Flame-Retardant Fabric Systems Based on Electrospun Polyamide/Boric Acid Nanocomposite Fibers

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ABSTRACT: To examine the feasibility of developing flame-retardant-textile coated fabric systems with electrospun polyamide/boric acid nanocomposites, fiber webs coated on cotton substrates were developed to impart-fire retardant properties. The morphology of the polyamide/boric acid nanocomposite fibers was examined with scanning electron microscopy. The flame-retardant properties of coated fabric systems with different nanoparticle contents were assessed. The flame retardancy of the boric acid coated fabric systems was evaluated quantitatively with a flammability test apparatus fabricated on the basis of Consumer Product Safety Commission 16 Code of Federal Regulations part 1610 standard and also by thermogravimetric analysis. The 0.05 wt % boric acid nanocomposite fiber web coated on pure cotton fabric exhibited an increment in flame-spreading time of greater than 80%, and this indicated excellent fire protection. Also, the coated fabric systems with 0.05% boric acid nanocomposite fiber webs exhibited a distinct shift in the peak value in the thermal degradation profile and a 75% increase in char formation in the thermooxidative degradation profile, as indicated by the results of thermogravimetric analysis. The results show the feasibility of successfully imparting flame-retardant properties to cotton fabrics through the electrospinning of the polymer material with boric acid nanoparticles. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: nanocomposites; nanofiber; polyamides

INTRODUCTION

Fire hazards have a great socioeconomic impact on society. Textile materials that are readily combustible can serve as one of the ingredients in a fire and pose a serious threat to human life and property in fire accidents. To provide additional protection from fires and to increase escape time when a fire occurs, methods to enhance the flame retardancy of consumer goods have been developed. They generally either lower ignition susceptibility or lower flame spread once ignition has occurred. Flame-retardation mechanisms occur by the following:

1. Inert gas dilution, which produces large volumes of noncombustible gases on decomposition and, hence, dilute the oxygen supply to the flame or dilute the fuel concentration below the flammability limit.
2. Thermal quenching, which is the result of endothermic decomposition.
3. The formation of a protective liquid or char barrier, which limits the amount of polymer available to the flame front and/or acts as an insulating layer to reduce heat transfer from the flame to the polymer.
4. Inert fillers and minerals acting as thermal sinks to increase the heat capacity of the polymer or reduce its fuel content.
5. Flame-retardant dissociation into radical species that compete with chain-propagating steps in the combustion process.

Growing awareness of fire protection has increased the demand for protective clothing materials.[1] Cotton is a widely used textile material and, particularly, is the best textile to wear in summer. However, lightweight cotton fabrics commonly worn in hot weather do not provide sufficient protection even against low-energy flame. Thus, imparting fire protection to cotton fabrics would be very useful for potential applications, such as clothing in hot environments and firefighting. Consumer Product Safety Commission (CPSC) 16 Code of Federal Regulations (CFR) part 1610 provides methods of testing the flammability of clothing and textiles intended to be used for clothing by the classification of fabrics into three classes of flammability on the basis of their speed of burning. This minimum standard specifies that class 3 textiles, the most dangerously flammable fabrics, are unsuitable for use in clothing because of their rapid and intense burning.[2]

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There is a group of polymers, including polyolefins, cellulose, and others, that undergo complete combustion in a medium that is poorer in oxygen than atmospheric air. Only a few polymers designed for special applications can be accepted as inflammable or flame retardant because of their chemical composition and molecular structure. Polyamides are commonly used in textiles, automotives, carpeting, and sportswear because of their extreme durability and strength. The flame-retardant chemicals are aluminum trihydroxide, magnesium hydroxide, ammonium polyphosphate, red phosphorus, halogenated chlorine and bromine, boron, and antimony compounds.

Nanocomposites are a new class of organic/inorganic hybrid materials showing impressive performance for multifunctional applications. Nanocomposites are being investigated widely for their flame-retardant effects on polymers. This is a promising route for flame retardancy, especially if it could be used as a flame-retardant approach for fibrous materials also.

Electrospinning is a fiber-forming technique that uses electrostatic force to produce polymer fibers with diameters in the range of micrometers to nanometers. The major advantage of the electrospinning process is that it can produce polymer fibers with diameters on the nanometer scale through a simple process compared with traditional fiber-forming methods. Nonwoven mats of electrospun nanofibers provide exceptionally high ratios of surface area to volume with very small pores; this makes them attractive for a wide range of potential applications, which range from filter media to biomaterials, reinforced composites, sensors, and protective clothing. Chronakis[3] produced the fibers in the range 50–500 nm using the electrospinning process. Wang et al.[4] developed a process for the fabrication of continuous fibers with diameters ranging from several micrometers down to a few nanometers. A study on the formation of silica nanofibers with the sol–gel method and electrospinning technique was conducted by Choi and Lee.[5] Lim et al.[6] prepared cellulose-based nanofibers using the electrospinning process.

Several researchers have incorporated nanoparticles into electrospun fibers to impart flame retardancy. Shanmuganathan et al.[7] studied the flame retardancy of nylon 6 coated with silicate nanocomposites and found that the flame-spreading rate was reduced by 30–40%. Lee[8] examined the flame retardancy of polyurethane fabrics with a coating of zinc oxide nanocomposites and found that ultraviolet protection and antibacterial functions to cotton fabrics were increased. Muralidhara and Sreenivasan[9] studied the burning behavior of cotton, polyester, and polyester/cotton blended fabrics after they were treated with phosphorous. Pielichowski et al.[10] prepared modified polyurethanes, and their thermal behaviors were tested to ascertain the flammability. Mostashari and Baie[11] also conducted a flame-retardancy study of cotton fabrics with a coating of lithium bromide and antimony trioxide. Grazyna Janowska, examined the flammability of butadiene (BR), butadiene-acrylonitrile (NBR) and butadiene-styrene (SBR) polymers.[12] The mechanical properties of nylon-6 nano fibres had been conducted by Satyajeet et al and found that tensile strength had increased marginally.[13] Janowska[13] examined the flammability of butadiene rubber, butadiene–acrylonitrile, and butadiene–styrene polymers. Kim et al.[14] prepared nylon 6/organoclay nanocomposite filament fibers and tested their mechanical properties.

As we concluded on the basis of a literature review of flame-retardant nanocomposites, nanoparticles of boric acid have not been used to impart flame retardancy to cotton substrates, and hence, this is a novel approach for imparting flame retardancy to cotton fabric through nanocomposite fibers of boric acid. In addition, boric acid was selected in this study because of its high flame-retardancy effects and fewer environmental effects. Boric acid also releases chemically bound water to further reduce combustion. Futons, mattresses, upholstered furniture, insulation, and gypsum board are common consumer items that use boric acid as a flame retardant. Plastics, textiles, specialty coatings, and other industrial products also contain boric acid to strengthen their ability to withstand exposure to flames.

The objective of this study was to examine the feasibility of imparting flame-retarding functions to a textile material through the application of polyamide/boric acid nanoparticles with electrospinning. Boric acid nanoparticles were incorporated into polyamide fibers to impart flame-retarding functions. The improvement in flame retardancy after the cotton fabric was coated with a very thin layer of functional nanocomposite fibers was assessed. Different concentrations of boric acid nanoparticles were examined to optimize the flame-retarding functions.

EXPERIMENTAL

Materials

Commercial-grade polyamide (nylon 6) pellets was used as the polymer, and a formic acid and ethanol mixture in a ratio of 80 : 20 was used as the solvent. Pure (99.99%) boric acid (H_3BO_3) was purchased from M/s Merck Chemicals (Mumbai, India) with diameters in the micrometer range. Further, the particle size of the boric acid was reduced by a ball-milling process (Fritsch, Pulverisette, Germany), and the particle size ranged between 160 and 200 nm, as shown in Figure 1. Electrospinning solutions were prepared by dissolution of the polymer in a solvent mixture. A polymer solution concentration of 20 wt %

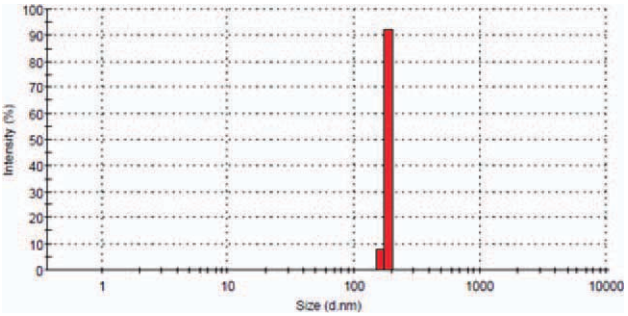

Figure 1 Particle distribution of boric acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polyamide was added to the solvent mixture. After complete dissolution, boric acid nanoparticles were added (0.05, 0.25, and 0.50 wt % polyamide) to the polymer solution under constant stirring. The resulting solution was then kept under constant agitation on a magnetic stirrer for 22 h. To form a coated fabric system, a 100% cotton, lightweight, plain-weave fabric was used as a substrate. The cotton fabric had a thickness of 0.40 mm and a weight of 81.6 g/m^2.

A scanning electron microscopy (SEM) micrograph of the boric acid nanoparticles is shown in Figure 2. The image shows that the particles were agglomerated in nature, and the particle sizes ranged from 160 to 210 nm throughout the matrix.

Electrospinning process

Electrospinning was conducted in a vertical electrospinning setup (Pico espin nano), which consisted of a syringe with its needle, a precisely controlled syringe pump, a high-voltage power supply capable of 0–50 kV, and a grounded collector. The polyamide/boric acid solution was loaded into the syringe, and a constant volumetric feed rate was maintained at a rate of 0.2–0.6 mL/h. A high voltage of 5–15 kV was applied to the needle. The needle diameter was kept at 0.2 mm for all concentrations of boric acid solution. As the applied voltage was increased, a droplet at the needle tip deformed into a conical shape. When the voltage was sufficiently high, an electrically charged jet was ejected from the tip. Fibers were laid down on the grounded collection plate, which was placed 80 mm from the tip and formed a nonwoven web. Boric acid nanocomposite fibers were electrospun from a formic acid–ethanol solvent mixture and deposited directly onto a cotton substrate to form a layered fabric system.

Fiber morphology

The morphology of the electrospun polyamide/boric acid nanocomposite fibers was examined with an SEM instrument (Hitachi SU1510, Japan) after the fibers were sputter-coated with Au. The SEM micrograph was taken at a magnification of 5000× and is shown in Figure 4(a) (shown later). The micrograph showed that the fiber diameter varied from 120 to 400 nm with a random orientation, and the fibers were aligned with one another. However, every strand of fiber maintained homogeneity in diameter throughout its length and, hence, was called a cylindrical fiber. The aspect ratio of the fiber varied from 100 to 500.

Flame-retardant behavior

The flame spread through the coated fabric systems was measured in accordance with CPSC Test Method CFR part 1610 standard for the flammability of clothing textiles. Measurements were carried out with the fabricated apparatus (Fig. 3) after dry cleaning and laundering. Four coated samples with the same concentration were tested to ensure precision of the flame-spreading time.

DTA/thermogravimetric analysis (TGA)

TGA was carried out to evaluate the flammability of the polymer-coated fabric samples. (TA Instruments Q600). The thermal stabilities of the samples were analyzed under the following test conditions:

- Maximum heating temperature = 700°C
- Time interval = 0.01 s

RESULTS AND DISCUSSION

Composite fiber morphology

On the basis of previous research, polyamide fibers were electrospun under various conditions to

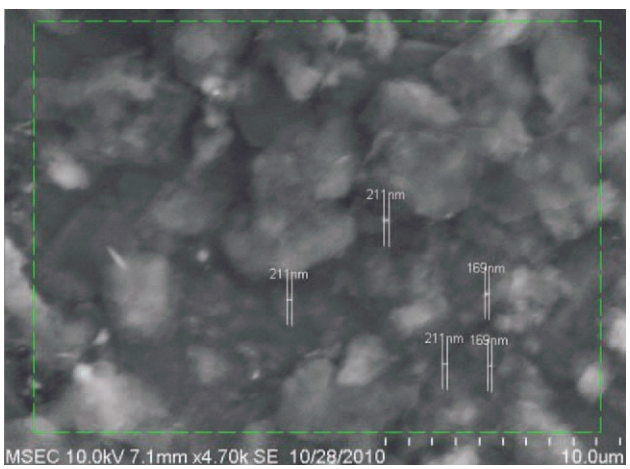

Figure 2 SEM image of boric acid nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

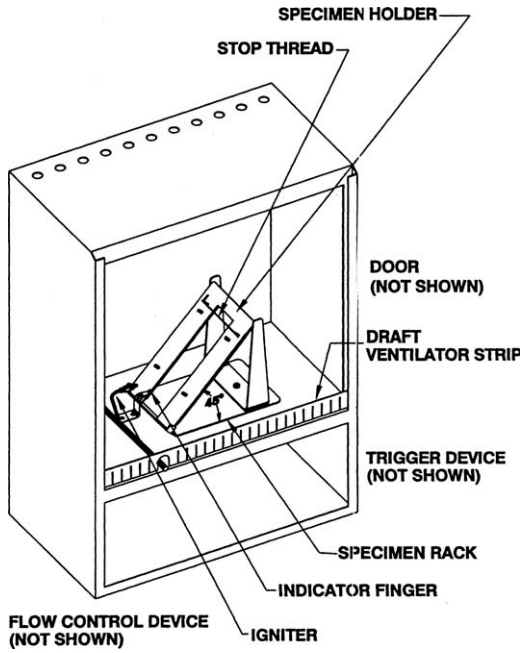

Figure 3 Flammability test apparatus.

determine the optimum spinning conditions; these conditions included the polyamide solution concentration, electric voltage, feed rate, collecting distance, and capillary diameter. Figure 4(a) shows an image of electrospun polyamide fibers obtained from a 20 wt % polyamide solution with a needle diameter of 0.2 mm at a feed rate of 0.5 mL/h, a voltage of 15 kV, and a collecting distance of 80 mm. These conditions yielded cylindrical fibers with diameters ranging from 120 to 400 nm. Figure 4(b–d) shows the electrospun polyamide/boric acid nanocomposite fibers obtained from 20 wt % polyamide solutions containing 0.05, 0.25, and 0.50 wt % boric acid nanoparticles, respectively. The fibers were fabricated with a needle diameter of 0.2 mm at a feed rate of 0.6 mL/h, a voltage of 10 kV, and a collecting distance of 70 mm. Boric acid particles are visible in Figure 4(b–d), and the diameter of the nanofibers ranged from 200 to 600 nm, as indicated in the figure.

Fire retardancy of the coated fabric systems

Coated fabric systems with electrospun boric acid nanocomposite fiber webs deposited on cotton

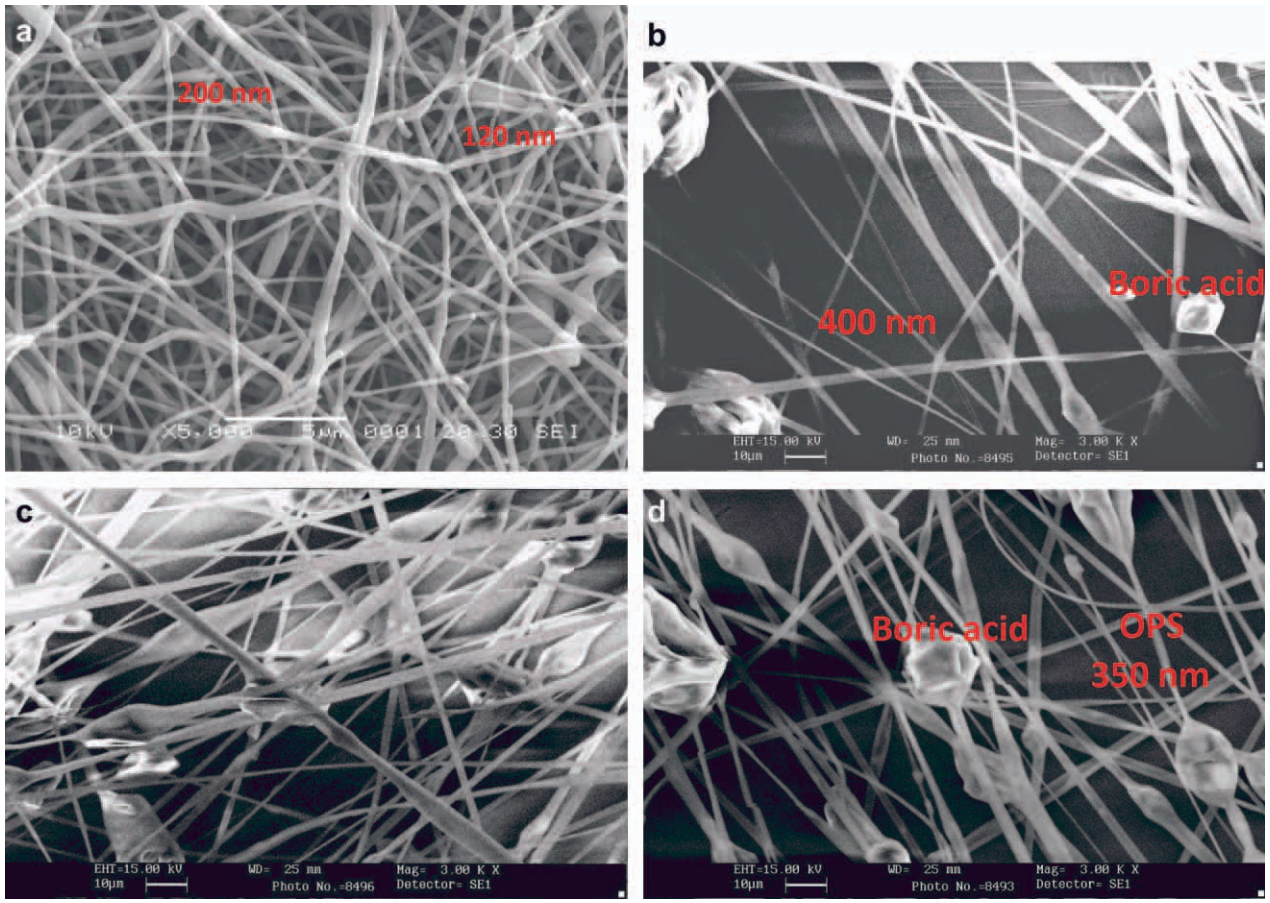

Figure 4 SEM images of (a) optimized polyamide solution (OPS), (b) OPS + 0.05 wt % boric acid, (c) OPS + 0.25 wt % boric acid, and (d) OPS + 0.50 wt % boric acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Flame Test Results of the Nanofiber-Coated (Electrospun) Fabrics

Sample	Flame-spreading time (s)
OPS	3.9
OPS + 0.05% boric acid	7.1
OPS + 0.25% boric acid	7.5
OPS + 0.50% boric acid	7.9

OPS = optimized polyamide solution.

substrates were fabricated for the development of a flame-retardant material via electrospinning. Boric acid nanoparticles at concentrations of 0.05, 0.25, and 0.50 wt % were added to 20 wt % polyamide solutions to impart flame retardancy. Under optimal spinning conditions, polyamide/boric acid nanocomposite fibers were electrospun directly onto the cotton substrate to form a coated fabric system. To examine the exact time of flame spread on the nanocomposite fiber web coated fabrics, four samples with the same weight percentage of boric acid were prepared and tested. The flame-spreading time of the untreated fabric was compared to those of the nanofiber coated fabrics treated with boric acid nanoparticles. This comparison confirmed that the fire-spreading time was increased considerably by the electrospun boric acid nanocomposite fiber webs. As mentioned earlier, the flame-spreading times were calculated according to the CPSC test method.

Table I clearly shows the increases in the flame-spreading times of the coated fabric systems with increasing concentration of boric acid nanoparticle content; these led to a corresponding increase in burn time. These also show that the flame-spreading time of the coated fabric sample with no boric acid content was 3.9 s; this indicated that it offered little protection against fire spread. However, a concentration of 0.05 wt % boric acid nanoparticles in the polyamide nanocomposite fiber web significantly improved the fire-retardant properties of the cotton substrate to 82%. Also, the spreading time continued

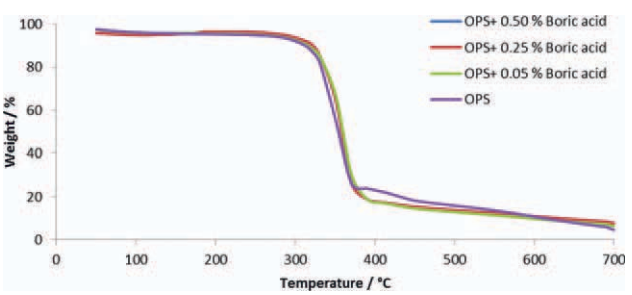

Figure 5 Weight loss versus temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

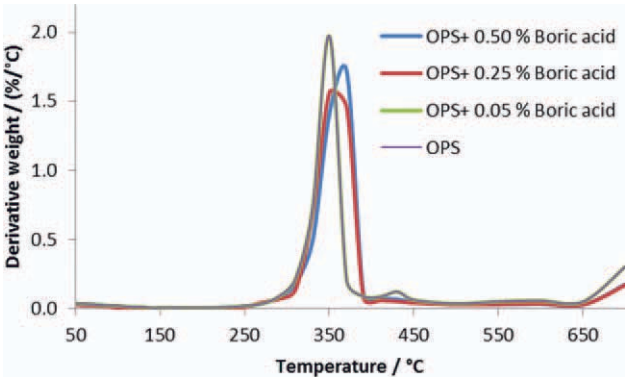

Figure 6 Effect of the derivative weight versus temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to increase gradually for an adverse addition of boric acid nanoparticles.

Thermal analysis of the coated samples

Thermogravimetric curves for the samples containing various percentages of boric acid are shown in Figures 5 and 6. The various temperatures and the char yield are shown in Figures 5 and 6 and are summarized for all of the samples in Table II. It was found that with an increase of boric acid in the polyamide solution, the unburned char yield increased from 4.6 to 7.8. Further, the initial temperature to ignite the fabric increased from 250 to 300°C with the addition of boric acid. The peak and end temperatures of ignition also changed considerably with the addition of boric acid.

During thermal degradation, the shift in the peak value and the initial temperature change confirmed that the addition of nanosized boric acid nanoparticles to the polyamide polymer increased the flame retardancy of the fabrics.

CONCLUSIONS

In this study, we examined the application of boric acid nanoparticles to cotton fabrics via electrospinning for the purpose of imparting flame-retardant properties. Fabric systems coated with electrospun polyamide/boric acid nanocomposite fiber webs

TABLE II
Observed Data from the Thermogravimetric Curves

Sample	Temperature			Unburned char (%)
	Initial (°C)	Peak (°C)	End (°C)	
OPS	250	350	375	4.610
OPS + 0.05% boric acid	290	360	380	6.388
OPS + 0.25% boric acid	290	360	390	7.644
OPS + 0.50% boric acid	300	360	390	7.801

OPS = optimized polyamide solution.

were developed by the electrospinning of a polyamide solution that contained different concentrations of boric acid nanoparticles onto a cotton substrate. A very low concentration of 0.05 wt % boric acid nanocomposite fiber webs coated onto the pure cotton fabric significantly increased the flame-spreading time, with an increase of greater than 80%. This indicated excellent fire protection. Also, the fabric systems coated with 0.5 wt % boric acid nanocomposite fiber webs exhibited a distinct shift in the peak value in the thermal degradation profile and a 38% increase in char formation in the thermooxidative degradation profile, as shown by the results of TGA. The results show that the successful imparting of flame-retardant functions to cotton fabrics was achievable through the electrospinning of the polymer material with boric acid nanoparticles.

It was demonstrated that functional nanostructures with tailor-made properties can be developed by the electrospinning of mixtures of polymers and functional materials, which is a relatively simple method in comparison to other conventional processes. This result opens the door for diverse possibilities in the preparation of new materials with desired functionalities in various fields and expands the potential applications of electrospun materials.

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