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COMPARATIVE EVALUATION EFFECTS OF THERMAL DEGRADATION, BURNING BEHAVIOR, AND INTUMESCENT CHAR FORMATION OF COTTON FABRICS COATED WITH ALKALINE AND ACIDIC CASEIN SOLUTIONS

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ABSTRACT

The present research work was aimed to investigate and study the effect of coatings of different concentrations and pH of aqueous casein solutions on thermo-oxidative properties, flame retardant performance, and intumescent char formation phenomenon of cotton fabrics. The flame retardant behavior of fabric samples was found to increase with an increase in the concentration of casein solutions in both alkaline and acidic pH conditions. The casein solution of acidic pH was found to yield more char residue than the alkaline casein solution, which evinced their better thermo-oxidative properties. The SEM micrographs of char residues also revealed the formation of stronger and coherent char with the presence of intumescence. Furthermore, the phenomenon of intumescence was largely observed in the case of cotton fabric samples coated with acidic casein solution.

KEYWORDS

Casein, cotton, thermos-oxidative stability, flame retardants, char residue.

INTRODUCTION

Cotton; a cellulosic fiber is one of the most important biopolymers in the world due to its availability in large quantities, good mechanical properties, biodegradability, and hydrophilicity. However, for further applications in transportation, automotive, protective garments, military, furniture upholstery, bed linen, and nightwear, it is necessary to improve the thermal degradation, ignition, and burning behavior of cotton based textile materials [1]. In recent years, intumescent flame retardant systems are considered the most performing solution available to withstand the fire threat. The term intumescence refers to the substances which can grow and increase in volume against the heat. Nowadays, the searches for environment-friendly flame retardants that ensure fire performances comparable to the conventional flame retardant compounds have gained significant importance [2]. This is because of the persistent, bioaccumulative, and environmentally toxic nature of some molecules employed in the formulation of traditional flame retardants. To overcome the limitations of intumescent flame retardant systems, searches for alternative environmentally-friendly intumescent materials containing all three components altogether (i.e. acid source, carbon source, and blowing agent) became important. In this context, the effectiveness of different biomacromolecules (whey proteins, caseins, hydrophobins, and deoxyribonucleic acid) has been assessed for textiles recently [3]. Among them, the application of casein as flame retardant could be an attractive solution for the valorization of the dairy industry by utilization of its by-product/waste. Casein is the major milk protein (80%) and is obtained as a co-product during the production of skim milk and cheese. The casein protein macromolecules are polyamino acids bearing several phosphate groups in their micellar structure [4]. While, the amino acids are ampholytes; i.e., they contain both the acidic and basic groups and exhibit amphoterism, i.e., amphoteric ionic behavior [5]. However, the amino acids are basic building blocks of proteins, hence, the amphoteric ionic behavior has also been considered one of the characteristics of proteins and attributed to the presence of amino ($–NH_2$; a basic group) and carboxyl (–COOH; an acidic group) groups in the side chains of the polypeptide chain. Contextually, to exploit this demeanor, casein was dissolved in water at alkaline and acidic pH conditions to prepare the solutions of different possible concentrations. Then these casein solutions were applied to cotton fabrics through the coating method to evaluate the comparative performance of flame retardant and char formation properties in conjunction with an intumescent phenomenon of casein coated cotton fabrics.

MATERIALS AND METHODS

Materials specifications: A bleached 100% cotton woven fabric having 145 g/m^2 areal density, purchased from Licolor, Czech Republic, was used in this research work. Bovine milk casein (technical grade) was received from Sigma-Aldrich, Czech Republic with approximate composition (g/l) of: α-s1 12-15, α-s2 3-4, β 9-11, and κ 2-4, as specified in the product information sheet. Sodium hydroxide (pearls, ≥99%) and hydrochloric acid (aqueous solution, 35%) of analytical grade were obtained from Lach-Ner, Czech Republic.

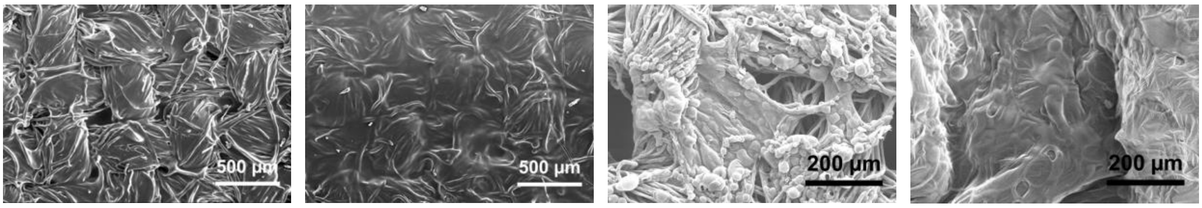
Preparation of casein solutions: The aqueous solutions of casein were prepared, under alkaline and acidic pH conditions, at three different concentrations such as 50, 100, 150 g/l. At first, the calculated quantity of casein powder was added to distilled water under continuous magnetic stirring/agitation (300 rpm) at room temperature for 10 min. Then, the temperature of the mixture was raised slowly and it was heated to 80°C in a thermostatic bath. Meanwhile, the pH was adjusted to 3 and 9 with a dropwise addition of 1M HCl and 1M NaOH respectively, under continuous magnetic stirring (600 rpm). The process was later stopped when the casein was completely dissolved in water.

Application of casein solutions on cotton fabrics: The coatings of different concentrations of casein solutions (prepared at alkaline and acidic pH conditions) were applied on cotton fabric by a coating method using the lab-scale bar/roller coating unit in a climatic chamber (30°C and 30% R.H.). After mounting the fabric sample over the frame, the casein solution was spread over the fabric sample with a spatula. While an excess of the solution was removed by pressing gently with a rotary bar. Casein solution coated fabric sample was then dried at 100°C in the lab-scale hot air dryer (stenter frame dyer) for uniform drying. The process was repeated to produce the replicas of coated cotton fabrics for each casein solution respectively. Then, the uptake (add-on/weight-gain) of casein for coated fabric samples was calculated according to the gravimetric principle from the oven-dry weight of fabric samples before and after coating.

Characterization and testing: Uncoated and casein coated cotton fabric samples were characterized and tested for ATR-FTIR, SEM, P content, TG analysis, flame retardancy, limiting oxygen index, radiant heat transmission, physiological comfort, mechanical properties, and washing durability.

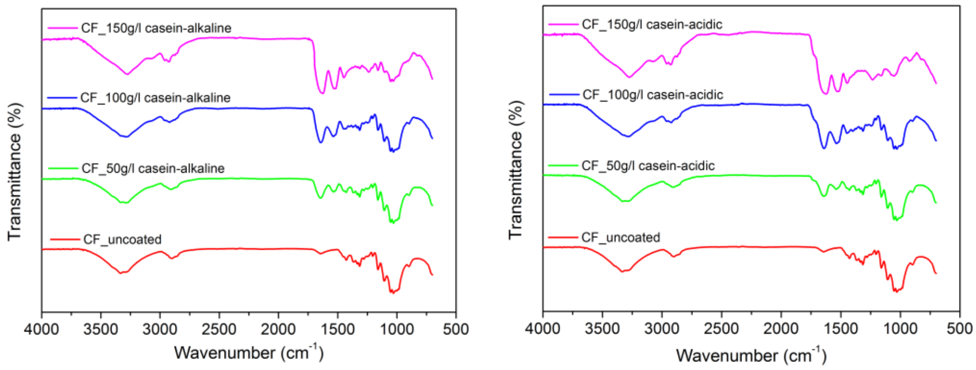
RESULTS AND DISCUSSION

Surface structure of casein coated cotton fabrics: The add-on (weight gain) was found to increase with an increase in casein concentration due to the maximum wetting and binding of individual fibers and yarns, and eventually seizing inside as well as depositing on the fabric structure after coating and drying as evidenced from the SEM images of casein coated cotton fabric samples (see Figure 1). Further, the solution of casein prepared under an acidic pH delivered a higher add-on of casein than that of the solution prepared under an alkaline pH, which was explained by the observed higher viscosity of casein solutions under the acidic pH conditions. The chemical structure, of uncoated and casein coated cotton fabrics' surfaces, was appraised by ATR-FTIR analysis, as shown in Figure 2. Apart from typical vibration modes of cotton cellulose, the two additional peaks, located at 1624 and 1528 cm^{-1}, were substantially attributed to the respective vibrations of amide I and amide II groups of casein [6]. Furthermore, the cotton fabrics coated with the acidic casein solutions exhibited one another band at 1710 cm^{-1}, which was manifestly endorsed for the protonation of casein protein macromolecules that were dissolved in water under acidic pH conditions.



(a) (b) (c) (d)

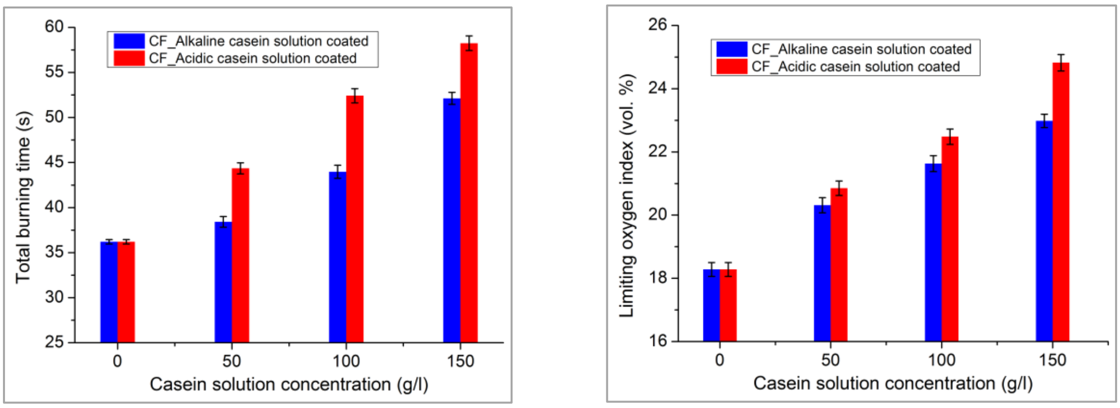
Figure 1. SEM images of; (a) CF_150g/l casein-alkaline (coated), (b) CF_150g/l casein-acidic (coated), (c) CF_150g/l casein-alkaline (char residues), (d) CF_150g/l casein-acidic (char residues).



(a) Alkaline casein coatings **(b) Acidic casein coatings**

Figure 2. ATR_FTIR spectra of uncoated and casein coated cotton fabrics.

Flame retardancy of casein coated cotton fabrics: As the limiting oxygen index (ISO 4589-2) and horizontal configuration flame spread (ASTM D4986) tests were employed, relating an actual fire scenario to test the flammability of textile fabrics during the prevalence of flame spread. The casein coating treatments were found to assist an increase in LOI values and total burning time while a decrease in burning rate and thus exhibited their ability for flame protection. Furthermore, the fabrics coated with acidic casein solutions burnt at a slower rate and resulted in stronger and higher char residues as compared to those coated with alkaline casein solutions. This behavior was also supported by the results of TGA. The char residues of fabrics coated with acidic casein solutions showed the formation of more expanded globular micrometric structures (i.e., global intumescence) in enlarged spaces, as revealed in Figure 1. These micrometric structures were phosphorus-rich bubbles that blow up during the combustion, exhibiting an intumescence phenomenon. The emergence of more bubbles, i.e., global intumescence, in the case of char residues of fabrics coated with acidic casein solutions, was ascribed to the release of ammonia [7], comparative in higher amounts, due to the protonation of casein protein macromolecules under acidic pH conditions.



(a) Total burning time **(b) Limiting oxygen index**

Figure 3. Flammability characteristics of uncoated and casein coated cotton fabrics.

Transmission of radiant heat through casein coated cotton fabrics: The effect of coatings, of different concentration casein solutions (both alkaline and acidic pH), for the thermal insulating characteristic of cotton fabrics as protection against the radiant heat, was assessed by exposing the cotton fabric samples to a radiant heat source at the specified incident heat flux density (Q_o). A drop in Q_c (transmitted heat flux density) and TFQ_o (heat transmission factor) values was observed for the casein coated cotton fabric samples as compared to that of uncoated cotton fabric, as given in Table 1. However, the reduction in Q_c and TFQ_o values was comparatively more in the case of cotton fabrics coated with acidic casein solutions than those coated with alkaline casein solutions.

Table 1. Radiant heat resistance parameters of uncoated and casein coated cotton fabrics.

Sample	Q_0 (kW/m^2)	$RHTI_{12}$ (sec)	$RHTI_{24}$ (sec)	$RHTI_{24}$-$RHTI_{12}$ (sec)	Q_c (kW/m^2)	TFQ_0 (%)
CF_uncoated	40	3.8±0.04	6.7±0.05	2.9±0.04	23.10±0.37	57.76±0.92
CF_50g/l casein-alkaline	40	4.3±0.05	7.5±0.08	3.2±0.04	20.66±0.28	51.66±0.70
CF_100g/l casein-alkaline	40	4.6±0.08	8.1±0.04	3.5±0.07	19.01±0.38	47.54±0.96
CF_150g/l casein-alkaline	40	4.9±0.07	8.7±0.09	3.8±0.05	17.33±0.25	43.32±0.61
CF_50g/l casein-acidic	40	4.4±0.05	7.7±0.08	3.3±0.04	20.04±0.26	50.10±0.66
CF_100g/l casein-acidic	40	4.8±0.04	8.4±0.05	3.6±0.05	18.18±0.27	45.45±0.68
CF_150g/ casein-acidic	40	5.4±0.08	9.5±0.04	4.1±0.09	16.39±0.36	40.98±0.89

CONCLUSION

The study presented the application of casein protein for an environment-friendly flame retardant finish of cotton fabrics. The effect of coatings of different concentrations and pH of aqueous casein solutions on intumescent flame retardant properties was investigated. The uncoated cotton fabric was found to undergo vigorous and rapid combustion without leaving any char. The samples coated with acidic casein solution produced a higher amount of residues than alkaline casein solution and it increased with an increase in casein concentration. From SEM microstructures, the residue of alkaline casein solution showed the formation of globular micrometric structures in localized spaces only. On the other hand, the uniform formation of more expanded globular micrometric structures (i.e. global intumescence) with the release of oily substances was observed for residues of acidic casein solutions.

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