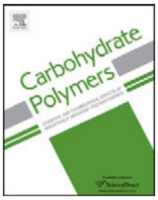
Carbohydrate Polymers 86 (2011) 922–927

Contents lists available at ScienceDirect

Carbohydrate Polymers

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



Cellulose/starch/HALS composite fibers extruded from an ionic liquid

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ARTICLE INFO

Article history:
Received 14 April 2011
Received in revised form 18 May 2011
Accepted 24 May 2011
Available online 1 June 2011

Keywords:
N-halamine
Hindered amine
Ionic liquid
Cellulose–starch
Composite fiber extrusion

ABSTRACT

The composite fibers of cellulose, starch, and a commercial hindered amine light stabilizer have been produced in various concentrations of the components using 1-butyl-3-methylimidazolium chloride as the spinning solvent in order to evaluate their physical properties. The composite fibers allowed desirable properties of both polymers to be retained, while producing fibers of reasonable physical properties. The halogenated hindered amine light stabilizer exhibited remarkably good resistance towards repeated ultraviolet light irradiation and halogenation cycles.

1. Introduction

Man made cellulose fiber is commercially produced by extrusion from different solvents. Because of the difficulty of dissolving cellulose, the processes that have been developed often use chemicals that pollute the air and the process water (Yamashiki et al., 1992). Molten organic salts, known as ionic liquids, are a class of solvents composed entirely of ions, and are particularly useful in dissolution of polar organic materials, even polymers like cellulose, that are difficult to dissolve (Hameed & Guo, 2010; Stevenson, Biswas, Jane, & Inglett, 2007; Swatloski et al., 2006; Swatloski, Spear, Holbrey, & Rogers, 2002). Ionic liquids are being intensively investigated because of their relatively environmentally friendly nature. It has been recently shown that cellulose fiber can be successfully extruded using bleached cotton dissolved in ionic liquids (Kilinc-Balci, Fan, Kocer, & Broughton, 2007; Lee, Broughton, Worley, & Huang, 2007). Beside cellulose, starch is also an abundant and biodegradable polysaccharide. It is well known that superabsorbent rayon (regenerated cellulose fiber) can be made with the inclusion of quantities of starch in the fiber (Lim, Yoon, & Kim, 2003). Recently, the preparation of composite materials from starch and cellulose in an ionic liquid was also demonstrated (Kadokawa, Murakami, Takegawa, & Kaneko, 2009). Having a common solvent for multiple polymeric materials leads to the consideration of making mixtures of the materials in order to form solids having properties of each component in the mixture.

Biocidal activity is one of the needed properties for the regenerated cellulose fibers being used in the healthcare industry (Hon, 1996). Quaternary ammonium salts (Ahmed, Hay, Bushell, Wardell, & Cavalli, 2008), metal ions (Nagar, 1989), and cyclic *N*-halamine compounds (Chen & Sun, 2005; Kocer, Worley, Broughton, & Huang, 2011; Makal, Wood, Ohman, & Wynne, 2006; Sun & Xu, 1998; Worley et al., 2005) are currently used in manufacturing numerous biocidal materials. Our research is concentrated on providing antimicrobial properties for various polymers, especially cellulosic substrates (Kocer, Worley, Broughton, Acevedo, & Huang, 2010; Ren, Kocer, Worley, Broughton, & Huang, 2009; Worley et al., 2005) using *N*-halamines. The use of an N–H functionality to allow halogenation of materials (Fig. 1) and production of regenerable biocidal materials is well known (Worley & Sun, 1996). The resulting broad-spectrum biocidal materials are effective against Gram-positive and Gram-negative bacteria, fungi, protozoa, and viruses. However, there remains one limitation of the *N*-halamine coatings: their stabilities under sunlight, UV irradiation (Kocer et al., 2010; Ren et al., 2008). An *N*-halamine is defined as a compound containing one or more nitrogen–halogen covalent bonds. Similar functional groups can be found in various commercial polymer structures in amine, amide or imide forms. Hindered amines are used as UV light stabilizers and have been investigated as halamine precursors for biocidal compositions (Barnes et al., 2007; Chen & Sun, 2005); however, their stability towards UV light after halogenation was not studied.

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doi:10.1016/j.carbpol.2011.05.046

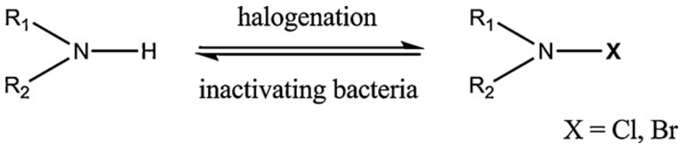

Fig. 1. Rechargeable *N*-halamines.

Table 1
The composition of the extruded solutions.

Sample	Cellulose (wt%)	Starch (wt%)	HALS (wt%)	Total solids in ionic liquid (wt%)
CH	96.00	0	4	4
CSH	47.50	47.50	5	5
CSSH	23.75	71.25	5	10

It has been discovered that a certain oligomeric hindered amine light stabilizer (herein referred to as HALS), as shown in Fig. 2, is soluble in a certain ionic liquid, 1-butyl-3-methylimidazolium chloride (IL), which is used for extrusion of polymers into fibers. In particular, the oligomeric hindered amine is less likely to be leached or washed from the fiber due to its high molecular size restricting its mobility. In this study composite fibers of cellulose, starch, and HALS have been produced in various concentrations of the components using IL as the spinning solvent in order to evaluate their physical properties. The UV light resistance of the halogenated composite fibers was examined.

2. Experimental

2.1. Materials

Bleached cotton cellulose, with a degree of polymerization of 1440, and a water soluble starch, Mallinckrodt Inc, were used. The cotton was ground to increase the rate of solution. The starch was dissolved in boiling water by stirring for 10 min. The solution was frozen and then dried in a freeze-dryer. The HALS (Chimassorb 2020®), having a number average molecular weight of 2900 g/mol, was provided by Ciba Chemical Co. The ionic liquid, 1-butyl-3-methylimidazolium chloride (IL), was purchased from Aldrich Chemical Co. and used without any further purification.

2.2. Preparation of cellulose/starch/HALS solutions

Bleached cotton, freeze dried starch, and HALS were dried at 70 °C for 12 h. Desired amounts of the compounds were added into the ionic liquid and then dissolved. For example, 1.9 g of cellulose and 0.4 g of HALS were added into 72 g of IL and stirred for 6 h at 2500 rpm with a speed-mixer (FlackTek Inc). Then 5.7 g of starch was added to the solution and stirred for an additional 14 h at 2500 rpm. The solution was then degassed under vacuum for 1.5 h at 100 °C to remove air bubbles, after which, it was poured into the extruder. All polymer solutions were clear and light amber in color indicating of a homogenous single phase solution. Undissolved material was detected via polarized light microscopy (Table 1).

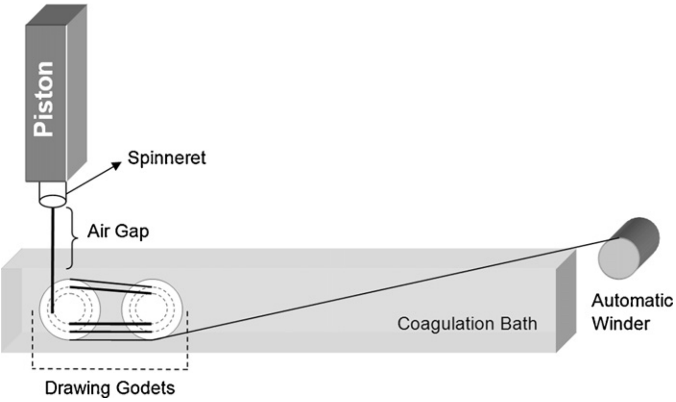

Fig. 3. Dry-jet wet spinning process.

2.3. Dry-jet wet spinning process

The dry-jet wet spinning equipment (Fig. 3) was composed of a piston pump (ISCO Series D), a Fischer Isotemp 3006 heating unit, a 500 μm diameter single-hole spinneret, a stepped godet with four levels (with diameters of 1.33, 2.65, 3.93, and 5.18 cm, for levels 1–4, respectively), a tap water coagulation bath, and a take-up winder. The solutions were extruded at 80 °C to inhibit the crystallization of IL in the extruder. The cellulose/starch/HALS-IL solutions had lower viscosity as compared to cellulose-IL solution, and could be extruded at lower temperatures (even at room temperature). However, the ionic liquid has the ability to crystallize at low temperatures. The solution was forced through a filter pack consisting of two screens having mesh size of 80 and 325 before the single hole spinneret. The air gap between the die and water was 5 cm and the length of coagulation route was around 150–210 cm according to used godet levels. The distance between two godets was 12.6 cm.

Extrusion conditions of the samples are summarized in Table 2. After the spinning process, the fibers were soaked in tap water at ambient temperature for 48 h to extract any residual ionic liquid and then dried at standard lab conditions for 24 h (21 °C, 65% relative humidity).

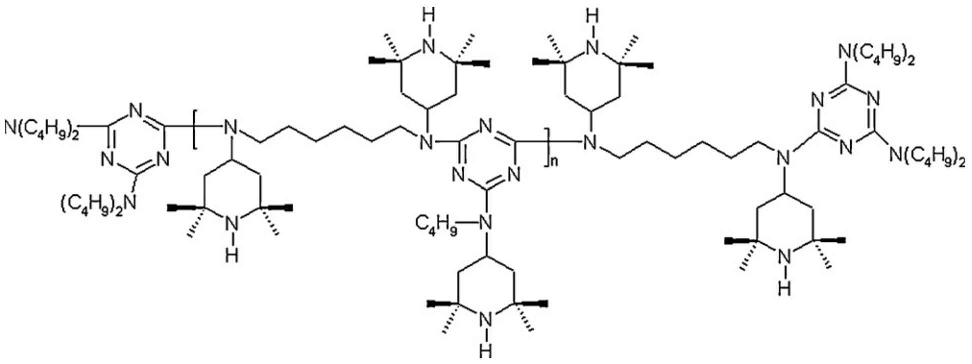

Fig. 2. Structure of the hindered amine light stabilizer (HALS).

Table 2
Mechanical properties of the composite fibers.

Sample	Throughput (mL/min)	Godet speed (rpm)	Draw ratio	Linear density (den)	Tenacity (g/den)	Strain at break (%)
CH	0.15	22	2.95	19.3 ± 1.4	2.9 ± 0.3	5.3 ± 1.6
CSH-1	0.20	9	2.95	38.4 ± 4.3	2.4 ± 0.3	8.8 ± 1.9
CSH-2	0.20	15	2.95	28.2 ± 2.8	2.3 ± 0.2	8.6 ± 1.9
CSH-3	0.15	15	2.95	20.6 ± 2.6	2.6 ± 0.4	8.4 ± 1.2
CSH-4	0.10	15	2.95	16.1 ± 1.7	2.5 ± 0.2	8.6 ± 1.3
CSSH-1	0.20	15	2.95	32.9 ± 2.5	1.6 ± 0.1	20.6 ± 3.2
CSSH-2	0.20	22	2.95	28.9 ± 1.7	1.7 ± 0.1	9.5 ± 1.3
CSSH-3	0.20	22	3.86	23.5 ± 1.2	1.8 ± 0.3	5.7 ± 1.3

2.4. Chlorination of the composite fibers

The fibers were soaked in a 10% solution of household bleach (pH buffered to 8.2 with sodium bicarbonate) at ambient temperature for 1 h, rinsed with distilled water, and dried at 45 °C for 1 h to remove any unbonded chlorine. For the determination of oxidative chlorine (Cl^+) content onto the fibers, a modified iodometric/thiosulfate titration procedure was employed (Kocer et al., 2010). The Cl^+% on the samples was calculated by the following formula

$$Cl^+\% = \frac{N \times V \times 35.45}{2W} \times 100 \qquad (1)$$

where Cl^+% is the weight percent of oxidative chlorine on the samples, N and V are the normality (equiv./L) and volume (L) of the titrant sodium thiosulfate, respectively, and W is the weight of the cotton sample in grams.

2.5. Property measurements

The IR data were obtained with a Nicolet 6700 FT-IR spectrometer using an ATR (Attenuated Total Reflectance) accessory. UV light stabilities of the bound chlorine and composite fibers were measured using an Accelerated Weathering Tester (The Q-panel Co., OH). The fiber linear density (denier) was measured on a vibroscope (Vibromat M) according to ASTM D1577 (07.01). The tensile properties of the fibers were investigated with an Instron 5565 Universal Tester according to ASTM D1774-94. 15 specimens were tested for each sample. The gauge length was 15 mm, and crosshead speed was 9 mm/min. The samples were conditioned at 21 °C and 65% relative humidity for 24 h before the tensile test.

3. Results and discussion

Bleached cotton has a limited solubility in IL of around 4.5 wt%. The water soluble starch was more soluble in IL, and allowed dissolving higher amounts of polymer solids (around 10 wt%) in the fiber extrusion solution. The composite fibers were successfully extruded into the coagulation bath, and the solution filters were very clean after the extrusion process confirming the lack of undissolved materials in the extrusion solutions. The composite fibers, CH, CSH, and CSSH, can be chlorinated up to chlorine loadings of around 0.33, 0.46, and 0.52% Cl^+, whereas the theoretical values for complete chlorination of all N–H sites were 0.50, 0.63, and 0.63%, respectively, showing that HALS is well trapped in the cellulose/starch mixture. Likewise, we expect that a water-soluble-starch/cellulose composite fiber would not allow the starch to dissolve out of the fiber, particularly since the starch is not soluble in cold water. The composite fibers having chlorine loadings between 0.3 and 0.5 would be expected to render good biocidal capability since this level of oxidative chlorine generally is antibacterial (Barnes et al., 2007; Ren et al., 2009; Worley et al., 2005), although the biocidal performances were not experimentally evaluated in this study.

The FTIR spectra of the composite fibers are shown in Fig. 4. Composite fibers CH, CSH, and CSSH have an additional band at around 1533 cm^{-1} which can be assigned to the C=N stretching vibration in the triazine ring of HALS. Due to the chemical similarities between starch (α-1,4-D-glucopyranose) and cellulose (β-1,4-D-glucopyranose), the FTIR spectra of the composite fibers were very complicated. Absorbed water in the amorphous region of the polysaccharides could be identified by a broad band at 1640 cm^{-1} (Kizil, Irudayaraj, & Seetharaman, 2002; Santha, Sudha, Vijaykumari, Nayar, & Moorthy, 1990). As the crystallinity of polysaccharides reduces, this band becomes stronger; therefore, less crystalline composite fibers and starch have more intense peaks around 1640 cm^{-1} as compared to bleached cotton. There are some slight differences in the region between 1100 cm^{-1} and 900 cm^{-1}. Bleached cotton exhibits several bands in this region, and this can be explained by the restricted conformation of the glycosidic bonds (C_1–O–C_4) in cellulose due to higher crystallinity compared to the composite fibers and starch (Caprona, Roberta, Colonna, Broglyb, & Planchot, 2007). X-ray diffraction patterns of the composite fibers (see Supporting information) also indicated the reduced crystallinity in the composite fibers compared to bleached cotton.

After the coagulation bath, the initial fiber diameters of the starch-containing composite fibers (CSH and CSSH) were surprisingly higher as compared to CH fiber. The initial diameter of CSSH was around 230 μm and reduced to 60 μm after water desorption. The initial water absorption of the CSSH was around 1500 wt% after the coagulation bath; however, its water absorbency character was reduced after drying. Water absorption of CSSH fibers after drying was around 135 wt% (see Supporting information). While the water absorption was high, it was not in the range of commercial superabsorbent polymers. Fig. 5 shows the SEM micrographs of the surface of CH and CSSH fibers after drying. The fibers have non-uniform fiber surface and diameter. There is a crenulated fiber surface for CH as is commonly seen for commercial regenerated cellulose fibers. The cross section of the composite fibers was ribbon-like in shape, and starch-containing fibers were more flat compared to CH fibers. Interestingly, no fibrillation on the surface was observed for the fibers, as is commonly seen for regenerated cellulose fibers.

The results in Table 2 show the mechanical properties of the composite fibers denier, tenacity, and strain at break. Starch-containing composite fibers exhibited lower tenacity and higher elongation at break compared to cellulose composite fiber CH. The effects of the extrusion parameters on the physical properties of composite fibers were also studied. For CSH-1 and CSH-2, increasing godet speed did not change any physical property, either tenacity or strain at break, but reduced the linear density (den) as expected. Reducing extruder throughput (0.20–0.10 mL/min), CSH-2 to CSH-4, reduced the linear density and again did not show any significant effect on physical properties. Composite CSH fibers have tenacity around 2.4 g/den and strain at break around 8.5% which are sufficient for many textile applications and compare favorably with rayon at 2.05 g/den and lyocell at 3.59 g/den (Kreze, Strnad, Stana-Kleinschek, & Ribitsch, 2001). CSSH-1 and CSH-2 samples

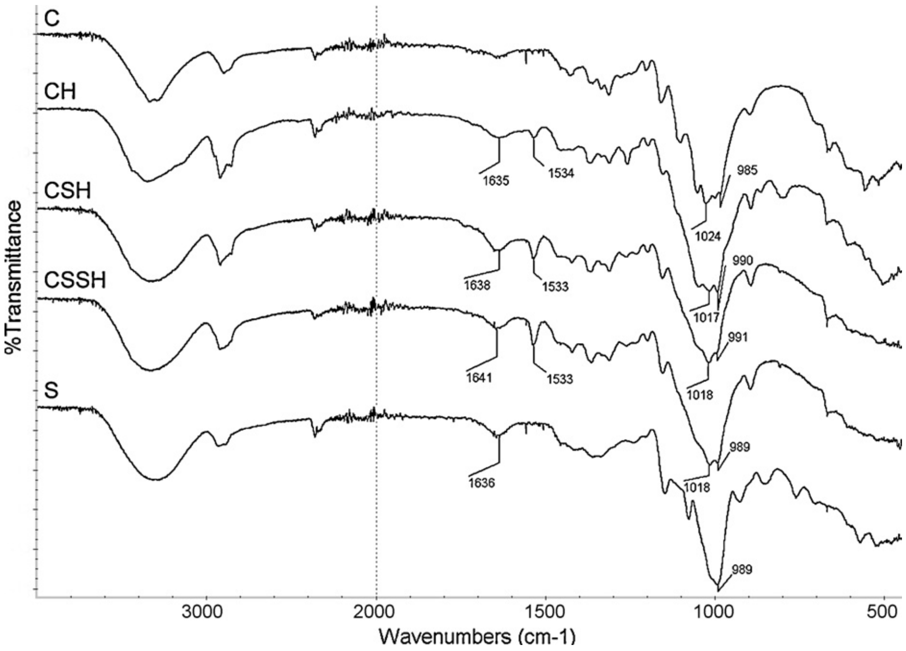

Fig. 4. FTIR spectra of bleached cotton (C), CH, CSH, CSSH, and water soluble starch (S).

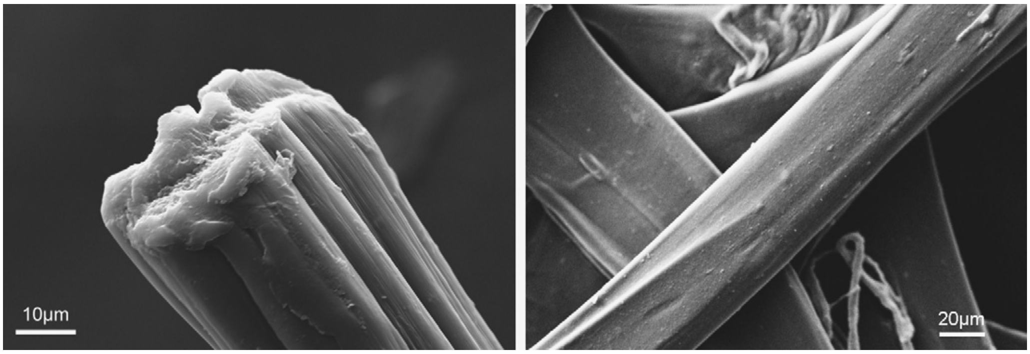

Fig. 5. SEM micrographs of CH (A) and CSSH (B).

have equivalent extrusion parameters allowing comparisons to be made between two different samples. CSSH-1 has a tenacity value around 1.6 g/den, while CSH-2 has 2.3 g/den indicating the tenacity of composite fibers was reduced by increasing the starch component amount.

The physical properties of the composite fibers were sufficient in the dry state for many textile processing and projected end-use applications. Fig. 6 shows the tenacity of CSH in dry and wet states. The tenacity of the fiber reduced in the wet state, as generally seen in commercial regenerated cellulose fibers. However, CSH fibers have good mechanical properties in the wet state when compared with other commercial regenerated cellulose fibers such as viscose rayon and modal which have tenacity values around 1.16 g/den and 1.72 g/den in wet state (Kreze et al., 2001).

One of the most promising characteristics of the composite fibers is the UV light stability of HALS. It should be noted that the stability of bonded chlorine and the structure itself should be considered separately. The bound chlorine on composite fibers was not very stable toward UV light exposure, as summarized in Table 3, similar to other *N*-halamines (Kocer et al., 2010; Ren et al., 2008).

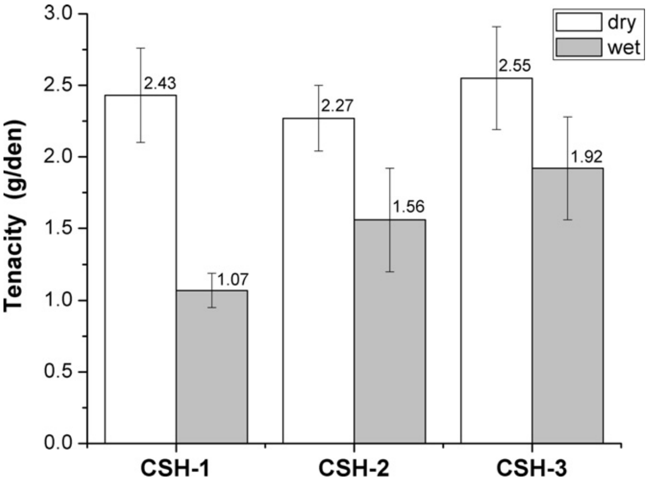

Fig. 6. Tenacity of CSH fibers in dry and wet states.

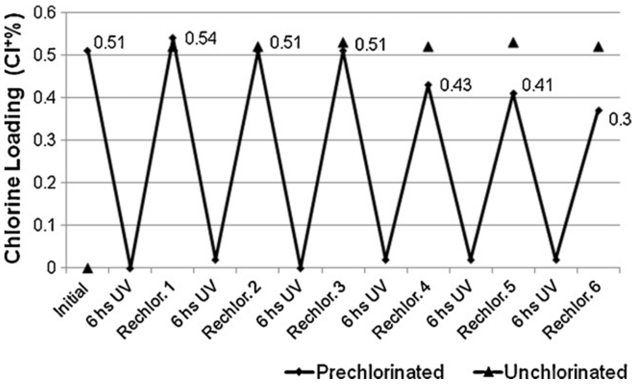

Fig. 7. Stability of bound chlorine on CSSH fibers toward UVA light exposure (Cl^+% remaining).

The chlorinated composite fibers (CSSH-Cl) lost all bonded chlorine within 6 h of UVA exposure. However, the chlorine loadings of rechlorinated fibers after the UV light exposure were remarkably high.

Since the stability of *N*-halamine precursors is higher compared to *N*-halamines, a stability test including several rechlorination cycles and exposure to UV light was employed to give more information about the stability of the chlorinated HALS structure. The stability toward UV light of CSSH-1 composite fibers is presented in Fig. 7. Two sets of samples were tested – prechlorinated samples were exposed to UV light and titrated and then rechlorinated and titrated – unchlorinated samples were only chlorinated and titrated after exposure to UV light. The prechlorinated samples were rechlorinated after each UV light exposure cycle. The unchlorinated samples were very stable towards UV light; they did not show any decomposition according to chlorine loadings. The prechlorinated samples lost all bound chlorine within 6 h in every cycle. Chlorine loadings after rechlorination for the first three cycles were around the initial chlorine loading; however, they started to decrease gradually after the third cycle. Although the chlorine loadings did decrease, the loss after 6 cycles was around 27%, which is remarkably good compared to previous cyclic *N*-halamines (Ren et al., 2008).

4. Conclusions

A method for the transformation of a commercial polymer (HALS) into durable and regenerable antimicrobial polymeric materials has been described. The method provides practical and environment friendly production of cellulose based fibers having durable and regenerable antimicrobial property with improved UVA light stability. The ability to form composite fibers having reasonable strength from an ionic liquid spinning solvent has been demonstrated, and the effects noted with changes in extrusion and drawing conditions followed expected trends. The composite fibers allowed desirable properties of both polymers to be retained, while producing fibers of reasonable physical properties. Use of starch allowed dissolving higher solid content (wt%) in the ionic liquid. The composite fibers might find applications in hospital clothing, hygienic products, and household products.

Table 3
Stability of bound chlorine on CSSH-Cl fibers toward UV light exposure (Cl^+% remaining).

Time	$[Cl^+]$%	Rechlorination
0	0.52	
1 h	0.26	
2 h	0.19	
3 h	0.08	
4 h	0.03	0.54
6 h	0.01	0.53
1 d	0	0.52
15 d	0	0.53
30 d	0	0.52
45 d	0	0.52

Acknowledgments

This work was supported by National Textile Center through Project Grant C05-AE05 and US Air Force through Grant FA8650-07-1-5908.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2011.05.046.

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