Polymer Degradation and Stability 128 (2016) 237–244

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

The chemical bonding and fire performance of the nylon/cotton blend fabrics treated with a hydroxy-functional organophosphorus oligomer

Qin Chen [a, b], Charles Q. Yang [a, *], Tao Zhao [b]

[a] Department of Textiles, Merchandising and Interiors, The University of Georgia, Athens, GA 30602, USA
[b] College of Chemistry, Chemical Engineering & Biotechnology, Donghua University, Shanghai, 201620, China

ARTICLE INFO

Article history:
Received 10 November 2015
Received in revised form
23 February 2016
Accepted 12 March 2016
Available online 14 March 2016

Keywords:
Chemical bonding
Cotton
Cotton/nylon blends
Crosslinked polymeric networks
Flame retardant finishing
Flame retarded textiles
Military protective clothing
Nylon

ABSTRACT

Nylon/cotton blend fabrics have long been used in military protective clothing. Because fire risk has drastically increased in recent warfare, developing flame retarded military nylon/cotton fabrics becomes extremely important for protecting military personnel. It was previously discovered that a hydroxy-functional organophosphorus oligomer (HFPO) was bound to a nylon fabric in the presence of dimethyloldihydroxylethyleneurea (DMDHEU) as a bonding agent. In this research, the bonding mechanism of HFPO/DMDHEU on the nylon/cotton blend fabrics was investigated. HFPO was bound to the nylon/cotton blend fabrics by (1) forming HFPO/DMDHEU crosslinked polymeric networks on both nylon and cotton and (2) forming a DMDHEU bridge between cellulose and HFPO on cotton. The relative quantity of the HFPO/DMDHEU crosslinked networks and that of the DMDHEU-bridging formed on the treated blend fabrics was controlled by the HFPO-to-DMDHEU ratio. The HFPO/DMDHEU system was an effective and durable flame retarding treatment system for nylon/cotton military blend fabrics. The treated fabrics passed the fabric vertical burning test after 50 home laundering cycles. The fire performance and hydrolysis-resistance of different nylon/cotton blend fabrics treated with HFPO/DMDHEU was fully evaluated, and the performance data were analyzed in relation with the bonding mechanism.

1. Introduction

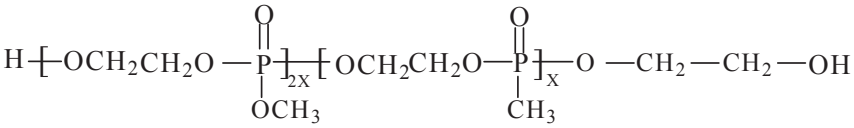
The 50/50 nylon66/cotton blend fabrics, known as “battle dress uniform” fabrics, have long been extensively used to make combat uniforms for the army and marine in the U.S. and in more than twenty other countries [1]. The major limitation for the nylon/cotton blends is their high flammability. Both nylon66 and cotton are flammable, and the melting of nylon in a blend caused by a fire represents additional risk for burn injuries. In conventional warfare, burn injuries caused 5–20% combat casualties [2,3]. A recent study on combat burns occurring in the wars of Iraq and Afghanistan has shown that burn resulted from explosions in combat have increased in frequency, size and injury severity [4].

Flame retarded fabrics can be used as barriers to protect military personnel from extremely high temperatures caused by fires and explosions in combat [5,6]. Therefore, developing flame retarded military protective clothing is extremely important for reducing the combat injury and mortality caused by fires. Flame retarded textile fibers used for protective clothing include cotton treated by flame retardants and inherently flame retardant fibers [5,7]. Cotton treated with a tetra(hydroxymethylol) phosphonium salt (THPX), urea and ammonia has exceedingly high laundering durability and is commercially available for use in industrial fire protection clothing [8]. However, low strength and low abrasion resistance of flame retardant cotton fabrics have made them not suitable for use in military protective clothing. Inherently flame retardant fibers, such as Nomex®, are currently used by tankers, aviators and submariners of U.S. military services [5,6,9]. However, high cost of Nomex® and similar fibers becomes prohibitive for their use by infantry.

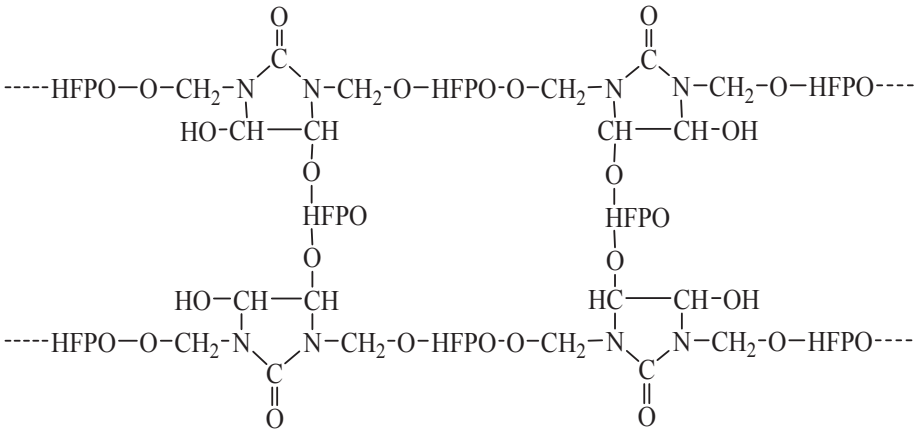
Blending cotton with nylon considerably improves affordability and serviceability of the fabrics used by infantry [9]. If the nylon/cotton blend fabrics can be treated with an effective flame retardant finishing system, those treated blends will become more affordable. The use of additives in the fiber-spinning stage has not been successful to produce flame retardant nylon fibers because adding additives often resulted in forming a separate phase, thus reducing the strength of melt-spun fibers [10]. Flame retardant finishing of nylon/cotton blends has only been successful when

* Corresponding author.
E-mail address: cyang@uga.edu (C.Q. Yang).

http://dx.doi.org/10.1016/j.polymdegradstab.2016.03.014
0141-3910/



Scheme 1. Structure of HFPO.



Scheme 2. The HFPO/DMDHEU crosslinked polymeric networks.

cotton constitutes the overwhelming majority of the blend such as the 88/12 cotton/nylon blend fabrics [6,11–13]. Patent literature indicates that the flame retardant finishing of cotton blends with as much as 35% nylon was possible by treatment with organophosphorus compounds [14]. As the relative quantity of nylon increases, the flame retardant finishing of the blend fabrics becomes more difficult. The flame retardant finishing of 50/50 nylon/cotton blend fabrics is still at the developmental stage today.

Previously, a durable flame retardant finishing system for cotton was developed based on a hydroxy-functional organophosphorus oligomer (HFPO) (Scheme 1) with dimethyloldihydroxyethyleneurea (DMDHEU) or trimethylolmelamine as bonding agents [15–17]. It was found that HFPO was bound to nylon66 when DMDHEU was used as a co-additive [18], and the 50/50 nylon66/cotton blend fabric thus treated achieved durable fire resistance [18,19]. The objective of this study was to investigate the bonding mechanism of HFPO/DMDHEU on the nylon66/cotton blend fabrics. The fire performance of the treated blend fabrics subjected to multiple launderings was also fully evaluated.

2. Experimental

2.1. Materials

The textile fabrics and chemicals used in this study are listed in Table 1, in which a ripstop fabric is a special light-weight woven fabric with interwoven reinforcement threads in a crosshatch pattern to achieve high resistance to tearing and ripping.

2.2. Fabric treatment and laundering procedures

A fabric specimen was first immersed in a solution containing HFPO, DMDHEU and the catalyst. The concentration of the catalyst was 2% of that of DMDHEU (based on 100% active reagent). The treated specimen was passed through a laboratory padder with two dips and two nips, dried at 90 °C for 3 min and finally cured in an oven at 165 °C for 2 min. All concentrations were based on weight (w/w, %). The wet pick-up of the 50/50 nylon66/cotton, 30/70 nylon6/cotton and 100% nylon66 was 75 ± 2%, 85 ± 2% and 60 ± 2%, respectively. After curing, the treated fabrics were subjected to a specified number of home laundering washing/drying cycles using a reference detergent ("AATCC Standard Detergent 1993") according to AATCC Test Method 124, and the water temperature of laundering was kept at ~46 °C.

2.3. Measurement of "percent fixation"

A fabric specimen was weighed (1) before treatment (W_0), (2) after treatment and before washing (W_1), and (3) after treatment and subsequent washing (W_2). All the specimens were weighed after being conditioned for 24 h. The fabric's percent fixation was calculated by Eq. (1). "Fixation %" represents the weight percentage of the applied (HFPO+DMDHEU) chemically bound to the fabric substrate with respect to their original prewash values.

$$\text{Fixation } \% = (W_2 - W_0)/(W_1 - W_0) \times 100\% \quad (1)$$

2.4. Quantitative analysis of phosphorus concentrations on the fabrics

Prior to analysis, textile fabric samples were first wet-digested using a procedure described by Feldman [20]. Five specimens taken from different areas on a fabric sample were cut and ground into a fine powder in a grinding mill, and the powder was fully mixed in the mill to improve homogeneity. The powder was kept under the standard condition for 24 h before analysis. Approximately 0.1 g of the powder sample was weighted with 4-significant figure precision. The weighed sample was then transferred to a 100 mL glass beaker.