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Graft copolymerization coating of methacryloyloxyethyl diphenyl phosphate flame retardant onto silk surface

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ABSTRACT

This paper reports an efficient surface modification methodology to increase fire resistance properties of silk fabric performed by radio frequency (RF) plasma-induced graft copolymerization of vinyl phosphate ester as nanometer coating. Methacryloyloxyethyl diphenyl phosphate (MEDP) monomer was prepared and graft-copolymerized onto the surface of silk fabric by argon RF plasma at ambient temperature. Under optimum RF power (30 W), amounts of MEDP and *N*,*N* methylenebisacrylamide cross linking agent were varied to obtain optimum graft copolymerization conditions. Untreated and treated silk were characterized by attenuated total reflectance infrared (ATR-IR) spectroscopy to investigate their functional group characteristics. This showed a strong covalent attachment between the surface of silk and flame retardant material as the carbonyl functionality of the MEDP was clearly observed in the spectra. Scanning electron microscopic (SEM) analysis also showed grafted material as nanometer residue on silk surface. Thermogravimetric analysis (TGA) revealed that the decomposition of phosphorus compound which occurs at lower temperature than that of silk itself resulted in the formation of char which covers the surface of the fabrics. This protects the fabric surface from further burning, therefore, higher amounts of remaining materials were observed as char in all cases. Furthermore, the limiting oxygen index (LOI) increased from 25.5 for untreated to 28.0 (ca. 10%) for the MEDP-grafted silk. Higher amounts of char were also observed in the case of MEDP-treated silk. After 5 dry cleaning cycles, the LOI of the treated silk dropped only very slightly. Detailed analysis on structural and thermal properties as well as surface grafting efficiency are presented.

1. Introduction

Silk has long been considered a natural yet luxurious and glamorous textile. Silk is widely used not only as fabric for fashionable clothes but also for interior household decoration such as curtains, furniture upholstery. Although silk (possessing an LOI of about 25.5) is relatively fire resistive among natural fibers, a high percentage of household fatality caused by fire prompted several countries to require for certain types of textile, for instance, domestic furnishing fabrics, to possess resistance to fire [1–5]. Methods in textile finishing which introduce specific properties are available and a sustainable fire proof quality of silk is the primary concern of this paper. In the case of a textile made from natural fibers such as silk, mostly only a surface treatment can be applied. Research have been carried out in order to find efficient means to introduce suitable flame retarding materials onto natural fibers. Interests have grown in improving various properties of natural textiles including silk and various reviews have been reported [6–9].Organophosphorus-based materials have been shown to give a high level of flame retardancy, in general usage as well as applications for fabrics, with lower toxicity as compared to halogenated counterparts [10–13]. More importantly, in general only a low phosphorus content is required for an efficient level of flame retardancy. A phosphorus containing flame retardant can function in the condensed (polymer) phase, the gas phase, or concurrently in both phases [14,15]. Recent improvement of fire resistance of silk with organophosphorus reagents have been reported by using solution polymerization or grafting [16,17], atom transfer radical polymerization (ATRP) [13], or plasma-induced graft polymerization [10,11]. Some have reported multifunctional properties by surface modification as well [11,13]. Durability in flame retarding properties of textile is also problematic especially after exhaustive cycles of laundering. Therefore, the incorporation of a phosphorus-based flame retardant to silk fabric by strong chemical bond formation should lengthen

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flame retardancy of the fabric. Moreover, since this is a surface treatment, the bulk properties of the fiber or fabrics will not change and the desirable properties of the fiber be retained.

The objectives of this research are to improve flame retardant property of silk by directly incorporating a flame retarding agent to the fabrics. This could be carried out by the graft copolymerization technique of an organophosphorus flame retarding monomer onto the fabrics. The target monomer was 2-methacryloyloxyethyl diphenyl phosphate (MEDP).

2. Experimental

2.1. Materials and methods

Degummed silk fabrics were purchased from Jim Thompson, Co., Ltd, Thailand. Phenyl dichlorophosphate (PDCP), 2-hydroxyethylmethacrylate (HEMA), phenol, and *N*,*N*-methylenebisacrylamide (MBAA) were purchased from Sigma–Aldrich and were used as received. The Irgacure 819 (bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, BAPO) reaction initiator was kindly supplied by Ciba Specialty Chemicals (Thailand). Flash column chromatography was performed on Merck 230-400 mesh ASTM silica gel.

2.2. Synthesis and characterization of the flame retarding monomer

The methacryloyloxyethyl diphenyl phosphate (MEDP) flame retarding monomeric agent was synthesized *via* a reaction of HEMA, PDCP, and phenol according to the method described earlier with a slight modification [15].

2.3. Plasma-induced graft-copolymerization method

The radio frequency inductively coupled plasma (RF-ICP) system used in this work is represented schematically in Fig. 1. The employed plasma system consists of five main parts, (i) the RF generator, (ii) the impedance matching network, (iii) the vacuum chamber in which the process takes place, (iv) a pumping system and, (v) unit mass flow controllers to regulate the gas flow. The reactor is a cylindrical chamber of stainless steel, which has several ports for feeding gas and plasma diagnostic equipments. The top stainless steel plate has a circular opening of 20 cm in diameter where a quartz window is mounted to isolate the vacuum and still be able to let the RF field from a planar coil placed above the quartz plate to couple into the plasma. A flat coil (7 turns) with maximum diameter of 150 mm is mounted directly on top of the quartz window to induce the plasma at 13.56 MHz. The power source operates at 50 Ω and delivers up to 1000 W of power. The matching network is placed inside a perforated aluminum cylinder which acts as a Faraday cage protecting the electronic instruments from the effect of stray RF fields. The power used could be adjusted by a variable capacitance-matching network. Before the plasma was generated, the pressure in the chamber was reduced to 4×10^{-2} Torr by rotary vane pump. After the base pressure was reached, Ar gas is allowed to enter the chamber *via* mass flow controller and the operating pressure in this work is at 3.0×10^{-1} Torr with the power of 30 W in 3 min.

The incorporation of MEDP flame retarding monomer onto silk fabrics was performed according to a modified method by Tsafack [18,19]. Silk fabrics were cut into a $11 \times 14\,\text{cm}^2$ size. A chloroform solution containing the monomer at various concentrations (100–300 mg/mL), the cross linking agent MBAA (at 5%, 7% and 10% w/w), and 5% w/w of Irgacure 819 (BAPO) initiator were prepared. A piece of fabric was immersed in a particular solution and was subsequently air-dried at room temperature to remove the solvent. The fabric was then placed on the sample holder located at a distance of 3 cm away from the quartz plate. The chamber was evacuated to a base pressure of 4×10^{-2} Torr before argon gas was allowed into the chamber *via* a mass flow controller. The RF power is inductively coupled through the quartz window. The argon plasma was generated at RF power of 30 W. A pressure of 0.3 T and the treatment time of 3 min were used with argon flow rate of 30 sccm.

After the treatment, the fabrics were extracted in a soxhlet apparatus with acetone to remove all non-grafted materials off of the fabrics, and air-dried at room temperature for one day and kept in the desiccators for future analysis.

The degree of grafting was calculated as follows:

$$\text{Degree of grafting}(\%) = \left[\frac{(W_g - W_0)}{W_0}\right] 100$$

where W_0 is the weight of the original fabrics, and W_g is the weight of grafted fabrics.

2.4. Analysis and charactization of the untreated and the MEDP-grafted silk

Attentuated total reflectance infrared (ATR-IR) spectroscopy was employed to investigate functional group characteristics of the untreated and MEDP-grafted silk surface. The spectra were recorded on a Nicolet iS10 ATR-FTIR spectrometry in the 4000–600 cm^{-1} range. Functional groups present in the MEDP phosphorus containing flame retardant monomer, as well as untreated and treated fabrics with flame retardant monomers can be detected by this technique.

Scanning electron microscopic (SEM) analysis was performed on a JEOL model JSM-6480LV to compare the surface morphology of the untreated and the MEDP-grafted silk.

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo thermogravimetric analyzer model TGA/SDTA 851. This was carried out to measure continuous weight loss of untreated and treated fabrics. The method started of with placing the sample into an aluminum pan suspended from the arm of a microbalance situated in the furnace tube. The measurement was carried out under a nitrogen atmosphere at the heating rate of $10\,^{\circ}\text{C min}^{-1}$ and the temperature was scanned from 25–600 °C. Percent char residues were also determined.

Limiting oxygen index (LOI) measurements were carried out according to the ASTM D2863-06a standard to preliminary assess the flame retarding properties of the obtained materials.

3. Results and discussion

3.1. Synthesis and characterization of MEDP monomer

Flame retarding methacryloyloxyethyl diphenyl phosphate (MEDP) was synthesized from a reaction of HEMA, PDCP, and phenol in the presence of TEA in THF at 0 °C according to the method described earlier [12] and as shown in the scheme below. After workup and chromatographic purification, MEDP was obtained in 45% yield as a colorless clear liquid.

3.2. Plasma-induced graft-copolymerization of MEDP onto silk

A ratio frequency (RF) plasma-initiated graft-copolymerization of flame retarding monomer MEDP onto silk was achieved in the presence of Irgacure 819 (BAPO) initiator and MBAA cross linking agent. A low RF power of 30 W in conjunction with the use of the initiator facilitated the copolymerization really well. Preliminary results showed that 5% of BAPO initiator and 10% of MBAA cross linking agent were appropriate for the copolymerization. The MEDP