Surface & Coatings Technology 305 (2016) 184–191

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Carbon nanotube-filled intumescent multilayer nanocoating on cotton fabric for enhancing flame retardant property

Xin Ding [a], Fei Fang [b], Tianxiang Du [c], Kang Zheng [a], Lin Chen [a], Xingyou Tian [a], Xian Zhang [a,*]

[a] Institute of Applied Technology, Hefei institutes of Physical Science, Chinese Academy of Sciences, Hefei 230088, People's Republic of China
[b] Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[c] School of Material Science & Engineering, Shandong University, Jinan 250002, People's Republic of China

ARTICLE INFO

Article history:
Received 29 April 2016
Revised 29 July 2016
Accepted in revised form 15 August 2016
Available online 16 August 2016

Keywords:
LBL assembly
Cotton fabric
Flame retardant
Physical barrier effect
MWNTs

ABSTRACT

In this work, hybrid organic-inorganic film of polyhexamethylene guanidine phosphate (PHMGP)/one kind of industrially available fluorescent whitening agents (VBL)-MWNTs was built via layer-by-layer assembly technique to protect cotton fabric from fire. The UV–vis spectra and the TEM images confirm that VBL could improve the dispersibility of MWNTs in water. Attenuated total reflection Fourier transform infrared spectroscopy and scanning electron microscopy prove that the PHMGP and VBL-MWNTs are successfully incorporated into the cotton fabric. Compared to the control fabric, the thermal stability, flame retardancy and residue chars of the coated fabrics are improved with the bilayer number increasing, which were assessed by thermo-gravimetric analysis, microscale combustibility experiments, vertical and horizontal flammability tests, respectively. The enhancements are ascribed to both the physical barrier effect of MWNTs and the intumescent flame retardant of PHMGP and VBL.

1. Introduction

Owing to the essential characteristics of smooth handle, good breathability and hygroscopicity, cotton fabric has been widely applied in clothing, ornaments and industrial textiles, etc. [1]. However, its intrinsic nature of inflammability could easily result in fire, which will pose immediate dangers to human health and environmental quality [2]. In order to decrease the potential fire hazard of this textile, several effective flame retardant treatments, such as surface grafting [3,4], ultraviolet curing [5,6] and sol-gel methods [7,8], have been developed. Unfortunately, these techniques generally require complex and rigorous reaction conditions, which will limit their practical applications.

Recently, layer-by-layer (LBL) assembly technique has been considered as a promising method capable of endowing flame retardant performance to various polymer materials [9–11], because it involves simple operational process and water is chosen as the solvent. In addition, it is a versatile functional modification method by depositing various self-assembly materials on substrates. Since 2009, LBL technique was applied to flame retardant treatment on cotton fabric by alternately depositing opposite charged flame retardant materials [12]. To achieve efficient flame retardant performance, researchers have constructed several flame retardant coating systems such as organic intumescent coating [13], inorganic nanoparticles coating [14,15] and organic-inorganic hybrid coating [11,16]. There into, intumescent coating is considered as one of the most popular assembled systems, due to its excellent flame retardant effect by the powerful combination of acid source, carbon source and blowing agent, which can generate an insulating layer on the combustible materials to interrupt the combustion process and heat transmission at burning. The first intumescent coating on cotton was made with poly(allylamine) and poly(sodium phosphate) to prevent the ignition of cotton [13]. Subsequently, various intumescent ingredients, such as ammonium polyphosphate (APP) [17] phytic acid [18], deoxyribonucleic acid (DNA) [19], were introduced in LBL coating on fabric substrates. Very recently, our research group has first introduced polyhexamethylene guanidine phosphate (PHMGP) coupling with ammonium polyphosphate (APP) [20] or Potassium alginate [21] into an LBL assembly coating to achieve intumescent flame retardant performance. Meanwhile, the incorporation of PHMGP also endows cotton with excellent antimicrobial property by electrostatic linking with the anionic carboxylate groups on cotton. However, the fire resistant performance of PHMGP-based assembly coating is not as good as that of reference reported [17–19,22–25], and still need to be further improved.

To further improve flame retardant performance, some inorganic nanoparticles were introduced into the intumescent systems [26]. For example, thermally shielding montmorillonite (MMT) was cooperated with intumescing poly(allylamine hydrochloride)/poly(sodium phosphate) to construct a unique trilayer brick wall nanocoating on polyurethane foam [27]. This complex nanocoating can completely eliminate

* Corresponding author.
E-mail address: xzhang@issp.ac.cn (X. Zhang).

http://dx.doi.org/10.1016/j.surfcoat.2016.08.035
0257-8972/

melt dripping phenomenon and dramatically decrease the heat release. Additionally, for the ceramic nature, silica nanoparticles were exploited as a thermal-protective layer combined with intumescent assembly chitosan/APP to form complex silica/silica/chitosan/APP quadlayer nanocoating [28]. By synergistic effect, the nanocoating performs a high flame retardant effect on polyester-cotton blends. In consideration of limited variety of nanomaterials composed with intumescent system, much effort has been devoted to introduce more novel and effective flame retardants into intumescent LBL coating.

Remarkably, as a novel inorganic flame retardant, multi-wall carbon nanotubes (MWNTs) can cooperate with intumescent flame retardant to form body-fitted intumescent network structure, which can effectively control the thermal transmission and release of cellulose's gaseous product [29]. However, MWNTs tend to form spontaneous aggregation due to high length/diameter ratio, and the poor dispersibility of MWNTs in water strongly limits its application in LBL assembly coating. The most common approach to enabling its charged is hydrophilic modification, which involves complex physical and chemical reactions. Now, according to the report [30], VBL as one kind of fluorescent whitening agents (the molecular structure is shown in Fig. 1), could modify the solubility of MWNTs in water by non-covalent interaction, and what's more, the mixed VBL-MWNTs solution presents negatively charged, which could be used as an anionic material in LBL assembly coating [31]. Besides, VBL contains abundant nitrogen and sulfur elements, which is potential for acid source and blowing agent and beneficial to improve the flame retardant property of the cotton fabrics [32].

In this work, anionic VBL-MWNTs were coupled with cationic PHMGP to construct an effective organic-inorganic hybrid flame retardant nanocoating on cotton fabric via LBL assembly technique. The growth of nanocoating was monitored by Attenuated total reflection Fourier transform infrared (ATR-FTIR). The thermal stability and fire resistance of the samples was evaluated by thermo gravimetric analysis (TGA) and flammability test (Vertical flame tester and Horizontal flame tester).

2. Experimental

2.1. Materials

Cotton fabric with a density of 230 g/m^2 was acquired from Guangzhou Huacheng Textiles Industry Co. Ltd. PHMGP solution (n > 60, 25 wt%) was purchased from Shanghai Scunder Industry Co. Ltd. VBL was supplied kindly by Shanxi Kingsun Chemical Co. Ltd. MWNTs (diameter: 20–30 nm, length: 30–50 mm, >90 wt%) were acquired from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. All reagents were used as received and without further purification.

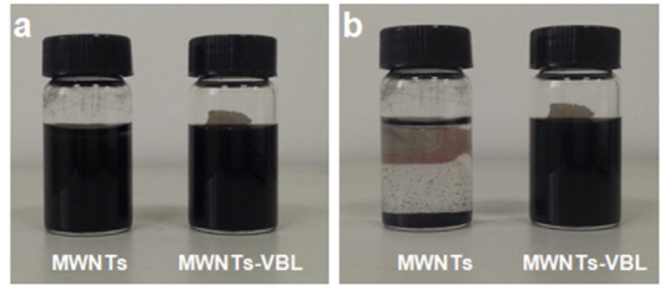

Fig. 2. Solubility of MWNTs and VBL-MWNTs with a concentration of 1 mg/ml, a and b represent the solution staying for 10 min and 1 week after 12 h sonication, respectively.

2.2. Layer-by-layer assembly

Prior to deposition, cotton fabrics were immersed in deionized water for 24 h, then rinsed several times and dried under vacuum at 60 °C. The original cationic PHMGP solution was diluted by deionized water to 0.1 wt% solution. The anionic VBL-MWNTs solution was prepared by adding 8 g VBL and 2 g MWNTs into 1000 ml deionized water, followed by magnetically stirred for 12 h, then filtered and washed repeatedly by deionized water. Finally, the concentration of MWNTs in anionic deposition solution is 0.1 wt%.

The typical LBL assembly process is shown in Fig. 1. Cotton fabric was alternately immersed into cationic (PHMGP) and anionic (VBL-MWNTs) solutions. After each immersion, cotton fabric was rinsed with deionized water for 30 s and dried in air at 60 °C for 30 min. One bilayer (BL) of PHMGP/VBL-MWNTs was obtained in the complete assembly cycle process. The immersion time for the first BL was set for 5 min to promote the uniform growth of the assembly coating on fabric. Subsequent immersion time was only 1 min, and repeated the same procedure until the desired BL numbers (5, 10, 20) were achieved.

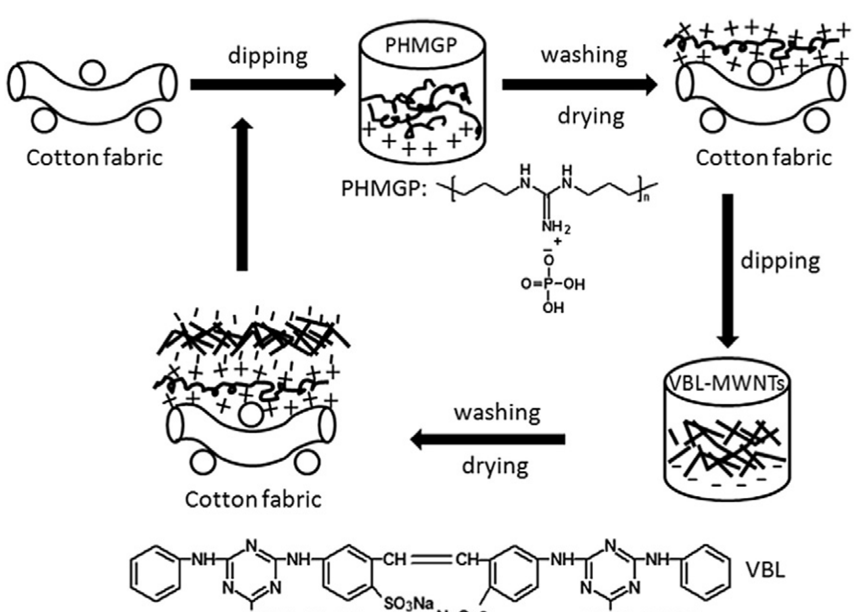

Fig. 1. Schematic illustration of PHMGP/VBL-MWNTs LBL assembly deposition on cotton fabric.