

Functionalized Poly(ether ether ketone): Improved Mechanical Property and Acellular Bioactivity

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ABSTRACT: Poly(ether ether ketone), PEEK, was functionalized by addition of pendant functional groups, that is, acetyl, carboxylic, acyl chloride, amide, and amine groups in the benzene ring of polymer backbone without substituting the parent (ether or ketonic) functional groups of polymer to improve the mechanical and surface adhesivity with acellular inorganic biomaterials. The functional groups of virgin PEEK and functionalized PEEK were identified by Fourier transform infrared spectroscopy and ¹³C nuclear magnetic resonance. The crystallinity was studied by X-ray diffraction and further supported by differential scanning calorimetry (DSC) analysis. Similarly,

the change in glass transition temperature was confirmed by the DSC and dynamic mechanical analysis (DMA). The improved mechanical property was also evaluated by DMA. The excellent surface adhesivity and bioactivity were revealed by acellular *in vitro* test using simulated body fluid. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1100–1111, 2012

Key words: functionalization; poly(ether ether ketone); Fourier transform infrared spectroscopy; nuclear magnetic resonance spectroscopy; *in vitro*; bioactivity; mechanical properties

INTRODUCTION

Poly(ether ether ketone), (PEEK) or poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), $[-O-C_6H_4-O-C_6H_4-CO-C_6H_4-]_n$, is a thermoplastic and semicrystalline polymer having outstanding properties, that is, high hydrolysis resistance, low flammability, low toxic gas emission, excellent heat resistance, good processability, excellent mechanical, electrical properties, etc.^{1–3} This material is thermally stable at the temperature of 400°C for 15 min in a nitrogen (N₂) atmosphere.^{4,5} The melting temperature (T_m) of PEEK is in the range of 335–395°C and glass transition temperature (T_g) varies from 143 to 160°C, depending upon the grade of polymer or crystallinity.⁶

PEEK has a wide range of application, like jigs for semiconductor process, various mechanical parts for automobiles, hardware, fasteners, and mechanical components for aircraft, wire and cable insulations, medical devices, oil and gas process equipment, etc.³ In recent years, several studies have been reported

the surface treated PEEK or PEEK based composites with an intention of improving adhesive bonding.^{2,7} The surface modification of aryl polymers for adhesive bonding has been carried out by several techniques namely, corona discharge treatment,¹ UV/ozone surface oxidation,⁷ low-energy ion-beam irradiation under a reactive O₂ environment, etc.¹ But most of the functionalizations of aryl polymers for membrane applications have been performed through chemical methods.^{8,9} The blends^{10,11} and composites^{12–15} of PEEK with various materials have been used in membrane, structural, and biomedical applications. Generally PEEK is produced by step-growth polymerization by the dialkylation of bisphenolate salts as reported elsewhere.^{3,16–18} Few researchers have investigated to functionalize the PEEK for several applications. To the best of author's knowledge, the nitration,¹⁹ amination,^{9,10,19} sulfonation,^{9,10} hydroxylation,^{9,10,19,20} and pendant sulfonic acid phenyl groups²¹ have been done to improve the performance of PEEK to date.

Concentrated sulfuric acid (0–5°C) and concentrated nitric acid (5–25°C) have been used as solvents during sulfonation and nitration of aryl polymers [polyether sulfone, polyether ether sulfone, polyether ketone (PEK), polyether ether ketone (PEEK), polyether ether ketone ketone (PEEKK)].¹⁹ Cui has used sodium dithionite (Na₂S₂O₄) to reduce –NO₂ to –NH₂ in the temperature range of 60–

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180°C.¹⁹ However in another report, Henneus-Boxus et al., have substituted the C=O group of backbone chain in PEEK by —OH group using NaBH₄ in dimethyl sulfoxide (DMSO) solvent at the temperature of 120°C.⁹ They have used various reagents (such as OHAc, R-CONH₂, LiOH, NaOH, etc) to convert this —OH group to —NH₂ groups.⁹ The pendant sulfonic acid phenyl group (—PhSO₃H) has also been incorporated in PEEK using other reagents (like bisphenol monomers, difluorinated monomers, ethanol, chlorobenzene, concentrated sulfuric acid, etc).²¹ Moreover, most of the studies have reported the substitution of either ether (—O—) or ketonic (carbonyl, C=O) group by the above functional groups. However, these two groups have a unique role to control the crystallinity, mechanical, and structural properties of this polymer.¹³ Hence, substitution of ether or ketonic group may deteriorate the performance of functionalized PEEK materials in the target applications.

Since PEEK polymer has good mechanical properties even at the high temperature,¹³ an attempt is made to further improve the performance of virgin polymer. If it shows some beneficial properties, the functionalized PEEK materials further can be used as matrix for composites in aerospace, automobile, biomedical, etc. However, it is known that the surface modification of PEEK by amine group significantly improves the membrane properties and the cellular adhesion properties for the biological applications.⁹ The amine group can also be grafted with conventional polymer (sulfonated PEEKs) to improve the mechanical properties of the membrane materials. Further mechanical behavior as well as hydrophilic detrimental effect of amine functionalized polymers can be improved by making of composites with porous inorganic compounds (silicon based or calcium phosphate compounds) for membrane applications. Hence, the surface modification of PEEK through proper functionalization, that is, acetyl (—COCH₃), carboxylic acid (—COOH), acyl chloride (—COCl), amide (—CONH₂), and amine (—NH₂) groups may improve the strength as well as bioactivity. In this context, the main objective of this investigation is to improve the mechanical properties and surface adhesivity of PEEK with acellular inorganic biomaterials and its characterization through dynamic mechanical analysis (DMA) and acellular *in vitro* test, respectively. The next objective is to identify the functional groups through Fourier transform infrared spectroscopy (FTIR) and ¹³C solid state nuclear magnetic resonance (NMR) spectroscopy. Furthermore, first time, this study aims to functionalize the PEEK with amine as well as carboxylic acid group without substituting the existing parent (ether or ketonic) groups present in the back bone chain of PEEK. Hence, this functionalized polymer can have better surface adhesivity properties along with mechanical properties. As a

result, it can be used as matrix to make composites for structural, membrane, and biological applications. The last objective in this study is to understand the improved mechanical properties through crystallinity using X-ray diffraction (XRD) and differential scanning calorimetry (DSC).

MATERIALS AND METHODS

Raw materials

The material used in this study was commercial PEEK powders (specific gravity: 1.30, water absorption for 24 h: 0.1%, melt flow index at a temperature of 400°C under a load of 2.16 kg: 3.0 g/10 min, and melting temp: 340°C) supplied by M/S Gharda Chemicals (India). Other reagents like glacial acetic acid (CH₃COOH), thionyl chloride (SOCl₂), anhydrous aluminum chloride (anh.AlCl₃), potassium permanganate (KMnO₄), ammonia solution (aq.NH₃), potassium hydroxide (KOH), and solid iodine (I₂) were supplied by M/S Glaxo Smith Kline Pharmaceuticals (India).

Functionalization of PEEK

The functionalization of PEEK was performed by the following steps.

Preparation of acetyl chloride

Acetyl chloride (CH₃COCl) was prepared by nucleophilic substitution reaction as shown in Scheme 1 (a, Fig. 1). CH₃COOH and halogenating agent, SOCl₂ using a ratio of 54.3 : 45.7 (w/w) was mixed at ice cold condition (0–5°C) with slight stirring. Then the product was refluxed at 45°C for 5 h. During refluxing at 45°C the acetyl chloride is separated out from the reaction vessel by left out higher boiling point (>100°C) by-product, that is, hydrochloric acid. The acetyl chloride is condensed as pure form during cooling. Another by product, SO₂, is easily left out from the liquid acetyl chloride during reaction as gaseous form. The yield of acetyl chloride is ~ 74% (mole) and mentioned in Table I.

Preparation of PEEK-COCH₃

PEEK (18.3 wt %) was heated in the temperature range of 70–80°C for 20 min with anhydrous AlCl₃ (3.7 wt %) and freshly prepared CH₃COCl (50.6 wt %) to produce PEEKCOCH₃ as shown in the Scheme 1(b, Fig. 1). Here, anhydrous AlCl₃ acts as a catalyst. Solvent was not used for this reaction, whereas deionized water (DI H₂O, 27.4 wt %) was added drop wise as a medium to dissociate the AlCl₃. The whole mixture was stirred by a glass rod for a

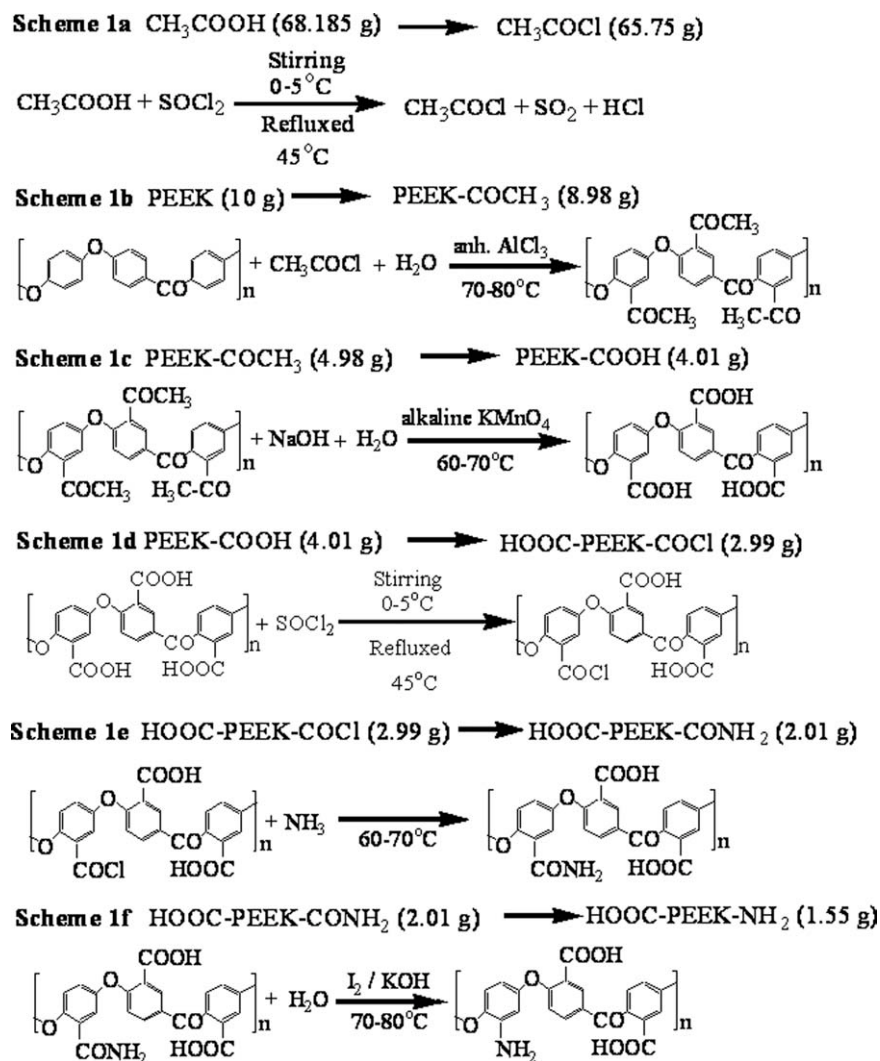


Figure 1 Reaction scheme used in functionalization of PEEK.

TABLE I
Yield of Various Functionalized PEEK Polymers

Reaction Scheme	Reactant or repeating unit of reactant (in case of polymer)	Molecular weight of reactant or repeating unit	Product and its molecular weight	Weight of reactant used in the reaction	Weight of the final product	Yield = $[(W_p/W_r) \times (M_r/M_p)] \times 100$
		M_r	M_p	W_r (gm)	W_p (gm)	(%)
1a: Preparation of CH_3COCl	CH_3COOH	60	CH_3COCl , 78.5	68.185	65.75	74
1b: Preparation of PEEK-COCH ₃	$\text{C}_{19}\text{H}_{12}\text{O}_3$	288	$\text{C}_{25}\text{H}_{18}\text{O}_6$, 414	10.00	8.98	63
1c: Preparation of PEEK-COOH	$\text{C}_{25}\text{H}_{18}\text{O}_6$	414	$\text{C}_{22}\text{H}_{12}\text{O}_9$, 420	4.98	4.01	79
1d: Preparation of HOOC-PEEK-COCl	$\text{C}_{22}\text{H}_{12}\text{O}_9$	420	$\text{C}_{22}\text{H}_{11}\text{O}_8\text{Cl}$, 438.5	4.01	2.99	72
1e: Preparation of HOOC-PEEK-CONH ₂	$\text{C}_{22}\text{H}_{11}\text{O}_8\text{Cl}$	438.5	$\text{C}_{22}\text{H}_{13}\text{O}_8\text{N}$, 419	2.99	2.01	70
1f: Preparation of HOOC-PEEK-NH ₂	$\text{C}_{22}\text{H}_{13}\text{O}_8\text{N}$	419	$\text{C}_{21}\text{H}_{13}\text{O}_7\text{N}$, 391	2.99	1.55	83

period of 10–15 min. This reaction is also known as Friedel-Crafts reaction, which allows the synthesis of monoacylated products from the reaction of arenes (i.e., aromatic hydrocarbons) and acyl chlorides or anhydrides. At the end of reaction the product was filtered and washed with DI H₂O several times to eliminate AlCl₃ and acid. The yield of PEEK-COCH₃ is ~ 63 (mole %).

Preparation of PEEK-COOH

Then PEEK-COCH₃ (15.5 wt %) obtained from previous step [Scheme 1(b), Fig. 1] was heated in the temperature range of 60–70°C for 20–25 min with a strong oxidant, that is, alkaline KMnO₄ (1.6 wt %), NaOH (5.6 wt %), and DI H₂O (77.4 wt %) to produce carboxylic acid functionalized PEEK or PEEK-COOH as shown in the Scheme 1(c, Fig. 1). Similarly it is also heterogeneous reaction. Here, this alkaline KMnO₄ solution acts as a medium. The yield of PEEK-COOH is ~ 79 (mole %).

Preparation of HOOC-PEEK-COCl

PEEK-COOH obtained from the Scheme 1(c) and SOCl₂ using a ratio of 19.6 : 80.4. (w/w) was mixed in the temperature range 0–5°C for 30 min followed by refluxed at 45°C for 2 h to produce –COCl functionalized PEEK-COOH or HOOC-PEEK-COCl as shown in the Scheme 1(d, Fig. 1). This is a nucleophilic substitution type addition reaction. Since the –COCl group is able to replace partly –COOH group from the PEEK-COOH polymer, therefore the product contains –COOH group along with –COCl group. The yield of HOOC-PEEK-COCl is ~ 72 (mole %).

Preparation of HOOC-PEEK-CONH₂

The HOOC-PEEK-COCl (13 wt %) was heated in the temperature range of 60–70°C for 15–20 min with nucleophile agent, that is, ammonia solution (aqueous NH₃, 43.5 wt %) and DI H₂O (43.5 wt %) to replace –Cl group from –COCl in HOOC-PEEK-COCl by amine (–NH₂) as shown in the Scheme 1(e, Fig. 1). Similarly here also no special solvent was used, whereas ammonia solution acts as a medium. In this heterogeneous reaction, amide (–CONH₂) group was formed along with the carboxylic acid in functionalized PEEK (HOOC-PEEK-CONH₂). The yield of HOOC-PEEK-CONH₂ is ~ 70 (mole %).

Preparation of HOOC-PEEK-NH₂

Finally, HOOC-PEEK-CONH₂ (11.6 wt %) was heated at 70–80°C for 20–30 min with I₂ (0.1 wt %), KOH (1.7 wt %), and DI H₂O (86.6 wt %) to produce

functionalized carboxylic amine PEEK or HOOC-PEEK-NH₂ as shown in the Scheme 1(f, Fig. 1). Here, the alkaline iodine solution acts as a solvent. This is also known as addition reduction reaction or Hoffman degradation reaction. The yield of HOOC-PEEK-NH₂ is ~ 83 (mole %).

All the above reactions, except Scheme 1(a) reaction, were heterogeneous type and at the end of the reaction the product was washed several times with DI H₂O to eliminate the excess reactants and/or unnecessary products.

CHARACTERIZATIONS

The existence of various functional groups in PEEK and functionalized PEEK polymers was analyzed in the spectral region of 4000–400 cm⁻¹ using Fourier transform infrared spectrophotometer, FTIR (Bruker make, model Vector 22). The KBr disk was made by using spectroscopic-grade KBr powder (sample : KBr = 1 : 30), which was dried at 100°C for 4 h.

The functional groups of PEEK were also analyzed by 300 MHz ¹³C solid state nuclear magnetic resonance (NMR, Bruker make, model DSX 300). This analysis was performed in the δ -shift range of –100–220 ppm.

The crystallinity of PEEK and functionalized PEEK was measured in the 2 θ range of 10–80° by X-ray diffractometer, XRD (Seifert Diffractometer, England, model: ISO DebyeFlex-2002) using CuK α radiation ($\lambda = 1.54056 \text{ \AA}$).

Differential scanning calorimetric (DSC) study was performed for virgin PEEK and all other functionalized PEEK polymers by a Pyris Diamond DSC (Perkin-Elmer make, model Pyris Diamond) in the temperature range of 40–350°C using nitrogen atmosphere (flow rate 200 mL/min). The glass transition temperature (T_g) was calculated directly through the Pyris software in the temperature range of 130–190°C. The weight of samples used for DSC experiments was in the range of 5–6 mg. Three scans were taken for each sample. The T_g values are almost identical with a repeated scan. The scan, which is shown in the figure, is the third scan.

DMA was carried out for virgin PEEK, PEEK-COOH, and HOOC-PEEK-NH₂ by a Pyris Diamond DMA (Perkin-Elmer make, model Pyris Diamond) in the temperature range of 35–310°C, nitrogen atmosphere (flow rate 150 mL/min), and shear mode. The glass transition temperature (T_g) was also calculated from $\tan \delta$ peak, which is nothing but a ratio of loss modulus (G'') to storage modulus (G'). Since most of the functionalizations are derived from carboxylic (–COOH) and amine (–NH₂) groups, only PEEK-COOH and HOOC-PEEK-NH₂ functionalized polymer have been compared with the virgin PEEK.

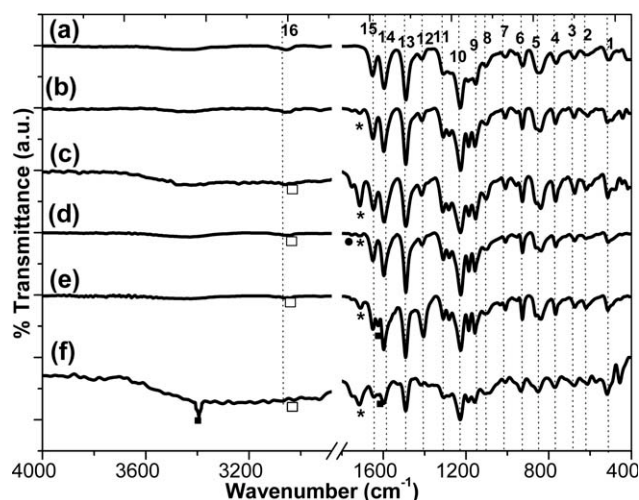


Figure 2 Fourier transformation infrared spectroscopy of (a) PEEK, (b) PEEK-COCH₃, (c) PEEK-COOH, (d) HOOC-PEEK-COCl, (e) HOOC-PEEK-CONH₂, and (f) HOOC-PEEK-NH₂.

To understand the performance of functionalized PEEK in bioapplication, acellular *in vitro* test was carried out on virgin PEEK, PEEK-COOH, and HOOC-PEEK-NH₂ pellets in simulated body fluid (SBF). The pellets were sintered at 370°C for 1 h in controlled N₂ atmosphere. The chemicals used in SBF are sodium chloride (NaCl), commercial grade potassium chloride (KCl), calcium chloride (CaCl₂·2H₂O), sodium bi-carbonate (NaHCO₃), dipotassium hydrogen phosphate (K₂HPO₄·3H₂O), sodium sulfate decahydrate (Na₂SO₄·10H₂O), and magnesium chloride hexa-hydrate (MgCl₂·6H₂O). All

these chemicals were dissolved in deionized water (DI H₂O). The samples were immersed into SBF solution maintaining the physiological conditions (at 37°C and pH = 7.4) at humid atmosphere (50%) for 7, 15, and 30 days.^{22–25} First data was taken after 7 days. The weight of wet samples was measured immediately after taken out from the SBF solution and again measured in the dry state (dried at 100°C for 2 h). The dried sample was again examined with the same SBF solution for 15 and 30 days.

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy

The various functional groups present in PEEK are studied through FTIR as shown in Figure 2. These peaks are summarized in Table II. The identification numbers, that is, 1–16 represent the various functional groups present in the virgin PEEK. The numbers 1–6 and 12–14 refer to aromatic (C=C) bond, 7–11 for aromatic ether (—O—), and 15 for ketonic (C=O) bond. In addition to these numbers, the other symbols, that is, (*), (□), (●), and (■) represent the C=O stretching bond for carboxylic acid, O—H bond for carboxylic acid, the —COCl of aromatic acyl chloride, and the N—H bond for amine group, respectively. These are also shown in Figure 2. The peaks at wave number of 509, 619, 676, 763, 846, and 925 cm⁻¹ are attributed to aromatic (C=C) bond; 1010, 1105, 1153, 1226, 1309, 1413, 1490, and 1595 cm⁻¹ for aromatic ether (—O—) group; 1652 cm⁻¹ for carbonyl (C=O) group; and 3062 cm⁻¹ for

TABLE II
Various Functional Groups Present in PEEK and Functionalized PEEK Polymers

Peak's Symbol	PEEK (cm ⁻¹)	PEEK-COCH ₃ (cm ⁻¹)	PEEK-COOH (cm ⁻¹)	HOOC-PEEK-COCl (cm ⁻¹)	HOOC-PEEK-CONH ₂ (cm ⁻¹)	HOOC-PEEK-NH ₂ (cm ⁻¹)	Bond	Compound
1	509	514	514	513	511	516	C=C	Aromatic
2	619	611	617	619	622	613	C=C	Aromatic
3	676	676	675	675	676	677	C=C	Aromatic
4	763	767	767	765	767	771	C=C	Aromatic
5	846	842	840	840	839	850	C=C	Aromatic
6	509	514	514	925	927	935	C=C	Aromatic
7	1010	1010	1008	1008	1008	1008	—O—	Ether
8	1105	1103	1103	1101	1103	1110	—O—	Ether
9	1153	1157	1155	1157	1157	1159	—O—	Ether
10	1226	1226	1226	1226	1224	1228	—O—	Ether
11	1309	1309	1311	1310	1309	1307	—O—	Ether
12	1413	1413	1415	1413	1413	1415	C=C	Aromatic
13	1490	1490	1490	1492	1492	1492	C=C	Aromatic
14	1595	1596	1596	1596	1596	1596	C=C	Aromatic
15	1652	1649	1647	1650	1650	1645	C=O	Ketone
16	3062	3062	3060	3062	3062	3072	C—H (sp ²)	Aromatic hydrogen
*	—	1712	1714	1716	1713	1714	—C=O or —C=OR	Carboxylic acid
□	—	—	3060	3051	3045	3072	O—H	Carboxylic acid
●	—	—	—	1755	—	—	—COCl	Acetyl chloride
■	—	—	—	—	1626	1621, 3392	N—H	Amine

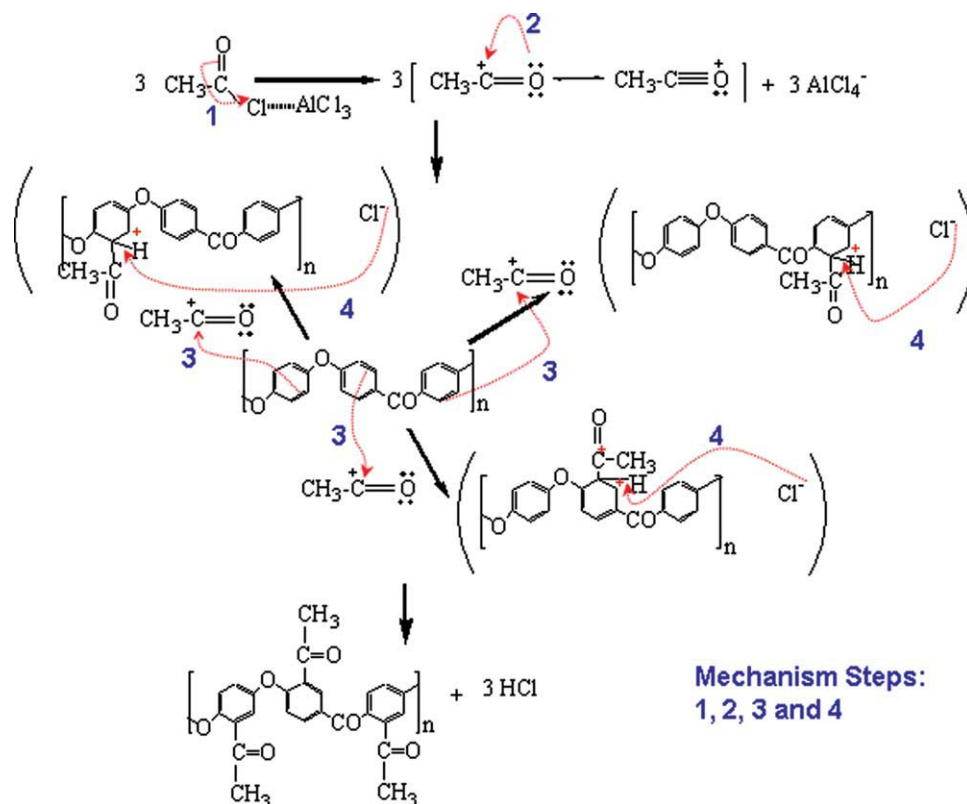


Figure 3 A probable mechanism for the formation of PEEK-COCH₃. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aromatic hydrogen (C–H, sp²) as reported in other studies.^{19,24} All these peaks are also common for all other functionalized PEEK. However, a small shift of these peaks is observed. The product, PEEK-COCH₃, as shown in reaction scheme 1(b, Fig. 1) shows an extra peak at 1712 cm⁻¹. This is attributed to the C=O bond of acetyl (–COCH₃) group.²⁴ The authors would like to mention that though the acetyl group is difficult to link in ortho of keto-group in benzene ring based on the principle of organic chemistry, but this structure is stable due to the combined effect of ether and ketonic groups. A probable mechanism for this reaction is proposed in Figure 3. The other product (PEEK-COOH) as shown in reaction scheme 1(c, Fig. 1) shows two extra peaks (strong in intensity) at 1714 and 3060 cm⁻¹. These are corresponding to the –C=O bond and –O–H stretching vibration of carboxylic (–COOH) group, respectively. This is a confirmation of –COOH group in functionalized PEEK, as stated in other reports.^{20,26,27} Then in the reaction Scheme of 1(d, Fig. 1), the product (HOOC-PEEK-COCl) shows another small peak at 1789 cm⁻¹. This is due to the aromatic acyl chloride (–COCl) group and the peak at 3062 cm⁻¹ is attributed to the –O–H stretching vibration of carboxylic (–COOH) group. Since, it is hard to substitute all the –COOH groups from the polymer (PEEK-COOH), therefore few parts of

–COOH group is replaced by –COCl group. In the next reaction, Scheme of 1(e, Fig. 1), the two small extra peaks at 1650 and 1625 cm⁻¹ of HOOC-PEEK-CONH₂ are attributed for ketone (>C=O) and amine (–NH₂) of the amide (–CONH₂) group, respectively. Another peak at 3062 cm⁻¹ is due the O–H stretching vibration of carboxylic (–COOH) group.²⁶ The final product (HOOC-PEEK-NH₂) shows two extra peaks at 1645 and 3392 cm⁻¹, these are for N–H bond of amine (–NH₂) group along with >C=O bond of carboxylic acid group at 1714 cm⁻¹ and O–H stretching vibration at 3072 cm⁻¹ as reported in other studies.^{19,20,24,26} Since substitution of all the –COOH groups from the polymer (PEEK-COOH) is very difficult, few parts of –COOH groups are replaced by –NH₂ group. This result also supports that the backbone of functionalized PEEK materials is not broken at all even in the final product (HOOC-PEEK-NH₂). Díez-Pascual et al. have calculated the degree of functionalization in PEEK-OH by taking the ratio between the area of the carbonyl peak and the area of a reference peak associated with the C–C stretching of the aromatic rings, and observed that the functionalized hydroxyl group reduces the carbonyl group with increasing the reaction time.²⁸ The degree of functionalization in a repeating unit of polymer are 0.65, 0.08, 0.06, and 0.056 of carboxylic group in PEEK-COOH, acyl

TABLE III
Calculation of —COOH, —COCl, and —NH₂ Functional Groups in the Functionalized PEEK Polymers

Samples	Area of the whole IR spectrum in the range of 4000–400 cm ⁻¹		Area% of the reference peak	Number of reference bonds in a repeating unit of polymer (as expected)	Weight of the reference bond in a repeating unit of polymer	Molecular weight of the repeating unit of polymer	Weight% of the (C=O) bond in a repeating unit of polymer	Number of (C=O) bonds for —COOH/COCH ₃ in a repeating unit of polymer
	(A ₀)	(A ₁)						
PEEK-COOH	528.4	23 (1714 cm ⁻¹)	4.34	3 (C=O)	84	420	20.00	0.65
HOOC-PEEK-COCl	315.7	1.62 (1755 cm ⁻¹)	0.51	1 (—C=O of COCl)	28	438.5	6.385	0.08
HOOC-PEEK-CONH ₂	375.16	0.8 (1626 cm ⁻¹)	0.21	1 (—NH)	15	419	3.58	0.06
HOOC-PEEK-NH ₂	362.51	0.76 (1621 cm ⁻¹)	0.21	1 (—NH)	15	391	3.836	0.055

Results verified by another method used by Díez-Pascual et al. ²⁸					
	Intensity of peak-13 (near 1490 cm ⁻¹), I ₁₃	Intensity of C=O bonds (near 1755 cm ⁻¹), I _x	% of relative intensity for CO group, I _R =(I _x /I ₁₃) × 100	Number of expected COCl group in a repeating unit of polymer, N _{ex}	Number of (C=O) bonds for —COCl in a repeating unit of polymer, N _{IR} =(I _R /100) × N _{ex}
HOOC-PEEK-COCl	0.62	0.06	9.68	1	0.09

group of HOOC-PEEK-COCl, amide group of HOOC-PEEK-CONH₂, and amine group of HOOC-PEEK-NH₂, respectively. These are summarized in Table III. Just to verify this method of calculation, the degree of functionalization data of HOOC-PEEK-COCl was verified by another technique proposed by Díez-Pascual et al.²⁸ No difference is observed. These data are also included in same Table III.

Nuclear magnetic resonance spectroscopy

Figure 4 shows the ¹³C solid state NMR spectra of PEEK (δ-shift in ppm: 1–152.569; 2–119.680; 3–161.561; 4–122.356; 5–133.989; 6–194.803), PEEK-COOH (δ-shift in ppm: 1–152.489; 2–119.723; 3–161.490; 4–122.363; 5–133.996; 6–194.803; 7–172.380), HOOCPEEK-CONH₂ (δ-shift in ppm: 1–152.527; 2–119.548; 3–161.529; 4–122.413; 5–133.998; 6–194.947; 7–172.285; 8–170.014), and HOOC-PEEK-NH₂ (δ-shift in ppm: 1–152.553; 2–119.809; 3–161.531; 4–122.022; 5–134.093; 6–194.787; 7–175.985) powders. The δ-shift for PEEK powder has also been reported in other reports.^{29,30} The extra peaks at 186, 189, and 201 ppm may be attributed for the c-atoms of neighboring monomer present in the same polymeric chain. The δ-shift peak 6 around 194 ppm is attributed for ketonic (>C=O) group present in the backbone chain. However, the δ-shift peak 5 is shifted to the

lower side in all functionalized PEEK, which is due to the presence of carboxylic acid (—COOH) pendant group. Whereas the δ-shift peak 7 at 172 ppm in all functionalized PEEK polymers are attributed to carboxylic (—COOH) group. The rest of all other peaks have remained unaltered. The δ-shift peak 8 at 172.285 ppm for amide (—CONH₂) group in HOOC-PEEK-CONH₂ forms doublet with carboxylic (—COOH) group at around 172 ppm as shown in Figure 4.³⁰ Since, it forms doublet, this amide functionalized PEEK may be atactic or syndiotactic polymer. However, the δ-shift peak 8 at 170 ppm is vanished in HOOC-PEEK-NH₂, which may be due to the absence of amide (—CONH₂) group. However, the peak 7 for carboxylic (—COOH) group is slightly shifted at 176 ppm. This is due to the amine (—NH₂) group as shown in Figure 4. Furthermore, this result also indicates that the functionalizations of PEEK have been perfectly carried out without disturbing the ketonic (>C=O) group, which is present in the main backbone of virgin PEEK. Therefore, the NMR study further strongly supports the results obtained from FTIR.

X-ray diffraction

The crystallinity (X_c) of PEEK, PEEK-COCH₃, PEEK-COOH, HOOC-PEEK-COCl, HOOC-PEEK-CONH₂,

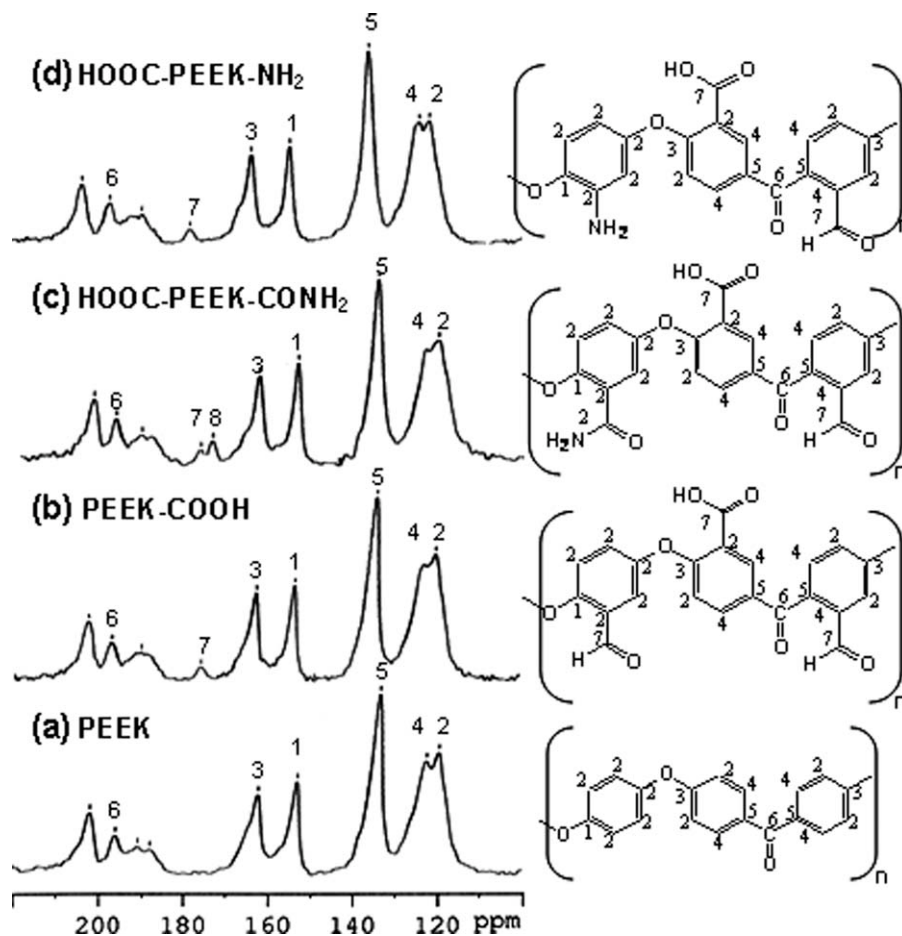


Figure 4 ^{13}C solid state NMR spectra for (a) PEEK (δ -shift in ppm: 1–152.569; 2–119.680; 3–161.561; 4–122.356; 5–133.989; 6–194.803), (b) PEEK-COOH (δ -shift in ppm: 1–152.489; 2–119.723; 3–161.490; 4–122.363; 5–133.996; 6–194.803; 7–172.380), (c) HOOC-PEEK-CONH₂ (δ -shift in ppm: 1–152.527; 2–119.548; 3–161.529; 4–122.413; 5–133.998; 6–194.947; 7–172.285; 8–170.014), and (d) HOOC-PEEK-NH₂ (δ -shift in ppm: 1–152.553; 2–119.809; 3–161.531; 4–122.022; 5–134.093; 6–194.787; 7–175.985).

and HOOC-PEEK-NH₂ was calculated from XRD graph using the following equation³¹:

$$X_c = (A_t - A_a)/A_t \quad (1)$$

where, A_a is the area under the amorphous part and A_t is total area including crystalline and amorphous parts. These values (crystallinity %) are 29.5, 41.8, 37.5, 39.2, 34.3, and 34.2 for PEEK, PEEK-COCH₃, PEEK-COOH, HOOC-PEEK-COCl, HOOC-PEEK-CONH₂, and HOOC-PEEK-NH₂, respectively. The semicrystallinity of PEEK is confirmed by XRD graph as shown in Figure 5. But the crystallinity of other functionalized PEEK polymers increase with surface modification, which is due to the addition of more polar functional groups like -COCH₃, -COOH, -COCl, -CONH₂, and -NH₂ in PEEK as described in Figure 1. The inter chain interactions of the functionalized PEEK are high due to the presence of these polar functional groups. As a result the polymer chains are rearranged and form a more order structure (A common example is nylon to justify the above explanation, where the polar amide

groups of the backbone chain of nylon (6,6) are strongly attracted to each other through hydrogen bonds and forms a crystal structure). The main

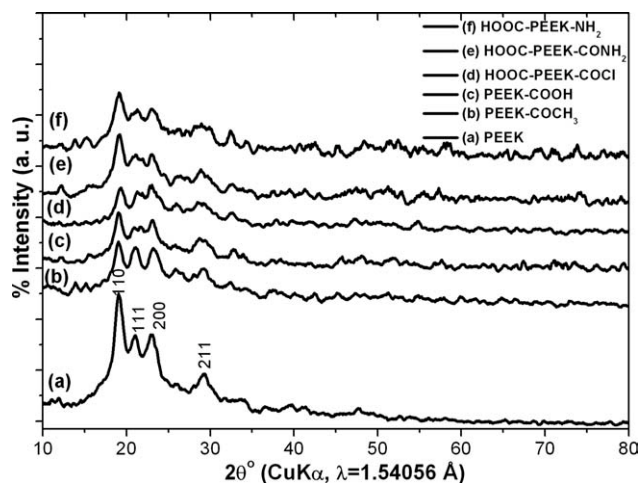


Figure 5 X-ray diffraction pattern of (a) PEEK, (b) PEEK-COCH₃, (c) PEEK-COOH, (d) HOOC-PEEK-COCl, (e) HOOC-PEEK-CONH₂, and (f) HOOC-PEEK-NH₂.

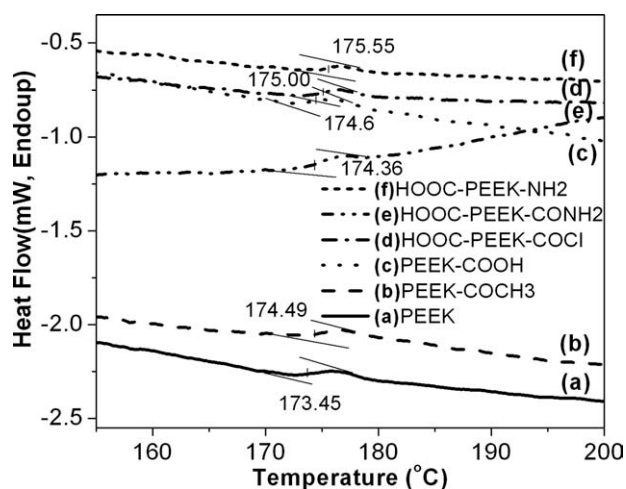


Figure 6 Differential scanning calorimetric plots for measurement of glass transition temperature ($^{\circ}\text{C}$) of (a) PEEK ($T_g = 173.5$), (b) PEEK- COCH_3 ($T_g = 174.5$), (c) PEEK- COOH ($T_g = 174.6$), (d) HOOC-PEEK-COCl ($T_g = 175$), (e) HOOC-PEEK-CONH $_2$ ($T_g = 174.4$), and (f) HOOC-PEEK-NH $_2$ ($T_g = 175.6$) polymers.

peaks, that is, (110), (111), (200), and (211) of virgin PEEK powder are also remained in the functionalized PEEK.^{32,33} Therefore, this XRD result shows that the backbone of functionalized PEEK polymers is not broken or disturbed at all even in the final product, that is, HOOC-PEEK-NH $_2$. This also supports the results obtained from the FTIR analysis. The highest crystallinity is observed in PEEK-COCH $_3$ followed by HOOC-PEEK-COCl.

Differential scanning calorimetry

The virgin PEEK and the functionalized PEEK specimens were further investigated by DSC. The glass transition temperature (T_g) was calculated from DSC thermo scan and is shown in Figure 6. The T_g of virgin PEEK is $\sim 173.5^{\circ}\text{C}$, whereas for all other functionalized PEEK, it is higher than that of virgin PEEK. The T_g of PEEK-COCH $_3$ is 174.5°C . This is due to the polar pendant group ($-\text{COCH}_3$), which is introduced in the backbone of PEEK. A similar result is also observed in PEEK-COOH with a T_g of 174.6°C . The polar groups, $-\text{COOH}$ may form hydrogen bond between the chains and enhance the restriction of chain mobility, which helps to increase the T_g . However, a higher T_g value (175°C) of HOOC-PEEK-COCl is seen again due to the presence of $-\text{COCl}$ group, which is highly polar and at the same time it is bulky, compared to the $-\text{COCH}_3$ and $-\text{COOH}$. Then HOOC-PEEK-CONH $_2$ shows a T_g of 174.4°C . However, the T_g value is again increased to 175.6°C in HOOC-PEEK-NH $_2$. This high T_g value is due to presence of highly polar carboxylic acid ($-\text{COOH}$) and amine ($-\text{NH}_2$) groups. Therefore, the DSC results strongly support the

functionalization of PEEK, which was previously supported by FTIR and NMR analysis.

The crystallinity (X_c) was calculated from DSC thermo scan using the following Eq. (2)³⁴:

$$X_c = (\Delta H_f / \Delta H_f^{\circ}) \times 100\% \quad (2)$$

where, ΔH_f° is heat of fusion for the 100% crystalline PEEK. It is 130 J/g .³⁴ The ΔH_f (in J/g) is calculated from the Pyris Diamond software. These are 41.77 , 44.36 , 41.96 , 51.48 , 44.28 , and 47.54 J/g for PEEK, PEEK-COCH $_3$, PEEK-COOH, HOOC-PEEK-COCl, HOOC-PEEK-CONH $_2$, and HOOC-PEEK-NH $_2$, respectively. The heat flow curve is shown in Figure 7. The values of crystallinity are 32.1 , 34.1 , 32.3 , 39.6 , 34.1 , and 36.6% for PEEK, PEEK-COCH $_3$, PEEK-COOH, HOOC-PEEK-COCl, HOOC-PEEK-CONH $_2$, and HOOC-PEEK-NH $_2$ polymers, respectively. The heat flow curve is shown in Figure 7. The values of crystallinity are 32.1 , 34.1 , 32.3 , 39.6 , 34.1 , and 36.6% for PEEK, PEEK-COCH $_3$, PEEK-COOH, HOOC-PEEK-COCl, HOOC-PEEK-CONH $_2$, and HOOC-PEEK-NH $_2$ polymers, respectively. The authors would like to point out that the value of ΔH_f° [used for calculation of crystallinity using Eq. (2)] should be 100% crystalline of PEEK-COCH $_3$, PEEK-COOH, HOOC-PEEK-COCl, HOOC-PEEK-CONH $_2$, and HOOC-PEEK-NH $_2$, not for 100% crystalline PEEK. As the data was not available in the literature, the value of PEEK was used here for the comparison purpose. The higher crystallinity in all these functionalized polymers is also supported by the peak height in DSC graph (Fig. 7). However, the melting temperature of all the functionalized materials is shifted to the low temperature compared with the virgin PEEK. The values are 341.7 , 335.7 , 335.5 ,

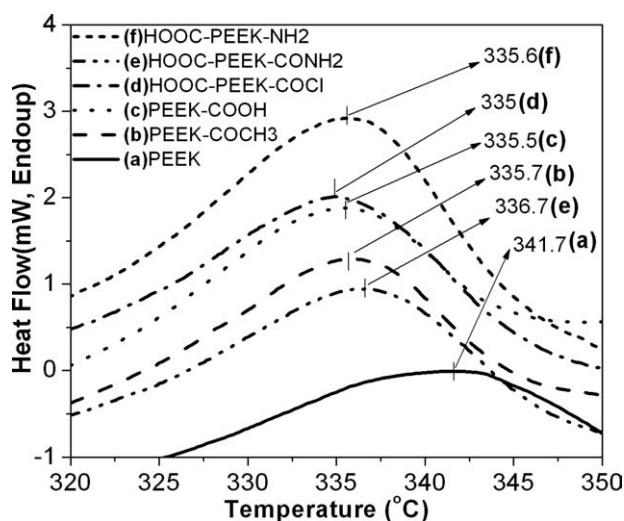


Figure 7 Differential scanning calorimetric plots for measurement of melting temperature ($^{\circ}\text{C}$) of (a) PEEK ($T_m = 341.7$), (b) PEEK-COCH $_3$ ($T_m = 335.7$), (c) PEEK-COOH ($T_m = 335.5$), (d) HOOC-PEEK-COCl ($T_m = 335$), (e) HOOC-PEEK-CONH $_2$ ($T_m = 336.7$), and (f) HOOC-PEEK-NH $_2$ ($T_m = 335.6$) polymers.

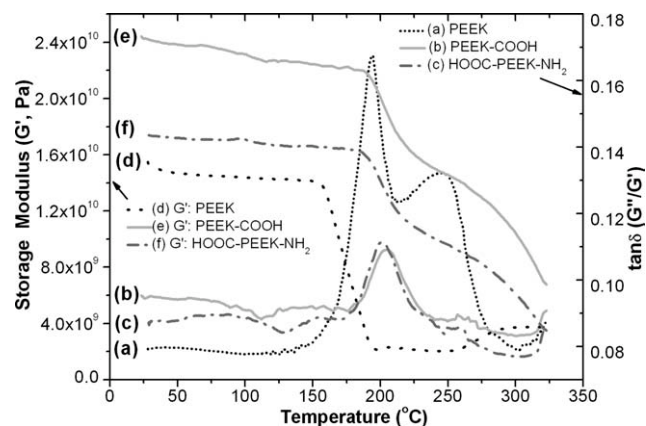


Figure 8 $\tan \delta$ characteristic of (a) PEEK ($\tan \delta = 0.167$ at $T_g = 194.6^\circ\text{C}$), (b) PEEK-COOH ($\tan \delta = 0.109$ at $T_g = 205.7^\circ\text{C}$), and (c) HOOC-PEEK-NH₂ ($\tan \delta = 0.111$ at $T_g = 201.5^\circ\text{C}$); and Storage shear modulus (G') characteristic of (d) PEEK ($G'_{\text{max}} = 1.5 \times 10^{10}$ Pa, at 35°C), (e) PEEK-COOH ($G'_{\text{max}} = 2.4 \times 10^{10}$ Pa, at 35°C), and (f) HOOC-PEEK-NH₂ ($G'_{\text{max}} = 1.7 \times 10^{10}$ Pa, at 35°C).

335, 336.7, and 335.6°C for PEEK, PEEK-COCH₃, PEEK-COOH, HOOC-PEEK-COCl, HOOC-PEEK-CONH₂, and HOOC-PEEK-NH₂, respectively. This study also indicates that the T_g of functionalized PEEK is increased with degree of crystallinity. At the same time, it suppresses the melting temperature (T_m). This fact can be advantageously used in near future for the production of net-shaped articles,³⁵ which have improved thermomechanical property and disused in the next section.

Dynamic mechanical analysis

The T_g is also determined from $\tan \delta$ in DMA to support the results obtained from DSC. A similar trend is also observed here. A T_g of 194.6°C is found for virgin PEEK, whereas 205.7°C is for PEEK-COOH as shown in Figure 8. The most interesting observation, that is, a small peak ($\tan \delta = 0.089$) around 155°C , is observed before the main $\tan \delta$ peak ($T_g = 201.5^\circ\text{C}$, $\tan \delta = 0.111$) in HOOC-PEEK-

NH₂ (Fig. 8). This small peak may be attributed to the β -transition. The presence of β -transition in functionalized polymer is due to the interchains crosslinking through amine ($-\text{NH}_2$) group, which is present in HOOC-PEEK-NH₂.³⁶ The $\tan \delta$ peak (the ratio of loss modulus to storage modulus) is found to be highest ($\tan \delta = 0.167$ at $T_g = 194.6^\circ\text{C}$) for virgin PEEK and lowest ($\tan \delta = 0.109$ at $T_g = 205.7^\circ\text{C}$) in PEEK-COOH materials as shown in Figure 8. The T_g value measured by DMA is different from DSC value due to the different principles used during analysis. The magnitude of this difference in T_g value also depends on the several factors like, machine conditions, heating rate, frequency, and so forth. However, the DMA result also shows higher values of storage modulus (G') for PEEK-COOH and HOOC-PEEK-NH₂ than that of virgin PEEK. Also, the G' value of PEEK-COOH is found higher than that of HOOC-PEEK-NH₂. The polar group present in the functionalized polymers increases the T_g value, which in turn increases the mechanical property (i.e., G'), that is, storage modulus. Since the HOOC-PEEK-NH₂ material contains more polar groups than PEEK-COOH, the modulus should be higher in HOOC-PEEK-NH₂ material. However, in practice, the modulus value is reduced in case of HOOC-PEEK-NH₂ material. This is probably due to the atactic or syndiotactic stereographic position of pendant groups ($-\text{COOH}$ and $-\text{NH}_2$), which ultimately reduces the crystallinity as observed in XRD. Therefore, both DSC and DMA results strongly support the functionalization of PEEK observed from FTIR and NMR analyses.^{37,38}

Acellular *in vitro*

The acellular *in vitro* test data is illustrated in Table IV. The dry weight (%), which is nothing but net weight change, increases with the immersion time as extended from 7 to 30 days for each specimen. For all the specimens, it is observed that the net weight change is more for all the functionalized

TABLE IV
A Acellular *In-Vitro* Study of Sintered PEEK, PEEK-COOH, and HOOC-PEEK-NH₂ polymers using SBF solution for 7, 15, and 30 days

Sample	Initial dry weight (gm)	Wet weight (gm)	Change in wet weight (wt %)	Dry weight (gm)	Change in dry weight (wt %)	Day
PEEK	0.132	0.142	+7.6	0.136	+3.0	7
		0.151	+14.4	0.139	+5.3	15
		0.192	+45.5	0.147	+11.4	30
PEEK-COOH	0.114	0.123	+7.9	0.118	+3.5	7
		0.132	+15.8	0.121	+6.1	15
		0.167	+46.5	0.129	+13.2	30
HOOC-PEEK-NH ₂	0.086	0.093	+8.2	0.089	+3.5	7
		0.100	+16.3	0.092	+7.0	15
		0.126	+46.5	0.098	+14.0	30

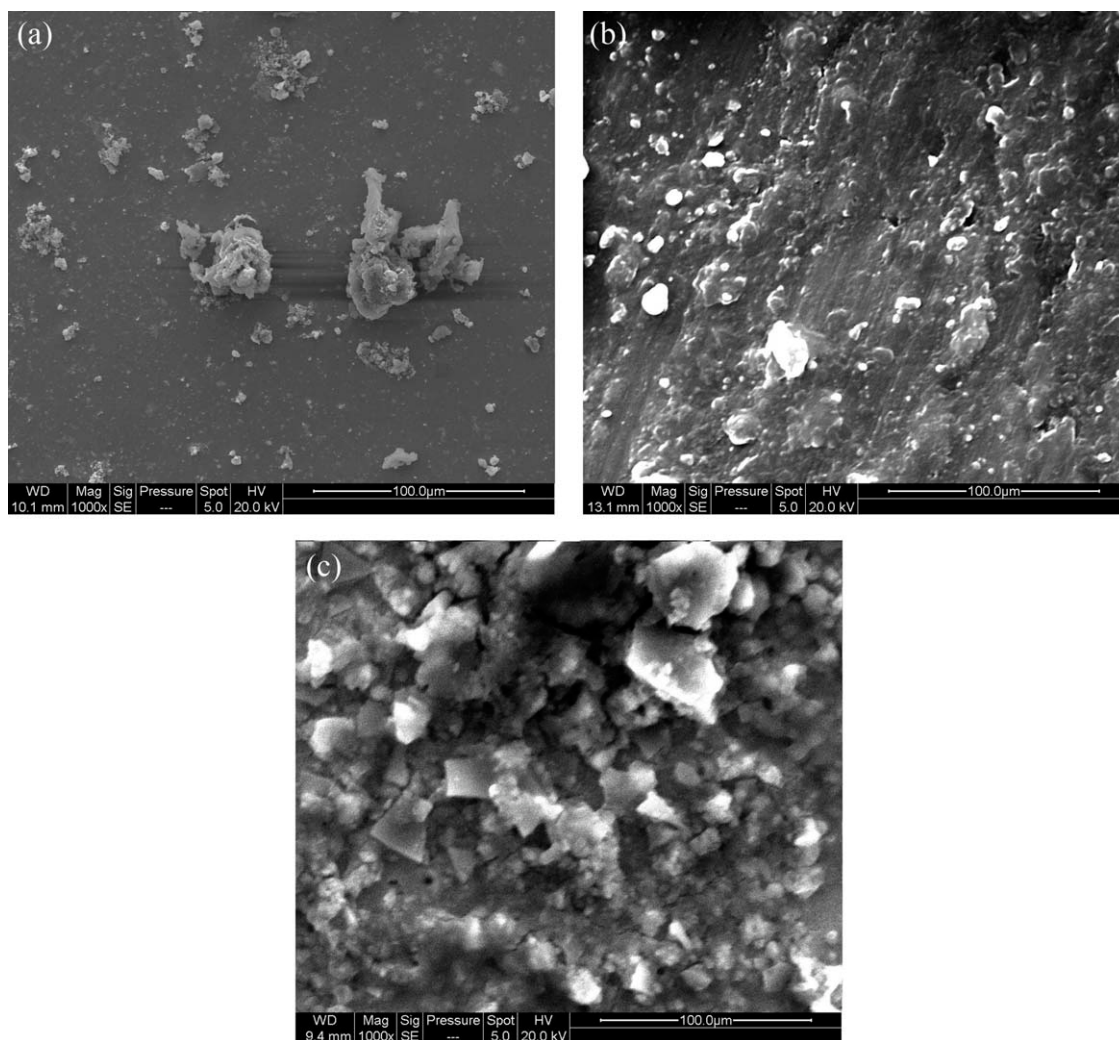


Figure 9 (a) Scanning electron microscopy of SBF crystals grown on PEEK. (b) Scanning electron microscopy of SBF crystals grown on PEEK-COOH. (c) Scanning electron microscopy of SBF crystals grown on HOOC-PEEK-NH₂.

polymers compared with the virgin PEEK. This is because of tiny SBF crystals, which is grown on the polymer surfaces. Figure 9 shows the SEM micrographs of SBF crystal, which is grown on PEEK

[Fig. 9(a)], PEEK-COOH [Fig. 9(b)], and HOOC-PEEK-NH₂ [Fig. 9(c)] respectively, (growth time was 30 days). The surface treatment of PEEK, that is, functionalization of PEEK enhances the formation of

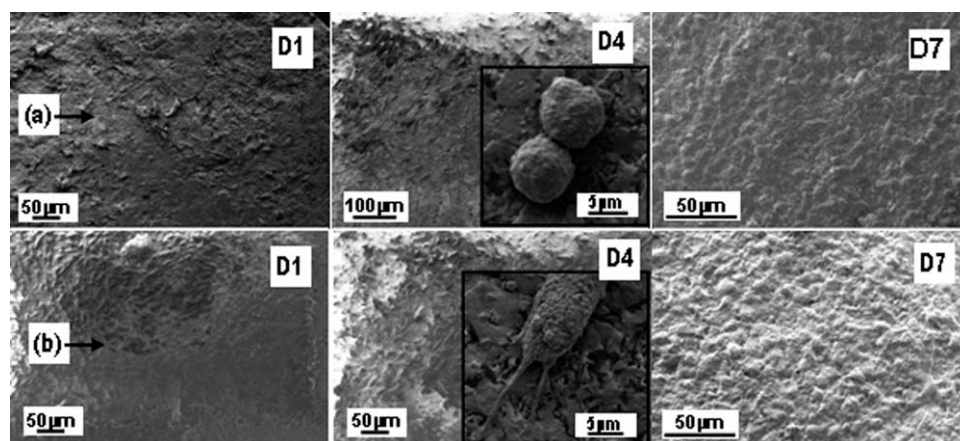


Figure 10 SEM micrographs of cell cultured (a) PEEK and (b) HOOC-PEEK-NH₂, sintered polymers after Day 1, 4, and 7.

the SBF crystals. This supports the higher adhesivity in terms of bioactivity for functionalized PEEK polymers than that of virgin PEEK polymer. Although the difference in weight is not so evident, but it is worth to mention that biocompatibility does not deteriorate with surface modification of PEEK. In addition to this, the SBF crystals grow uniformly throughout the surface as in the case of functionalized polymer. This is not seen in the case of virgin PEEK [Fig. 9(a)]. As these functionalized polymers have shown good surface adhesivity with SBF crystals, the host tissues in the leaving body can be easily grown onto the implant made of these functionalized PEEK having high surface adhesivity. These functionalized polymers can be an excellent candidate for implant materials. The cell adhesivity with material's surface reveals in SEM micrographs after 1, 4, and 7 days of cell culture assay test using L929 fibroblast cells. The cells are observed to grow and strongly attached onto the surfaces of HOOC-PEEK-NH₂ polymer compare to virgin PEEK and shown in Figure 10. However, the trend is observed to become highest value at day 4 and after that it again decreases at day 7 due to the excessive cell division has taken place after day-4. The higher surface adhesivity of the final functional polymer, which contains amine and carboxylic acid groups, can also be used in biomembrane applications. These amine and carboxylic acid groups have active surface that will lock amino acid biomolecules like, glutamate, aspartate, etc.³⁹ In case of polymer electrolyte membrane fuel cell application, the hydrophilic detrimental effect of this functional polymer as membrane can be improved by making of composites/hybrids with inorganic or organic compounds as seen in a recent report.⁴⁰ The amine group of this functional PEEK can also be grafted with conventional membrane materials (sulfonated PEEKs) to improve the mechanical properties.

CONCLUSIONS

Functionalization of PEEK polymer by addition of pendant functional groups, that is, acetyl, carboxylic, acyl chloride, amide, and amine in the benzene ring of backbone chain without substituting the parent (ether or ketonic) functional groups of PEEK is successfully carried out. Each group of the virgin and functional PEEK polymers has been identified by FTIR analysis, which is again strongly supported by NMR study. Improvement in crystallinity, T_g , dynamic mechanical property and surface adhesivity of the functionalized polymers are observed, which are supported by XRD, DSC, DMA, and acellular *in vitro* tests.

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