Multifunctional coatings on fabrics by application of a low-pressure plasma process

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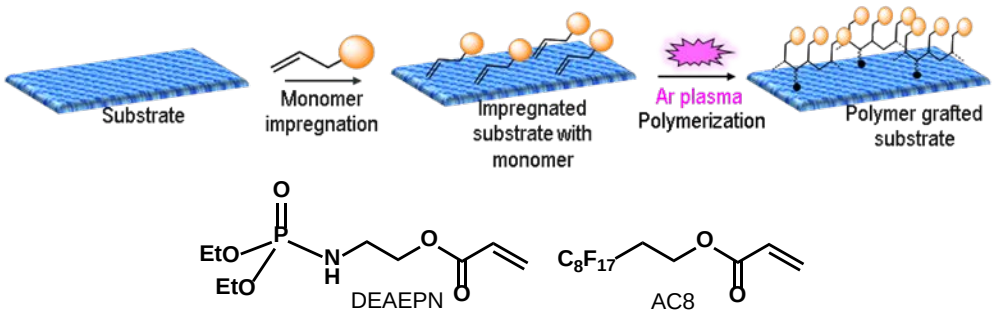
Abstract

Nowadays, there is an increased demand to produce highly-performant fabrics combining multiple properties such as flame retardancy, hydrophilicity/hydrophobicity, antibacterial, UV resistance, etc. In order to produce a wash-resistant-flame-retardant-water-repellent-dyed multifunctional coating on natural fabrics like cotton and silk, various protocols involving the Ar plasma-induced graft-polymerization (PIGP) process of suitable monomers were investigated. The burning behaviour of treated fabrics is discussed using LOI measurements. The water repellent behaviour is evaluated by means of Schmerber pressures ($P_{Sch.}$) and dyeing properties by spectrophotometric measurements. The wash-resistance of the coatings was tested by using an accelerated laundry method. The obtained results have shown that for each protocol, the flame retardant monomer is compatible with a water repellent or a dyeing treatment.

1. Introduction

The challenge to confer wash-resistant flame retardant properties to textiles remains[1]. This is even more relevant when textiles of natural origin like cotton or silk fabrics are concerned. Indeed, the flame retardant finishing could only be applied by surface modification technologies. Among all of them, the plasma induced graft polymerization (PIGP) process we have developed and refined in our laboratory over the last years has proven to be an efficient tool for that purpose[2-6]. The substrate is immersed into a solution containing a monomer (acryloyl- or methacryloyl derivative) bearing the requested property. Under Ar plasma the monomer is simultaneously grafted and polymerized onto the surface of the substrate (scheme 1). The thin homogeneous layer of grafted polymer onto the surface exhibit excellent wash-fastness properties thanks to the covalent bonding created during this process between the polymeric layer and the substrate. By using this process, we were already able to confer excellent wash-resistant-flame retardant behaviour to cotton and silk[6] fabrics without altering their bulk properties. The flame retardant monomer used for this application which has been synthesized in our laboratory is the diethyl(acryloyloxyethyl)phosphoramidate (DEAEPN) (scheme 1). However it was of interest to know whether this new property conferred to cellulosic fabrics allows further treatment like a water repellent treatment or a dyeing process. Therefore the FR-cotton fabrics obtained by this process where submitted either to a water repellent treatment or a dyeing process. In both cases, the added functionality has been evaluated by the relevant technique and the flammability of the bi-functional fabric has been further assessed as well as the durability of the new finishing.



Scheme 1: PIGP process and flame retardant (DEAEPN) and water repellent (AC8) monomers used in this study

2. Experimental

The textiles (twill woven bleached cotton 210 g/m^2) were kindly supplied by EMPA Testmaterialien AG (Switzerland) or obtained from TESTEX Prüfmaterialien (Germany). The synthesis of the monomer diethyl(acryloyloxyethyl)phosphoramidate (DEAEPN) is depicted elsewhere[2-6]. The photoinitiator Irgacure 819 was obtained from BASF AG Schweiz. EGDA (ethyleneglycoldiacrylate) and 1,1,2,2, tetrahydroperfluorodecylacrylate (AC8) were purchased from Aldrich and used as received. Solvents, chemicals and textile auxiliaries were obtained from the usual laboratory suppliers (Fluka, Baker and Merck) and were purified prior to use, if necessary, by standard methods. Remazol brilliant Blue R was used (Dyestar Textilfarben GmbH&CO) for reactive dyeing experiments.

PIGP on cotton textiles: The PIGP process which takes place in a Europlasma DC300PC MW-generator (2.46 GHz) is described elsewhere[2-4]. The samples (50 mm x 100 mm) were weighed and then impregnated at RT with 0.7 ml of an ethanol solution containing up to 30% on the weight of the fabric (w_{of}) of monomer, 10% on the weight of the monomer (w_{om}) of cross-linking agent (EGDA) and 5% w_{om} of photoinitiator. After padding and drying in air the fabrics were placed on a glass plate and exposed to a MW argon plasma treatment (F_{Ar} = 125 sccm; P = 100 W; p = 500 mT; t = 20 min). Then after several cycles of washing (Soxhlet ethanol, water) the samples were dried at room temperature and stored under standard conditions for at least 24 hours before measurements.

Dyeing experiments: A Polymat 1000 (Ahiba) was employed for dyeing experiments with a rotation rate of 40 rpm. A liquor-to-goods ratio of 25:1 was used with 50 g/L Na_2CO_3 and dyed in different shades for 60 min at 60 °C followed by soaping (liquor-to-goods ratio 40:1, 1 g/L Nekanil 910, 98 °C, 30 min).

Water repellent treatment: Two different procedures were followed involving the low pressure plasma process: (i) the FR-cotton fabrics are submitted to a CF_4 plasma treatment (F_{CF4} = 36 sccm, working pressure = 0.66 mb, P = 300 W). (ii) PIGP process of a perfluorinated acrylate monomer (AC8) (F_{Ar} = 125 sccm. P = 100 W; p = 500 mT; t = 5 min; [AC8] = 50g/L) on FR-cotton fabrics

3. Results and discussion

3.1. Combination of dyeing and flame retardant finishing

In dyeing processes the affinity of the dyestuff to the fibres is plays a important role and is sensitive to any surface modifications. Therefore it has to be investigated to ensure whether the flame retardant finishing by PIGP can be integrated into the whole textile finishing process. Reactive[5] dyes are one of the most applied in the cotton finishing processes, therefore they were employed in this study. Figure 1 presens the spectrophotometric measurements obtained for FR-cotton with increasing amounts of DEAEPN add-on and deeply dyed with Remazolbrilliant blue, 3% w_{of}.

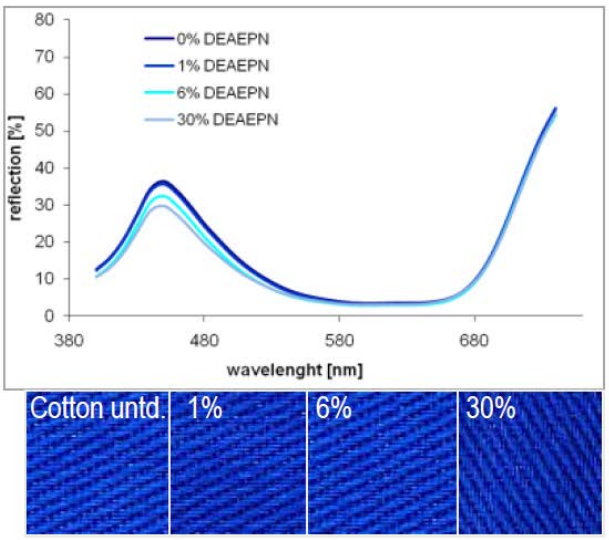


Figure 1: Spectrophotometric results and photographs of 3%w_{of} RB blue dyed FR treated cotton with various amount of grafted FR-polymer.

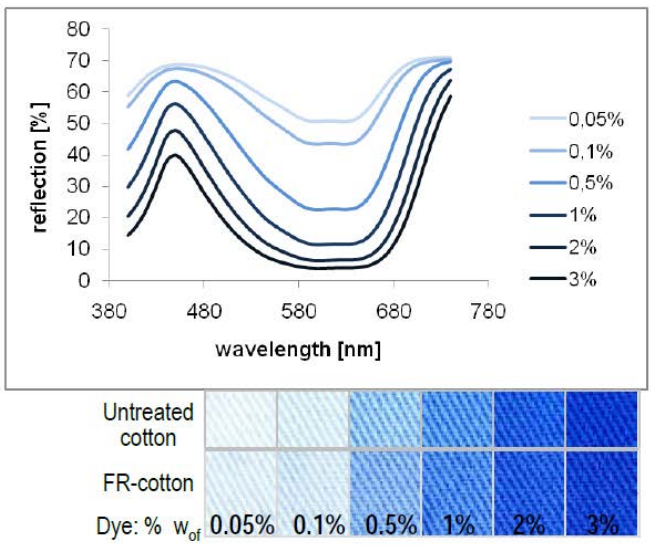


Figure 2: Reflexion curves and photographs of different RB blue dyed shades on untreated and FR-treated cotton (DEAEPN: 17.5% w_{of}).

At a first glance, a good match of the reflection curves can be seen at low amount of grafted flame retardant (< 6%). However, while reaching high degree of grafting (30%) a slight decrease of the absorption is observed in the blue range region. The samples become darker. Nevertheless, this deviation is hardly visible from human eyes. This indicates that the presence of the flame retardant polymer on the surface of the cellulosic fabric allows a post dyeing treatment. A good diffusion of the dye into the pores of the cotton fabric is maintained and sufficient cellulosic-OH groups remain for the reactivity with the dye.

In a second step the colour shade was varied by using increasing amount of RB blue dye (0.05 to 3% w_{of}) on flame retardant finished cotton (17.5% w_{of}). The results presented in figure 2 indicate that even for high FR-grafting excellent colour shades are possible with respect to the original colour and correlate with the amount of dye. The affinity of the dyestuffs is not influenced by the thin polymer film.

LOI measurements performed on the dyed fabrics have indicated that the dyeing process does not alter the flame retardant properties of the fabric even after several cycles of washing and soaping.

3.2. Flame retardant and water repellent cotton fabrics

(i) CF_4 plasma treatment of flame retarded cotton fabrics with DEAEPN

Perfluorocarbon plasmas are well known to be effective for waterproofing polymeric substrates[7]. Virgin and FR-cotton fabrics were submitted to a CF_4 plasma (F_{CF4} = 36 sccm, working pressure = 0.66 mb, P = 300 W) during 5 minutes. Before and after the plasma treatment, the Schmerber pressures ($P_{Sch.}$) were measured. The results obtained are given in Table 1.

Cotton fabric	LOI_1	P_{sch1}	P_{sch2}	LOI_2
Untreated	19.0	0	2	19.0
DEAEPN (200g/L)	27.5	0	2	27.5

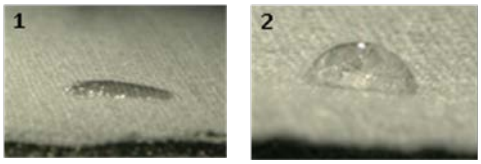


Table 1: LOI and Schmerber pressures (P_{Sch}) before (LOI_1/P_{Sch1}) and after (LOI_2/P_{Sch2}) the CF_4 plasma treatment on untreated- and FR-cotton fabrics and photographs of droplets of water on FR-cotton before (1) and after (2) CF_4 plasma treatment.

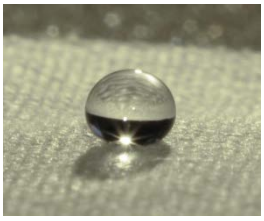
Before the CF_4 plasma treatment, the FR-cotton fabrics are totally absorbent ($P_{Sch.1}$ = 0 mb). After the CF_4 plasma treatment, the $P_{Sch.}$ values of the FR-sample increases slightly up to 2 mb. Droplets of water remain but do not roll on the surface of the treated fabrics. However, by heating the fabrics during 1h at 100°C in an oven, P_{Sch} double from 2 to 4 mb. The droplets of water slightly roll on the surface of the fabrics. This is due to the increase of the chain mobility with the temperature as already observed[7]. Interestingly, LOI values are the same before and after the CF_4 plasma.
CF_4 plasma treatment of flame retarded (FR) fabrics leads to a decrease of the surface energy of the treated fabrics compared to the untreated ones. However this can be attributed only to a simple surface fluorination, since there is no noticeable difference in IR and weight measurements between FR-cotton samples before and after the CF_4 plasma exposure. This CF_4 plasma treatment is not sufficient to impart a good water repellent character.

(ii) Plasma-induced graft polymerization of AC8 on FR-cotton fabrics

In this approach the (AC8)[2, 7] monomer is grafted and polymerized via the PIGP process onto the surface of FR-cotton. The amount of grafted polymer the $P_{Sch.}$ values and the corresponding LOI values are listed in Table 2.

Cotton	$\%G_{FR}$	LOI_1	P_{sch1}	$\%G_{FR+AC8}$	LOI_2	P_{sch2}
Untreated	-	19	0	3.03	19	11
DEAEPN	24	26.5	0	29.36	27	15

Table 2: Grafting percentage (%G), LOI and Schmerber pressures (P_{Sch}) before (LOI_1/P_{Sch1}) and after (LOI_2/P_{Sch2}) the PIGP of AC8 on untreated- and FR-cotton fabrics. Photograph of the water-repellent-FR-cotton fabric.



The results clearly indicate that both the degree of grafting and the $P_{Sch.}$ values increase after the PIGP of AC8 on the FR-cotton fabrics. This indicates the presence of a fluorinated polymer on the surface of the fabrics. The droplets of water roll onto the surface of the double-layer treated fabrics. This observation confirms the good water repellent character of the cotton textiles. The LOI of the flame retarded fabrics remain almost the same after water repellent treatment.

From these results, it can be concluded that it is possible to confer good water repellent properties to FR-cotton fabrics with only 3% of grafted polyAC8 using the PIGP procedure. This occurs without affecting the flame retardant character of the fabrics.

4. Conclusion

From these results we have shown that the Plasma Induced Graft Polymerization process of a flame retardant monomer can be easily integrated in a cotton fabric finishing process as it is totally compatible with reactive dyeing process and water repellent treatment. Moreover, the flame retardant properties are not affected by these post plasma treatment and exhibits excellent wash-fastness properties after 50 cycles of laundry[8].

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