SURFACE AMINATION OF POLYPROPYLENE FABRICS UNDER MELAMINE-RF-COLD-PLASMA CONDITIONS

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ABSTRACT

Saturated and unsaturated amines were used for plasma induced reactive amine group implantation onto polypropylene films and fabrics. Significant primary amine implantation was achieved. Wettability, contact angle and scanning electron microscopy measurements indicated significant increase in the surface polarity and surface roughness of the plasma treated samples.

INTRODUCTION

Polypropylene (PP) is the most significant olefinic macromolecule. It is inexpensive and exhibits excellent mechanical properties. The weight to strength ratio of PP fibers is the best among common fibers. Due to the advanced symmetry of PP macromolecules and to the absence of polar functional groups in their structure, they are chemically inert, moisture insensitive and exhibit advanced crystallinity. These properties and their inherent surface smoothness are associated with low adhesion characteristics, which also limit their application. Coventional chemistry deos not offer adequate solutions for the functionalization of PP substrates. Cold plasma conditions open up new possibilities for surface activation and grafting of these materisals. Abundant literature data indicate that even the most inert polymeric surfaces can be functionalized under carefully selected plasma conditions without altering the basic bulk properties of the substrates [1-5].

Reactive amine group implantation into polymeric surfaces represents one of the promising possibilities for enhancing surface characteristics of polyolefinic fibers and fabrics. These groups provide basic characteristic to the surface and promote interactions with acidic nature counterparts. Amino and imino groups are reactive nucleophilic functionalities which can initiate second stage surface modification reactions of plasma treated textiles. Successful plasma induced primary amine implantations has been reported and discussed earlier [4, 6], by using ammonia, and saturated and unsaturated amine-plasmas. Unfortunately some of the potential aminating candidates, and especially multi-amino group containing aromatic derivatives, exhibit low volatilities which require high volatilization temperatures and consequently specially designed plasma reactors with elaborate handling procedures. In many cases adequate vapor pressures cannot be established even in these cases, due to the thermal decomposition of these materials.

Recently a new technical approach to this problem was proposed in our laboratories, that is, the inert-plasma surface modification of low-volatility-derivatives precoated polymeric substrates. In this contribution the argon plasma treatment of melamine-coated PP fabrics will be discussed.

EXPERIMENTAL

Materials and Methods: Aldich 99+% melamine was used in all of the experiments. PP fabrics were acetone extratcted to remove possible technical additives from the fiber surfaces.

200 mm diameter substrates (having a 25 mm central hole) were considered for all plasma irradiations. High purity argon (Liquid Carbonic) was used both for plasma treatments and for cleaning operation purposes. Aldrich toluene diisocyanate (TDI), tetrahydrofurane (THF), polyethylene glycol (PEG) and dibutyltin dilaureate (DD) were employed for carrying out the post plasma grafting reactions. The plasma treated and controll fabrics were dyed with (20 mg/ml) Acid Red 1 (AAKASH Chemicals & Dye Stuffs Inc.), to evaluate the extent of amine group implantation according to an ion-exchange technique develped by Allred and coworkers [7]. PP fabrics were melamine coated by immersing them in a 1% melamine solution, at 80°C, followed by drying in a vacuum oven. An average of 0.32 mg/cm^2 melamine layer was deposited on the substrates.

The post plasma grafing reactions were carried out according to the following procedure: melamine-argon-plasma treated PP samples were immersed in 100 ml of TDI/THF solution (5 ml TDI and 95 ml THF) and vigorously stirred for one hour at 60°C, then 150 ml PEG/THF/DD solution was added, and the mixture was kept another hour at 60°C. The PP samples were then removed and oven-cured for 35 hours at 95°C. The polyurethane grafted PP substrates were then extracted with THF, dried under vacuum oven conditions, and stored in a vacuum dessicator for analytical estimations.

Plasma induced molecular fragmentation of melamine was simulated by low-energy-electron mass spectroscopy (LEE-MS; GC-Carlo Erba Fractovap 4162; MS Kratos MS-25, experimental conditions: column-fused silica, length-30 m, ID-0.32 mm, coating- 5% phenyl and 95 % vinyl polysiloxane, injector-splitter trremperature-100°C, temperature profile of the column-1 minute at room temperature then heated up to 300°C at 20 °C/min, electron energy: 30eV). Chemical structure of unmodified, plasma treated and grafted PP surface layers was investigated with the aid of an ATR-FTIR spectrometer (Galaxy Series FTIR 3000, Resolution 4 cm^{-1}).

Surface atomic composition of virgin, plasma treated and post-plasma grafted samples was evaluated by using X-ray photoelectron spectroscopy (ESCA, Perkin Elmer Physical Electronics 0 5400 Small Area System; Mg source; 15 kV, 300 W; pass energy: 35 eV, angle: 45 degrees). The measurements involved: C1s, O1s, and N1s. Contact angle values were estimated

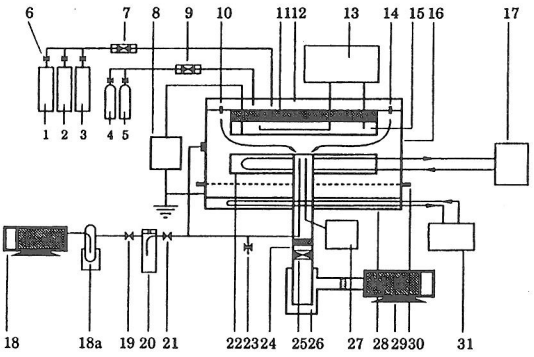

Figure 1. 1, 2, 3. Gas and $SiCl_4$ Reservoirs 4. Argon Reservoir 5. Monomer Reservoir 6, 19, 21, 23. Stainless Steel Needle valves 8. HF Generator 7, 9. Flow Controller 10, 14. Monomer and/or Gas Inlet Orifices, Located Circularly Around The upper electrode (Shower Type Feeding) 1. Electric Insulator 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

by using a CAHN Dynamic Contact Angle Analyzer (2X30 mm samples, elevator speed: 150 um/s, humidity: 50 %, temperature: 25°C).

Surface morphologies of untreated, plasma modified and post-plasma grafted samples were analyzed by scanning electron microscopy (SEM-JEOL JSM-35°C; electron beam accelerating voltage: 15 kV, electron gun-target distance: 40 mm; vacuum: 10^{-6} mmHg), from gold-coated substrates.

Plasma Reactions: All plasma treatments were carried out in a 30 KHz, parallel-plate, capacitively coupled stainless steel reactor, discussed earlier (Figure 1). In a typical experiment the melamine coated PP substrate was placed on the lower electrode (grounded), the system was evacuated to basic pressure level, and by operating proper valves and flow meter controllers the argon pressure was established. The plasma was then ignited at the desired power level and sustained for the preselected treatment time. At the end of the reaction the PP sample was removed, washed in hot water, dried in vacuum, and stored for analytical purposes, and for evaluating second step grafting reactions. The plasma parameters employed during the experiments were as followes: pressure in the absence of plasma: 100-200 mT; RF-power dissipated to the electrodes: 50-100 W; argon flow rate: 6.0 sccm; treatment time: 0.5-10 minutes; temperature of the substrate: 25°C.

RESULTS AND DISCUSSIONS

LEE-MS simulation of plasma induced molecular fragmentation of melamine is shown in Figure 2. One can observe that besides the molecular ion of melamine (m/z=126) m/z=85, 84 and m/z=43, 42 are the most significant ionic fragments. It also can be noticed that m/z=85 represent a 41 mass lost (secondary amine fragment) and it is predominant, while m/z=84 results from a primary amine fragment cleavage (42). These results suggest that both secondary and primary amine-type fragments are present during the plasma treatments. It consequently can be assumed that these molecular fragments will be grafted and/ or modified and grafted under the action of plasma species onto PP surfaces.

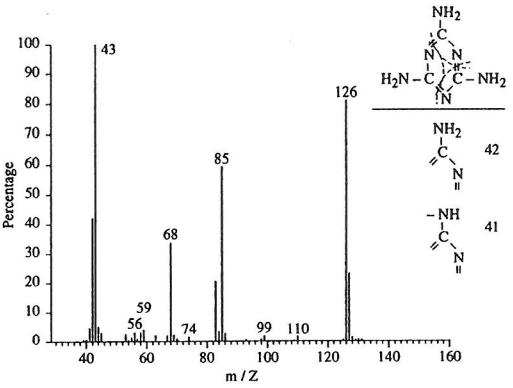

Figure 2. LEE-MS fragmentation pattern of melamine and the corresponding electron-energy depended ionic-fragment coposition

Characterization: Figures 3, 4 and 5 exhibit the influence of plasma parameters on the newly gained surface atomic composition of plasma treated substrates. It can be remarked that the highest nitrogen atom contents are reached at treatment times as low as 2 minutes (longer exposure period does not bring significant changes for this parameter), and that higher powers (50 W, 200 mT and 100 W, 200 mT) lead to more significant nitrogen atom incorporation (Figure 3). The influence of pressure on the plasma induced surface chemistry is also important (Figure 4). Pressures lower than 50 mT are high enough to complete most of the nitrogen atom incorporation processes; higher values of this parameter do not significantly modify thre surface atomic composition. Similar results can be observed in the cases of C/O ratios. Dramatic changes of this parameter can only be noticed in the first two minutes, while longer treatment time periods add less significant oxygen atom incorporations. These data indicate that the most intense plasma induced surface activations undergo in the first couple of minutes, which consequently initiate the most intense post plasma oxydation reactions.

Plasma-parameters-related contact angle data are in good agreement with surface atomic composition (Figure 6). Lower treatment time values determine a more intense decrease of the

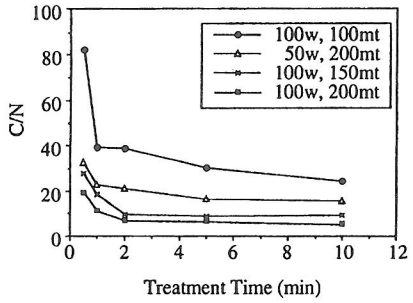

Figure 3. C/N Ratio For Plasma Treated PP Fabrics Under Various Experimental Conditions

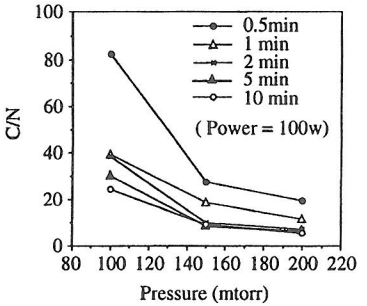

Figure 4. C/N Ratio vs. Plasma Pressure for Melamine-Plasma Treated PP Fabric

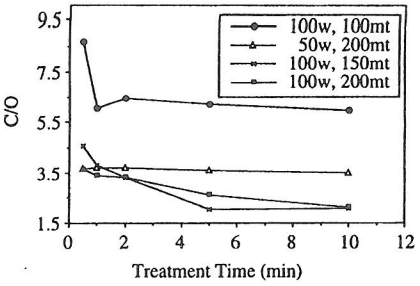

Figure 5. C/O Ratio For Plasma Treated PP Fabrics Under Various Experimental Conditions

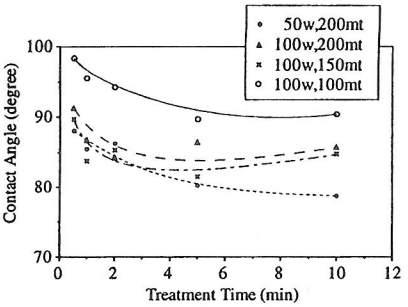

Figure 6. Contact Angle Of Melamine Plasma Treated PP Fabrics

contact angles regardless of power or pressure conditions. Higher treatment times result however, in an increse of this parameter. This phenomenon can be explained through the development of plasma induced crosslinking processes. Exception from this behaviour represent the low power conditions (50 W), where the energies of plasma species are not high enough, we believe, to induce intense decomposition and crosslinking reactions. The influence of pressure on the contact angle at the longest exposure time is presented in Figure 7. It is noteworthy that the contact angle is decreasing until a 150 mT pressure level and then increases with the increase of this parameter. More experimental data is required to understand this phenomenon.

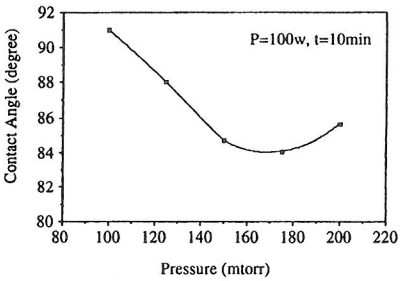

Figure 7. The Wettability vs. Plasma Pressure for Melamine-Plasma Treated PP Fabrics

Figure 8 (a and b) shows the comparative ATR-FTIR spectra of standard and melamine-argon-plasma treated PP samples. Besides the peculiar C-H stretching (CH_2 and CH_3, 2913 and 2916 cm^{-1}) and deformation (CH_2 and CH_3, 1450 and 1380 cm^{-1}) vibrations of PP, the presence of intense C-O-C (1018 cm^{-1}) and C=O (1737 cm^{-1}) stretching absorbtions can be remarked in the case of plasma modified PP samples. One also can notice the existence of intense NH stretching absorptions both for primary and secondary amines (3200-3500 cm^{-1}) and the existence of

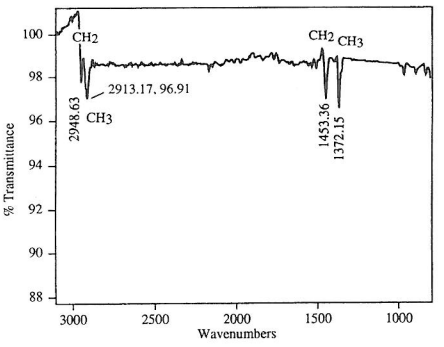

Figure 8A. ATR spectra of untreated PP

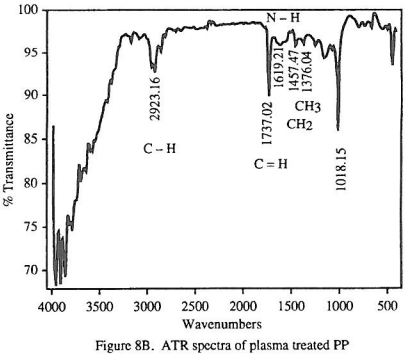

Figure 8B. ATR spectra of plasma treated PP

(weak) deformation vibrations for the same functionalities (1550-1650 cm^{-1}). Due to the post plasma oxydation reactions the presence of amide-type structures cannot be excluded.

Comparative SEM data emphasize different surface morphologies for virgin and plasma treated PP substrates (Figure 9, a and b). Contrary to the smooth surface of untreated PP fibres a deposition-based rough surface structure can be observed in all cases of plasma treated samples. It is suggested that melamine origin molecular-fragment recombination processes are responsible for the formation of surface layers.

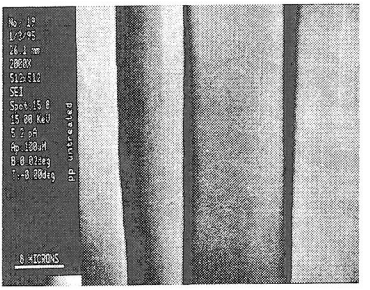

Figure 9A. Untreated PP fabric

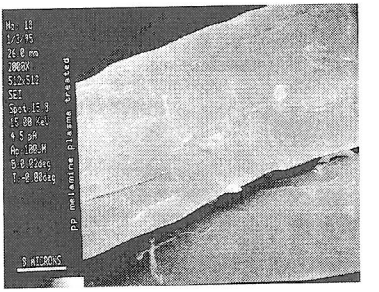

Figure 9B. Melamine plasma treated PP fabric

Calibration-curve-based primary amine group estimations carried out for plasma treated samples for different exposure times are shown in Figure 10. It can clearly be observed that the most intense primary amine group implantation develops in the first few minutes; this is in good agreement with the general trend of the intensity of plasma iduced surface chemistry.

Post plasma graft-polymerization: Table 1, exhibits the relative surface atomic composition and C/N, and C/O ratios for polyurethane (theoretical), melamine-argon-plasma-treated samples and plasma treated and polyurethane grafted substrates. The similar surface atomic compositions and atomic ratios of polyurethane and plasma treated and grafted samples evidence that the grafting reactions were succesful.

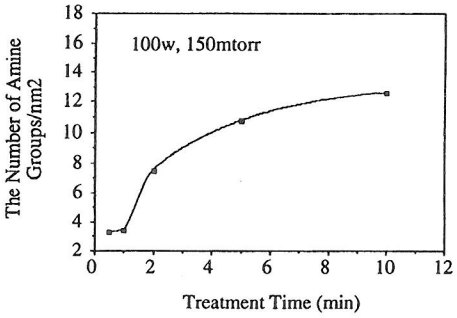

Figure 10. Amino Group Estimation for Different Time

CONCLUSIONS

Primary amine group implantation onto PP fabrics surfaces can effectively be developed from melamine precoated substrates, under RF-plasma conditions.

The specific primary amine concentration of the PP substrate surfaces sesitively depends on the employed plasma parameters. Exposure times as low as 2 minutes and power and pressure levels not higher than 100 W and 150 mT are adequate for completing of plasma induced surface chemistry.

Table 1. ESCA comparison of atomic concentrations

	C%	O%	N%
Polyurethane Grafted	64.44	32.09	3.46
Polyurethane	66.00	31.00	3.00
Plasma Treated	60.54	28.37	11.08

The presence of primary amine groups on PP fabric surfaces permits the development of TDI and PEG based graft-polymerization reactions on plasma modified PP fabric surfaces.

Potential applications can be envisaged in the area for developing PP fabrics- and polyurethane-based composites.

ACKNOWLEDGEMENTS

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