Graft Polymerization of Acrylic Acid onto Polypropylene Monofilament by RF Plasma

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ABSTRACT: Plasma-induced graft polymerization of acrylic acid onto polypropylene monofilament was carried out to introduce carboxyl groups on its surface. The monofilament was treated with oxygen plasma to create hydroperoxide groups and subsequent graft polymerization of acrylic acid on exposed filament was carried out. An increase in the plasma power led to higher graft levels. It was observed that the hydroperoxide build up on PP surface follows linear increase with the increase in the plasma treatment time only up to 180 s beyond which it slowed down significantly. The formation of oxygenated species was ascertained by X-ray photoelectron spectroscopy, and the peroxide content was measured by the 2′-diphenylpicrylhydrazyl (DPPH) estimation. The grafting was observed to be considerably influenced by the plasma exposure time, plasma power, reaction temperature, monomer concentration and the storage temperature. A maximum in the degree of grafting was observed at 40% monomer concentration beyond which grafting tended to decrease very fast. The grafting was also found to be maximum at 50°C followed by a sharp decrease, subsequently. The storage of the exposed filament at −80°C led to the identical grafting all along the 16 days. However, the storage at 25°C showed significant reduction in the degree of grafting. The atomic force microscopy showed that surface morphology is transformed into a nonhomogeneous one after the plasma exposure, but tends to flatten out after the grafting process in the form of globular structures. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 2884–2892, 2010

Key words: polypropylene; monofilament; acrylic acid; plasma; graft polymerization; suture

INTRODUCTION

Polymeric materials with bioactive characteristics have generated considerable interest in human healthcare systems. The prominent application of these materials, commonly known as biomaterials, lies in the fabrication of implants, catheters, wound dressings, scaffolds, and sutures where infection control is the crucial consideration.[1–4] Most of the polymers, conventionally, do not show activity against microbial infection and hence are needed to be modified in such a way that the bioactive nature is introduced without much variation in the inherent physical properties of these materials. There are several ways to develop such polymers, such as by blending, coating, and immobilization of an active component within the matrix. However, the compatibility of the bioactive additive with the polymeric matrix and the stability of the component at high processing temperatures become the prime constraint to develop a required material.[5] It is the surface of a biomaterial that remains in contact with the tissues where surface functionality, morphology, and the wettability plays an interesting role in its performance.[6] Therefore, the most feasible way to design a material is to fabricate the surface in such a way that it acquires bioactive nature.

The surface modification needs to be followed in a way that the physical and chemical properties of the biomaterial surface are not adversely affected while achieving the antimicrobial nature through the modification process. The radiation-induced graft polymerization of a monomer onto the polymer matrix is an interesting route to the chemical functionalization of a biomaterial irrespective of its shape and size.[7–9] The attractive feature of the grafting process is that the extent of modification can be precisely controlled by proper selection of the irradiation parameters and the reaction conditions. However, the radiation grafting has the limitation in biomaterial development because of the fact that it brings about the bulk modification in a polymer due to the high energy of the electromagnetic waves. This is where, plasma grafting offers an innovative feature in terms of the nanoscale modification of the surface layers so that the inherent properties of the biomaterial remain intact while surface acquires desired functionality.[10]

Polypropylene (PP) has found enormous applications in hernia repair, wound dressings, sutures, biocomposites, blood contacting surfaces, and thermoresponsive materials.[11–14] In most of these domains

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such as sutures, the bacterial infection needs to be controlled to overcome postsurgical complications. The plasma grafting of an appropriate monomer followed by the immobilization of an antimicrobial drug or a bioactive molecule onto the modified surface makes it a formidable combination towards the development of a material which would prevent the bacterial infection at the surgical site.[15] The radiation grafting of acrylic acid on PP followed by the chitosan immobilization has been found to be effective approach to achieve antimicrobial fabric.[16,17] Although, radiation grafting process has been observed to produce PP suture with antibacterial behavior, the loss in mechanical strength due to extensive bulk degradation is a serious problem.[18–20] Plasma processing has the advantage over radiation treatment option. As the changes are confined to the surface layers, the mechanical properties of the material are preserved. The plasma treatment has been studied by several workers to investigate the changes in the surface chemistry *vis-à-vis* the nature of the ionizing medium.[21] The ionizing species and the radicals constituting the plasma interact with the material surface and create oxidative species, such as hydroperoxides and initiate the polymerization of a monomer to produce a graft copolymer.[22]

The grafting of various monomers on PP surface has been reported by a number of workers.[23–25] In a recent study, Liao et al.[23] carried out the grafting of acrylic acid on PP nonwoven fabric using microwave plasma. The resultant surface was coupled with chitosan to develop an antimicrobial surface. These surfaces were also evaluated for their coagulant behavior toward the adhesion of red blood cells and platelets. Similar studies on the acrylic acid grafting in PP nonwoven fabric have been carried out by Wang et al.[24] The grafted surfaces were immobilized with collagen/chitosan mixture. It was observed that the antimicrobial nature of the surfaces enhanced as the chitosan content in the collagen/chitosan mixture increased. The plasma grafting of acrylic acid on microporous PP membranes has also been carried out by Choi and moon,[25] and surprisingly, a very high graft level of 155% has been reported by the group. These materials have been projected to be cation exchange membranes of very low resistance (0.4 Ωcm^2). The incorporation of the carboxyl groups onto the polymer surface by plasma grafting has been very attractive for the immobilization of biological molecules and has been investigated for a number of polymers other than the PP matrix. The studies of Choi et al.,[26] Kang et al.,[27] and Kim et al.[28] are worth mentioning toward the development of bioactive surfaces for various applications. Although, significant studies involving the influence of the plasma parameter on the graft variations onto PP surfaces have been carried out by various groups, the precise information on the graft management as a function of the reaction parameters is inadequate.[22–25]

To overcome the mechanical loss due to gamma radiation-induced grafting, we have followed the plasma activation route to initiate the grafting process for the suture development.[29] It has been observed that the reaction medium plays a significant role in the graft management on the surface and the contact angle variation truly is influenced by the organic and inorganic additives present in the grafting medium. We have extended our studies to the influence of the plasma parameters as well as the reaction conditions so that the precise conditions for designing a suture may be accomplished. In this investigation, the PP filament was exposed to RF plasma for different durations and the graft polymerization of acrylic acid was studied under various reaction conditions. The influence of the plasma and the reaction conditions on the degree of grafting has been investigated.

EXPERIMENTAL

Materials

Polypropylene (PP) used for this study was supplied by Indian Petrochemicals Limited, India. The monofilament was prepared by melt spinning of PP at 230°C under nitrogen atmosphere. The filament had a diameter of 0.26 mm and denier of 428. The monofilaments were soxhlet extracted with acetone to remove impurities adhering to the surface.

Acrylic acid (Merck India Ltd.) was purified by distillation under vacuum. Methanol obtained from Qualigens Fine Chemicals, India, was used as received. Toluidine Blue O (TBO) was supplied by Spectrochem. Toluene was also supplied by Merck India Ltd. and was used as such. 2,2-diphenyl-1-picrylhydrazyl (DPPH) was received by Fluka. Distilled water was used for all experiments.

Plasma treatment

Plasma treatment of PP monofilaments was carried out under oxygen plasma as reported earlier.[29] The system consisted of RF reactor operating at 13.6 MHz. The unit is a reactor consisted of two cylindrical electrodes of 13 cm diameter and 2.6 cm apart in a cylindrical vacuum vessel. The system was evacuated to 10^{-5} Torrr and oxygen was introduced into the chamber at a flow rate of 20 sccm. The chamber pressure was subsequently maintained at 0.05 Torr and plasma was generated at the required electric power for half the period of the total exposure time. Subsequently, air was introduced into the chamber and the sample was reverted for the remaining

exposure on the other side. 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 15 min.

Determination of amount of peroxide

The amount of peroxide formed on the surface of PP filament after oxygen plasma treatment was quantified with DPPH.[30,31] The samples were put in $1 \times 10^{-4}M$ toluene solution of DPPH in a glass ampoule of 2×10 cm^2 size. Nitrogen was purged into the ampoule to remove air trapped inside the reaction mixture and the ampoule was kept at 70°C for 3 h to decompose peroxides formed on the surface of the polymer substrate. The DPPH molecules consumed were measured from the difference in absorbance at 520 nm between the control and the peroxidized sample by using the spectrophotometer. The concentration of peroxides was measured by calibration plot using different concentration of DPPH solutions in toluene.

Grafting procedure

A weighed amount of plasma-treated monofilament was placed into ampoule containing monomer and the solvent. Nitrogen was purged into the ampoule to remove air trapped inside the reaction mixture. The ampoule was subsequently placed in a water bath maintained at a specific temperature. After a desired period, the ampoule was removed and the sample was soxhlet extracted with water to remove any homopolymer adhering to the sample surface. The sample was dried in an oven at 50°C under vacuum and the degree of grafting was estimated.

Determination of homopolymer yield

The homopolymer yield was determined gravimetrically. When the grafting reaction was over, the complete homopolymer was collected by precipitating the homopolymer in a nonsolvent like 2-butanone. The homopolymer was vacuum dried at 50°C overnight. The dried homopolymer was accurately weighed.

Determination of degree of grafting

The degree of grafting was determined by colorimetric method with TBO staining, as reported in the literature.[32] TBO solution at pH 10 was prepared and the grafted filament was placed into this solution for 6 h at 40°C. The filament was subsequently removed and washed with sodium hydroxide solution of pH 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 polyacrylic acid content (degree of grafting) was obtained from the calibration plot of the optical density vs. dye concentration with the assumption of 1 : 1 ratio between the dye and the carboxylic acid groups.

UV-visible spectrophotometer

The dye content was measured on Perkin Elmer Lambda E Z 201 spectrophotometer at 623 nm.

Atomic force microscopy

Topographical studies of the sample surface were carried out in air using atomic force microscope (AFM), Nanoscope IIIa (Digital Instruments, Veego Metrology Group) and was operated in the contact mode using an etched silicon tip attached to the end of a cantilever (115–135 μM in length). The AFM measurements were carried out at a cantilever resonant frequency of around 277.5 kHz and a scan rate of 0.5 Hz. The spring constant of the cantilever was in the range of 20–80N/m.

X-ray Photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) analyses were performed on a Physical Electronics Quantum 2000 Scanning ESCA Microprobe using a monochromatic Al X-ray source. The detection angle was 45° and the pass energy was 23.50 eV.

RESULTS AND DISCUSSION

Peroxidation of PP monofilament

The grafting of acrylic acid onto polypropylene monofilament has been carried out to introduce carboxyl groups on the surface. It was observed that the grafting of acrylic acid is strongly governed by the presence of organic or inorganic additives in the grafting medium.[29] The inorganic additives such as ferrous sulfate has been found to produce very low graft levels and very little hydrophilicity as compared with those of the organic additives such as methanol, butanone, and acetone addition. The most appropriate additive was found to be methanol in the water-organic mixture, which allows smooth grafting reaction to take place. In a grafting reaction, both the plasma treatment conditions as well as the reaction conditions influence the graft levels on the filament surface, significantly. The plasma exposure follows the generation of hydroperoxides along the polymer backbone, which is the general observation

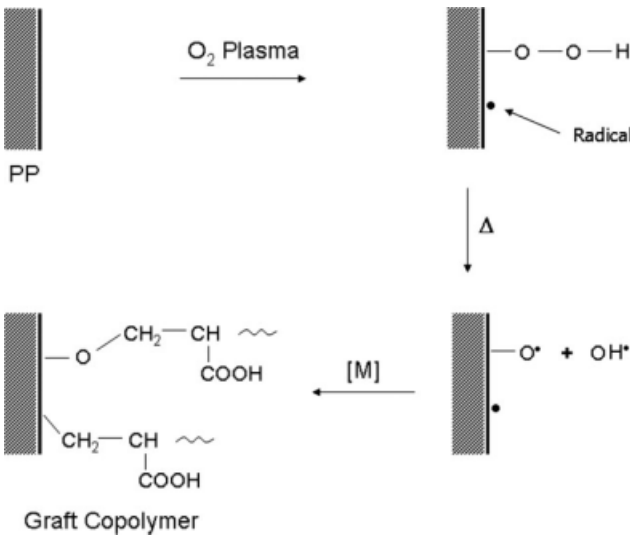

Figure 1 Schematic representation of the plasma grafting process.

for hydrocarbon polymers, such as polyethylene and polypropylene, and represent the active species for initiating the grafting process via its homolytic cleavage as presented in Figure 1.[33]

It is observed that there is a steady increase in the peroxide content with the plasma exposure time up to 180 s beyond which the deviation from the linear increase is observed. This indicates the slower rate of peroxide build-up beyond 180 s exposure time (Fig. 2). It may be proposed that the radical formation and their interaction with the oxygen proceeds smoothly as the exposure time increases. This leads to a linear build-up of the hydroperoxides on the PP surface up to 180 s. May be, a fraction of these peroxides undergoes deactivation due to the bombardment of various species present in the plasma. The ablation of the filament surface may also eat away some of the hydroperoxides. So there is equilibrium between the hydroperoxide generation and their deactivation leading to a slower peroxide build-up. Huang et al.[33] also observed that the peroxide concentration during plasma treatment of polypropylene films increases with the plasma exposure only for a couple of minutes and decreases rapidly up to the exposure time of 30 min, supporting our observation for the peroxide generation and their partial deactivation during plasma treatment of PP filament. The generation of oxygenated species is strongly supported by XPS analysis on plasma-treated samples (Table I). There is a significant increase in the oxygen content (O_1s/C_1s, 0.23) for the exposure period of 180 s indicating the formation of oxygenated species. Surprisingly, we have observed a minute amount of nitrogen in our plasma-treated and the grafted samples which may be due to the contamination on our samples. The virgin PP has $\sim$ 16% oxygen which seems to be originated from the stabilizers and a partial degradation during the melt spinning process. However, the grafting of acrylic acid to a level of 119 $\mu g/cm^2$ further enhances the oxygen content to 24.46% and may be attributed to the incorporation of carboxyl groups on the surface. These studies are in line with the observation of Wang and Chen[34] for AA grafting on Teflon films.

Influence of the plasma exposure and the reaction conditions on the degree of grafting

Both the plasma exposure parameters and the grafting reaction conditions exert significant influence over the grafting process. The variation of the degree of grafting with the monomer concentration is presented in Figure 3. The grafting increases with the increase in the monomer concentration up to 40% and subsequently tends to decrease. Similar maxima in the grafting of acrylic acid onto PTFE films have been observed by Wang and Chen[34] and the results have been attributed to the "Trommsdorff effect" in the grafting medium which originates due to the sudden increase in the viscosity of the grafting medium and subsequent slowing down of the termination of the growing chains. We, however, do not visualise such an effect operating in our grafting system. Instead, the grafting trend in the Figure 3 seems to be a fall out of the high level of homopolymerization and depleting monomer content in the grafting medium. The initial increase in the degree of grafting with the increase in the monomer concentration is probably due to the unhindered accessibility of the monomer to the primary radicals $P^{\bullet}$, resulting in a smooth initiation step and the propagation step [eqs. (1) and (2)].

$$P^{\bullet} + M \xrightarrow{k_i} PM^{\bullet} \quad \text{initiation} \tag{1}$$

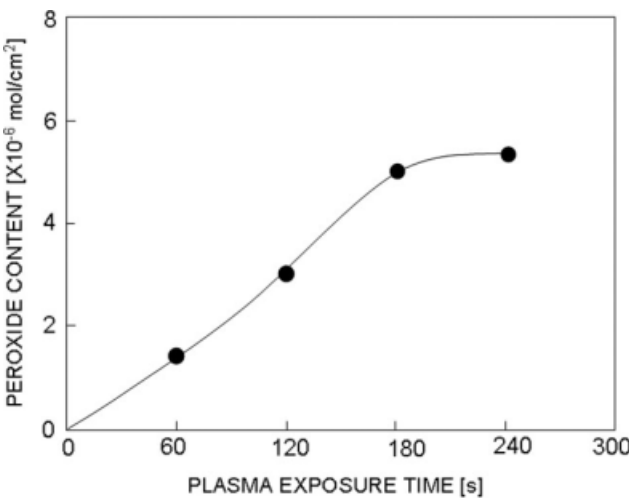

Figure 2 Variation of the peroxide content with the plasma exposure time. Plasma power, 60 W; O_2 pressure 20 sccm.

TABLE I
XPS Analysis of Samples

S. no.	Sample description	Degree of grafting (μg/cm)	C_1s	O_1s	N_1s	O_1s/ C_1s
1.	Original PP Fiber	–	84.11	15.89	0	0.19
2.	Oxygen plasma-treated PP fiber (180 s)	–	80.86	18.60	0.53	0.23
3.	PP-*g*-AAc	116	74.11	24.46	1.43	0.33

$$PM^{\bullet} + nM \xrightarrow{k_p} PM^{\bullet}_{n+1} \quad \text{propagation} \qquad (2)$$

(represented as $PCHX^{\bullet}$ subsequently).

Hydroperoxides decomposes into $PO^{\bullet}$ and $OH^{\bullet}$, it is the $PO^{\bullet}$ radicals which initiates the graft polymerization. However, it is the $OH^{\bullet}$ radical which is involved in the homopolymerization. No homopolymerization takes place at 10% monomer concentration (Table II). The homopolymerization is still very little (4%) for 20% monomer concentration. At 30–40% monomer concentrations, a large fraction of the monomer is transformed into the homopolymer, but still leaves behind some monomer for the grafting process to follow. With the subsequent increase in the monomer concentration (>40%), the homopolymerization becomes extensive and the viscosity of the reaction medium increases significantly which causes the monomer depletion and hence diminishing monomer accessibility to the grafting sites. It is, therefore, the competition between the chain propagation and the homopolymerization process which influences the grafting process.[35] As a result, the rate of propagation (k_p) decreases considerably, and the growing chains are deactivated by mutual combination [eq. (3)] or by chain transfer to another species [eq. (4)] and primary radicals [eq. (5)]. The degree of grafting, as a result, shows a decreasing trend. The homopolymerization is so intense beyond 60% monomer concentration that the grafting does not takes place at all. Similar trend has been observed in our study on the acrylic acid grafting on PET films treated with the argon plasma.[36]

$$PCHX^{\bullet} + PCHX^{\bullet} \xrightarrow{k_t} \text{dead polymer} \qquad (3)$$

$$PCHX^{\bullet} + Q \xrightarrow{k_t} \text{chain transfer} \qquad (4)$$

$$PCHX^{\bullet} + P^{\bullet} \xrightarrow{k_t} \text{deactivation} \qquad (5)$$

The grafting increases with the increase in plasma power from 60 to 100 W (Fig. 4). This reflects an enhancement in the radical formation by oxygen plasma at the PP surface with the increase in the plasma power. The increased plasma power transfers more energy to the gaseous medium.[22] This causes more ionization of the plasma gases which leads to the generation of more active species in the plasma and hence results in the increased rate of initiation. The observed trend is the reflection of the steady increase in the radical sites and hence smooth build-up of the hydroperoxide functionality with the increase in the plasma power, leading to the higher graft levels.[34] Poncin-Epaillard et al.[22] have also observed an increased grafting yield with plasma power up to 80 W beyond which the grafting diminished, indicating the deactivation of the reactive species once power increases more than a crucial dose.

The variation of the degree of grafting with the reaction time for various plasma treatment time is presented in Figure 5. The graft variation shows identical behavior for exposure time in the range of 60–240 s. The degree of grafting increases linearly with the increase in the reaction time up to 6 h and then levels off, as observed by Lee et al. for the grafting of 2-hydroxyethyl methacrylate onto silicone rubber.[37] It may be stated that the growing chains are exhausted within 6 h and lead to the equilibrium degree of grafting. The grafting yield increases with the increase in the plasma treatment time due to the enhanced number of active species involved in the grafting reaction at higher plasma treatment time. Similar trend was observed by Kou et al.[38] in the grafting of α-allyl glucoside on microporous

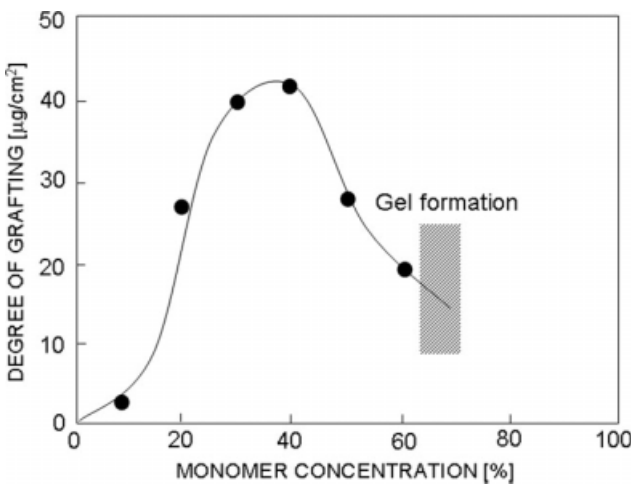

Figure 3 Variation of the degree of grafting with the monomer concentration. Plasma treatment conditions: exposure time, 60 s; plasma power, 60 W; O_2 pressure, 20 sccm. Grafting conditions: Water–Methanol, 60 : 40; temperature, 50°C; time, 2.5 h.

TABLE II
Homopolymer Yield at Different Monomer Concentrations

Monomer concentration (%)	Homopolymer yield (%)	Degree of grafting (μg/cm)
10	0	2.5
20	4	26
30	36	39
40	55	41
50	72	23
60	gel	19

polypropylene hollow fiber membrane by nitrogen plasma.

The equilibrium degree of grafting at various plasma treatment time is presented in the Figure 6. The rate of grafting was obtained from the slope of the plots in Figure 5. The grafting increases almost linearly up to 180 s and thereafter tend to slow down a bit. The initial rate of grafting also follows a linear trend and increases with the increase in the exposure time. This behavior may be ascribed to the higher number of initiating centers at higher plasma exposure time. The deviation in the grafting trend from the linear relationship beyond 180 s suggests that number of initiating centers beyond this exposure time is not linear. One has to understand that the oxidation process is also accompanied by the surface ablation process which means that a fraction of the generated oxidative species are deactivated as the plasma treatment proceeds for a longer period. This is what may be happening more intensively beyond 180 s of exposure time. The peroxide build-up with the exposure time also follows a similar pattern as that of the degree of grafting (Fig. 1). A correlation between degree of grafting and peroxide content is presented in Figure 7. The straight line relationship justifies the assumption that peroxide content at specific exposure time is responsible for the graft variation in this study investigation.

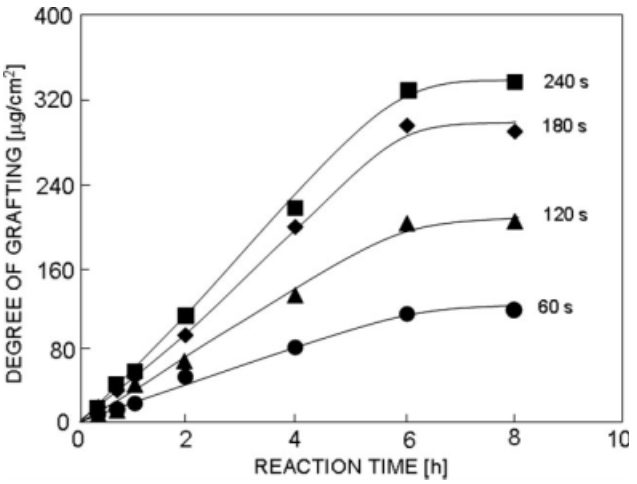

Figure 5 Variation of the degree of grafting with reaction time at different plasma treatment time. Plasma treatment conditions: plasma power, 100 W; O_2 pressure, 20 sccm. Grafting conditions: Water–Methanol, 60 : 40; monomer concentration, 40%; temperature, 50°C.

The reaction temperature has profound influence on the degree of grafting (Fig. 8). The grafting was carried out from 40 to 80°C. The degree of grafting initially increased and reached maximum at 50°C followed by sharp decrease with the further increase in the reaction temperature. The initial increase in the grafting with the temperature is due to the fact that the higher temperature can accelerate the diffusion of monomer within the PP surface layer and better accessibility of the monomer to the growing

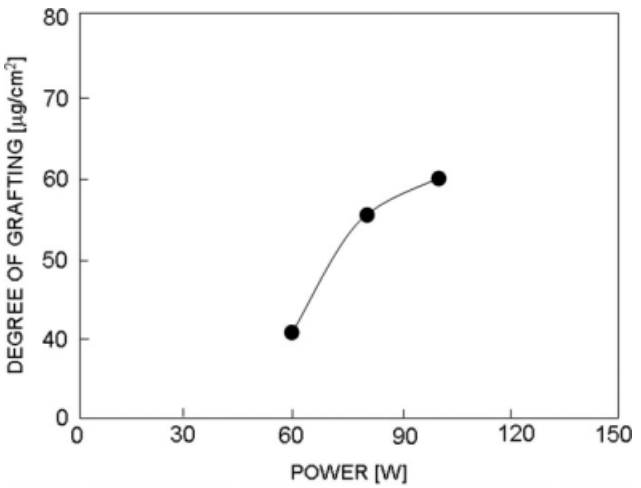

Figure 4 Variation of the degree of grafting with the plasma power. Plasma treatment conditions: exposure time, 60 s; O_2 pressure, 20 sccm. Grafting conditions: Water–Methanol, 60 : 40; monomer concentration, 40%; temperature, 50°C; time, 2.5 h.

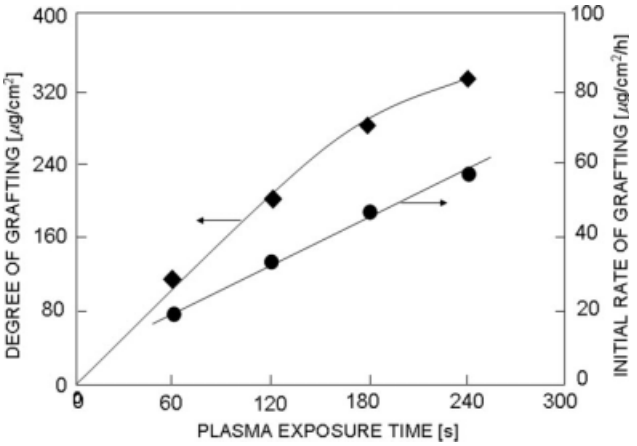

Figure 6 Variation of the equilibrium degree of grafting and initial rate of grafting with the plasma exposure time. Plasma treatment conditions: plasma power, 100 W; O_2 pressure, 20 sccm. Grafting conditions: Water–Methanol, 60 : 40; monomer concentration, 40%; temperature, 50°C; time, 6 h.

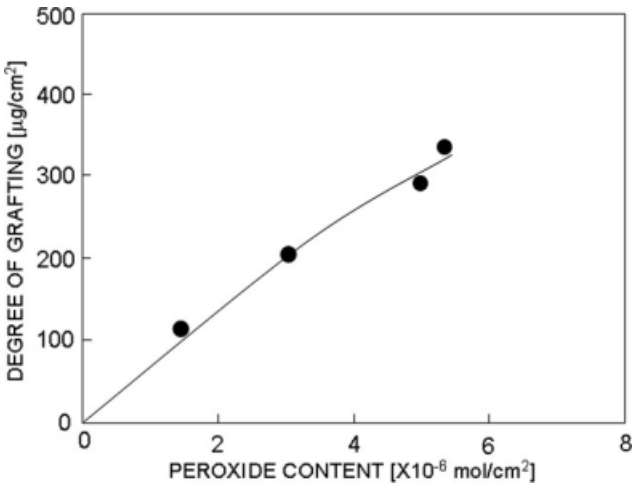

Figure 7 Correlation of the equilibrium degree of grafting with the peroxide content. Plasma treatment and grafting conditions are same as in Figure 6.

chains leading to the higher rate of propagation [eq. (2)].[34] The reactivity of radicals toward the monomer also increases with the increase in the temperature. The homolytic decomposition of peroxides into radicals is also accelerated at higher temperature resulting into higher grafting level.[34]

$$P^{\bullet} + P^{\bullet} \longrightarrow P - P \quad (6)$$

$$POO^{\bullet} + P^{\bullet} \longrightarrow POOP \quad (7)$$

$$POO^{\bullet} + POO^{\bullet} \longrightarrow POOP + O_2 \quad (8)$$

Although, the termination of primary radicals ($P^{\bullet}$) and peroxy radicals ($POO^{\bullet}$) by mutual recombination as per eqs. (6) and (7) would increase with the increase in the temperature, it seems that this deactivation is negligible as compared to the propagation reaction [eq. (2)] up to a temperature of 50°C which ensures higher degree of grafting. Beyond 50°C, the deactivation of primary radicals as well as the growing chains is more pronounced which diminishes the grafting levels. Another factor contributing to the observed behavior is the extent of homopolymerization. The acrylic acid homopolymerization proceeds quite fast at high reaction temperatures. This homopolymerization not only diminishes the monomer concentration but also increases the viscosity of the reaction medium which inhibits the diffusion of monomer to the radical sites. We see a reasonable similarity with our earlier plasma grafting studies on PET-acrylic acid system where peak maxima was observed at 50°C in spite of the fact that the initial rate of grafting increased with the increase in reaction temperature.[36] The grafting of acrylic acid onto Teflon has also been observed to follow similar trend where the grafting tends to decrease beyond 60°C.[34] If we compare these three studies of acrylic acid grafting on PP, PET, and teflon, the trend in the graft variation is identical with maxima being somewhere between 50–60°C. This suggests that it is primarily the monomer reactivity with the backbone radical and subsequent propagation that governs the grafting process while the chemistry of the base polymer has little significance, at least in the current scenario.

The polypropylene filament was stored at various storage conditions for specific period of time after plasma exposure. Figure 9 shows the effect of storage temperature and time on the degree of grafting for the plasma exposure time of 180 s. The grafting level in filament stored at room temperature was found to decrease rapidly with the storage time. On the other hand, the grafting yield at the storage temperature −80°C remained fairly constant up to 16 d. A constant grafting yield at −80°C is the reflection

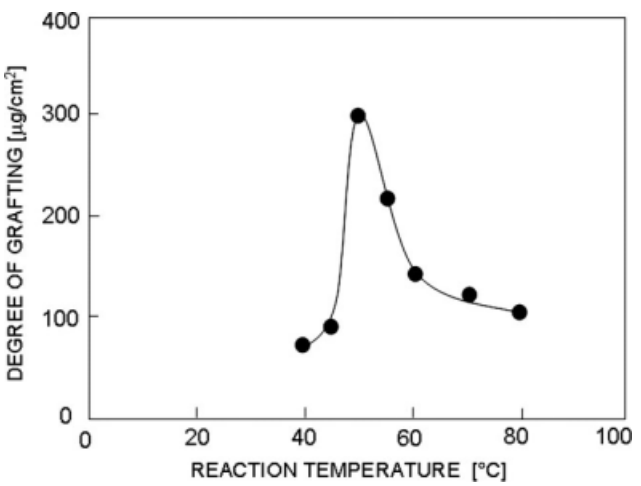

Figure 8 Influence of on the degree of grafting. Plasma treatment conditions: exposure time, 60 s; plasma power, 100 W; O_2 pressure, 20 sccm. Grafting conditions: Water–Methanol, 60 : 40; monomer concentration, 40%; time, 6 h.

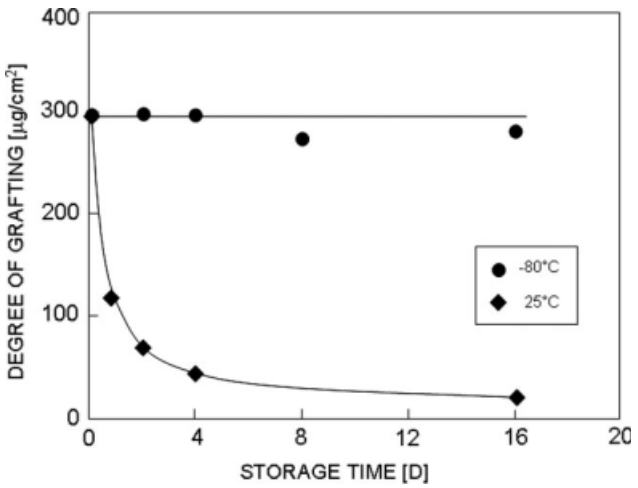

Figure 9 Influence of storage time on the degree of grafting. Plasma treatment conditions: exposure time, 60 s; plasma power, 100 W; O_2 pressure, 20 sccm. Grafting conditions: Water–Methanol, 60 : 40; monomer concentration, 40%; temperature, 50°C; time, 6 h.

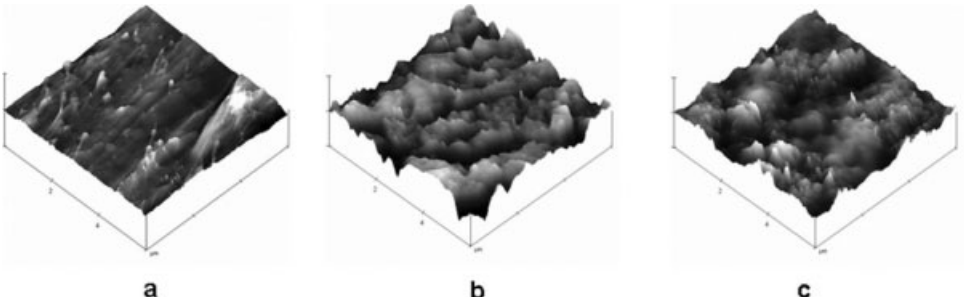

Figure 10 AFM images of (a) original PP filament (b) plasma-treated filament (180s) (c) grafted filament (24 μg/cm^2 PAA).

of the stability of the initiating species during the storage which comes from the restriction of chain segmental motion at such a low temperature. The termination rate of various active sites increases at higher storage temperature and leads to low graft levels [eqs. (7)–(9)]. Similar results were obtained by Park et al. for the grafting of acrylic acid onto polypropylene (PP) fabric by preirradiation method using 60Co gamma ray.[39]

It may be proposed that radical sites are created during the oxygen plasma exposure which may be either P$^\bullet$ or POO$^\bullet$. The radical sites have been found to be active even at a temperature of −20°C as observed the group of Chin et al. using ESR spectroscopy.[31] As the time between plasma exposure and storage was a couple of minutes, it may be understood that the active sites in PP would be both the hydroperoxides and the radical sites. Because of the restriction on the chain mobility and the oxygen diffusion, these sites remain protected in their form (POOH and P$^\bullet$) and offer constant graft levels all along the storage period.[40] However, the storage at 25°C would transform the free radical sites into some other stable species by reacting with the atmospheric impurities along with hydroperoxides. This deactivation seems to be responsible for the sharp decrease in the graft levels. Under such a scenario, the grafting would be accomplished solely by the decomposition of the stable species, such as POOP and POOH. The results in Figure 9 show that within a couple of days, the active sites are transformed into the inactive sites and lead to the low graft level.

The evolution of surface morphology during the grafting process was observed by AFM and is presented in Figure 10. The PP surface shows a quite smooth pattern with occasional and low aptitude structures. However, the plasma exposure leads to the formation of a rough morphology and a Hill–Valley structure becomes evident. This is a regular feature in the plasma etching process and has been observed in other systems as well.[41,42] The grafting of acrylic acid onto the plasma activated filament leads to the formation of globular domains and the flattening of the valleys. This may be assumed that the grafted PAA chains form independent domain on the surface and fill up in the valleys to flatten it out. Because of the incompatibility of the hydrophilic PAA chains and hydrophobic PP matrix, the phase separation between these two components follows. As a result, the grafted domains remain as isolated islands on the filament surface.

CONCLUSION

The plasma grafting of acrylic acid on PP filament is an interesting approach to introduce carboxyl functionality on its surface. The degree of grafting is significantly influenced by both the plasma exposure conditions as well as the reaction conditions during the grafting step. The plasma treatment leads to the formation of oxygenated species on the filament surface as measured by XPS analysis. The degree of grafting is governed by the plasma treatment time and the power. The grafting increases as the treatment time increased from 60 to 240 s. The rate of grafting was higher for the higher plasma treatment time due to the presence of more initiating species on the surface. The monomer concentration has profound influence over the degree of grafting. A maximum in the grafting at 40% monomer concentration was observed beyond which a sharp decrease in the grafting follows. This seems to be the outcome of a cumulative effect of the monomer accessibility to the grafting sites, primary as well as growing chain termination and the extent of homopolymerization. The homopolymer formation is so pronounced that inseparable gel formation takes place beyond 60% monomer concentration. The reaction temperature also shows strong influence over the degree of grafting. A sharp maxima in the degree of grafting is observed at 50°C. It seems that there is competition of the primary radical formation and propagation with the growing chain termination and the homopolymerization. Below, 50°C the propagation proceeds smoothly due to regular availability of the monomer to the growing chain. Beyond 50°C, the homopolymerization proceeds to a large extent and the termination of chains dominates due to little monomer availability for the grafting.

The grafting degree remained at almost the same level up to 16 days when the treated monofilament sample stored at −80°C but a sharp loss of grafting ability of the filament stored at 25°C was observed. This has been attributed to the loss of initiating species while storage at 25°C.The surface morphology as observed by AFM shows that the hill-valley structure is created due to the surface etching by plasma. Once the grafting proceeds, the graft fill up in the valleys produced by the plasma exposure and flattens onto the surface. The inherent incompatibility between the hydrophilic PAA chains and the hydrophobic PP matrix lead to the formation of islands on the filament surface.

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