SURFACE MODIFICATION OF CELLOPHANE FILMS BY PLASMA TREATMENT FOR MEMBRANE APPLICATIONS

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ABSTRACT

The cellophane films were modified and also grafted with PAN for various durations of time in RF air plasma. The rates of etching and polymer deposition were studied. The angle of contact of water was found to decrease with time of deposition revealing that the surface became hydrophilic. The ATR-IR spectroscopic studies confirmed the grafting of cellophane surface by PAN. The pervaporation studies for control and modified films showed that the permeation rate increased as a effect of treatment retaining the selectivity.

INTRODUCTION

Polymer films find increasing use in various areas such as packaging, separators, coating layers etc. These films can be used as membranes in waste water treatment, desalination, ion exchange and pervaporation. The commercial usefulness of polymeric membranes in the separation process is often limited by the cost and the compatibility under extreme conditions. Pervaporation is a technique of great promise for separation of organic materials from waste. The tailoring of such membrane materials has to be done very selectively by introducing functional groups or reactive sites in the parent polymer. Use of gaseous plasma is one of the routes for modifying such membranes so that their use can be enhanced [1]. The method of plasma treatment has many advantages over the conventional chemical process in that it is dry, quick and highly controllable. The effect of gaseous plasma treatment on the surface modification of films, fibers and fabrics has been reported from our laboratory.

Polymerization and treatment of surfaces of materials using plasma have been recognized as a very good process for the modification of surfaces. Glow discharge has the capability of producing sufficiently energetic species to cause the rupture of molecular bonds at the top few hundred A° of the polymer surface. This allows both surface modification by treatment and polymer deposition [2]. The formation of thin polymer films in a high frequency glow discharge have been carried out over a wide variety of monomers and has been discussed in a number of research publications [3,4]. It is well established that interfacial phenomena such as wetting and adhesion can be controlled and modified by introducing surface functional groups.

In the present paper we report the effect of plasma treatment on the surface properties of cellophane film. In addition, the cellophane film was modified by grafting with polyacrylonitrile to gain special advantages.

EXPERIMENTAL

Materials: Cellophane films were obtained from M/s Kesoram Industries, India which had thickness of 25 μm. Acrylonitrile obtained from S.D. Fine Chemicals, India (AR Grade) was used without further purification. Deionized double distilled water and acetic acid (AR Grade) were used for pervaporation (PV) studies.
Plasma Reactor: The plasma reactor consisted of a pyrex glass tube of inner diameter 5 cm and length 30 cm with a monomer inlet, a rotary pump, a Pirani gauge and RF power supply (13.56 MHz) with a matching network. Pieces of cellophane films were placed inside the tube and the system was evacuated to 0.05 torr. The substrate was treated in air plasma at 0.1 torr. Alternately, acrylonitrile vapours were introduced into the system to get a working pressure of 0.5 torr. The plasma discharge was initiated by applying RF power of 5 watts. The polymerization was carried out for different durations of time varying from few seconds to 30 minutes.
Characterisation: Etching and deposition rates were calculated from the measurements of weights. ATR-IR spectra were recorded using Hitachi Spectrophotometer with KRS-5 crystal. The angle of contact of water was measured using sessile drop method.
Pervaporation Studies: The PV apparatus is shown in the Fig.1. It consists of a stainless steel cell with membrane surface area of 17.35 cm², the permeant collection traps to condense the permeant vapours and a rotary vacuum pump. The experiments were performed at 25°C and at a downstream vacuum of 2 torr. The permeant vapours were condensed in traps cooled to -35°C. The weight of condensed liquid was measured for time durations of 2-6 hours and was used for calculation of permeation flux. The composition of

permeate was measured using refractive index method.

RESULTS AND DISCUSSION

Etching and Deposition

Plasma processing has a capability as a dry and quick process and is capable of giving thin layer as low as few hundred A°. Since plasma consists of ions, electrons and neutral species the bombardment of the surfaces by these leads to the phenomenon of etching. It has been observed that there is a competitive ablation and polymerization when plasma is struck in presence of monomer vapours. The rates of etching and polymerization are governed by various parameters such as time of treatment, type of monomer, type of substrate, power, pressure etc. If a monomer is not present in the plasma reactor and an inert gas or air is used the etching phenomenon is predominant. Fig.2 shows the etching of cellophane due to air plasma as well as the changes in the weight of cellophane film as a result of exposure to acrylonitrile plasma. The graph shows that there is a weight loss observed due to treatment with air plasma implying that cellophane is a highly etchable substrate. The loss of weight may be the effect of interaction with the reactive radicals in air plasma, the dominant effect being due to oxygen [5]. The graph also indicates that as the PAN film grows on the surface of cellophane the etching diminishes and deposition process predominates leading to a relative weight gain.

ATR-IR Spectroscopy

The typical ATR-IR spectra of cellophane control, air plasma treated cellophane and PAN grafted cellophane are shown in Fig.3. The spectrum of air plasma treated cellophane shows a broad band at about 1600 cm^{-1} which may be on account of oxidation due to air plasma treatment as well as further oxidation due to exposure to the atmosphere after the treatment. The spectrum for PAN grafted cellophane film shows various characteristic peaks. Most important among these are a typical characteristic absorption band at 2250 cm^{-1} (-C≡N) and 1640 cm^{-1} (-C=N) confirming the grafting of cellophane surface by polyacrylonitrile (PAN) [6].

Contact Angle Of Water

The change in the surface energy can be determined by the extent of wetting of a surface by a polar solvent such as water. For this purpose sessile drop method is a simple and most appropriate one. The changes in the angle of contact of water (θ°) due to plasma processing are shown in Fig.4, from which it can be seen that there is a sharp decrease in θ which tends to saturate for higher durations of treatment time. Similar behaviour is observed for the

PAN grafted cellophane films, which indicates that in both types of treatments the surface has become hydrophilic. This can be explained on the basis of roughening of the surface by etching as well as non-uniform deposition. The oxidation of the surface due to air plasma and exposure to atmospheric oxygen leading to formation of polar groups such as (-C=O) and (-COO) will also result in lowering of angle of contact of water.

Pervaporation Studies

The PV experiments carried out on cellophane film for acetic acid-water mixture reveals that the membranes are selective towards water than acetic acid. The PAN grafted samples show higher flux values than the control sample and is depicted in Fig.5. The figure also shows the changes in the separation factor (α) for control and PAN grafted cellophane films for various feed concentrations of acid (in %). It can be observed that α increases with the increase in acid concentration in the feed. This result may be explained on the basis of competitive ablation and polymerization process so that there is etching combined with deposition. The increase in flux is due to etching away of skin exposing internal porous matrix and the increase in the selectivity may be explained on the basis of pore flow model [7].

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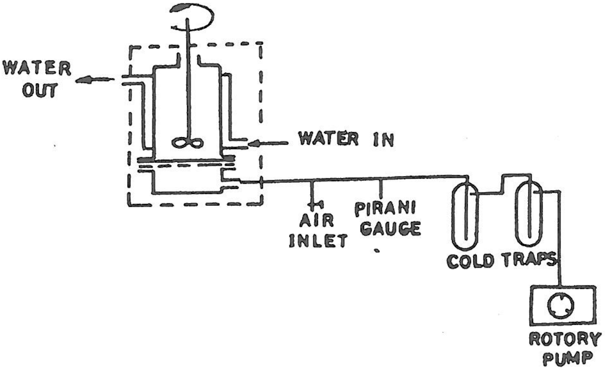

Fig. 1: The schematic of PV assembly.

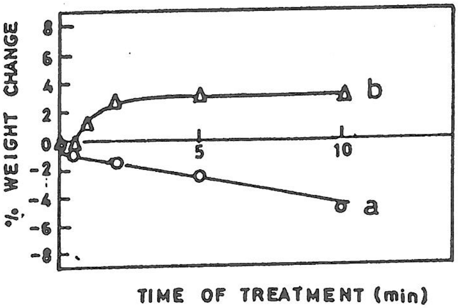

Fig. 2: % Weight changes in cellophane with time of treatment. (a) air plasma treatment, (b) PAN grafting.

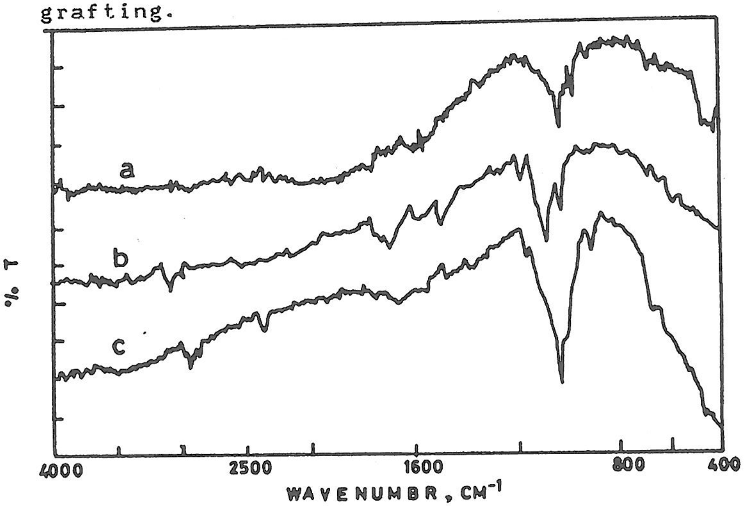

Fig. 3: The ATR-IR spectra of Cellophane for (a) control (b) air plasma treated and (c) PAN grafted.

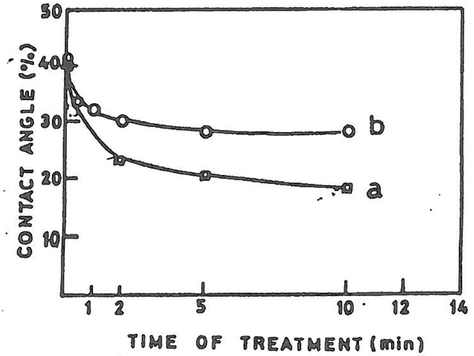

Fig. 4: The changes in angle of contact of water for (a) Air plasma treated. (b) PAN grafted.

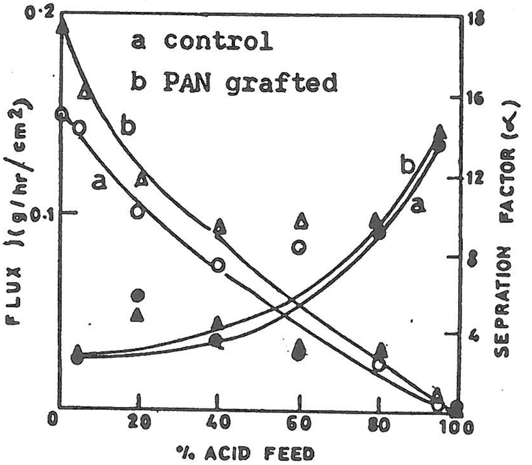

Fig. 5: Changes in flux and separation factor (α) with % acid concentration in feed.