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Plasma induced graft polymerization of acrylic acid onto poly(ethylene terephthalate) monofilament

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The graft polymerization of acrylic acid has been carried out on poly(ethylene terephthalate) (PET) monofilament to introduce carboxylic acid groups. The filament is treated with oxygen plasma for the introduction of peroxides and subsequently grafted with acrylic acid. The influence of monomer concentration, plasma exposure time and reaction temperature on the degree of grafting has been investigated. The grafted filament is subsequently immobilized with chitosan. ATR-FTIR confirms the immobilization of chitosan. The contact angle decreases from 72° for virgin PET to 38° for 180s plasma exposured sample, 42° for the grafted and 36° for the chitosan immobilized sample which shows significant improvement in the wettability. The surface topography of filaments is characterized by atomic force microscopy.

Keywords: Acrylic acid, Graft polymerization, Plasma, Poly(ethylene terephthalate)

1 Introduction

Plasma treatment has been found to be an extremely attractive way to modify the surface chemistry and morphology of polymeric materials[1]. The plasma modification may be carried out in the presence of specific gases, such as oxygen, argon, nitrogen, and hydrogen. This results in the generation of active species which can activate and modify the material chemistry depending on the nature of the gaseous medium[2-5]. An interesting aspect of plasma treatment is that the changes are confined to a depth of a few nanometers at the surface because of the low level of penetration. This opens up possibilities for producing a wide spectrum of surface chemistry with desired compositions. The most attractive feature of the plasma processing is that by exerting proper control over the exposure conditions, a tailored surface with desired chemical functionality and morphology may be produced[4].

Radicals are formed on the surface of the polymeric materials by plasma surface treatments, and some of them can initiate graft polymerization of vinyl monomers. These reactions have been recognized for a long time and applied for the surface modification of polymers such as polyesters[5,6]. However, plasma graft polymerization has not been considered as often as plasma surface treatments and plasma polymerization. This is because of the fact that the total reaction process involved in the plasma graft polymerization is much more complicated. However, the advantage of plasma graft polymerization is the durability of the properties of the modified surface. The surface characteristics enhanced by the graft polymerization do not change easily, while the properties caused by plasma surface treatments often suffer from the recession with aging. Plasma modification of poly(ethylene terephthalate) (PET) has been studied by several workers and changes in the physical behavior and surface morphology have been reported[7-17]. It was found that under oxygen environment, the surface acquired oxygen containing polar functional groups such as -C=O, -OH and -OOH. During storage, the treated films underwent significant surface reorganization, where both the time and temperature contribute to the increase in the contact angle[2,4]. The nature of plasma also has significant impact on the surface behavior. It has been observed that the surface morphological changes are more severe with low pressure plasma as compared to the atmospheric plasma treatment and have been visualized in terms of the contact angle measurements and the atomic force microscopy[18]. Friedrich *et al.*[6] studied ageing and degradation of PET in an oxygen plasma and observed that the degradation reactions of PET in an oxygen plasma displayed many similarities to photo- and thermo-oxidative degradation reactions.

Plasma discharges have been extensively used as a means to modify the surface characteristics and to improve the blood compatibility of polymeric

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materials[19]. Grafting of vinyl monomers onto PET has been frequently used for various biomedical applications such as urinary bladder[20,21], artificial vascular prosthetic parts[22,23], surgical mesh[24,25], sutures[26,27], and components for percutaneous access devices[28]. The plasma-induced graft polymerization of monomers onto PET has been investigated by a number of workers[5,7,17,19,29-31]. In our previous studies, we have carried out the plasma induced graft polymerization of acrylic acid on PET films and subsequently allow collagen (type I and type III) immobilization and human smooth muscle cell expansion[5,30,31]. In the present study, the graft polymerization of acrylic acid onto PET monofilament has been carried out using oxygen plasma to activate the PET surface for graft polymerization of acrylic acid and chitosan immobilization.

2 Materials and Methods

Poly(ethylene terephthalate) (PET) chips of grade G-5761 were supplied by Reliance Industries Ltd., Hazira. Acrylic acid monomer, procured from Merck India Ltd., was purified by distillation under vacuum. Methyl ethyl ketone (MEK) was received from Qualigens Private Ltd. and chitosan (M_w 4,00,000) from Fluka.

2.1 Spinning of PET Filament

PET filament was produced by spinning the polymer on a melt spinning machine, followed by two stage sequential drawing. Vacuum dried PET chips (120°C for 2 days) were used for spinning the filament at 285°C. The length and diameter of single orifice of the spinneret was 2mm and 1mm respectively. Take up speed was maintained at 90 rpm. Drawing of PET monofilament on "Cybertex" drawing machine was carried out at a draw ratio of 5.0 and drawing temperature of 80°C for first heater and 95°C for the second heater.

2.2 Plasma Treatment

Plasma treatment of PET monofilaments was carried out under oxygen plasma (Fig. 1). The system consisted of RF reactor operating at 13.6 MHz. The unit consisted of two cylindrical electrodes of 13 cm diameter kept 2.6 cm apart in a cylindrical vacuum vessel. The bottom electrode and the reactor walls were grounded. The chamber diameter was 22 cm. The monofilament of specified length was mounted zigzag over a sample holder and was placed on the grounded electrode. The system was evacuated to 10^{-5} Torr and oxygen was introduced into the chamber at a flow rate of 20 ml/min. The chamber pressure was subsequently maintained at 0.05 Torr and plasma was generated at the electric power of 100 W for different exposure time. Finally, the air was introduced into the chamber and the sample was removed for the grafting reaction. The time between the plasma treatment and the beginning of the grafting reaction was around 30 min.

2.3 Grafting Procedure

Grafting was carried out in glass ampoules of 2×10 cm^2 size. A weighed amount of plasma treated monofilament was placed into ampoules containing monomer and the solvent. Nitrogen was purged for 15 min into the ampoule to remove air trapped inside the reaction mixture. The ampoule was subsequently placed in a water bath maintained at required temperature. After a desired period, the ampoule was removed and the sample was soxhlet extracted with water to remove any homopoylmer adhering to the sample surface. The sample was dried in an oven at 60ºC under vacuum and the degree of grafting was estimated by TBO (toluidine blue O) staining method[2]. TBO solution at *p*H 10 was prepared and the grafted filament was placed into this solution for 6 h at 40°C. The filament was subsequently removed and thoroughly washed with sodium hydroxide solution of *p*H 9 to remove any noncomplexed dye adhering on the filament surface. The dye was desorbed from the filament in 50% acetic acid solution and the optical density of the solution was measured by using an UV-Visible spectrophotometer at 623 nm. The poly (acrylic

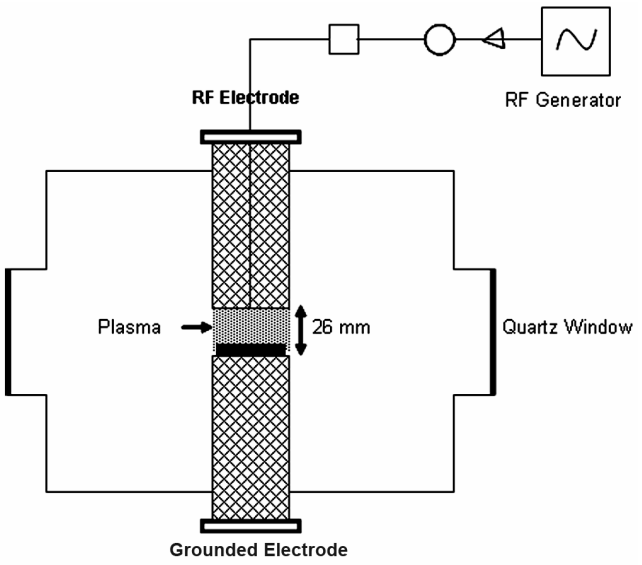

Fig. 1—Schematic representation of plasma treatment unit

acid) content (degree of grafting) was obtained from the calibration plot of the optical density versus dye concentration with the assumption of 1:1 ratio between the dye and the carboxylic acid groups.

2.4 Immobilization of Chitosan on Grafted PET Filament

Chitosan immobilization on PET filament was carried out by dipping the grafted filament in 0.5% chitosan solution in 2% acetic acid for 4 h. The filament was taken out of the chitosan solution and heat set at 130°C for 20 min. After the heat setting, chitosan immobilized filament was thoroughly washed with water at *p*H 3 to remove the excess amount of chitosan from the filament. The sample was dried at 60°C under vacuum.

2.5 Contact Angle Measurement

Contact angle measurements on filaments were made on DCAT 21 Tensiometer from Dataphysics using Wilhelmy method[2]. The sample was mounted on the holder and the force exerted on the contact of the filament with water surface was measured. The contact angle of the sample was obtained from the force using the in-built software[2].

2.6 Atomic Force Microscopy

The surface characteristics of unmodified and modified PET samples were studied with the help of VEECO atomic force microscopy (AFM).

3 Results and Discussion

The variation in grafting with the monomer concentration is shown in Fig. 2. Grafting reactions were carried out with monomer concentration of 20-80% for a reaction time of 4 h at 50°C. The degree of grafting increases and reaches maximum at 40% monomer concentration and then decreases with the further increase in monomer concentration. The initial increase in the degree of grafting with the increase in monomer concentration was caused by the unhindered accessibility of the monomer to the primary radicals (PO·), resulting in the smooth initiation and propagation steps, as shown in following Eqs (1) and (2):

$$PO\cdot + M \xrightarrow{k_i} P\text{-}OM\cdot \text{ (initiation)} \quad \ldots (1)$$

$$PCHX\cdot + M \xrightarrow{k_p} PCHX\text{-}M\cdot \text{ (propagation)} \quad \ldots (2)$$

The reaction medium involves MEK which is nonsolvent for poly(acrylic acid) and maintains the viscosity of the grafting medium by separating the homopolymer but complete phase separation does not occur. As a result, smooth grafting proceeds in the system. Beyond 40% of the monomer concentration, viscosity is increased and hinders the diffusion of monomer to the propagating sites. At the same time, effective concentration of monomer is reduced by extensive homopolymerization. As a result, the rate of propagation (k_p) is suppressed considerably and chain transfer (k_{tr}) to another species (Q), such as homopolymer in solution, dominates over the chain propagation. The degree of grafting, as a result, shows a decreasing trend[5].

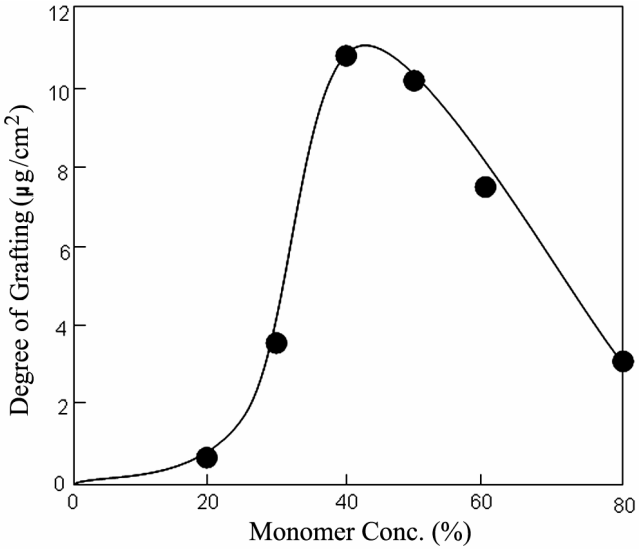

Fig. 2—Influence of monomer concentration on the degree of grafting [Conditions: plasma exposure time, 180s; plasma power, 100 W; MEK, 60%; temperature, 50ºC; and reaction time, 4 h]

The variation in degree of grafting of acrylic acid with reaction time at different plasma exposure time is shown in Fig. 3. It is evident that for 60s and 180s plasma exposure time, the degree of grafting increases with the increase in reaction time up to 6 h, whereas at 240s of plasma exposure time, the degree of grafting increases up to 3 h and then levels off. The increase in graft levels with the increase in reaction time is due to the availability of more time for propagation reactions of growing chains. As the treatment is carried out in oxygen plasma, the active sites are consisting of peroxides[6]. The increase in graft levels is achieved due to an increase in the number of active sites, resulting from increasing plasma exposure time.

The influence of reaction temperature on the degree of grafting is shown in Fig. 4. The grafting was carried out from 50°C to 80°C at a 40% monomer concentration. The equilibrium degree of grafting is

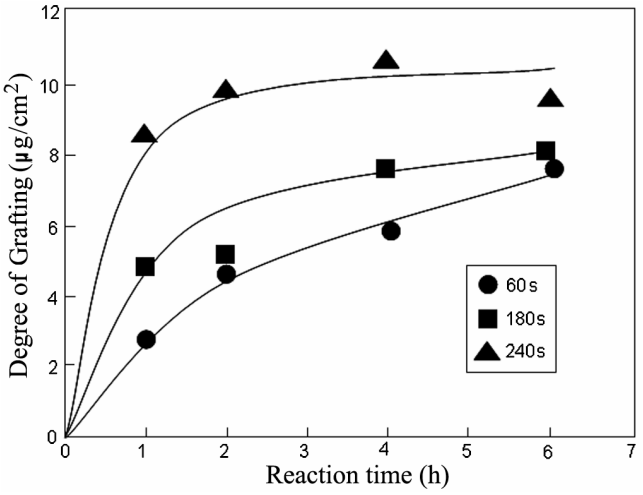

Fig. 3—Influence of reaction time on degree of grafting at different plasma exposure time [Reaction conditions: MEK, 60%; monomer conc., 40%; and temperature, 50ºC]

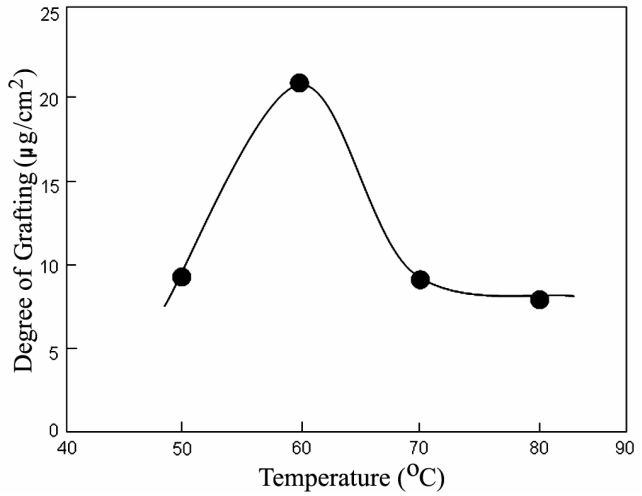

Fig. 4—Influence of reaction temperature on degree of grafting [Reaction conditions: plasma exposure time, 180s; plasma power, 100 W; MEK, 60%; monomer, 40%; and reaction time, 6 h]

increased up to 60°C and thereafter tends to decrease. It is proposed that in the early stages of reaction, the homopolymer formation is very limited which is separated by nonsolvent MEK and the local stationary concentration of monomer around the growing chain is maintained. This ensures fast initiation and propagation. However, with the increasing temperature, the concentration of propagating chains increases because of a higher peroxide decomposition rate, and the termination of two growing chains by mutual recombination becomes a major factor. Once the homopolymer formation is extensive, the monomer depletion favors more chain transfer in the system. It is possible that the chain transfer steps given by Eqs (3) and (4) at temperature higher than 60°C dominates to such an extent that the degree of grafting is reduced. It may also be possible that some of the primary radicals (PO·) become deactivated in the reaction medium [Eq (5)], contributing to the reduced degree of grafting at higher temperatures. Glass transition temperature seems to be an important factor in the observed behavior of reaction temperature. Schamberg and Hoigne[32] observed that at T_g, the polymer chains become more mobile. PET has T_g of approximately 70°C. It can be assumed that with increasing temperature beyond 60°C, more and more radicals combine and therefore they cannot react with the monomer. Additionally, chain termination may be favored due to an increased diffusion rate. This would lead to a lower kinetic chain length. An increase in the rate of chain termination could explain the decrease in the degree of grafting above T_g.

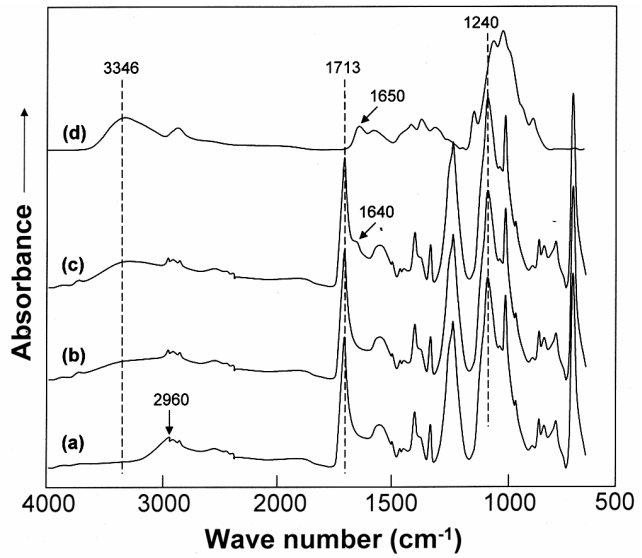

Fig. 5—ATR-FTIR of PET monofilament (a) virgin, (b) acrylic acid grafted (10.5 µm/cm^2), (c) chitosan immobilized, and (d) chitosan powder

$$PCHX\cdot + PCHX\cdot \xrightarrow{k_c} \text{dead polymer} \quad \ldots (3)$$

$$PCHX\cdot + Q \xrightarrow{k_{tr}} \text{chain transfer} \quad \ldots (4)$$

$$PO\cdot + PCHX\cdot \longrightarrow \text{deactivation} \quad \ldots (5)$$

The ATR-FTIR of different PET monofilaments is presented in Fig. 5. PET showed characteristic peaks at 2960 cm^{-1} of CH_2 stretching, 1713 cm^{-1} of –C=O stretching of aromatic ester, and a strong band at 1240

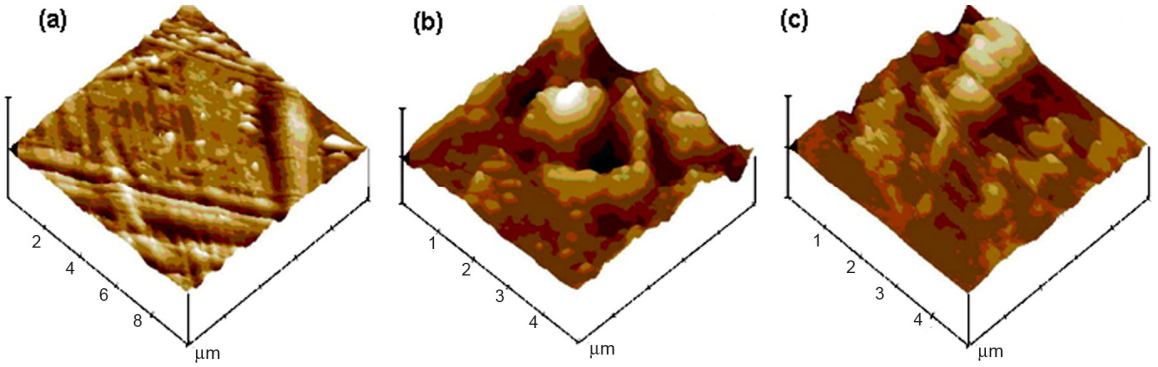

Fig. 6—AFM images (10 µm × 10 µm) of (a) virgin, (b) acrylic acid grafted (10.5 µm/cm^2), and (c) chitosan immobilized PET monofilaments

cm^{-1} of aromatic ester. Chitosan shows characteristic peaks at 3300-3600 cm^{-1} of –NH_2, and 1650 cm^{-1} of –C=O. The appearance of peak at 3300-3600 cm^{-1} (hydrogen bonding of –COOH) in PET-*g*-AA shows that acrylic acid had been grafted on the PET fabric. The appearance of peak at 1640 cm^{-1} in chitosan immobilized PET-*g*-AA, which is characteristic peak of –C=O of chitosan, indicates the presence of chitosan on the grafted sample.

The effect of plasma treatment time on contact angle of PET filament is also studied. The contact angle decreases from 72° for virgin PET to 38° for 180s of exposure which shows significant improvement in the wettability. The increase in wettability of surface is due to the presence of varieties of oxygen containing groups on the surface, such as -C-O, -C=O, -O-C=O, -OH, -OOH, etc after plasma treatment[33]. The contact angle of acrylic acid grafted (5.4 µg/cm^2) and chitosan immobilized filament is found to be 42° and 36° respectively at 120s plasma treatment time. It may be stated that the hydrophilicity becomes identical on plasma treatment and acrylic acid grafting as well as by chitosan immobilization.

The surface topography of filaments was observed by AFM (Fig. 6). The virgin filament is quite smooth in nature. The RMS value of surface roughness is increased from 3.7 Å for virgin PET to 51.5 Å for acrylic acid grafted PET. This is because of the fact that poly(acrylic acid) chains form their own domains and morphology at the surface which gives a characteristic hill-valley structure[31]. When chitosan is immobilized onto the grafted surface, it fills the valleys and leads to the flattening of the surface. The RMS value of roughness of chitosan immobilized PET is 34.8 Å which clearly reflects flattening behavior.

4 Conclusions

The plasma induced graft polymerization of acrylic acid onto PET monofilament is strongly influenced by the addition of different monomer concentration. The maximum grafting is observed at 40% of monomer concentration. The degree of grafting increases with the increase in plasma exposure time; this is due to an increase in the number of active sites, resulting from the increase in plasma exposure time. The reaction temperature influences the grafting significantly. Abrupt fall in the equilibrium degree of grafting takes place beyond 60°C. The appearance of carbonyl peak at 1640 cm^{-1} in chitosan immobilized PET-*g*-AA sample confirms chitosan immobilization. The contact angle is decreased from 72° for virgin PET to 38° for 180s of exposure of plasma treatment. The surface roughness is increased on grafting of acrylic acid. This is because poly(acrylic acid) chains form their own domains and morphology at the surface. This observation is clearly shown by atomic force microscopy.

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