electron Microscopy (SEM, Hitachi S4800, operated at 4.0 kV) with a conductive gold layer on the surface.

3. Results and discussion

3.1. Characterization of coated ramie fabric

The surface morphologies of the ramie fabrics with or without flame retarding modification were imaged by SEM and the results are shown in Fig. 1a and b. It can be clearly seen that the surface of cellulose fibers for pristine ramie fabric is smooth and the fiber edge is distinct. While for the flame retardant modified ramie fabric, the sidewalls of cellulose fibers are coated with the coatings and the interspaces between fibers are also filled. The SEM micrographs show that a thick and dense coating is built on the flame retardant modified fabric.

The energy-dispersive X-ray (EDX) analyzer was used to confirm the element composition of ramie fabrics and the results are summarized in Fig. 1c and d. The EDX analysis obviously exhibits that P element is detected in the flame retardant coated ramie fabrics compared with the pristine one, indicating the presence of APP on the surface of the coated fabrics. The SEM-EDX results confirm the presence of the assembled coatings on the surface of the flame retardant modified ramie fabrics.

3.2. Flame retardancy of the composites

The LOI value of the ramie/benzoxazine resin laminate without flame retarding modification (Laminate-1) is 26.5%. As we know, ramie fabric is more flammable than benzoxazine resin and it is the limiting factor for the flame retardancy of composites. Therefore, the flame retardancy of the laminates can be improved with the flame retardant modified ramie fabric as reinforcement. Indeed, the LOI value of Laminate-2 (made by LBL assembled ramie fabrics) reaches up to 38.9%, showing a remarkably improved flame retardancy for Laminate-2.

The flame retardancy of the composites was also assessed by the vertical flame test and Fig. 2 presents the photographs of the laminate specimens after the test. During the test, dropping

Download English Version:

<https://daneshyari.com/en/article/820011>

Download Persian Version:

<https://daneshyari.com/article/820011>

[Daneshyari.com](https://daneshyari.com)