

Structural Characterization of Alpha Methyl Styrene-Butyl Acrylate-Grafted Polyetheretherketone Films

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ABSTRACT: Radiation-induced graft copolymerization of alpha methyl styrene (AMS)-butyl acrylate (BA) mixture onto poly(etheretherketone) (PEEK) was carried out to develop films of varying copolymer compositions. The characterization of films was carried out with fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The presence of AMS and BA units within the film matrix was confirmed by FTIR. The intensity of the characteristic peaks for AMS and BA increased with the increasing grafted component in the films. The crystallinity of the films as observed from DSC and XRD decreased with the increasing graft levels. On the other hand, the melting temperature of the base polymer was almost unaffected by irradiation and the grafting process. The glass transition temperature (T_g) of the grafted film increased as compared to the virgin PEEK. Ungrafted film showed a stable thermogram up to $\sim 500^\circ\text{C}$. However, the grafting introduced a new decomposition range in the copolymer, due to the presence of the AMS/BA. AFM images showed the formation of domains on the grafted PEEK film surface. The SEM also showed domain formation of the grafted component within the PEEK matrix. However, the fracture analysis did not show any prominent phase separation. Mechanical characterization of films in terms of tensile strength, elongation, and modulus was also carried out.
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INTRODUCTION

The membrane is considered to be the heart of a fuel cell and the performance of a fuel cell depends largely on the physico-chemical nature of the membrane and its stability in the intimidating environment at elevated temperatures. Currently, perfluorinated membrane materials, such as Nafion[®] (DuPont, USA), Flemion (Asahi Glass, Japan), and Aciplex (Asahi Kasei, Japan) are used principally in polymer electrolyte fuel cells, due to their attractive conductivity and chemical stability. Consequently, the search for new membrane materials with low cost and required electrochemical characteristics, along with good performance has become the most focused research area.¹

The functionalization of polymers by radiation grafting of appropriate monomers offers an attractive way to develop materials for a wide range of applications.^{2–6} The preirradiation grafting involves the irradiation of polymer substrates in air or inert gas and then immersion in a monomer solution to initiate graft polymerization. The process of radiation grafting offers

enormous possibilities to design polymers by careful variation of the irradiation and the grafting conditions. Polymers can be altered into materials with a unique combination of features, which are otherwise not exerted by the individual polymers. This process of polymer functionalization has been widely recognized for a large number of films, such as polyethylene, polypropylene, and fluoropolymers.^{7–15}

Poly(tetrafluoroethylene-co-ethylene) (ETFE) films were grafted with styrene/1,3-diisopropenylbenzene (DIPB) and the interfacial properties, dimensional stability, and hydrogen barrier properties of the membranes were found to improve substantially by increasing DIPB concentration.¹⁶ At the same time, ETFE films have been modified through graft copolymerization of styrene and vinyl trimethoxysilane (VTMS), or styrene and 3-(trimethoxysilyl) propyl methacrylate (TMSPM) binary system using simultaneous irradiation method. The resulted membrane indicated and exhibited not only lower water uptake and dimensional change but also high proton conductivity at low

humidity conditions as compared to the noncrosslinked styrene-sulfonic acid grafted ETFE.¹⁷ Graft copolymerization of fluoropolymer films by polystyrene with subsequent sulfonation has also been carried out and their structural properties have been investigated.¹⁸

Poly(etheretherketone) (PEEK) films are known for their excellent thermal stability, mechanical strength, and high chemical resistance. The radiation grafting of PEEK films has been investigated recently in such a way that the copolymers with desired functionality are developed.^{19–21} PEEK films have been modified by thermal grafting of divinylbenzene (DVB) followed by radiation grafting of ethyl styrene sulfonate (ETSS), to develop a polymer electrolyte membrane (PEM) for use in direct methanol fuel cells (DMFCs).²² In another development, PEEK film was crosslinked by the electron-beam irradiation to enhance its insolubility and DVB was added to enhance the radiation-induced styrene grafting. The subsequent sulfonation resulted in lower methanol permeability and higher mechanical properties.²³ Hasegawa et al. carried out the grafting of styrene into PEEK polymer and subsequently sulfonated to introduce sulfonic acid groups into the matrix.²⁴ Studies of Scherer and co-workers have suggested that the grafting of alpha methyl styrene (AMS) offers better fuel cell stability as compared to the styrene grafting.²⁵ However, looking at the problems associated with the AMS polymerization, it is easier to polymerize AMS in combination of methacrylonitrile. AMS and dimethylaminoethyl methacrylate (DMAEMA) have also been grafted into poly(vinylidene fluoride) (PVDF) followed by sulfonation and protonation and the resulted membranes have found to have higher ion exchange capacity and conductive nature for the vanadium redox flow battery.²⁶

The presence of grafted microdomains into the film may produce considerable changes in its inherent properties depending on the infrastructure of the two polymeric components. The bulk properties of the modified film, therefore, will be dependent on the chemical nature of the monomer, and the distribution of grafted chains in the copolymer matrix.²⁷ Our approach for the grafting process is to use butyl acrylate (BA) in combination with AMS as the monomer system. BA is expected to enhance the polymerization of AMS on one hand, while some flexibility may be achieved into the grafted films because of the presence of BA moieties along the PEEK backbone. However, the grafting of AMS-BA may produce certain structural changes in the inherent structure of the PEEK films, which could be an important factor governing the overall membrane characteristics. It will be, therefore, interesting to determine the grafting-induced structural changes in the PEEK film and correlate them with the membrane behavior. The preparation of the AMS/BA grafted PEEK films has been reported in our earlier publication.²⁸ The present investigation aims at studying the characteristics and structural changes in the PEEK films induced by the AMS-BA grafting.

EXPERIMENTAL

Irradiation

A ⁶⁰Co gamma radiation source (dose rate of 0.16 kGy/h), supplied by Bhabha Atomic Research Centre, India, was used for

the irradiation of the samples. Irradiations were carried out in air under ambient conditions. A dose of 100 kGy was used to prepare these samples.

Graft Copolymerization

Graft copolymerization of AMS-BA (60 : 40) mixture on the PEEK films was carried out by preirradiation grafting method.²⁸ Grafting was carried out at the monomer concentration of 30% at a temperature of 50°C. The irradiated sample (~400 mg) was placed in a reaction tube containing aqueous monomer solution. The tube was deaerated by bubbling nitrogen for 15 min and was sealed. Subsequently, tube was placed in a thermostated water bath for a desired period. After the reaction was over, sample was washed with toluene at ~70°C to extract homopolymer as well as unreacted monomer formed during the grafting reaction. The grafted sample was dried under vacuum and the degree of grafting was determined gravimetrically, as per the following expression.

$$\text{Degree of Grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where, W_0 is the weight of the ungrafted film; W_g is the weight of the grafted film.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of samples were recorded on Perkin-Elmer FTIR System Spectrum GX over the 400–4500 cm^{-1} range.

Differential Scanning Calorimetry (DSC)

DSC measurements were made using DSC-204 phoenix (Netzch) under nitrogen atmosphere. The thermograms for all the samples were obtained in the range of 0–400°C. A constant heating and cooling rate of 10 K/min was maintained during the whole processes. The heat of fusion (ΔH_f) was obtained from the area under the melting thermogram. The melting point of samples was obtained as the peak temperature from the melting endotherm and the crystallinity of the samples was obtained by the following expression²⁹:

$$\% \text{Crystallinity} = \Delta H_f / \Delta H_f(\text{crys}) \times 100 \quad (2)$$

Where, $\Delta H_{f(\text{crys})}$ is the heat of fusion of 100% crystalline PEEK and has been taken as 130 J/g and ΔH_f is the heat of fusion of the sample from the thermogram.²⁴

Thermogravimetric Analysis (TGA)

TGA studies were carried out using a Perkin-Elmer TGA-7 in the range of 50–800°C. The heating rate was 10°C/min. The measurements were made under a constant flow rate (20 mL/min) of nitrogen.

X-Ray Diffraction (XRD)

XRD patterns of samples were recorded on PHILIPS, Holland, CuK α X-ray generator to study the morphological changes in the material. Scanning was carried out in 2θ range of 10°–40° at the wavelength of 1.54 Å, filament current of 30 mA and voltage of 40 kV.

Mechanical Strength

Mechanical strength was monitored over Universal Testing Machine for Tensile, INSTRON, model no: 3365. The extension

speed was 5 mm/min with the load cell of 1 kN and Gauge length of 22 mm.

Scanning Electron Microscopy (SEM)

SEM images were monitored on HMMM FEI Quanta 3D with field emission gun (FEG) on 40,000× magnification.

Atomic Force Microscopy (AFM)

The surface topography of films was investigated in air under at room temperature by AFM imaging with Solver Pro SPM (NT-MDT, Russia). It is operated in the semicontact mode using a NSG 10 series tip. Four to five different locations, free of any manufacturing defect, on each sample were analyzed and roughness observations were quantified in terms of RMS values, S_q . Scanning size of each image for comparison was kept $2.5 \times 2.5 \mu\text{m}^2$ and these were scanned at a rate of 1 Hz.

RESULTS AND DISCUSSION

The grafting of AMS-BA mixture was carried out on PEEK films to develop copolymer structure for the membrane preparation. The degree of grafting in the films was achieved in the range of 4–27%. The characterization of the grafted films was carried out to investigate the structural changes in copolymer films as a function of the graft composition.

Fourier Transform Infrared Spectroscopy

The grafting of AMS-BA mixture onto PEEK film was ascertained by FTIR and has been presented in Figure 1. Significant differences between the virgin PEEK film and the grafted films were observed in the range of 1500–1800 cm^{-1} and 3000–3600 cm^{-1} . Although, a new peak has been observed at 1725 cm^{-1} due to ester group after the grafting reactions, the intensity of this band shifted to 1731 cm^{-1} with the increase in the grafting. Both virgin and the grafted films had an absorption peak at 869 cm^{-1} , which is characteristic of the out of plane bending of two

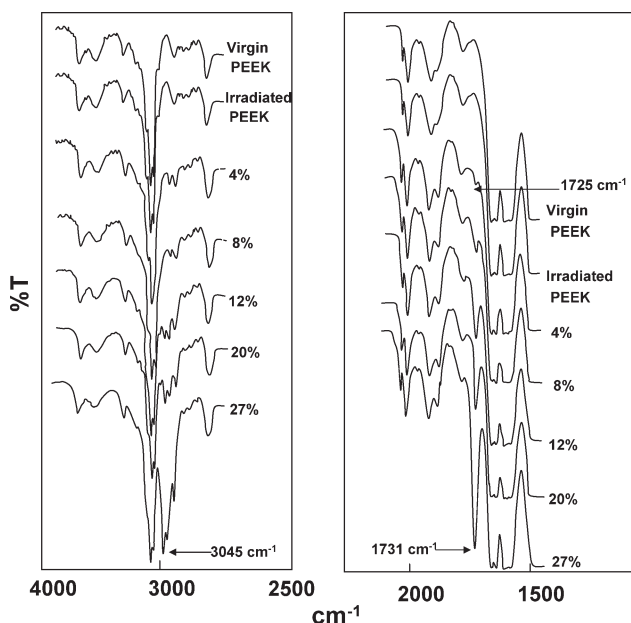


Figure 1. FTIR of (a) virgin film; (b) irradiated film and grafted film with the degree of grafting of (c) 4%; (d) 8%; (e) 12%; (f) 20%; and (g) 27%.

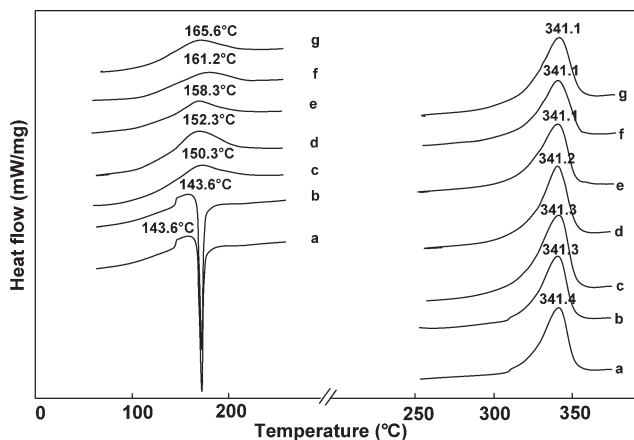


Figure 2. DSC thermograms of (a) Virgin PEEK; (b) Irradiated PEEK and grafted PEEK with degree of grafting of (c) 4%; (d) 8%; (e) 12%; (f) 20%; and (g) 27%.

hydrogen of 1,4-disubstituted benzene ring. The absorption band at 2873 cm^{-1} splits into two peaks, which signify the absorption band of stretching vibration of the single bond to —CH. As the degree of grafting increases, the intensity of these peaks increases, which is attributed to the fact that AMS is incorporated more and more as the grafting progresses.

Differential Scanning Calorimetry

DSC thermograms of virgin, irradiated and grafted PEEK films with different graft levels have been presented in Figure 2. The melting temperature of PEEK was found to be 341.1°C and did not show any variation in grafted films. This indicates that the perfection of crystallites is not influenced by the grafting process under our experimental conditions. The heat of fusion values of copolymer samples are accessible in Figure 3. The heat of fusion as obtained in the thermograms decreases with the increase in the degree of grafting. However, we have to look at the PEEK content in the copolymer films. The weight fraction of PEEK in films decreases with the increase in the degree of grafting. Hence, the heat of fusion of grafted films should follow a relationship as per eq. (3).²⁹

$$\Delta H_f^* = 35.8 \times \left[\frac{1}{1 + G} \right] \quad (3)$$

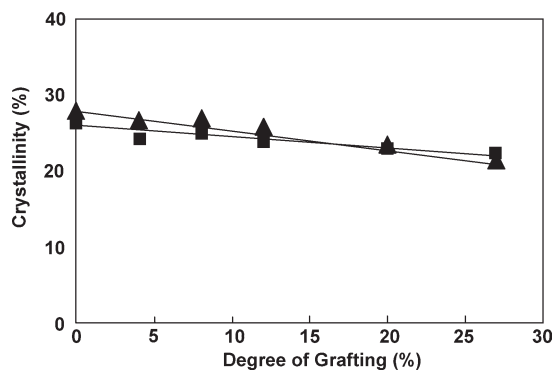


Figure 3. Variation of the heat of fusion with the degree of grafting (▲): calculated heat of fusion (■): experimental heat of fusion.

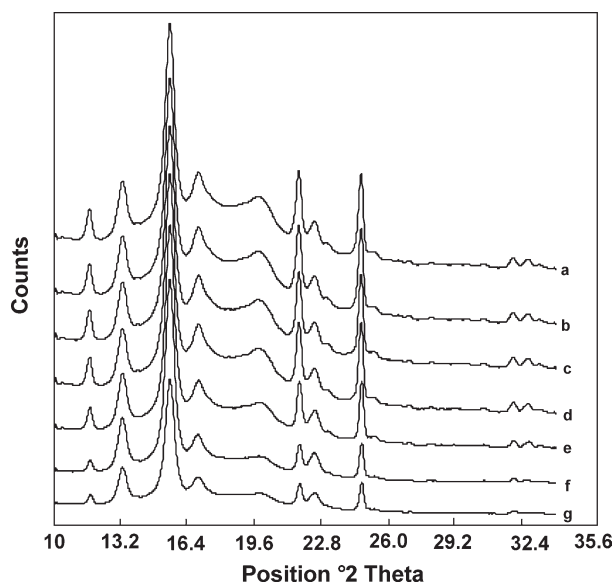


Figure 4. XRD patterns (a) virgin film; (b) irradiated film and PEEK-g-poly(AMS-co-BA) film with the degree of grafting of (c) 4%; (d) 8%; (e) 12%; (f) 20%; and (g) 27%.

Where, ΔH_f^* is the calculated heat of fusion based on the weight fraction of PEEK in copolymer samples, G is the degree of grafting and $[1/1 + G]$ is the weight fraction of PEEK in copolymer films.

The heat of fusion of irradiated film is 35.8 J/g, which is obtained from the thermogram. The open circles in the figure corresponds to the calculated heat of fusion of grafted samples based on the PEEK fraction in copolymer films, according to eq. (3). The heat of fusion values of grafted samples obtained from the thermogram (ΔH_f) fall on this trend and are very close to the one calculated as per eq. (3). These observations indicate that the poly(AMS-BA) grafts are amorphous in nature and do not disrupt the inherent crystal structure of the PEEK during the grafting process. The decrease in the heat of fusion is, therefore due to the dilution of inherent crystallinity in the PEEK film by the incorporation of amorphous poly(AMS-BA) moiety in the noncrystalline region of the PEEK films. These observations are well in agreement with the studies of other workers for the grafting in various polymer-monomer systems.^{29–32} It was observed that the grafts are confined to the amorphous region of the base matrix and diminish the crystallinity solely by the dilution effect.

The DSC thermograms for the glass transition temperature (T_g) of the films has been presented in Figure 2. The irradiation of PEEK, to 100 KGy does not influence the T_g of the polymer film however, a significant change in T_g is observed from 150.3 to 165.6°C as the graft level increase from 4 to 27%. It is observed that the T_g of grafted film increases as compared to ungrafted film. The increase in the glass transition temperature is due to the insertion of a graft chain, which stiffens the chain by impeding rotation so that more thermal energy is required to set the chain in motion. A restriction is imposed by steric effects, which arises when the bulky pendent groups hinder the

rotation about the backbone and causes T_g to increase. The grafted films do not show independent T_g for the virgin PEEK and for the grafted chains. The presence of single T_g in the grafted sample is the indication of the compatibility of the system. PAMS and PBA exhibit T_g at the temperature of 168°C and -60°C , respectively.³³ A copolymer of these two monomers should show T_g somewhere in their temperature range. This suggests that the enhancement in the T_g is only due to the hindrance in the chain mobility of PEEK and in grafted chain (PAMS-PBA) is not visible in the grafted film.

X-Ray Diffraction Patterns

The diffraction patterns of PEEK films with different graft levels (4–27%) have been compared with irradiated film. The irradiation of PEEK to 100 kGy did not show any appreciable difference in the diffraction pattern (Figure 4). The diffraction peaks of the crystalline phase present in the original and grafted PEEK films were observed with different intensities. The diffraction peaks at 17, 15.5, 25.5, 28.7 position ($^\circ 2\theta$) were found to be decreasing with low intensity in grafted films. This indicates that after the grafting process, PEEK film is getting into a more amorphous structure. The crystallinity of the film was obtained from the diffractograms and has been found to show a decreasing trend with the increasing degree of grafting. Interestingly, identical trend has been observed for the crystallinity variation by XRD and DSC (Figure 5).

Thermogravimetric Analysis

TGA thermograms of virgin, irradiated and grafted PEEK films are shown in Figure 6. Virgin and irradiated films show a stable thermogram up to $\sim 500^\circ\text{C}$. The high thermal stability of PEEK is evident from the aromatic rings in the polymer backbone. The grafting process changes the overall degradation pattern of the PEEK film and introduces a new decomposition at 160°C . These results indicate that the grafting of poly(AMS-BA) onto PEEK film diminishes the thermal stability of the film. In contrast to one step degradation, the grafted film exhibits two-step degradation, i.e., the first degradation occurs at $\sim 150^\circ\text{C}$, followed by the second decomposition at $\sim 540^\circ\text{C}$. The first degradation step corresponds to the degradation of the grafted

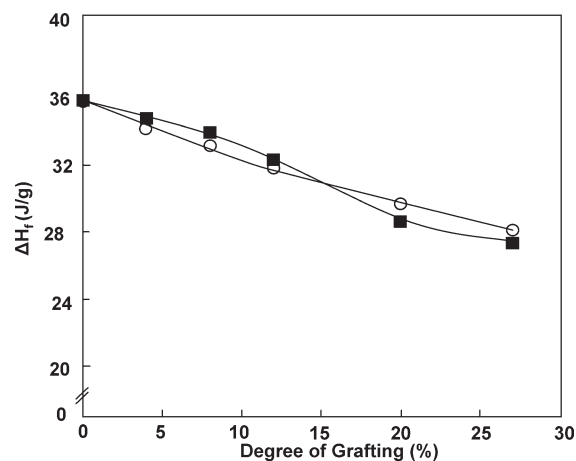


Figure 5. Variation of the percent crystallinity with the degree of grafting (○): calculated from DSC (■): calculated from XRD.

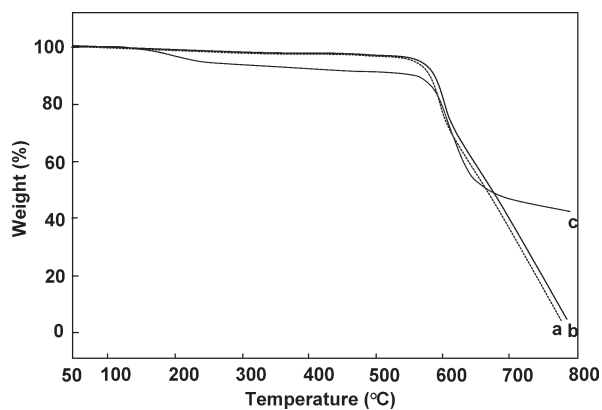


Figure 6. TGA Thermograms of (a) irradiated film; (b) virgin film; (c) PEEK-g-poly(AMS-co-BA) film with the degree of grafting of 27%.

monomers and the second step corresponds to the degradation of the PEEK components in the copolymer film.

Scanning Electron Microscopy

SEM images of virgin PEEK and the grafted PEEK with different graft level are shown in Figure 7. With the increasing graft level, the nodular spherical structures are observed. There is a noticeable increase in the size of each spherical unit. The nodular spherical structures in these films have been observed in the fractured state after keeping them in liquid nitrogen.

The structure becomes a bit nonhomogeneous and the small domains are formed within the matrix. The domain formation becomes more dominant as the grafting increases. However, this may not be termed as the phase separation within the copolymer matrix. The understanding from these observations is that there is low level of the compatibility between the grafted domains with the base matrix and this leads to the formation of some domains within the base matrix. It seems that the

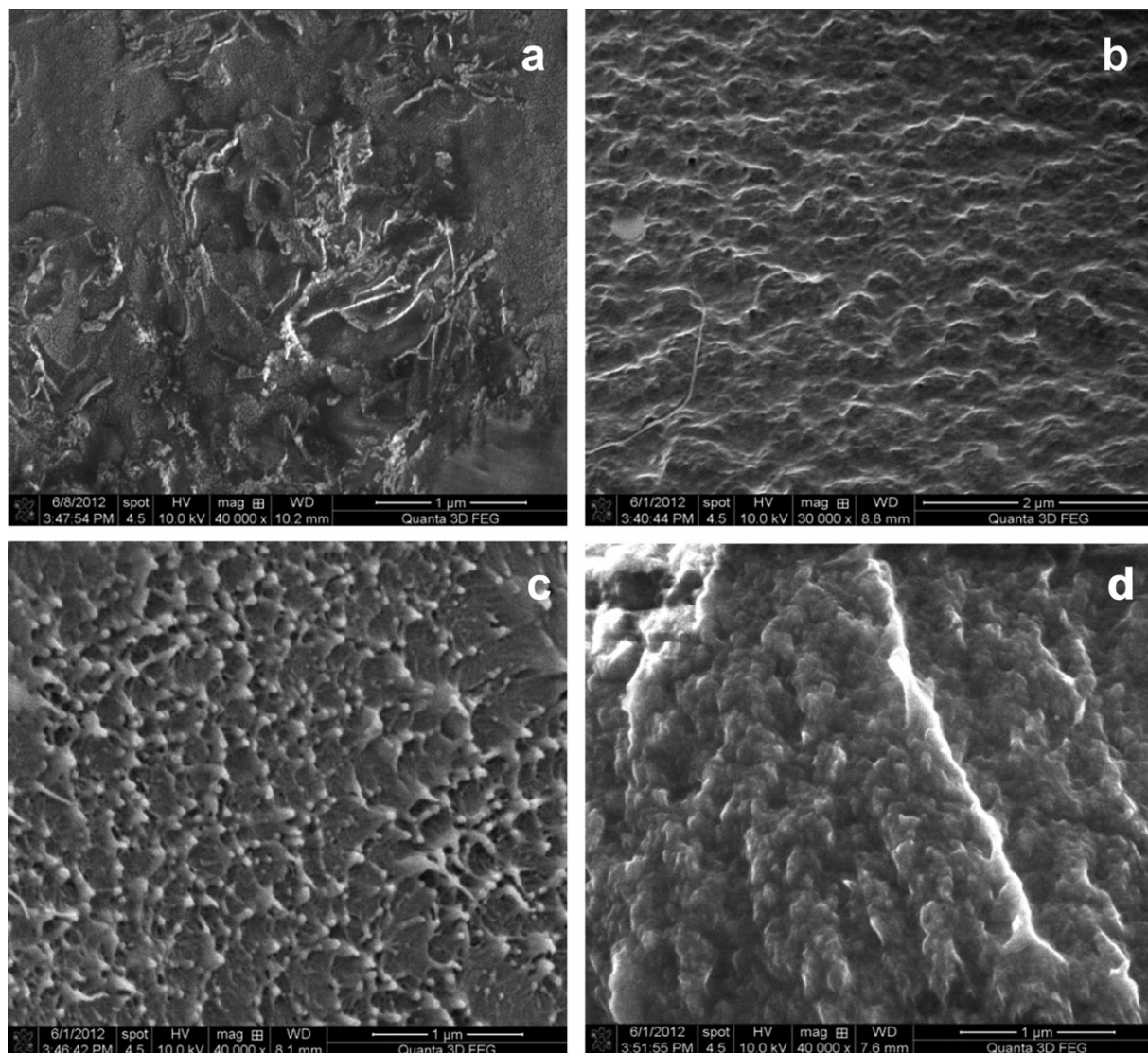


Figure 7. SEM images of (a) virgin film and PEEK-g-poly(AMS-co-BA) film with the degree of grafting of (b) 4%; (c) 12%; and (d) 27%.

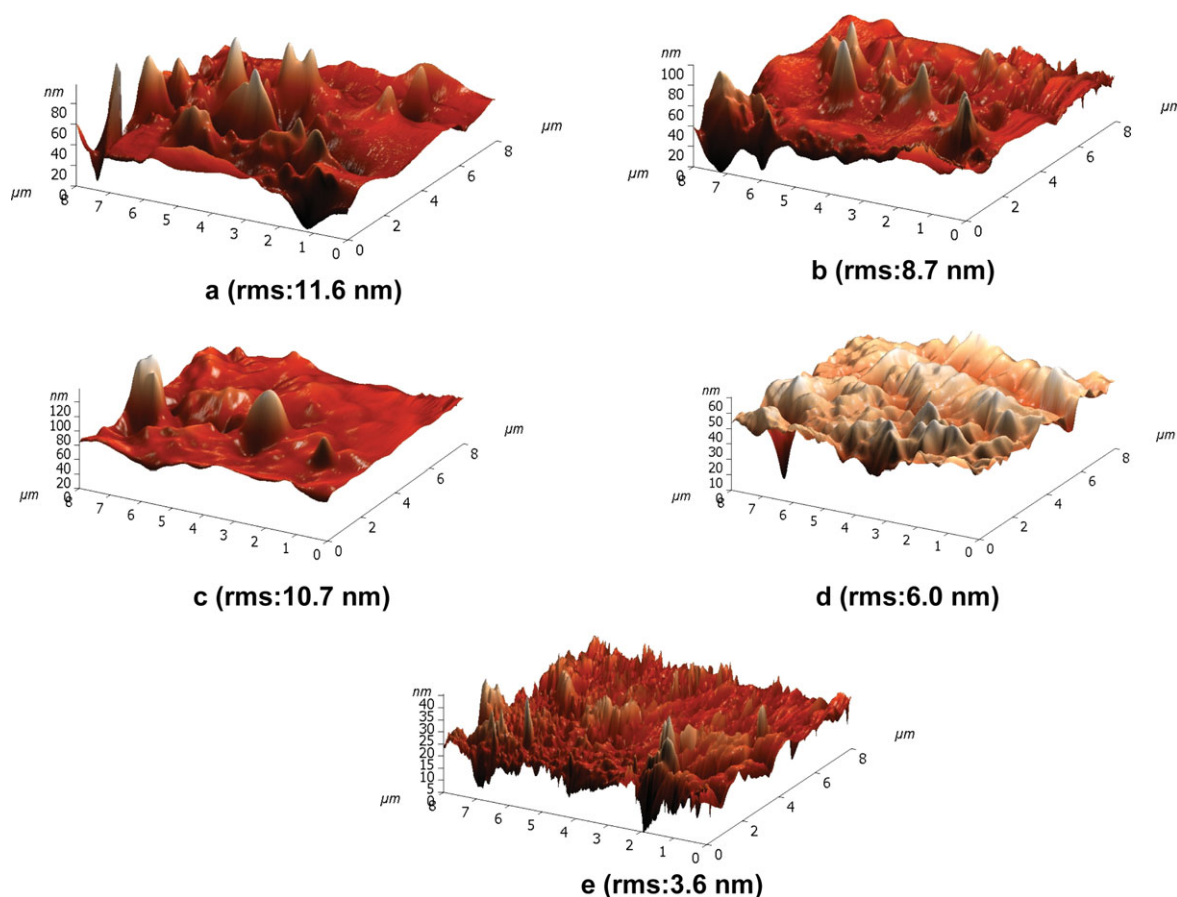


Figure 8. AFM of (a) virgin film; (b) irradiated film; PEEK-g-poly(AMS-co-BA) film with the degree of grafting of (c) 4%; (d) 12%; and (e) 27%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

limited compatibility between the PEEK matrix and the grafted domain is due to the aromatic and oxygenated structure of the grafted chain, which exerts compatibility with the aromatic and oxygenated structure of the base film.

Atomic Force Microscopy

The topography of the PEEK film, as observed by AFM, underwent significant changes after grafting process, RMS shows a

decreasing trend as the grafting progresses (Figure 8). Roughness is a measure of the texture of a surface. It is quantified by the vertical deviations of a real surface from its ideal form. Therefore, when the grafting takes place, there are large vertical deviations in comparison to the virgin surface. The increase in surface roughness may be because of the formation of domains

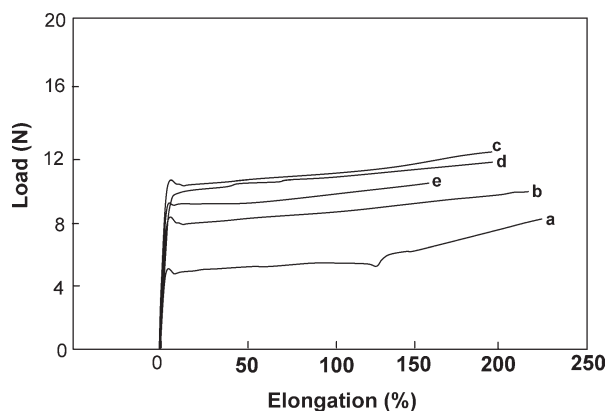


Figure 9. Stress-strain plot of (a) virgin film; PEEK-g-poly(AMS-co-BA) film with the degree of grafting of (b) 4%; (c) 12%; (d) 20%; and (e) 27%.

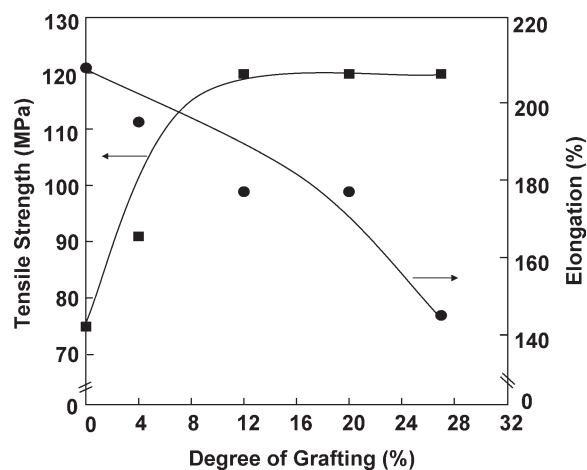


Figure 10. Variation of the tensile strength and the elongation with the degree of grafting.

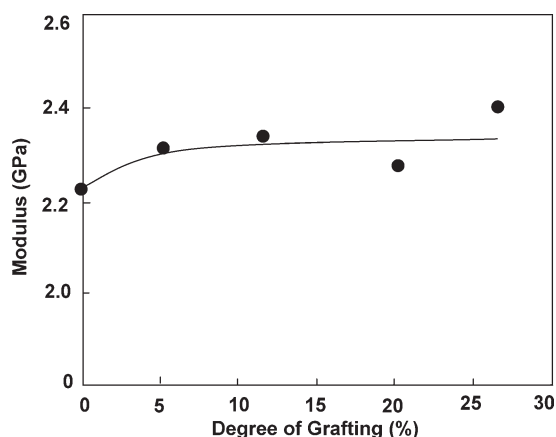


Figure 11. Variation of the modulus with the degree of grafting.

and morphologies by the grafted AMS-BA chains. As the grafting increases, the domain formation becomes significant and is reflected in the nonhomogeneity over there.

Mechanical Strength

The stress–strain plots of the virgin and the grafted films are presented in Figure 9. Virgin PEEK film shows a typical thermoplastic nature with well defined yield point, breaking load and the intermediate drawing region. However, the drawing region of the grafted samples becomes slightly different in shape. The tensile strength, elongation, and the modulus of the samples is presented in Figures 10 and 11. The tensile strength increases while the elongation shows a decreasing trend. On the other hand, modulus increases appreciably if not significantly. These results are the indication of the incorporation of some rigidity in the material as the grafting proceeds. There seems to be a good correlation between the SEM observations and the tensile deformation. It seems that the grafted microstructures are distributed within PEEK matrix and offer reinforcing effect against the deformation. Moreover, the grafted chains are incorporated within the amorphous region and reinforce them. Moreover, these graft chains, which diminish the mobility of the chains and hence contribute to the increase in modulus, but a decrease in elongation. The contribution of the mobility loss will be in addition to the reinforcing effect of the grafted microstructures.

CONCLUSION

Radiation induced grafting of poly(AMS-BA) onto PEEK films was carried out to develop materials for the membrane preparation. Melting temperature of the grafted PEEK films was found to be unaltered with increasing graft level and it has been observed that the T_g of the grafted PEEK increases as compared to ungrafted PEEK. The crystallinity of the films decreases, systematically with graft level and the fact has been supported with XRD patterns. However, the loss in crystallinity of the film is due to the incorporation of the amorphous grafted chains within the noncrystalline region. Thermal behaviour of PEEK-g-poly(AMS-co-BA) was also investigated and compared with the irradiated PEEK. The films were found to have two-step degradation patterns because of the grafted AMS-BA. It seems that

the grafted domains experience limited compatibility with the PEEK matrix, because of which small domains are formed within the grafted matrix. Strength and modulus of the grafted films increases while elongation decreases, it seems to be the outcome of the diminishing mobility of the chains and the reinforcing effect of the grafted component on the film matrix and the base matrix is not very important. The fracture analysis of the films also suggests phase separation between the grafted moieties.

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