

# Degradation in Thermal Properties and Morphology of Polyetheretherketone-Alumina Composites Exposed to Gamma Radiation

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Sheets of polyetheretherketone (PEEK) and PEEK-alumina composites with micron-sized alumina powder with 5, 10, 15, 20, and 25% by weight were fabricated, irradiated with gamma rays up to 10 MGy and the degradation in their thermal properties and morphology were evaluated. The radicals generated during irradiation get stabilized by chain scission and crosslinking. Chain scission is predominant on the surface and crosslinking is predominant in the bulk of the samples. Owing to radiation damage, the glass transition temperature,  $T_g$  increased for pure PEEK from 136 to 140.5 °C, whereas the shift in  $T_g$  for the composites decreased with increase in alumina content and for PEEK-25% alumina, the change in  $T_g$  was insignificant, as alumina acts as an excitation energy sink and reduces the crosslinking density, which in turn decreased the shift in  $T_g$  towards higher temperature. Similarly, the melting temperature,  $T_m$  and enthalpy of melting,  $\Delta H_m$  of PEEK and PEEK-alumina composites decreased on account of radiation owing to the restriction of chain mobility and disordering of structures caused by crosslinks. The decrease in  $T_m$  and  $\Delta H_m$  was more pronounced in pure PEEK and the extent of decrease in  $T_m$  and  $\Delta H_m$  was less for composites. SEM images revealed the formation of micro-cracks and micro-pores in PEEK due to radiation. The SEM image of irradiated PEEK-alumina (25%) composite showed negligible micro-cracks and micro-pores, because of the reinforcing effect of high alumina content in the PEEK matrix which helps in reducing the degradation in the properties of the polymer. Though alumina reduces the degradation of the polymer matrix during irradiation, an optimum level of ceramic fillers only have to be loaded to the polymer to avoid the reduction in toughness.

**Keywords** degradation, irradiation, morphology, PEEK composite, polyetheretherketone, thermal properties

## 1. Introduction

In nuclear power plants polymeric components are extensively employed in a radiation environment. High energy radiation can bring major changes in the molecular structure and macroscopic properties of the polymers. The radiation dose required to bring changes in physical properties of polymers is considerably less than that required to cause any significant change in glasses, ceramics, or metals. Nevertheless, in numerous applications polymers are specifically needed in environments of ionizing radiation because of specific polymer properties such as elasticity, light weight, and formability.

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In such cases the polymer is required to be as radiation resistant as possible. Radiation resistance is strongly influenced by the basic molecular structure, the presence of certain additives and the particular environmental exposure condition. The radiation effects are manifested as changes in appearance, chemical and physical states and mechanical, electrical and thermal properties. However, not all properties of a polymer are affected to the same degree by radiation. The radiation stability of a polymer is dependent upon the chemical structure of the material because radiation induced excitation is not coupled to entire chemical system, but is localized at a specific bond. The addition of energy absorbing aromatic rings to the chemical structure significantly increases the radiation stability of some polymers by aiding in the redistribution of the excitation energy throughout the material. Conversely, those polymers with highly aliphatic structures are least resistant to radiation. Radiation resistance is characterized by the half-value-dose of significant mechanical properties. Half-value-dose is defined as the absorbed dose, which reduces a property to 50% of the initial value under defined environments (Ref 1). The relevant properties to characterize the radiation resistance are the elongation at break for flexible plastic and elastomers and flexural strength for rigid plastics. The properties can be affected in different modes and therefore more than one property should be considered.

The performance of the polymers in high radiation field deteriorates because their radiation resistance is in the range of

1 kGy to about 100 MGy, beyond which they become brittle and making them not suitable for further use. It was reported in literature that the radiation resistance of polymer materials could be increased appreciably when aluminum flakes, radical stabilizers, ceramic fiber, inorganic fillers, etc., are added to polymer matrix (Ref 1–5). The radiation resistance of polycarbonate could be improved by incorporating an effective amount of benzylic alcohol (Ref 6) in the resin. This improved the resistance to yellowing and to the formation of haze induced upon exposure to gamma radiation. Polyaniline, a conducting polymer exhibits antioxidant effect in rubber mixtures when subjected to gamma irradiation (Ref 7) and thermo oxidative aging (Ref 7, 8). Some intrinsically conducting polymers show radical scavenger property. The sensitivity of polymers to degradation during exposure to high energy radiation is mitigated by the use of radical trapping stabilizers. Polyetheretherketone (PEEK) and polyimide (PI) have the highest radiation resistance of 10 and 100 MGy, respectively. The high performance PEEK is a derivative of polyaryletherketones and is a melt processable aromatic polymer. Its melting point,  $T_m$  lies between 330 and 385 °C depending on the relative proportion of ether-ketone group linking the phenylene rings. It can be processed by conventional methods such as injection molding, extrusion, compression molding, and powder coating. PEEK has outstanding thermal stability, wear resistance, mechanical properties, excellent resistance to chemicals and has the advantage over epoxy resin-based composites because of its high fracture toughness and excellent resistance to moisture. Therefore, PEEK and its composites are reported for use in aerospace, automotive, structural, high temperature wiring, tribology, and biomedical applications.

In the aqueous reprocessing of spent mixed carbide/oxide fuels of fast reactors, radiation tolerant polymers are widely used as coating materials, cable/wire insulation, electrical connectors, O-rings, seals, and in critical components such as motors (Ref 9, 10). As radiation-induced aging affects the properties and performance of these polymer materials, a program was initiated to develop PEEK composites with alumina fillers to improve the resistance of PEEK to gamma rays. The radiation damage on PEEK and its composites was evaluated by measuring the mechanical properties before and after irradiation and the results were reported elsewhere (Ref 11). The effect of radiation on the thermal properties and morphology of PEEK and its composites with alumina is reported in this work.

### 1.1 Effect of Radiation on Polymers

The deposition of radiation energy in an organic material triggers a complex set of events (Ref 12–15). High energy photons, such as  $\gamma$ - or X-rays are deposited in a material by the three modes: the photoelectric effect, Compton scattering, and pair production. The energy of the incident radiation and the atomic composition of the absorbing medium determine which of the above modes predominate. Compton scattering is the principal mechanism for most of the organic polymers. The ions and excited-state molecules generated during irradiation can give rise directly to chemical reactions, the predominant intermediate in radiation chemistry of organic molecules is the free radical. Radiation-induced radicals in polymers are extensively studied and well documented (Ref 15, 16).

## 2. Experimental

### 2.1 Materials

Commercially available, linear aromatic, semi-crystalline, color natural, fine powdered thermoplastic, and unreinforced polyetheretherketone, 450PF from M/s. Victrex, UK was used for making PEEK sheets. Its melt viscosity was 450 Pa s; density: 1.3 kg/dm<sup>3</sup> and average particle size of 50  $\mu$ m. Alumina powder from M/s. Alpha Aesar used for reinforcement had purity better than 99% and average particle size was 10  $\mu$ m.

### 2.2 Fabrication of Sheets of PEEK and PEEK-Alumina Composites

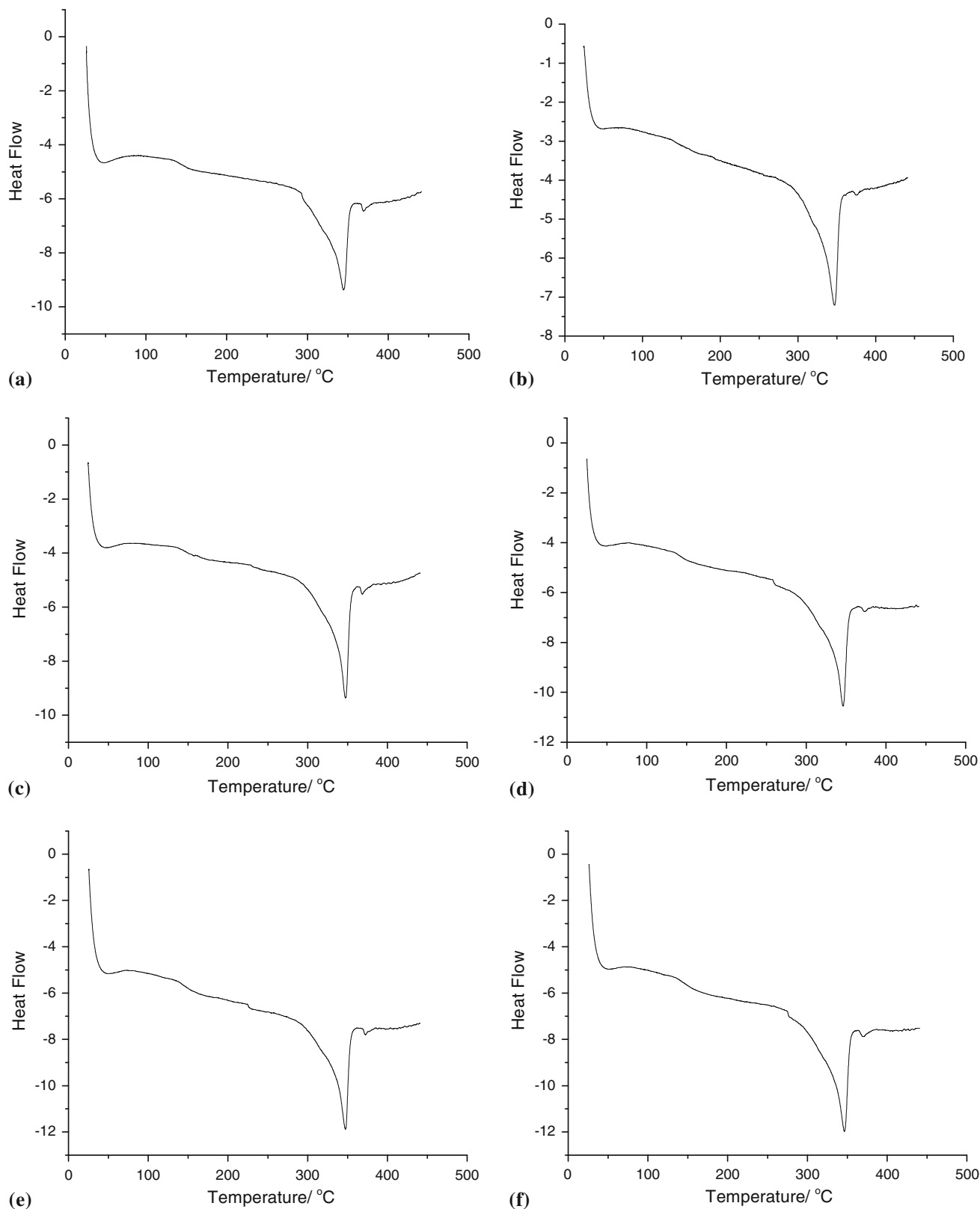
Hydraulic upthrust compression molding machine of capacity 1500 kN with two platens of 500 °C temperature rating each was used for fabricating sheets of PEEK and PEEK-alumina composites. Aluminum foil of thickness 0.15 mm was placed over stainless steel die of dimensions 21  $\times$  19 cm. About 60 g of PEEK powder was weighed accurately, spread uniformly on the die, covered further by another aluminum foil and was compacted in the compression molding machine at a pressure of 15 MPa. The mold was subjected to programmed heating to 400 °C and soaked for 8 min. The polymer completely melts at this temperature. The mold was allowed to natural cooling and the PEEK sheet was taken out carefully after removing the aluminum foil. This procedure for the fabrication of PEEK sheets was adopted for making PEEK-alumina composite sheets with alumina content 5, 10, 15, 20, and 25% by weight. PEEK and PEEK-alumina composite sheets fabricated by compression molding had a thickness of 1.6 mm. Homogeneity of alumina in each of the composite sheets was ascertained by incinerating an accurately weighed quantity of the PEEK-alumina blend (a domestic mixer was used for proper mixing of PEEK and alumina powders) and determining the wt.% of alumina from the weight of the residue. Scanning electron microscopic (SEM) pictures of the composite sheets before irradiation also confirmed the uniform distribution of alumina particles in the sheets.

### 2.3 Irradiation Experiments

Samples of dimensions 70  $\times$  100 mm cut from the sheets were exposed to gamma rays in the presence of atmospheric air at room temperature in a gamma chamber, with Co<sup>60</sup> as the source, supplied by Board of Radiation and Isotope Technology (BRIT), Mumbai, India at a dose rate of 4.11 kGy/h. Samples were taken out from the chamber at cumulative dose intervals of 1.0, 2.5, 5.0, 7.5, and 10.0 MGy for the purpose of thermal and surface characterization.

### 2.4 Measurement of Thermal Properties

Differential scanning calorimetric (DSC) measurements were carried out using Setaram Instruments, France; Model: DSC 131 EVO. Specimen of weight about 5–7 mg was used for each run. Prior to the experimental runs, the instrument was calibrated with pure indium and zinc standards for temperature and thermal scale. The measurements were carried out in commercial N<sub>2</sub> atmosphere in the temperature range 25–450 °C



**Fig. 1** DSC thermograms of (a) pure PEEK, (b) PEEK-5% alumina, (c) PEEK-10% alumina, (d) PEEK-15% alumina, (e) PEEK-20% alumina, and (f) PEEK-25% alumina composites

at the heating rate of 20 °C/min. Enthalpy of melting ( $\Delta H_m$ ) of irradiated and unirradiated samples were determined from the area of the corresponding transitions in the DSC scans.

### 2.5 Morphology by SEM

Morphology of PEEK and PEEK-alumina composites before and after irradiation was studied by Philips XL 30

**Table 1** Values of  $T_g$ ,  $T_m$ , and  $\Delta H_m$  measured from the DSC curves for PEEK and PEEK-alumina composites before and after irradiation to 10 MGy

Description of sample	Before irradiation			After irradiation to 10 MGy		
	$T_g$ , °C	$T_m$ , °C	$\Delta H_m$ , J/g	$T_g$ , °C	$T_m$ , °C	$\Delta H_m$ , J/g
PEEK	136	344.2	33.8	140.5	340.5	23.3
PEEK + 5% Al <sub>2</sub> O <sub>3</sub>	137.1	347.3	34.3	140.3	342.5	25.8
PEEK + 10% Al <sub>2</sub> O <sub>3</sub>	137.7	347.6	33.4	138.7	342.9	24.6
PEEK + 15% Al <sub>2</sub> O <sub>3</sub>	137.7	346.9	31.7	139.0	343.4	26.2
PEEK + 20% Al <sub>2</sub> O <sub>3</sub>	138.2	347.5	32.4	138.4	344.7	26.7
PEEK + 25% Al <sub>2</sub> O <sub>3</sub>	139.7	347.1	32	140.0	345.3	29.0

ESEM, at an accelerating voltage of 30 keV. As the specimens were non-conducting, the surface of the polymer samples was coated with 10-20 nm of gold before the analysis.

### 3. Results and Discussion

#### 3.1 Thermal Properties

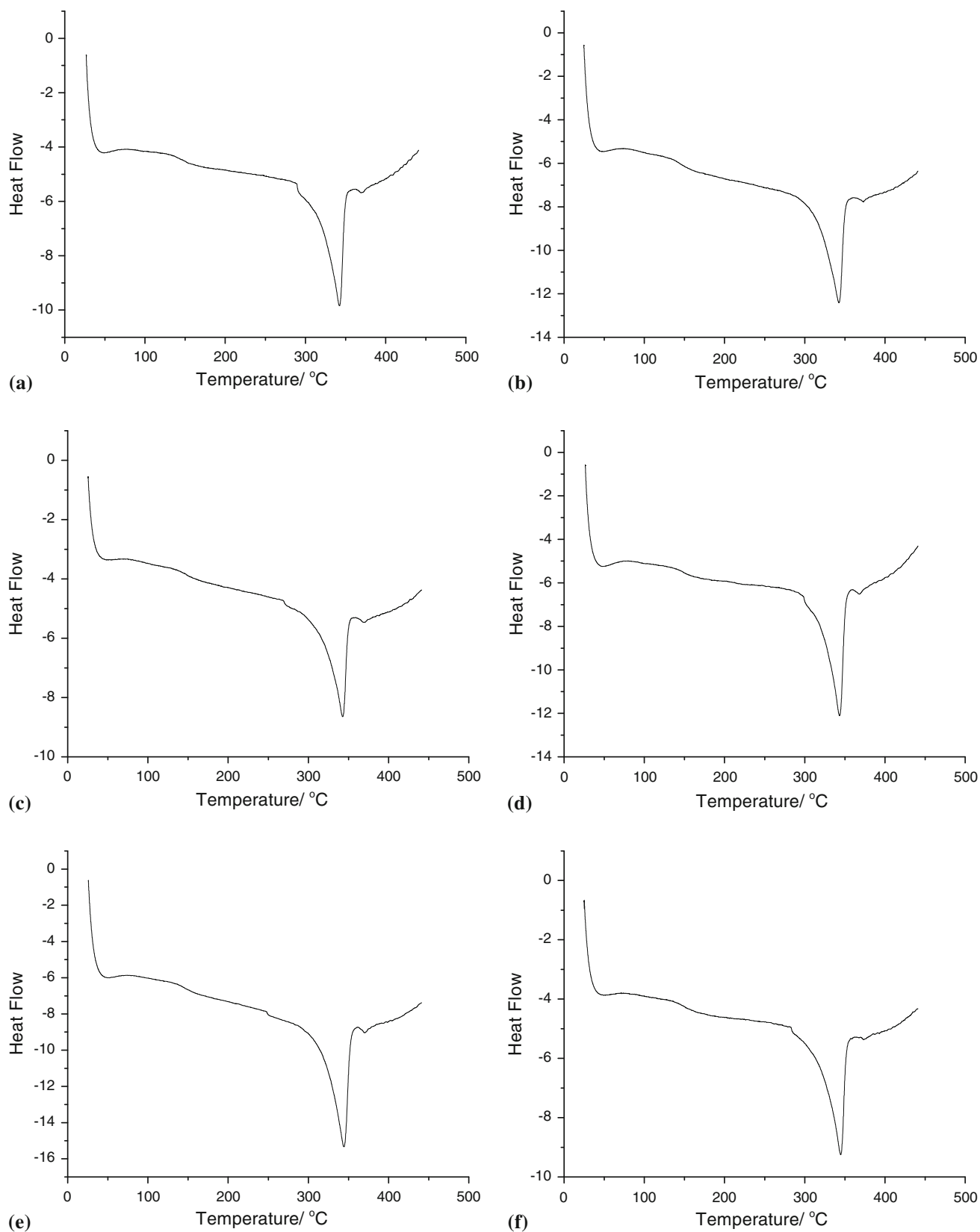
The DSC heating curves recorded in the temperature range 25-450 °C for PEEK and PEEK-alumina composites are shown in Fig. 1(a)-(f).  $T_g$  and  $T_m$  were measured accurately with precision of  $\pm 0.1$  °C. The precision in the measurement of the enthalpy of melting of PEEK and its composites is ascertained to be within  $\pm 1$  J/g based on the measurements of  $\Delta H_m$  carried out with calibration standards In, Sn, and Zn. From the slope change in the heating curves, glass transition temperature ( $T_g$ ) and from the endothermic peaks, melting temperature ( $T_m$ ) and enthalpy of melting ( $\Delta H_m$ ) were calculated and are tabulated in Table 1. The value of  $T_g$  measured for pure PEEK (given in Table 1) is 136 °C and it was found to increase gradually by the addition of alumina to PEEK and yielded a value of 139.7 °C for PEEK with 25% alumina. This observation of the shift in the  $T_g$  value of PEEK towards higher temperature by the addition of alumina is upheld by the results reported by Hanchi and Eiss Jr. (Ref 17) wherein the  $T_g$  value increased from 148 to 159 °C when PEEK was reinforced with 30 wt.% short carbon fiber. However, shift in  $T_g$  was not observed in carbon nanofibre reinforced PEEK (Ref 18) and mica filled in poly(aryl-ether-ether-ketone) (Ref 19) composites. Weak interaction between the two components, i.e., filler and the matrix might be the reason for not changing the  $T_g$  temperature in the two latter studies. On account of strong interaction between alumina and the matrix, the macromolecular mobility of polymer chains is affected resulting in the shift of  $T_g$  towards higher temperature as well as increasing the crystallinity (Ref 20–22). It is well known that in particle reinforced polymer composites, particles are surrounded by two regions; first by mesophase which is a tightly bound polymer or constrained polymer chain and second, by loosely bound polymer chains or unconstrained polymer chain, i.e., regions of a continuous phase of polymer having restricted mobility. With the incorporation of large amount of filler particles, the average inter-particle distance decreases and the loosely bound polymer gradually transforms to the tightly bound polymer. Hence, the volume fraction of loosely bound polymer decreases, thereby increasing the  $T_g$  (Ref 23). Presence of crystallinity in the polymer matrix contributes to a considerable increase in the breadth of the

relaxation as compared to the initially amorphous specimen, which leads to a corresponding decrease in intensity (Ref 21).

The melting temperature of pure PEEK was observed to be 344.2 °C. For the composites,  $T_m$  values were found to be increasing. The increase in melting temperature could be because of better interaction between the polymer and the dispersed alumina particles. The resultant interaction makes the PEEK segmental motion towards attaining perfect crystallinity (Ref 21). In PET/SiO<sub>2</sub> (97.5/2.5) nano-composite, an increase of 18 °C was observed in the melting temperature (Ref 24).

The DSC heating curves for irradiated PEEK and PEEK-alumina composites are reproduced in Fig. 2(a)-(f). From the heating curves, the thermal properties glass transition temperature, melting temperature, and enthalpy of melting ( $\Delta H_m$ ) were calculated and the values are listed in Table 1 along with those values calculated for unirradiated specimens. In  $\gamma$ -ray irradiation in air, probably chain scission occurs mainly on the surface and crosslinking occurs mainly inside the polymer (Ref 25). Since PEEK and PEEK-alumina composites were irradiated in the presence of air, chain scission is predominant on the surface and crosslinking is predominant in the bulk of the sample. It is evident from Table 1 that  $T_g$  increases upon irradiation of PEEK. PEEK-alumina composites also show an increase in  $T_g$  on irradiation. As  $T_g$  is governed by the chemical structure of repeating units of the polymer, bulkiness, interaction of chains and presence or absence of crosslinks, it is probable that the shift in  $T_g$  to higher temperatures by irradiation is due to the restriction of chain mobility caused by the crosslinking network structure formed on irradiation. It is well known that radiation has a significant effect on the amorphous region rather than on the crystalline region. While radicals form uniformly throughout the whole polymer, they cannot form crosslinks in the rigid lattice, but do so in the amorphous polymer or amorphous regions of the semi-crystalline polymer (Ref 26). Changes in the amorphous regions are indicated by increase in  $T_g$  with dose, which suggests that crosslinking is the important radiation damage mechanism in the inside of PEEK and its composites with alumina. It is clear from Table 1 that with increase in alumina content, increase in  $T_g$  due to radiation decreases. Alumina acts as an excitation energy sink (Ref 4) thereby reducing the crosslinking density, which in turn reduces the shift in  $T_g$  towards higher temperature.

Table 1 also reveals that on irradiation, the melting temperature as well as the heat of melting decrease in pure PEEK and its composites. The decrease in  $T_m$  is attributed to the inhibition of crystallization above  $T_g$  by the presence of crosslinks. Molecular changes in the crystalline regions cause reduction in  $\Delta H_m$ . Owing to the formation of crosslinks on irradiation, there

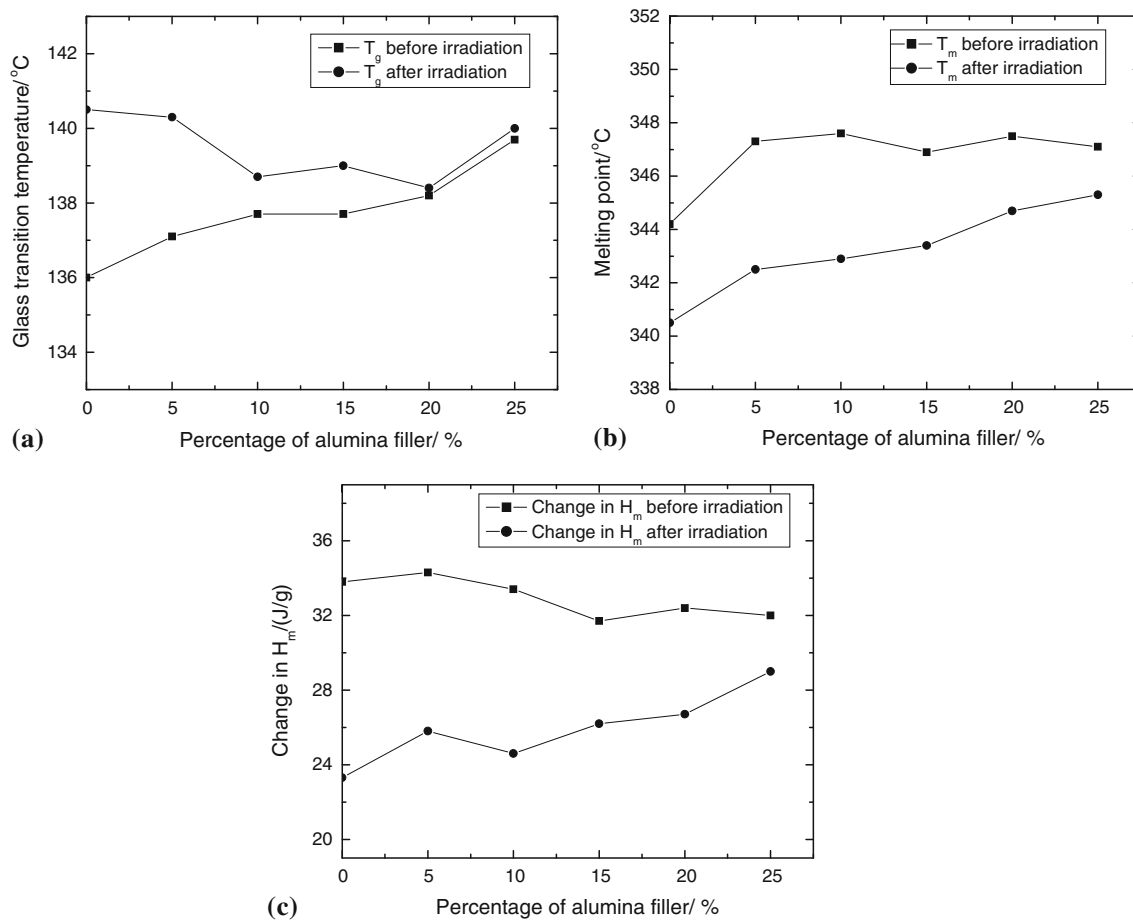


**Fig. 2** DSC thermograms of irradiated (a) pure PEEK, (b) PEEK-5% alumina, (c) PEEK-10% alumina, (d) PEEK-15% alumina, (e) PEEK-20% alumina, and (f) PEEK-25% alumina composites

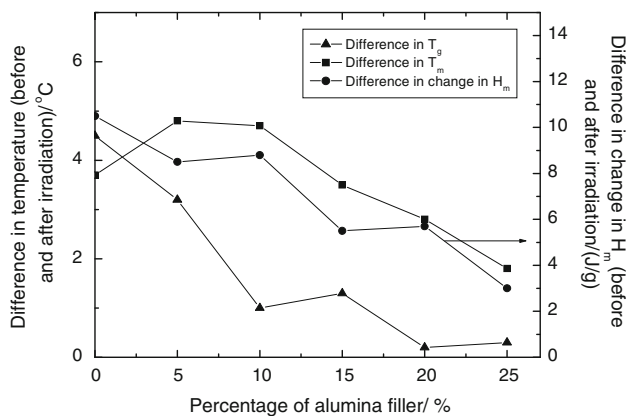
is a decrease in crystalline content and also the crosslink in amorphous domains can constrain the crystallites which results in the decrease in  $T_m$ . Therefore, decrease in  $T_m$  and  $\Delta H_m$  for

PEEK and PEEK-alumina composites is due to the restriction of chain mobility and disordering of their structures caused by such crosslinks. The decrease in  $T_m$  and  $\Delta H_m$  is more





**Fig. 3** Plot of (a)  $T_g$  before and after irradiation, (b)  $T_m$  before and after irradiation, and (c)  $\Delta H_m$  before and after irradiation with filler concentration



**Fig. 4** Plot of difference (before and after irradiation) in  $T_g$ ,  $T_m$ , and  $\Delta H_m$  with filler concentration

pronounced in pure PEEK and the decrease gets reduced with increase in alumina content. As the inorganic filler reduces the crosslinking density, the decrease in  $T_m$  and  $\Delta H_m$  of the composites is less.

The values of  $T_g$ ,  $T_m$ , and  $\Delta H_m$  of PEEK and PEEK composites before and after irradiation are plotted with filler concentration and is given in Fig. 3(a)-(c). From the figure it is seen that the curves before and after irradiation are approaching each other with increasing alumina filler concentration which

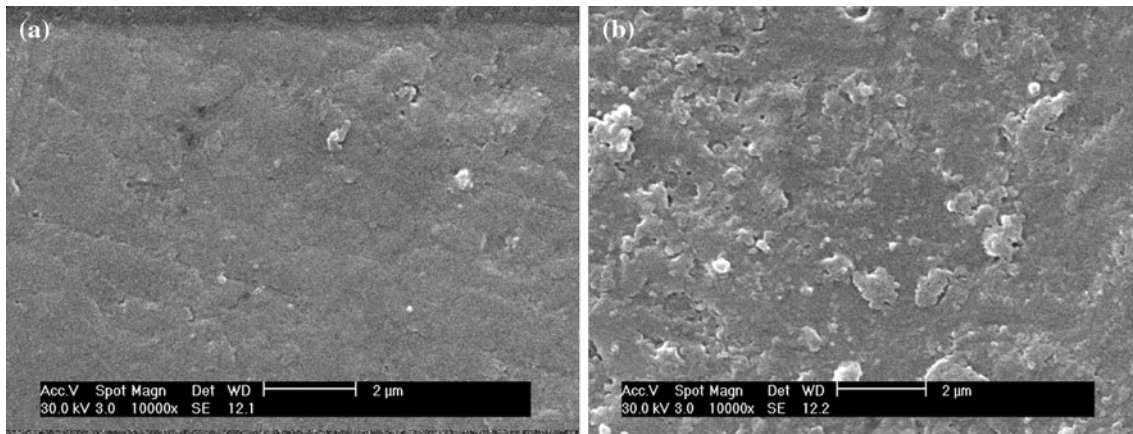
shows that with increase in filler concentration degradation is less and change in  $T_g$ ,  $T_m$ , and  $\Delta H_m$  due to radiation is reducing. Figure 4 shows the plot of difference (before and after irradiation) of  $T_g$ ,  $T_m$ , and  $\Delta H_m$  with alumina filler concentration. From the figure it is evident that the difference (before and after irradiation) of  $T_g$ ,  $T_m$ , and  $\Delta H_m$  due to irradiation is reducing with increase in filler content.

### 3.2 Morphology of the PEEK and Its Composites

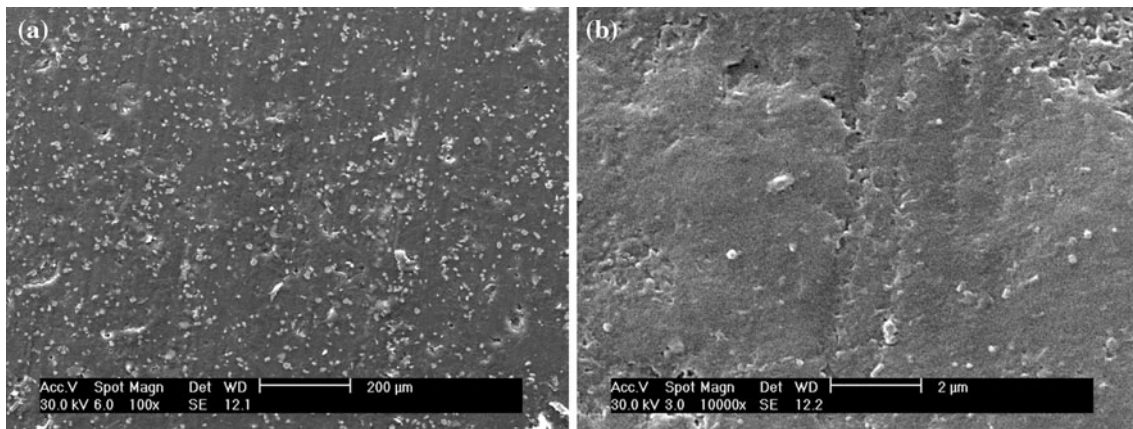
The morphology and particles distribution in PEEK matrix were studied using SEM. The SEM images of PEEK and PEEK-alumina composites are shown in Fig. 5(a)-7(a). Defects and pores are negligible in the SEM image of pure PEEK (Fig. 5a). It could be observed in the SEM image of PEEK with 10% alumina composite shown in Fig. 6(a) that alumina particles are uniformly dispersed in the PEEK matrix and aggregates of alumina particles are absent, which is expected due to good processing condition during sample preparation. Alumina particles were uniformly distributed without any agglomerates in 25% alumina composite also as evidenced from Fig. 7(a).

### 3.3 Effect of Radiation on Morphology

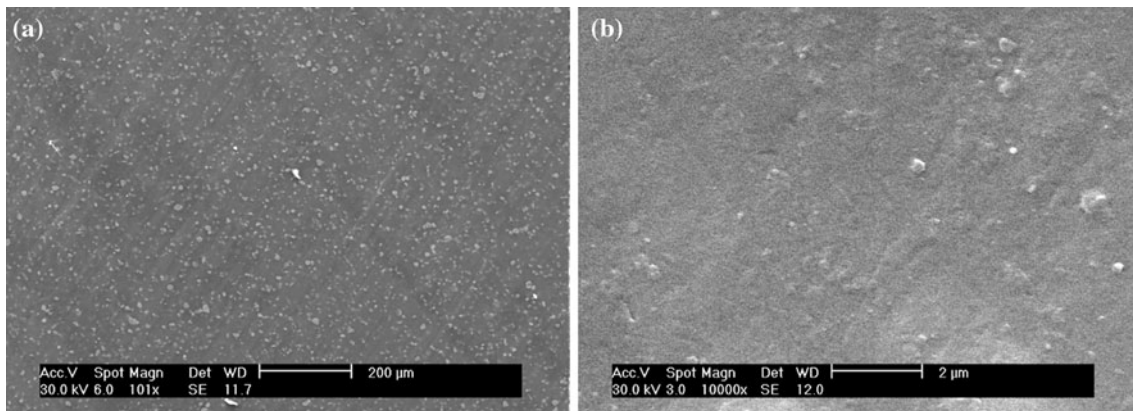
The SEM pictures of PEEK and PEEK-alumina composites, given in Fig. 5(b)-7(b) show the effect of radiation on the polymer matrix. Micro-cracks and micro-pores are observed in



**Fig. 5** (a) SEM image of pure PEEK. (b) Morphology of irradiated PEEK



**Fig. 6** (a) SEM image of PEEK + 10% alumina composite. (b) Morphology of irradiated PEEK + alumina (10%) composite



**Fig. 7** (a) SEM image of PEEK + 25% alumina composite. (b) SEM image of irradiated PEEK-alumina (25%) composite showing the absence of pores

the SEM image of degraded PEEK (Fig. 5b). The formation of micro-cracks on the polymer surface is mainly due to the chain scission reaction occurring in degraded samples. Breaking of polymer bonds produces fragments which occupy more volume than the original macromolecules. This causes strains and stresses responsible for the formation of micro-cracks and damaging the irradiated polymer. The cracks are frequently initiated from the breakdown of crazes formed at internal

defects as voids or impurities (Ref 27). The high degree of surface erosion leads to the loss of mechanical properties of polymers. It should be noted that the surface of undegraded (pure) PEEK (Fig. 5a) is smooth, without any visible structural defects and does not exhibit any special microstructure. During irradiation of polymers volatile, gaseous degradation products (Ref 28, 29) evolved from the sample leave behind micro-pores with different shapes and sizes. The volatile, low-molecular

weight products are mainly H<sub>2</sub>, CO, CO<sub>2</sub>, and aliphatic hydrocarbons. Similar results concerning morphology changes were reported by Kaminska et al. (Ref 30) for UV-irradiated, modified poly(vinylchloride), in which numerous blisters and holes were observed on the film surface, resulting from HCl evolution. Micro-cracks and micro-pores are seen due to degradation in the SEM image (Fig. 6b) of irradiated PEEK-alumina (10%) composite also. The SEM image of degraded PEEK-alumina (25%) composite in Fig. 7(b) shows negligible micro-cracks and micro-pores. This is due to the reinforcing effect of high alumina content in the PEEK matrix which helps in reducing the degradation in the properties of the polymer due to radiation (see Fig. 5-7).

## 4. Conclusion

PEEK sheet and PEEK-alumina composite sheets were fabricated by compression molding and samples were irradiated in gamma chamber to 10 MGy. The effect of gamma radiation on the thermal properties of PEEK and PEEK-alumina composites were studied. When exposed to radiation, the thermal properties such as glass transition temperature  $T_g$ , melting temperature  $T_m$ , and enthalpy of melting  $\Delta H_m$  of PEEK and PEEK-alumina composites were found to be affected owing to radiation damage. The shift in  $T_g$  towards higher temperature and the decrease in  $T_m$  and  $\Delta H_m$  values for pure PEEK were found to be more pronounced when compared to those changes for the PEEK-alumina composites. In the PEEK composites, the degradation in the thermal properties was observed to be less as more of alumina was loaded in the polymer matrix. Morphology of the PEEK and PEEK-alumina composites before and after irradiation was analysed with the aid of SEM images. Chain scission of PEEK leading to the formation of crazes and cracks and the formation of voids and holes owing to the evolution of volatile, low-molecular products were confirmed in the SEM picture of irradiated PEEK. Micro-cracks and micro-pores were negligible in the composites as alumina acts as an excitation energy sink and serves to add structural strength to the polymer during irradiation.

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