

# Plasma Induced Graft Polymerization of Acrylic Acid onto Polypropylene Monofilament

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**ABSTRACT:** Plasma induced graft polymerization of acrylic acid onto polypropylene (PP) monofilament was carried to introduce carboxyl functionality on its surface. The monofilament was treated with oxygen plasma to create hydroperoxide groups and subsequent graft polymerization was initiated on this exposed monofilament. It was observed that in the absence of an added inhibitor, the grafting did not proceed because of the extensive homopolymerization which left behind hardly any monomer for the grafting reaction. The addition of ferrous sulfate to the grafting medium led to the homopolymer free grafting reaction. The addition of organics, such as methanol, butanone, and acetone led to complete inhibition of the homo-

polymerization at 60% content. However, the addition of butanone led to much lower degree of grafting than methanol and acetone. The contact angle of the monofilament showed drastic reduction by plasma treatment and by the subsequent grafting of acrylic acid. The grafting in ferrous sulfate medium showed higher contact angles as compared to the grafting in organic medium. The surface morphology was significantly influenced by the nature of the additive in the grafting medium. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 324–330, 2008

**Key words:** polypropylene; monofilament, acrylic acid; plasma; graft polymerization

## INTRODUCTION

Polypropylene (PP) is one of the most versatile materials because of its chemical inertness, better tensile strength, and low cost. However, the hydrophobic nature of the polymer restricts its application in a number of technologically important areas, such as in composites, packaging materials, and biomaterials. The medical applications of PP in surgery as suture or as prosthetic implant are due to its optimum tensile strength and low level of tissue reaction.<sup>1,2</sup> However, the microbial infection on the implanted site often has been observed to lead deterioration of the wound and related complications.<sup>3</sup> Therefore, the development of the antimicrobial suture may provide necessary environment for the infection free healing process. The key requirement of development process is that the modification of PP sutures should be carried out in such a way that it acquires functional groups where a drug may be immobilized. This drug is released from the suture once in contact with the biosystem and provides antimicrobial action at the stitch site.

The functionalization of polymeric materials by plasma and high energy radiation has attracted wide attention to introduce desirable functional properties in the material surface.<sup>4–7</sup> Both the morphological and the chemical changes take place during the plasma exposure.<sup>8</sup> The etching leads to the surface roughness and at the same time, functional groups are created on the surface depending on the nature of the gases. The chemical changes on PP surface are reflected in the form of changes in surface energy and contact angle.<sup>9–13</sup> 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.<sup>8</sup>

The most common gases used for plasma exposure are water, argon, nitrogen, ammonia, and oxygen which lead to the formation of a wide range of functional groups, such as hydroxyl, amino, amide, carboxyl, hydroperoxide, and carbonyl.<sup>8</sup> The hydroperoxide groups are thermally labile groups and can induce the graft polymerization of a monomer onto the PP surface. The plasma-induced graft polymerization of monomers onto PP has been investigated by a number of workers.<sup>14–17</sup> Research group of Poncin-Epaillard has reported the graft polymerization of acrylic acid onto PP films.<sup>15</sup> The PP film was

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treated with nitrogen plasma and was subsequently grafted with acrylic acid using the postgrafting method. The degree of grafting and the rate of grafting were shown to be dependent on the generated amino groups.<sup>15</sup> Sciarratta et al.<sup>16</sup> on the other hand, activated the PP surface by hydrogen plasma and subsequently introduced acrylic acid vapors into the plasma chamber to initiate the grafting process. However, the relative efficiency of the vapor phase *in situ* or two step *ex situ* grafting processes has been observed to be dependent on the nature of the monomer to be grafted.<sup>17</sup>

In our previous work, we carried out the grafting of 2-hydroxyethylmethacrylate (HEMA) onto PP monofilament suture to immobilize 8-hydroxyquinoline as the antimicrobial drug.<sup>18,19</sup> However, The inherent incompatibility of the grafted component with the nonionic PP matrix led to the significant loss in tensile strength. In order to overcome this problem, we carried out the grafting of nonionic monomer, acrylonitrile onto PP monofilament using preirradiation.<sup>20</sup> The grafted PP monofilament was subsequently hydrolyzed to get carboxyl groups for subsequent antimicrobial drug immobilization.<sup>21–22</sup> In a subsequent work, the grafting of vinyl imidazole was accomplished on PP filament using simultaneous radiation method to develop antimicrobial sutures.<sup>23,24</sup> However, the gamma irradiation leads to the bulk modification of the material and a significant degradation as well as the loss of mechanical strength was observed even before any grafting could be initiated. This is where the plasma activation offers advantage over the gamma irradiation. Here the modification remains confined to nano layers on the surface without any influence on the bulk structure, thereby producing a material with retention in the mechanical properties.

One of the most critical observations in the graft polymerization has been the formation of homopolymer during the grafting reaction both in plasma and radiation-induced graft modifications.<sup>15,18,19</sup> Efforts have been made to overcome this problem by the addition of ferrous sulfate to the grafting medium.<sup>14,15</sup> However, the ferrous ions may interact with the grafted component by complexation and may not be possible to remove them completely from the modified polymer. This is where the need for an organic additive has arisen which would hinder the homopolymerization and would ensure the smooth grafting reaction. Our earlier studies on acrylamide grafting on polyethylene has shown that organic additives such as methanol and acetone inhibit homopolymer formation and ensure smooth grafting reaction.<sup>24</sup>

In the present study, the graft polymerization of acrylic acid onto PP monofilament has been carried out using oxygen plasma to activate the PP surface.

The influence of various organic additives in the reaction medium on the degree of grafting and homopolymerization has been investigated. A correlation between the surface morphology as a function of the degree of grafting and the grafting medium has been made.

## EXPERIMENTAL

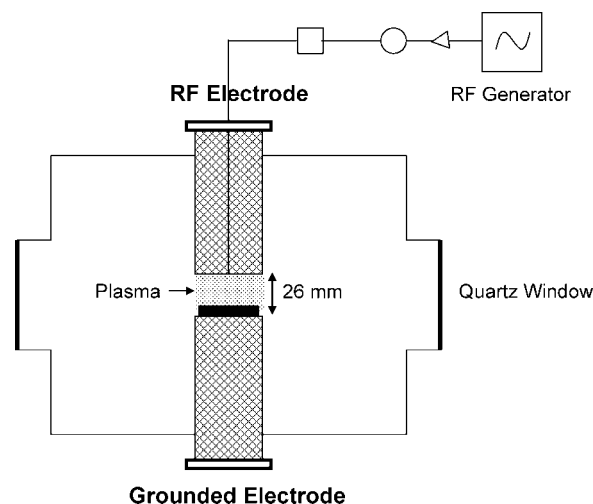
### Materials

PP, MFI of 16, 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 monofilament was collected on bobbins and was further drawn to 1 : 5 ratio. The filament had a diameter of 0.30 mm and denier of 720. The monofilaments were soxhlet extracted with acetone to remove any impurity adhering on the surface.

Acrylic acid monomer was received from GS Chemicals, India and was purified by distillation under vacuum. Ferrous sulfate was received from Merck, India. Methanol, acetone and 2-butanone obtained from GS Chemicals India. were used as received. Distilled water was used for all experiments.

### Plasma treatment

Plasma treatment of PP monofilaments was carried out under oxygen plasma as depicted in Figure 1. The system consisted of RF reactor operating at 13.6 MHz. The unit consisted of two cylindrical electrodes of 13 cm diameter and 2.6 cm apart in a cylindrical vacuum vessel. The bottom electrode and the reactor walls were grounded. The chamber diameter



**Figure 1** Schematic representation of the plasma treatment unit.

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 sccm. The chamber pressure was subsequently maintained at 0.05 Torr and plasma was generated at the electric power of 60 W for 60 s. 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.

### Grafting procedure

Grafting was carried out in glass ampoules of  $2 \times 10$  cm<sup>2</sup> size with B-24 joints. A weighed amount of plasma treated monofilament was placed into ampoules 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 50°C. 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 degree of grafting

The degree of grafting was determined by colorimetric method with Toluidine Blue O (TBO) staining, as reported in the literature.<sup>25</sup>

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 thoroughly 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 versus dye concentration with the assumption of 1 : 1 ratio between the dye and the carboxylic acid groups.

### Contact angle measurement

Contact angle measurements on filaments were made on DCAT 21 Tensiometer from Dataphysics using Wilhelmy method.<sup>26</sup> 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 by in-built software.

### Scanning electron microscopy

The surface characteristics of unmodified and grafted monofilaments were studied using STEREO-SCAN 360 (Cambridge Scientific Industries Ltd.), scanning electron microscope, after coating them with silver. Thick layer of silver metal is used to provide conduction.

## RESULTS AND DISCUSSION

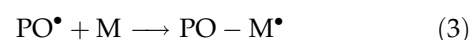
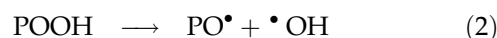
In the present investigation, the plasma induced graft polymerization of acrylic acid onto PP monofilament was carried out to investigate the influence of the reaction medium on the degree of grafting and surface morphology. An effort has been made to develop a grafting system where homopolymerization is completely inhibited. This has been accomplished by the addition of different inorganic and organic additives to the grafting medium. The homopolymer free grafting reaction would make the process highly efficient on the economic front.

The oxygen plasma exposure of PP monofilament leads to the formation of hydroperoxides [Eq. (1)]. The hydroperoxides are thermally labile functional groups and undergo decomposition and initiate graft polymerization of acrylic acid to create polyacrylic acid brushes on the polymer surface [eqs. (2)–(4)]. The graft management on the filament surface is strongly influenced by the reaction conditions employed at any stage. The variation of the degree of grafting with ferrous sulfate concentration is presented in Figure 2. It is important to mention that no grafting takes place in the absence of an added inhibitor since homopolymerization is so intense that hardly any monomer is left behind for the grafting reaction to take place.

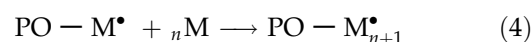
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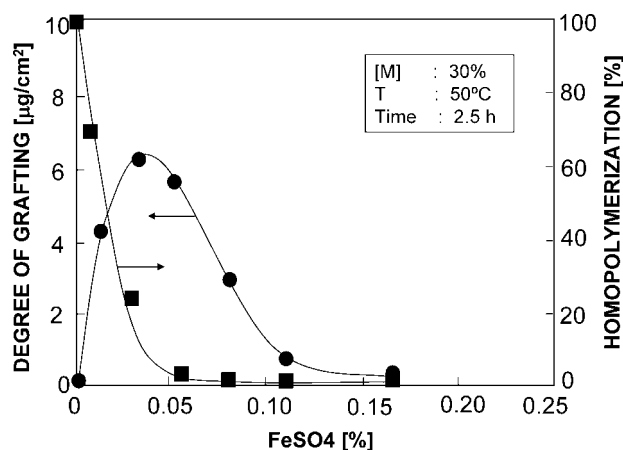
Initiation:



Propagation:

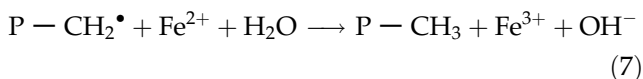
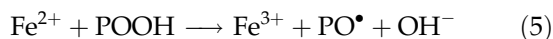


In the presence of ferrous sulfate as inhibitor, a reasonable amount of grafting takes place. However,

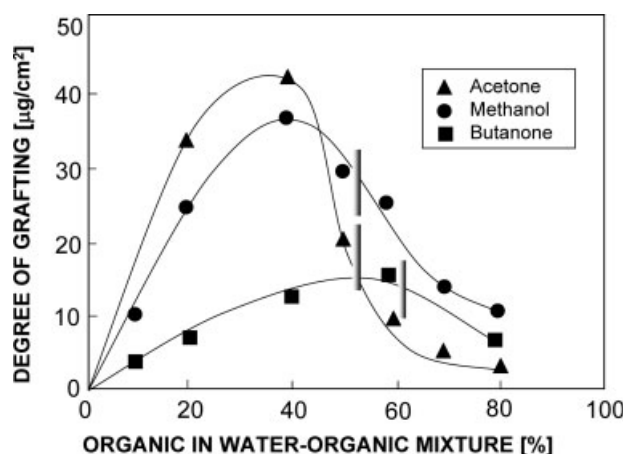


**Figure 2** Variation of the degree of grafting and the homopolymerization with the ferrous sulfate concentration. Plasma treatment conditions: exposure time, 60 s; plasma power, 60 W; O<sub>2</sub> flow rate, 20 sccm.

as the ferrous sulfate concentration increases the grafting increases initially, reaches its maximum and then decreases fast (Fig. 2). The homopolymer formation is also inhibited as the ferrous sulfate concentration increases. Virtually no homopolymer formation takes place at the ferrous sulfate concentration of 0.06%. The initial increase in the grafting is because of the diminishing homopolymerization with the increasing ferrous sulfate concentration so that sufficient monomer remains available for the grafting reaction. The maximum grafting is achieved at 0.06% ferrous sulfate concentration beyond which a drastic reduction of the degree of grafting occurs. It may be stated that in spite of free monomer availability for grafting, the ferrous sulfate not only hinders the homopolymerization by deactivating the hydroxyl radical into hydroxyl anion [eq. (5)] but also deactivates the primary PO radicals as well as propagating polyacrylic acid chains [eqs. (6) and (7)] leading to very little degree of grafting.<sup>24</sup> These observations show that the use of ferrous sulfate in the grafting medium is bound to produce material with low level of grafts on the PP surface.

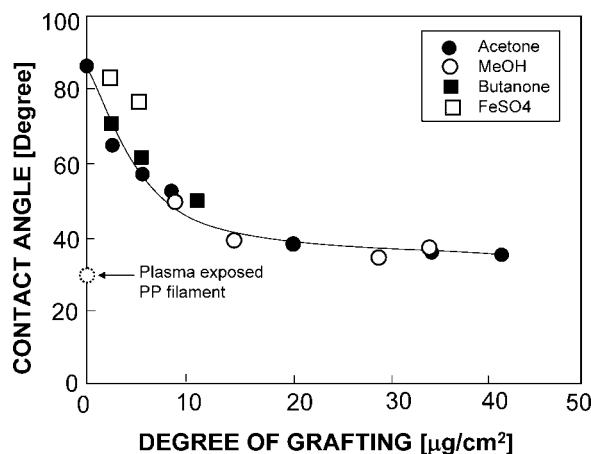


To replace ferrous sulfate by organic additives, different solvents were added to the grafting medium and a precise monitoring of homopolymerization was done. A comparative investigation on the addition of methanol, acetone, and butanone on the degree of grafting is presented in Figure 3. A maxi-

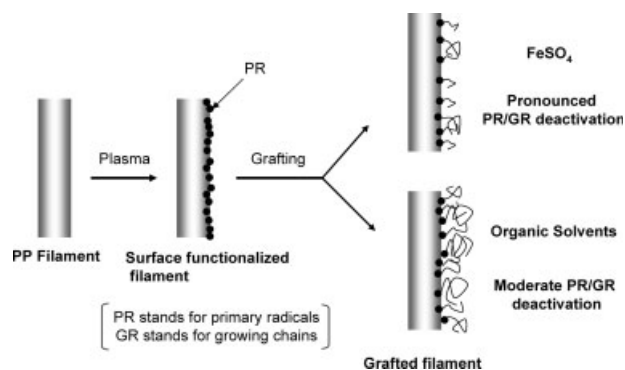


**Figure 3** Variation of the degree of grafting with the water-organic composition. Plasma treatment conditions: exposure time, 60 s; plasma power, 60 W; O<sub>2</sub> flow rate, 20 sccm. Grafting conditions: monomer concentration, 30%; temperature, 50°C; time, 2.5 h.

mum of 42 µg/cm<sup>2</sup> graft level was achieved for the acetone addition under our experimental conditions. All additives are able to inhibit the homopolymer formation during the grafting reaction as represented by bar on each plot beyond which the reactions tend to be homopolymer free. The homopolymer formation has always been higher in acetone medium as compared to methanol. For example at 40% solvent addition, the homopolymer is 3.5% as compared to 0.6% in methanol. Although, the homopolymer yield seems to be low, the viscosity of the grafting medium will be highly affected because of the hydrogel nature of acrylic acid. Acetone and Methanol show almost identical trend in the graft variation with their content in the grafting medium. The grafting increases with the additive content, reaches maximum at 40% and then tends to decrease. The favorable aspect is that the inhibitory action of methanol



**Figure 4** Variation of the contact angle with the degree of grafting under different additives.



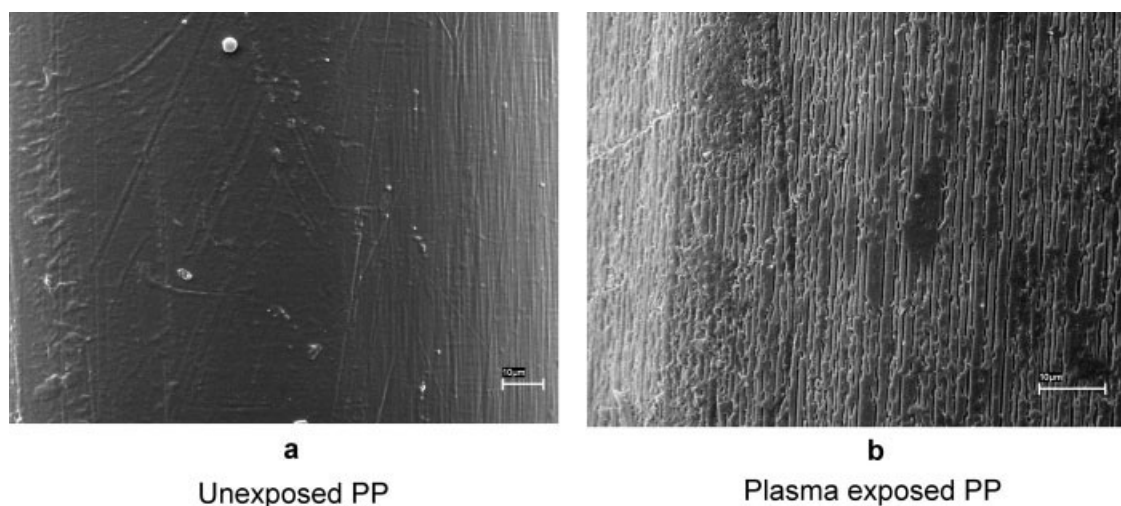
**Figure 5** Schematic representation of the grafting process under different reaction conditions.

and acetone helps in maintaining sufficient monomer accessibility to the grafting reaction. It seems that the inhibitory action of both the additives on one hand helps in homopolymer inhibition, and on the other hand, deactivates a fraction of the growing polyacrylic acid chains and is reflected in the form of a decrease in the degree of grafting.

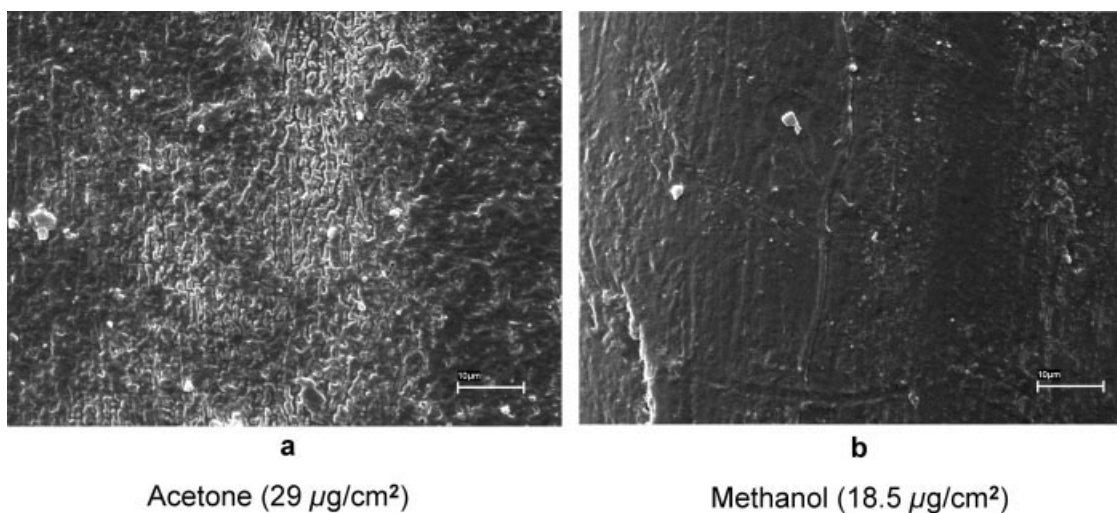
The addition of butanone shows the grafting trend similar to the methanol and acetone but with a maxima at 60% concentration. It is observed that the homopolymerization is completely inhibited beyond 60% butanone content. The degree of grafting is much lower than the one obtained for acetone and methanol addition. Unlike methanol and acetone, butanone acts as the nonsolvent for the growing polyacrylic acid chains. This precipitates out the polyacrylic acid as soon as it is formed in the reaction medium. As a result, the viscosity of the grafting medium is considerably maintained. In spite of the fact that this regulates the monomer diffusion to the grafting sites for smooth grafting reaction, the degree of grafting is much lower. May be due to the nonsolvent nature of butanone towards polyacrylic

acid chains, the grafted layer on PP surface does not swell and the enrichment of the grafted layer with monomer does not proceed well. The growing chain termination, as a result, follows instantaneously, providing low graft levels. These observations on the inhibitory influence of organic additives acetone, methanol and butanone are interesting in achieving homopolymer free grafting reaction. It is difficult to predict any precise mechanism for these observations.

The contact angle of filaments shows interesting behavior depending on the grafting with acrylic acid under specific conditions. The exposure of the filament with the oxygen plasma leads to significant reduction in the contact angle from  $88^\circ$  for original filament to  $32^\circ$  for the exposed sample for a treatment time of 60 s as represented by open circle on Y-axis in Figure 4. Similar observations have been made by Huang et al.<sup>26</sup> for the plasma treatment of the PP filament (contact angle,  $91^\circ$ ) where oxygen plasma reduces it to  $43^\circ$  and argon plasma reduces to  $55^\circ$ . This is the indication of the surface functionalization of PP by plasma treatment which involves various groups such as carbonyl, hydroxyl, and hydroperoxides. However, this history of functional groups on the surface changes as the polyacrylic acid chains are incorporated. The contact angle of the samples having different graft levels and prepared under different reaction mediums is presented in Figure 4. The contact angle decreases with the increase in the degree of grafting. The results show that the transition to a minimum contact angle takes place beyond  $\sim 20 \mu\text{g}/\text{cm}^2$  graft level and a minimum contact angle of  $23^\circ$  was achieved for a graft level of  $42 \mu\text{g}/\text{cm}^2$ . As compared to ferrous sulfate and butanone, both the acetone and methanol produce high graft levels and show identical contact angle values. A precise evaluation of the contact angle of samples grafted in ferrous sulfate and buta-



**Figure 6** SEM of (a) unexposed PP and (b) plasma exposed PP filament (60 s).

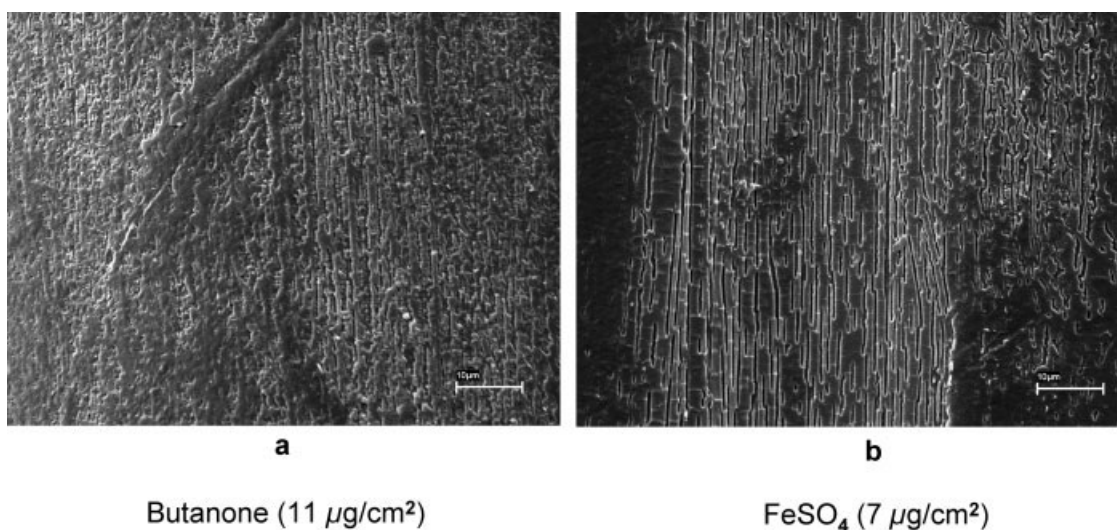


**Figure 7** SEM of PP-g-PAA filament prepared in (a) methanol and (b) acetone in the grafting medium. Values in bracket represent the degree of grafting.

none (having close graft levels) shows very interesting observations. Ferrous sulfate produces surfaces which have relatively higher contact angle as compared to the butanone. For instance, the contact angle is 72° and 60° for a graft level of  $\sim 8 \mu\text{g}/\text{cm}^2$  for ferrous sulfate and butanone addition, respectively. Probably, the inhibitory action of ferrous sulfate is so pronounced that it deactivates primary radicals or the radicals produced by hydroperoxide decomposition even before the grafting process is initiated. Moreover, whatever the grafting is initiated from the remaining sites, the propagating chains are also deactivated fast leaving behind short chains. This reflects that the ferrous sulfate addition introduces lower hydrophilicity as compared to the butanone addition. The influence of organic additives is

so mild that it allows chains to propagate before terminating them and this leaves behind relatively a more hydrophilic surface. Keeping these observations, a tentative mechanism of surface management under ferrous sulfate and butanone is proposed in Figure 5.

The surface morphology of the resultant filament is strongly governed by the nature of the additive in the grafting medium (Figs. 6–8). The unmodified filament is quite smooth in nature [Fig. 6(a)]. The plasma treatment leads to significant changes on the surface and the roughness originates as observed in Figure 6(b). The etching of the surface takes place that leads to the formation of fissures on the surface. This is a typical feature of the plasma exposure and has been observed in our earlier studies on PET films.<sup>27,28</sup> The subsequent grafting of acrylic acid



**Figure 8** SEM of PP-g-PAA filament prepared in (a) butanone and (b) ferrous sulfate in the grafting medium. Values in bracket represent the degree of grafting.

onto the plasma treated surface results the surface morphology depending on the nature of the medium (Figs. 7 and 8). In general, the flattening of the surface takes place because of the grafting process. The grafted polyacrylic acid chains form independent domains and sit on the surface and fill up the space. This observation is in line with the studies of Basarir et al.<sup>29</sup> for the grafting of acrylic acid onto porous PP surfaces. The grafting under ferrous sulfate causes the least changes on the plasma treated sample. However, methanol, acetone, and butanone lead to similar but more flattening of the surface as compared to ferrous sulfate addition. Although, the degree of grafting is not identical in all the systems, the polyacrylic acid chains are long enough to form an independent domain in organic medium and a general trend may be visualized in the form of grafts filling into the fissures leading to the filament surface to a more smooth morphology. With ferrous sulfate, by virtue of its strong chain deactivation effect, the chains may be shorter and do not form isolated structures. As a result, a strong morphological visualization is not evident. This reflects the interesting role of the specific additive on the surface management on plasma grafted system.

### CONCLUSION

The plasma-induced graft polymerization of acrylic acid on PP filament surface is strongly influenced by the nature of the additive in the grafting medium. The grafting is completely interrupted because of strong homopolymerization that follows in the absence of an added inhibitor. However, the inorganic additive, ferrous sulfate, and organic additives, methanol, acetone, and butanone offer inhibitory action on the homopolymerization beyond certain concentrations in the reaction medium and ensure optimum grafting to take place. On one hand, methanol, and acetone lead to much higher graft levels as compared to the ferrous sulfate, the butanone addition gives graft levels very similar to the ferrous sulfate. Butanone acts as the nonsolvent for the polyacrylic acid chains, thereby ensures high monomer availability in the reaction medium. In spite of this the grafting tends to be very low. It seems that the as soon as the initial grafting takes place, the grafted layer does not swell in the reaction medium because of the nonsolvent nature of the butanone towards the growing polyacrylic acid chains. Therefore, the monomer interaction with the growing chains is drastically lowered and leads to low graft levels.

The contact angle of the grafted samples decreases as the degree of grafting increases. Ferrous sulfate leads to relatively higher contact angle as compared to the organic additives. The surface morphology on

the grafted surface is significantly influenced by the nature of the additive. In general, the grafting results into flattening of the surface. However, ferrous sulfate addition produces little changes on the filament surface. This may be due to the formation of independent polyacrylic acid domains filling up the valleys on the surface. These observations suggest a precise role of an additive in designing the surface morphology of the filament in plasma grafting process.

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