Functionalisation of cotton fabrics with (meth)acrylate monomers by glow discharge plasma

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Influence of the nature of the process gas on macroradicals' generation

Mercerised cotton samples were treated by different gas plasmas at fixed RF power and treatment time (250 W; 180 sec); after treatment, samples were placed into a reaction flask containing GMA (glycidilmethacrylate) to carry out the grafting reaction. **Table I** shows the relation between the amount of GMA grafted onto the cotton sample (related to the amount of free radicals generated onto the cotton surface) as a function of the kind of gas used in the plasma processing.

Table I - Functionalisation of cotton with GMA by different gas plasmas

Sample	*Power (W)*	*Time (sec)*	*Gas*	*GMA add-on[a] (g)*	*GMA add-on (%)*
Cot1-1	250	180	Ar	0,1829	5,30
Cot1-2	250	180	air	0,0487	1,43
Cot1-3	250	180	O_2/Ar (1:1)	0	0
Cot1-4	250	180	O_2	0	0
Cot1-5	250	180	N_2	0,0613	1,83

[a]GMA add-on (%) = $[(W_2-W_1)/W_1]x100$ where W_2 is the dry weight of the grafted sample and W_1 is the dry weight of cotton fabric after the plasma treatment

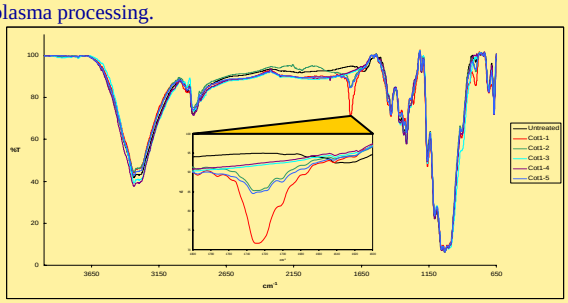


Figure 1- ATR spectra of plasma treated cotton samples using different gases

The Maximum amount of grafted material was obtained by Argon treatment. Being an inert gas Ar is able to generate stable radicals not undergoing side reactions with the process gas itself (as for air or nitrogen) leading to radical inactivation and chemical etching. IR Spectra of treated samples (**Figure 1**) are quite complex: a diagnostic band ($\nu_{C=O}$) at 1740 cm^{-1} indicate the presence of grafted poly-GMA. The signal is absent in untreated cotton and its intensity in treated samples is qualitatively in accordance with the amount of grafted polyGMA determined by gravimetry.

ESR study of radicals formed by Ar-plasma treatment

In order to verify the nature of the radical species onto the cotton surface an ESR study on some samples of cotton treated by argon-plasma for 180 seconds, at varying RF powers and contact time with air (simulating the conditions for continuous plasma treatment) was carried out. Results are shown in **Table II** and **Figure 2**. Radical species held for responsible for spectra reported in Figure 2 are sketched in **Scheme I**.

Table II– Argon-plasma treatment of cotton fabrics

Sample	RF power (W)	Air exposition
1	150	YES
2	250	YES
3	350	YES
4	450	YES
5	550	YES
6	100	NO
7	200	NO
8	300	NO

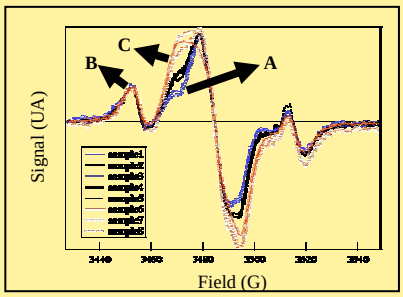
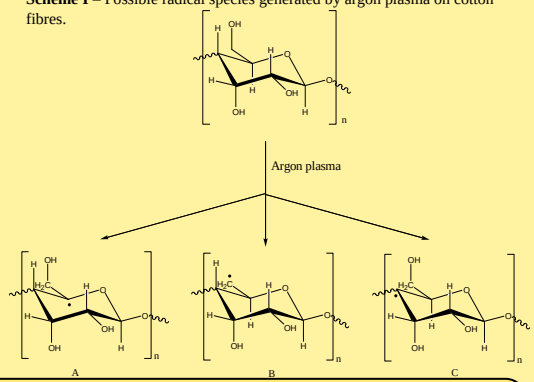


Figure 2 – ESR spectra of cotton samples treated by argon-plasma and typical bands of radical species A, B and C.

Scheme I – Possible radical species generated by argon plasma on cotton fibres.



Effect of Plasma Power and Time of Treatment on percent Graft Add-on in batch Plasma Process

The plasma-treated cotton sample was placed into a reaction flask containing a 500 ml of a 20% (v/v) GMA solution in methanol/water (1:1). The flask contents were kept in a thermostatic oil bath at the temperature of 85 °C under methanol reflux for 4 hours. After the reaction time was over, the sample was removed and consecutively washed with: a hot solution (T=85 °C) of methanol/water (1:1) for 1 h; a solution of methanol/water (1:1) at ambient temperature for 1 h; and with acetone at ambient temperature for 1 h twice. The sample was then squeezed and dried in an oven at 105°C for a period of 4 h, cooled over silica-gel in a desiccator and weighed.

Figure 3a shows the effect of RF power on the graft add-on. The percent of graft add-on decreases by increasing the power, probably because at higher power a higher instantaneous concentration of radicals is generated, promoting coupling reaction that lead to the inactivation of active sites.
Moreover, at higher RF power radicals are generated in a shorter time so that etching reaction have higher chances to occur.
Figure 3b shows the effect of time on the graft add-on. At long treatment time and lower RF power higher % of graft add-on is observed. In these conditions the generation of radicals is continuous and therefore radical coupling reactions are less likely to occur and the formation of stable active sites is favoured.

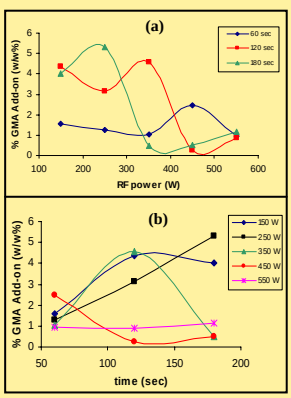


Figure 3 – Percent graft add-on of GMA as function of: **(a)** RF power; **(b)** plasma treatment times.

Effect of Plasma Power and Time of Treatment on percent Graft Add-on in one-step Plasma Process

After the plasma treatment of the cotton sample, the valve of gas inlet was turned off, while the vacuum pump valve was still opened: when a pressure of 0.04 mbar was attained, the monomer (GMA) in vapour phase was introduced into the system. The monomer was previously degassed with Argon for 2 hours. The time of treatment was in the range from 60-300 min. After the reaction time, the sample was removed and washed as described in batch plasma process.
The graft add-on (**Figure 4**) shows a similar trend to that observed in the discontinuous process, as the maximum yield is recorded at RF powers between 200 and 250 W.

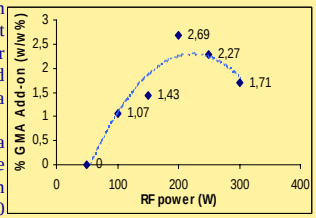


Figure 4 - Percent graft add-on of GMA as function of RF power at constant treatment time (180 sec.).

Conclusions

Plasma treatment is a promising technique for the modification of fabric surfaces for commercial purposes in the apparel sector. The present work confirmed the possibility to graft an acrylic monomer on natural fibers by either continuous or discontinuous treatment through plasma surface activation. Future work is in progress to extend the precisely established operating conditions for GMA to a wider palette of acrylic monomers carrying functionalities which will be able to improve different characteristics of fabrics according to the more stringent requirements of