Polymer Degradation and Stability 99 (2014) 111–117

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Caseins and hydrophobins as novel green flame retardants for cotton fabrics

Jenny Alongi [a,*], Riccardo Andrea Carletto [b], Francesca Bosco [b], Federico Carosio [a], Alessandro Di Blasio [a], Fabio Cuttica [a], Vincenza Antonucci [c], Michele Giordano [c], Giulio Malucelli [a]

[a] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Viale Teresa Michel 5, 15121 Alessandria, Italy
[b] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[c] IMCB, Istituto per i Materiali Compositi e Biomedici, Consiglio Nazionale delle Ricerche, Piazzale Vincenzo Tecchio, 80-80125 Napoli, Italy

ARTICLE INFO

Article history:
Received 2 September 2013
Received in revised form
21 October 2013
Accepted 24 November 2013
Available online 4 December 2013

Keywords:
Cotton
Green flame retardants
Caseins
Hydrophobins
Flammability
Combustion behaviour

ABSTRACT

Despite the use of toxic and not environmentally-friendly chemicals, some proteins derived from animal or microbial sources have been investigated as novel green flame retardants for cotton fabrics. In particular, phosphorus- and sulphur-rich proteins (i.e. caseins and hydrophobins) have been homogeneously deposited on cotton fabrics starting from protein aqueous suspensions/solutions. These surface treatments, based on the use of species able to favour the dehydration of cellulose instead of its depolymerization, have strongly enhanced the production of a thermally stable carbonaceous structure (*char*), hence significantly enhancing the flame retardancy of the fabrics, as assessed by thermogravimetry and flammability tests.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

In the last four decades, both industrial and academic researchers have focused their efforts to design and develop chemicals able to prevent the combustion of polymers or at least to delay the spread of fire after ignition. The most efficient flame retardants (FRs) have been identified as those containing halogens and halogen-based derivatives, phosphorus, nitrogen, aluminium and magnesium, boron, antimony, molybdenum, or recently developed nanofillers [1]. Although very efficient and widely used, some molecules employed in the formulation of the halogen-based FRs such as pentabromodiphenyl ether, decabromodiphenyl ether (or oxide) and polychlorinated biphenyls, have proven to be persistent, bioaccumulative, and/or environmentally toxic for animals and humans [2]. Among the currently commercial available flame retardants, phosphorus-based compounds represent a suitable alternative to halogen-based FRs. Furthermore, as far as fabrics are concerned, the current attention is focused either on the production of effective halogen-free substituents for coatings and back-coated textiles or on the use of hydroxymethylphosphonium salts (Proban®) and N-methylol phosphonopropionamide derivatives (Pyrovatex®) for cellulosic textiles. A historical and comprehensive review of the progress achieved during the second half of the twentieth century has been recently published by Horrocks [3]. In the continuous seek for novel cost-effective and environmentally sustainable FRs, the use of biomacromolecules like proteins and nucleic acids may represent a worthy alternative to the traditional approaches. To this aim, our group has already demonstrated that whey protein isolate (WPI) and herring sperm DNA can be deposited on cotton fabrics, achieving a homogeneous coverage. The WPI treated fabrics have shown an increased total burning time, together with a reduced burning rate [4]; furthermore, DNA has conferred a flame suppressant character to the treated cotton fabrics [5,6]. These systems have demonstrated that biomacromolecules may represent a challenging, innovative and promising "green" finishing treatment for cellulosic substrates. In addition, their origin from renewable natural sources represents a further advantage from an environmental point of view. Among the proteins derived from animal or microbial sources, caseins and hydrophobins, which contain phosphorus and sulphur elements,

---

[*] Corresponding author. Tel.: +39 0131229337; fax: +39 0131229399.
E-mail address: jenny.alongi@polito.it (J. Alongi).

0141-3910/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymdegradstab.2013.11.016

respectively, exhibit a great potential as flame retardant systems for textiles.

Casein is the major milk protein (80%) and is obtained as a co-product during the production of skim milk; it is made up of many components, among which αs1-casein, αs2-casein, β-casein, and κ-casein are prevalent. αs-Caseins are the major casein proteins containing 8-10 seryl-phosphate groups, while β-casein contains about 5 phosphoserine residues [7]. Casein is the main product of dairy industry and, despite its relevance as a nutritional product, it has been used for a long time in non-food applications, particularly as a binding material for plastics, man-made fibres, coatings and dyes [8]. Quite recently, this protein has been exploited for preparing films in the presence of different crosslinking agents for tissue engineering applications [9].

Hydrophobins are produced by filamentous fungi and consist of a large family of small cysteine-rich proteins with a molecular mass of ca. 10 kDa [10]. Due to the cysteine distribution and the clustering of hydrophobic and hydrophilic aminoacid residues, two main classes have been identified: namely, class I (such as SC3 and EAS) and class II (HFBI and HFBII) [11,12]. Despite the low sequence similarity, the two classes have a characteristic pattern of eight cysteine residues forming four non-sequential disulphide bonds that stabilize the tertiary structure. Similarly to caseins, hydrophobins exhibit the ability to adhere spontaneously to several substrates by self-assembling at hydrophobic/hydrophilic interfaces [13,14]. Recently, they became attractive as special surfactants, and foaming agents, for protein immobilization in the food industries, in the biosensor field, in pharmaceutical formulations and in tissue engineering [14].

When cotton fabrics are ignited by a flame or exposed to a strong irradiative heat flux, degradation phenomena occur: more specifically, the degradation may involve the depolymerization of the glycosyl units to volatile species able to further fuel the process and/or the dehydration of such units to form a thermally stable carbonaceous structure, called *char* [15]. One possible strategy for confining the degradation process is to favour the dehydration instead of the depolymerization: this could be achieved by using species capable to interfere with the described degradation process.

In this context, both the phosphate groups of caseins and the disulphide bonds of hydrophobins could lead the cellulose pyrolysis towards the formation of char, instead of the production of combustible volatile species. By this way, they may prevent the combustion of cotton or at least delay the spread of fire after ignition.

In the present work, we have chosen to deposit caseins or hydrophobins on cotton fabrics starting from their aqueous suspensions/solutions. The resulting morphology of the coatings has been observed by Scanning Electron Microscopy (SEM) and correlated to the final properties exhibited by the protein-treated cotton fabrics. The thermal and thermo-oxidative stability of such materials, as well as their flame retardancy properties have been thoroughly investigated by thermogravimetric analysis (in nitrogen and air) and flammability tests, respectively.

2. Experimental part

2.1. Materials

Cotton (COT, 200 g/m^2) was purchased from Fratelli Ballesio S.r.l. (Torino, Italy).

Caseins (reagent grade) were purchased from Sigma–Aldrich (Italy); their approximate composition is as follows: 12–15 α-s_1, 3–4 α-s_2, 9–11 β and 2–4 κ (concentration expressed in g/l, as stated in the product information sheet).

Commercial hydrophobin solutions (H Star Protein B liquid®) were kindly supplied from BASF (Italy). The aqueous solution contains 5% hydrophobins (a mixture of class I and class II: the composition is unknown). Hereafter, the fabrics treated with caseins or with hydrophobins will be coded as COT_caseins and COT_hydrophobins, respectively.

2.2. Application of protein coatings to cotton fabrics

The caseins powder (5 wt.-%) was dissolved in distilled water under magnetic stirring (300 rpm); after that the suspension was heated at 80 °C in a thermostatic bath and the pH was corrected to 8.5. Before the application on cotton samples, the suspension of caseins was cooled to 30 °C. The treatment of cotton fabrics was carried out in a climatic chamber (30 °C and 30% R.H.): the suspension was spread on samples with a spatula, the excess was removed by gently pressing with a rotary drum and samples were dried to constant weight.

The commercial hydrophobin solution was employed for cotton samples treatment without further dilution. The treatment was carried out in a climatic chamber (30 °C and 30% moisture), the bath ratio (cotton/hydrophobin solution) was 1:26. The samples were dipped in the hydrophobin solution for 1 min, after that they were collected and gently pressed with a rotary drum in order to remove the suspension excess. Finally, the samples were dried to constant weight.

The total dry solids add-on on cotton samples (A, wt.-%) was determined by weighing each sample before (W_i) and after the impregnation with the solution and the subsequent thermal treatment (W_f), using a Gibertini balance ($\pm 10^{-4}$ g). The uptake of COT_caseins and COT_hydrophobins (approximately 20%) was calculated according to the following equation:

$$A = \frac{W_f - W_i}{W_i} 100$$

2.3. Characterization techniques

The chemical structure of the prepared samples and residues left after TG analyses was assessed by Attenuated Total Reflectance (ATR) spectroscopy. ATR spectra were recorded at room temperature in the range 4000–600 cm^{-1} (32 scans and 4 cm^{-1} resolution), using a Frontier FT-IR/FIR spectrophotometer, equipped with a diamond crystal (penetration depth: 1.66 μm).

The surface morphology of the treated samples was studied using an LEO-1450VP Scanning Electron Microscope (beam voltage: 5 kV); an X-ray probe (INCA Energy Oxford, Cu-Kα X-ray source, $k = 1.540562$ Å) was used to perform elemental analysis. Fabric pieces (5 × 5 mm^2) were cut and fixed to conductive adhesive tapes and gold-metallized.

The thermal and thermo-oxidative stability of the fabrics was evaluated by thermogravimetric (TG) analyses in nitrogen and in air, respectively, from 50 to 800 °C with a heating rate of 10 °C/min. A TAQ500 analyzer was used, placing the samples (ca. 10 mg) in open alumina pans, in inert or oxidative atmosphere (gas flow: 60 ml/min). The data collected were $T_{\text{onset}10\%}$ (temperature at 10% of weight loss), $T_{\max}$ (temperature at maximum rate of weight loss) and the residue at 600 °C.

Flammability tests in horizontal configuration were carried out by applying a 25 mm methane flame for 3 s on the short side of the specimen (50 × 100 mm^2). These tests were repeated 3 times for each formulation. Total burning time and rate after the flame applications as well as the final residue were measured.

The combustion behaviour of square fabric samples (50 × 50 mm^2) was investigated by cone calorimetry (Fire Testing Technology, FTT). The measurements were carried out under a 35 kW/m^2 irradiative heat flow in horizontal configuration,

Download English Version:

https://daneshyari.com/en/article/5202094

Download Persian Version:

https://daneshyari.com/article/5202094

Daneshyari.com