Improvement of the graft and dyeability of linen by DBD treatment in ambient air

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ABSTRACT

Plasma treatment can effectively modify the surface characteristics of fabrics, such as wettability, dyeability and adhesion strength. In this paper, dielectric barrier discharge (DBD) in ambient air is applied to modify linen surface and improve the grafting efficiency and dyeability. Scanning electron microscope (SEM) shows that DBD treatment can effectively change the surface morphology of the treated linen. Raman spectrum, SEM and Fourier transform infrared spectroscopy conform that graft reaction certainly takes place on the DBD-treated linen surface. The dyeability improves with the increase of grafting efficiency, which shows that graft has a great effect on dyeability. For the grafting efficiency and dyeability, the optimal DBD treatment time is 30 s in this experiment. The possible reason may be that, with the increase of the treatment time, the surface degradation will become strong, which will lead to the invalidation of some already modified results.

1. Introduction

Due to its good wettability, permeability to air and electrostatic resistance, linen has been widely used in garment industry. However, the low dyeability limits its further applications in high-level garment industry. Low-temperature plasma treatment has been proved to be a good method to modify the surface and improve the surface characteristics of fabrics, such as wettability, adhesion and dyeability (Cui and Brown, 2002; Tanaka et al., 2001; Kan et al., 1998; Poletti et al., 2003; Rahel et al., 2003).

Low-temperature plasma can be produced at low and high gas pressure. For the modification of fabric, low-temperature plasma produced at atmospheric pressure is ideal. Dielectric barrier discharge (DBD) can be performed at atmospheric pressure and the produced plasma is low-temperature or non-thermal plasma. Recently, DBD is widely used to modify the surface of fabrics and some interesting results have been obtained in the improvement of the wettability, adhesion and dyeability (Esrom et al., 2001; Massines et al., 2001).

In this experiment, DBD in ambient air was applied to modify the surface and improve the graft and dyeability of linen. Scanning electron microscope (SEM), Raman spectrum, Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopy and visible absorption spectroscopy were used to analyze the surface morphology, surface chemical compositions, grafting efficiency and dyeability of the treated linen samples, respectively.

2. Experimental

2.1. Specimen preparation and experiment treatment

The linen fabric was cut into pieces with the dimensions of 2 cm × 2 cm and then kept in an acetone solution for 24 h to...
dissolve and dispel the attached impurities. After that, the specimens were put into a de-ionized water solution to clean the acetone. The cleaned specimens were dried at the temperature of 105 °C and then put into a desiccator for use.

The experimental setup is schematically shown in Fig. 1. The main chamber, made of stainless steel, has a dimension of 20 cm × 20 cm × 20 cm. Two parallel plane electrodes, 3.0 cm in diameter and covered by quartz barriers, are mounted in the central area of the main chamber. The upper and the bottom barriers are both 7.0 cm in diameter and 1.0 cm in thickness. The specimen is placed on the surface of the grounded electrode. The gas gap, discharge frequency and peak–peak voltage amplitude are fixed and the values are 3.0 mm, 1.5 kHz and 28 kV, respectively in the experiment. The experiment was performed under a batch system in ambient air.

2.2. Graft experiment

The DBD-treated specimens were put into an acrylic acid (AAc) monomer solution (prepared with de-ionized water) with the volume concentration of 30%, at the temperature of 70°C for 2 h to graft AAc onto the linen surface. After that, the specimens were put into boiling de-ionized water for 8 h to dispel the absorbed AAc and the possible homopolymers. The graft-treated specimens were analyzed by the methods of SEM (S-366, Cambridge, England), Raman spectrum (RABRAM-HR, JY Co., France), FTIR-ATR (560ESP, Nicolet Instrument Co., USA) and visible absorption spectroscopy (UV-240, Shimadzu Co., Japan). The measurement of visible absorption spectroscopy was performed as follows: the graft-treated specimens were put into a cationic dye solution (prepared by de-ionized water and cationic Red α-GR2) with the liquor volume ratio of 1:80 and the dye dosage of 1% of the specimen weight, at the temperature of 65°C for 15 min and then 85°C for 45 min. Comparing the value of the absorbance of the original solution with that of the remained, lower the value of the absorbance of the remained solution is, higher the grafting efficiency is. The grafting degree is got by this method: the absorbance value of the remained solution minus that of the original, then the difference is divided by the absorbance value of the original solution, and the final value represents the grafting degree. Because cationic dye will react with the acidic site of the grafted co-polymerization AAc one by one, the measurement can correctly indicate the grafting efficiency. The reason why we did not evaluate the grafting efficiency by directly measuring the absorbance of the graft solution is that, not only the grafted co-polymerization AAc but also some adsorbed AAc monomers and some possible homopolymers will contribute to the measured value which will lead to incorrect measurement results. But in the dyeing process, homopolymer will not be produced, so the measured results are more precise.

Fig. 1 – Schematic show of the experiment setup.

Fig. 2 – SEM pictures of (a) original, (b) air-DBD-treated and (c) DBD-graft-treated linen samples. DBD treatment time is 30 s.
2.3. The dyeability measurement

The graft-treated specimens were kept in an active dye-bath (prepared by de-ionized water and active aurantium X-GN) with the liquor ratio of 1:80 and the dye dosage of 2% of specimen weight, at room temperature for 10 min. Then NaCl salt with the weight of the linen specimens was added into the dye solution and the specimens were kept for 20 min. After that, the specimens were taken out of the dye solution and sodium carbonate (Na₂CO₃) with the weight half of the linen specimens had been put into the solution. Thereafter, the specimens were put into the solution again and kept for 30 min to solidify the dye. The dyeability of the specimens was evaluated by the absorbance measurement of the remained dye solution using visible absorption spectroscopy by the method just as mentioned in Section 2.2. The difference of the experiments in Section 2.2 and Section 2.3 is that, the solution preparation and the dyeing in Section 2.3 are based on practical production, whereas that is only for evaluating the grafting efficiency in Section 2.2. The photos of the dye-treated specimens were taken with a digital camera.

3. Results and discussion

Fig. 2 is the SEM pictures of the linen specimens of (a) untreated, (b) DBD-treated and (c) DBD-graft-treated. From Fig. 2(a), some flaws on the surface of the linen are found. This may be caused by the bombardment of the electron beam with high energy in the process of SEM view. Comparing Fig. 2(a) with Fig. 2(b), it can be found that there are small fragments on the surface of the DBD-treated linen. The fragments are believed to be caused by the chemical sputtering of the air-DBD plasma and the morphology will contribute to the improvement of the grafting efficiency. From Fig. 2(c), it can be found that the fragments previously existing on the DBD-treated sample’s surface disappear. Because the physical absorbed AAc has been cleaned out, the change of the surface
morphology of the graft-treated linen can only be attributed to the grafted co-polymerization AAc. 

Fig. 3 shows the Raman spectrum of (B) DBD-graft-treated and (C) only DBD-treated linen specimens. The Raman spectrum of the original specimen (not shown in the figure) is almost same with that of the DBD-treated. The possible reason is that, modification degree is low and the modification only happens on the surface, so it is difficult to show the composition change by Raman spectrum analysis. What the dispersion peak displacement at about 1126 cm$^{-1}$ in Fig. 3(B) corresponds to is not clear now, however, it must come from the linen itself. One dispersion peak displacement at 2875 cm$^{-1}$ corresponding to the vibration of –CH$_2$ in Fig. 3(B) is found and this should come from the grafted copolymerization AAc.

Fig. 4 shows the FTIR-ATR spectra of (A) original and (B) graft-treated specimens. Comparing A with B, it can be seen that a new absorption peak near the wave number 1730 cm$^{-1}$ presents for the grafted linen sample and this should be the vibration of COO of AAc. Plasma treatment can lead to the production of some radical sites (Wilken et al., 1999; Kuzuya et al., 1999). These radical sites (Cell–, here, Cell denotes cellulose molecule of linen) will take oxidation reaction with oxygen molecules in air and produce peroxides (Cell–OO, Cell–OOH, Cell–OO–Cell) (Chung et al., 2004). Due to pyrogenation, the peroxides will become CellO– and graft reaction will take place between CellO– and AAc monomer (CH$_2$CHCOOH) to form the copolymer of CellO–(CH$_2$CHCOOH)$_n$– (Choi et al., 2004; Huang and Chen, 2002).

Fig. 5 shows the dependence of the grafting efficiency on the DBD treatment time. From the picture, it can be found that there is an optimal time of 30 s for DBD treatment. With the treatment time increasing beyond 30 s, the grafting efficiency decreases quickly and then undergoes a slow increasing process with the treatment time extending further. The possible reason for the phenomena is that, within the treatment time of 0–30 s, air-DBD plasma treatment mainly causes the formation of some radical sites. With the treatment time increasing, chemical sputtering starts to happen, and which will lead to the degradation of the treated linen sample. Degradation will lead to the disappearance of some already formed radical sites (Chapiro, 1995). The phenomenon that the grafting efficiency slowly increases after the treatment time 150 s may indicate that, with the increase of the treatment time, the plasma modification will go deep into the linen bulk.

The effect of the treatment time on the dyeability of linen is shown in Fig. 6. It can be seen that the dyeability improves with the increase of grafting efficiency and this indicates that grafting efficiency is the key for the improvement of dyeability. The reasons may come from the following two aspects: the main component of linen is cellulose (Sefain et al., 1995) and cellulose contains many hydroxyl sites (Tindall et al., 2002). The positive electrical characteristic of carboxyl of grafted AAc in alkaline solution will attract more active dye to reach the surface of linen to form covalent chemical bonds with hydroxyl sites (Tam et al., 1997). Besides, electron donor characteristic of carboxyl of grafted AAc in an alkaline solution can decrease the speed of the hydrolysis of active dye and this can also correspondingly improve the dyeability (Tam et al., 1997). Contrarily, cationic dye shows positive electrical characteristic in water solution, and the main approach that cationic dye combines with the graft-treated linen specimen is the covalent combination between cationic dye and the carboxyl sites of the grafted AAc (Chao et al., 2004). This is the reason why the experiment in Section 2.2 can correctly evaluate the grafting efficiency.

Fig. 7 is the photos of the dyed linen samples of (a) original, (b) DBD-treated and (c) DBD-graft-treated. From the picture, it can be found that the dyes of the original and DBD-treated sample are almost same and the dyes are light and non-uniform. At the same time, the dye of the graft-treated sample is heavy and more uniform. This gives an intuitionistic proof that graft can improve dyeability.

4. Conclusions

Linen fabric is treated by DBD plasma in ambient air. The treatment can change the morphology and compositions of the linen surface, and this then increases the grafting efficiency of AAc onto the treated linen surface. The graft process will greatly affect the dyeability of the linen sample and the dyeability of the DBD-graft-treated linen has been greatly improved. An optimal DBD treatment time of 30 s for the grafting efficiency and dyeability has been obtained in this experiment and this may attribute to the dynamic equilibrium of modification and chemical sputter-
The dye of DBD and graft-treated linen becomes more uniform.

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References