IMPROVED DYEING PROPERTIES OF $SiCl_4$-PLASMA TREATED POLYESTER FABRICS

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ABSTRACT

PET fabrics were treated under $SiCl_4$-RF plasma conditions by varying experimental parameters. ESCA, wettability and EM data indicated surface implantation of $SiCl_X$ functionalities associated with improved wettability, dyeability and increased surface roughness. Dyeing of treated fabrics is discussed.

INTRODUCTION

Polyester (PET) fibers are the world's leading synthetic fibers; they are produced at an annual rate of over 1.5 million tons only in the United States. The properties of these fibers are related not only to the chemical nature of the constituting macromolecules but also to physical characteristics like molecular weight distribution, extent and distribution of crystallinity, nature and quantities of incorporated additives, etc. Fiber characteristics (tensile strength and high modulus) can only be achieved from high molecular symmetry (linear chains) and high cohesive energies between the macromolecules; these factors, are usually associated with high density and advanced crystallinity. Fiber-forming processes add to the natural organization of macromolecules even a more advanced orientation and packing. These characteristics accompanied by the absence of reactive functionalities and polar sites in the macromolecular chains, and by the stiffening effect of the phenylene groups, make PET fibers relatively chemically inert and less penetrable to solvents and solutions. This is the reason why disperse dyeing is almost the only technological option for PET fibers and fabrics. During this dyeing technique the PET substrates are exposed to temperatures higher than Tg (80-120°C; no motion of macromolecules exist, except the stretching or distortion of covalent bonds below Tg) in order to increase their specific volume, and to pressures higher than 1 atm, to force the dye molecules into the structure of the fibers. Disperse dyeing technologies are conse-

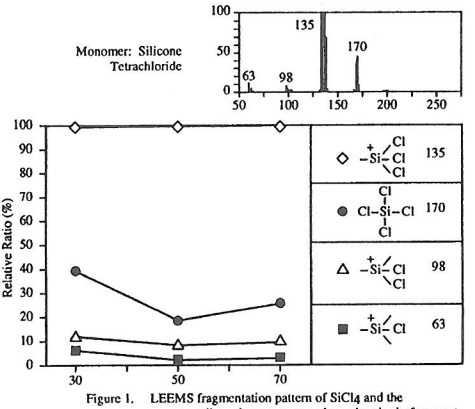

Figure 1. LEEMS fragmentation pattern of $SiCl_4$ and the corresponding electron-energy dependent ionic-fragment composition

quently energy-intensive and require batch-type systems. Plasma induced surface functionalization PET substrates opens up new possibilities in this field. Previous experimental data [1,2] indicate that RF-plasma generated sillylium cations ($SiCl_x^+$) can efficiently be implanted even into the most inert polymeric surfaces. $SiCl_3^+$ ions are predominant in the ST-RF plasma (Figure 1), are extremely reactive, and are readily converted into $Si(OH)_x$ functionalities in the presence of moisture. In this contribution the wettability and dyeing characteristics of $SiCl_4$-RF-plasma modified PET substrates are discussed.

EXPERIMENTAL

Materials and Methods: High purity Aldrich silicon tetrachloride (ST) (Silicon-IV chloride, packed under nitrogen in sure seal bottles) was used in all of the experiments. The stainless steel ST feeding reservoir was handled under glove box (Labconco) conditions (argon blanket), and ST was degassed by cooling it to liquid nitrogen temperature and vacuumed to base pressure level. During the experiments the reservoir was kept at room temperature. Liquid Carbonic argon (99.9 %) was employed for the reactor cleaning operations both in the absence and presence of plasma (Each run was preceded by an argon plasma cleaning procedure in order to remove possible contaminants from previous experiments: 150 W, 200 mT; 5 minutes). Additive-free (cetone extracted) PET samples were used in all experiments.

The surface atomic compositions of ST-plasma modified PET substrates were analyzed by using X-ray photoelectron spectroscopy (ESCA, Perkin-Elmer Physical Electronics 0 5400 Small Area System; Mg source; 15 kV, 300 W; pass energy: 89.45 eV; angle: 45 degrees). C1s, O1s, Cl2p and Si2p were investigated during the measurements. Surface charge neutralization techniques were not employed during the analyses, however recalibrations of binding energy values, by referring to C1s peak were performed.

The morphology of untreated and plasma modified PET fabrics was investigated by scanning electron microscopy (SEM-JEOL JSM-35°C; electron beam accelerating voltage: 15 kV; electron gun-target distance: 39 mm; vacuum: 10^{-6} mmHg). Gold coated substrates were used in all of the SEM estimations. Contact angle data were collected from 2X30 mm PET fabrics, by using a CAHN Dynamic Contact Angle Analyzer (elevator speed: 150 μm/sec; humidity: 52%; temperature: 25°C).

Plasma treated and virgin PET substrates were dyed in an AHIBA dyeing system with C.I. Basic Blue 7 dye by using the following conditions: dyeing time: 15 minutes; temperature: 107°C (boiling temperature of dyeing solution); dyestuff composition: 1g Basic Blue- 7, 0.75 ml acetic acid, 1 droplet of TritonX100 and 2000 ml water; dyeing solution composition: 1ml TritonX100, 30 ml dyestuff and 169 ml distilled water; substrate/dye solution ratio: 0.5g PET fabric/ 200 ml dye solution. At the end of the dyeing the samples were rinsed at room temperature, for 10 minutes in a washing solution composed of: 2g/l acetic acid and 1g/l TritonX100, in order to remove unbounded dye molecules. Color saturation (K/S values) of dyed fabrics was estimated with the ACS Chromosensor system.

Plasma Treatments: ST-plasma treatments of PET fabric samples were carried out in a capacitively coupled, stainless steel, 30 kHz reactor described earlier (Figure 2). In a typical experiment a 200 mm diameter PET fabrics sample, provided with a centrally located 25 mm hole was placed on the lower (grounded) electrode (22), then the reactor was closed and vacuumed to base pressure level by using large capacity vacuum

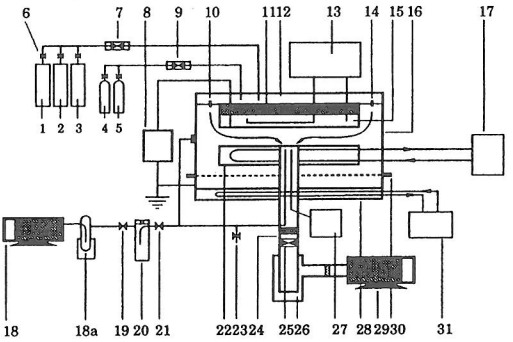

Figure 2. 1, 2, 3. Gas and $SiCl_4$ Reservoirs 4. Argon Reservoir 5. Monomer Reservoir 6, 19, 21, 23. Stainless Steel Needle valves 8. HF Generator 7, 9. Flow Controller 10, 14. Monomer and/or Gas Inlet Orifices, Located Circularly Around The upper electrode (Shower Type Feeding) 1. Electric Insulator Disc 12. Gas Mising-Chamber 13. Programmable Refrigerated Circulator 15. Drum-Type Stainless Steel Upper Electrode 16. Cylidrically Shaped Upper Part of Reactor 17. Temperature Controller for the Built-In Electric Heater of the Lower Electrode 18. Mechanical Vacuum Pump 20. Stainless Steel Liquid Nitrogen Trap for Collecting the Plasma Generated Molecular Mixture 22. Grounded Lower Stainless Steel Electrode 24. One Inch diameter Stainless Steel Connecting Tubing 25. Large Cross Section Battefly-Type Valve 26. Stainlees Steel Liquid Nitrogen Trap for Protecting Vacuum Pump 27. Vacuum Gauge 28. Drum-Type Stainless Steel Lower Part of the Reactor 29. High Capacity Mechanical Vacuum Pump 30. Rubber O-Ring Mediated Circular Vacuum Tight Sealing 31. Refrigerated recirculator

line (24, 25, 26, 30). During this operation, argon (9) and ST (7) connecting lines were open. Flow meter valves were then closed and the system was argon-plasma washed for decontamination. Base pressure was reestablished in the next step and then the pre-selected ST pressure and flow rate were created in the reactor. The plasma was then ignited and sustained for the desired time period. At the end of the reaction the PET sample was removed from the reactor and stored in vacuum desiccator for analytical purposes. The experimental conditions used during the plasma treatments were: RF-power dissipated to the electrodes: 100-175 W; pressure in the absence of plasma : 100-175 mT; pressure in the presence of plasma: 100-175 mT; flow rate of ST: 7.5 sccm; treatment time: 30 sec.-10 min.; temperature of substrate: 25°C.

RESULTS AND DISCUSSIONS

Figures 3, 4 and 5 show the influence of plasma parameters on the relative surface atomic composition of untreated and ST-plasma modified samples. One can notice that treatment times as low as 1 minute (Figure 3) are high enough to complete most of the plasma induced surface chemistry. A significant increase in silicon and oxygen content of the plasma treated substrates in comparison to virgin samples can be noticed in this interval, accompanied by the obvious diminuation of carbon percentage. The presence of high oxygen content can be related both to post plasma surface oxidation mechanisms and to the hydrolysis of Si-Cl linkages. Less sig-

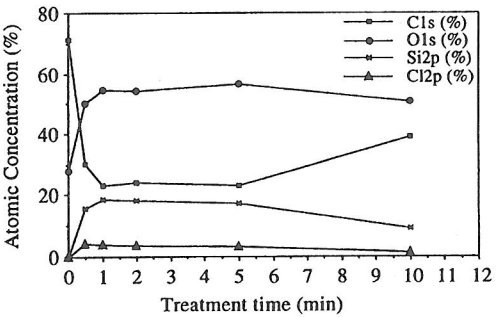

Figure 3. The Influence of Treatment Time on the Atomic Concentration (Power=100W, Pressure=100mT)

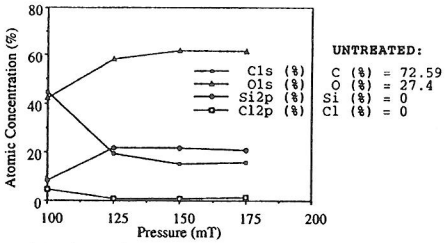

Figure 4. The Influence of Pressure on the Atomic Concentration

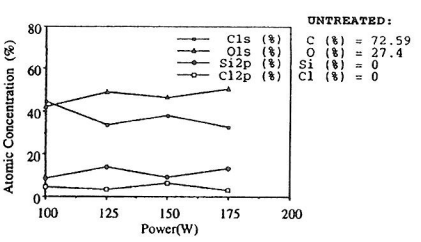

Figure 5. The Influence of Power on the Atomic Concentration

nificant is the implantation of chlorine atoms, which can be explained through surface dehydrochlorination reactions and by the high reactivity of $SiCl_x$ (x<3) species. Treatment times longer than six minutes lead to a slight decrease in both the oxygen and silicon atom contents, due probably to the presence of a more advanced cross-linking mechanism. The effect of pressure on the surface atomic composition, at the longest treatment time (Figure 4), is significant only in the 100-125 mT range, where a 10% increase for silicon and 18% for oxygen is evident. The influence of power at the highest plasma irradiation time value is even less significant (Figure 5). It consequently can be suggested that treatment periods as low as 1 minute and power and pressure levels not higher than 125 W and 125 mT are sufficient to complete the plasma induced surface modifications.

The plasma-parameters-related contact angle data are in good agreement with these observations (Figures 6,7 and 8). Low treatment times (1 minute) and low pressure (100 mT) and power (100 W) conditions (at the longest irradiation periods) can reduce the contact angle of PET to around 50% of its original value. It also can be observed that

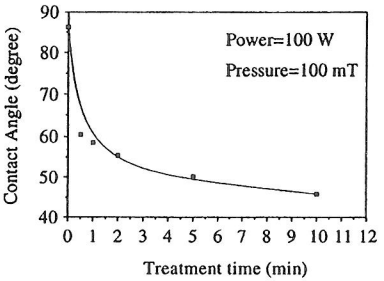

Figure 6. Contact Angle Values for Different Treatment Times

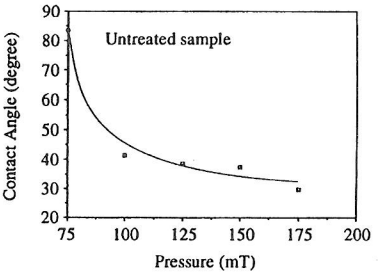

Figure 7. Contact Angle Values for Different Pressure Conditions (Power = 100 W, Treatment time = 10 min)

the lowest contact angles are associated with the highest silicon and oxygen atomic contents (Figures 9 and 10). The presence of $Si(OH)_x$ functionalities on the plasma treated PET surfaces can explain this phenomenon.

Dyeing characteristics of untreated and plasma-treated substrates are presented in Table 1. The plasma parameter related K/S values led to a conclusion similar to that obtained from the wettability data. In the first minute of treatment the K/S values recorded the highest increase rate (0.4 for untreated substrate and 1.2 and 1.7 for 0.5 and 10 minutes treated samples respectively). The influence of power is also less significant for a treatment time of 10 minutes. Relatively high K/S values (1.6) are recorded even at

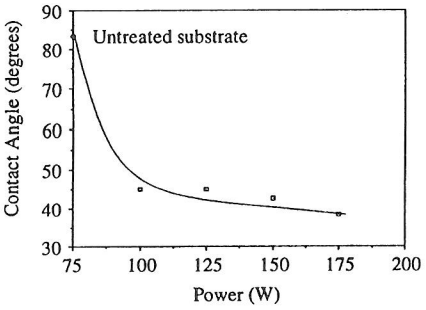

Figure 8. Contact Angle Values for Different Power Conditions (Pressure = 100mT)

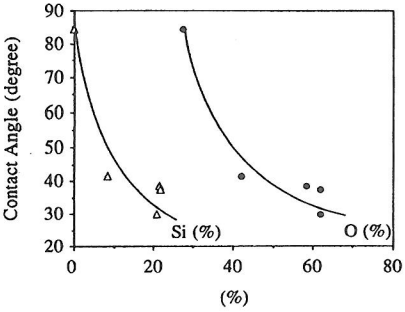

Figure 9. Contact Angle Values Relative to the O (%) And Si (%) (Pressure = 0, 100, 125, 150, 175 mT, Power=100W , Treatment time=10min)

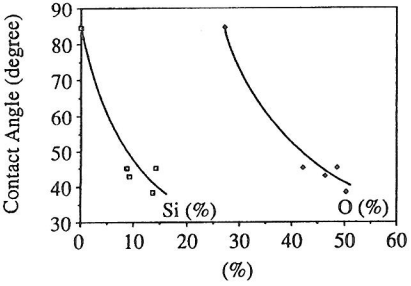

Figure 10. Contact Angle Values Relative to the O(%) and Si (%) (Power = 0, 100, 125, 150, 175 W, Pressure = 100 mT, Treatment time=10 min

Table 1. Dyeing characteristics

Sample	K/S Values	
Untreated	0.4	
Treated 0.5 min	1.2	
Treated 1 min	1.3	100W,
Treated 2 min	1.4	100 mT
Treated 5 min	1.6	
Treated 10 min	1.7	
100 W, 100 mT	1.6	
125 W, 100 mT	1.4	10 minutes
150 W, 100 mT	1.6	
175 W, 100 mT	1.9	
100 mT, 100 W	1.6	
125 mT, 100 W	1.3	
150 mT, 100 W	0.8	10 minutes
175 mT, 100 W	0.8	

power as low as 100 W. Low pressure conditions (100 mT) led to high K/S values (1.6) as well, however, higher levels of this parameter resulted in a significant diminuation of this characteristic (e.g. K/S=0.8 for 175 mT). We believe that more experimental data is required in order to understand the influence of pressure on the dyeing behavior.

Figures 11, 12 and 13 exhibit SEM images of unmodified, and 2 and 10 minutes treated PET substrates. A peculiar smooth surface is evident in the case of untreated substrate (Figure 11), while the two minute plasma exposed sample (Figure 12) exhibits an intensive coating. The surface atomic composition of plasma treated substrates suggests the existence of a polysilicic acid type structure. Less uniform depositions evidenced at longer plasma exposure (Figure 13) suggests that the presence of a competitive ablation process.

CONCLUSIONS

$SiCl_4$-RF-plasma conditions are suitable for improving the surface wettability and dyeing characteristics of PET fabrics.

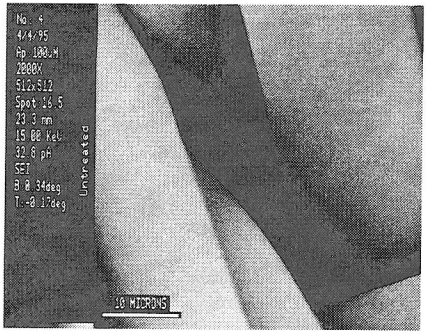

Figure 11. Untreated PET fabric

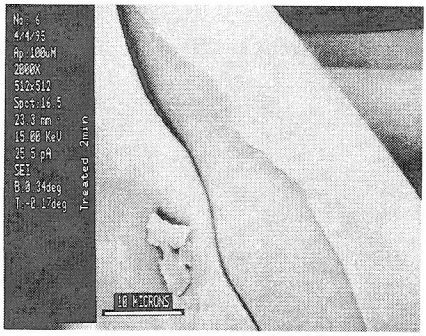

Figure 12. $SiCL_4$ - plasma treated PET fabric (2 min, 100W, 100mT)

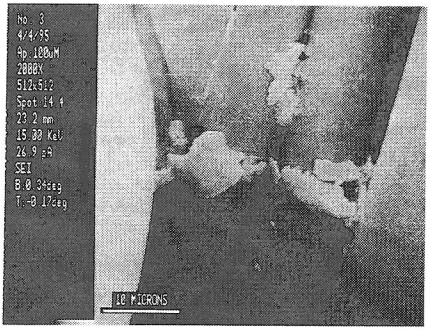

Figure 13. $SiCL_4$ - plasma treated PET fabric (10 min, 125W, 100mT)

The discharge parameters (power, pressure and treatment time) have a significant influence on the surface atomic composition of the plasma modified substrates. Treatment times as low as 1 minute and power and pressure as low as 100 W and 100 mT are adequate for effective surface modification.

The lowest contact angle values are recorded at the highest silicon and oxygen atom contents.

ACKNOWLEDGMENTS

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