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Preparation of high performance composites based on aluminum nitride/poly(ether–ether–ketone) and their properties

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Abstract

Novel high performance aluminum nitride (AlN)/poly(ether–ether–ketone) (PEEK) composites containing 0–50 wt.% fractions of AlN were prepared by solution blending method followed by hot pressing to evaluate their density, melting temperature, crystallization, thermal stability, morphological behavior and Vickers hardness by using different characterization techniques. Differential scanning calorimetry results indicated that the AlN particles are very effective nucleating agent, which results in increase in melting point, hot crystallization temperature and crystallinity of composites as the AlN content increases. Thermogravimetric analysis showed enhanced thermal stability of the composites with respect to PEEK. Density and X-ray diffraction techniques showed that crystallinity of the composites increases as the wt.% of AlN content increases in polymer matrix. Scanning electron microscopy revealed that AlN particles were well dispersed with no porosity in composites. Vickers hardness of the samples increased from 24 kg/mm^2 for the pure PEEK to 35 kg/mm^2 for AlN/PEEK composites.

Keywords: High performance composites; PEEK; Hardness; Density; Crystallization

1. Introduction

In recent years, high performance thermoplastic polymer matrix composites (PMCs) have attracted the attention of researchers towards the thermally conducting but electrically insulating materials in electronics applications, which has led to their use as substitutes for thermosetting matrix. PMCs reinforced with ceramic particles known as particulate composites results in attractive combination of properties, such as high thermal conductivity, low CTE, good thermal stability and low dielectric constant.

The mechanical and physical properties of particulate composites are influenced strongly by many parameters such as particle shape [1], particle size [2], particle distribution [1–3], loading of filler concentration, type of matrix [4], microstructure and interfacial interaction between particle and matrix [5]. The addition of

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inorganic filler or particle has been a common practice in PMCs to improve the properties such as heat distortion temperature, hardness, toughness and mould shrinkage. Among inorganic fillers, calcium carbonate has been one of the most commonly used fillers for thermoplastics, such as HDPE [5], and polypropylene (PP) [6] to reduce the cost of the expensive resins. In order to keep pace with the modern technological innovations for operating under stringent condition of temperature and hazardous environments, specialty polymers PEEK, polyimides, PTFE, LCPs, PPS, PES etc., with good thermal stability and mechanical properties are required for the applications where performance is more important than cost.

In the past, thermoplastics have not been widely used as matrix materials for high performance applications because of poor solvent resistance and failure to maintain adequate strength and stiffness at elevated temperatures. In addition, component parts made out of composite materials are subjected to mechanical stress and to attacks from environment factors such as temperature, radiation, and moisture. However, two decade ago commercially developed poly(oxy-1,4-phenyleneoxy-1,4 phenylenecarbonyl-1,4-phenylene) more commonly known as poly(ether–ether–ketone) [herein after referred to as PEEK] could overcome these problem due to good resistance to moisture, chemical and hard radiation [7,8] and exceptional high temperature thermal stability [9,10]. It possesses high melting point (T_m = 335 °C), high glass transition temperature (T_g = 143 °C) and high continuous service temperature (250 °C) as a result the material is used in high temperature engineering applications [11–13] such as in high temperature wiring. PEEK coated wire offers lifetime many years at 200 °C [8]. It shows higher Young's modulus at temperatures above 220 °C then PES, which loses it as its T_g is approached but PEEK retained some rigidity until the temperature is reached in the region of 300 °C [12].

PEEK composites have been reported to have higher mechanical properties at elevated temperature, outstanding resistance to creep, de-lamination, moisture and organic solvents [12–15] as *compared* to the CF/epoxy composites. Susceptibility of the CF/epoxy to impact damage in multiple de-lamination through thickness is the limiting factor in structures [16]. PEEK exhibits moisture absorption less than 0.5 wt.% at ambient temperature [17] as compared to 4–5% for conventional aerospace epoxies. In plastic packages, moisture diffusion above a threshold limit through epoxy is the cause of (i) corrosion of metals in electronic packaging (ii) and increase of dielectric constant of epoxy materials [18]. The absorbed moisture decreases the polymer glass transition temperature and increases interface failure of continuous carbon fiber reinforced epoxy composites whereas CF/PEEK were not affected by moisture due to low moisture uptake of the PEEK matrix [7]. As a results PEEK may replace epoxies in many aerospace composites because of its excellent mechanical, electrical, thermal stability [19] and moisture resistant properties [11].

Wang et al. have studied the wear properties of PEEK with various weight fraction of SiC [20], SiO_2 [21], Si_3N_4 [22] and ZrO_2 [23]. They found that addition of less than 10 wt.% nanoparticles improved the wear resistance and reduced the friction coefficient. Hanchi et al. investigated the effect of operating temperature on the dry sliding friction and wear performance of a short carbon fiber reinforced (SCFR) PEEK composite. They reported that SCFR-PEEK exhibited coefficient of friction two to three order of magnitude lower than neat PEEK above T_g [24]. Kurokawa et al. [25] reported superior load capability of gear made of CF/PEEK under a high temperature condition as compared to polyamide composite gear or polyphenylene sulphide (PPS) gear. However, melting, crystallization and thermooxidative stability behavior was not discussed in their studies. Stuart et al. [26] have studied the scratch hardness of amorphous, semicrystalline and organic solvent induced PEEK. Sandler et al. [27] have studied the thermal and mechanical properties of carbon nanofibers reinforced poly(ether–ether–ketone) nanocomposites.

Earlier work on AlN/polymer matrix composites was limited to the use of epoxy [1,15] and polyimide [28,29] as high temperature thermosetting polymer matrix and polyvinyledene fluoride [1] and polystyrene [30,31] as low temperature thermoplastic polymer matrix for electronic packaging applications. AlN particulates are widely used as ceramic particulate for polymer matrices on account of its high thermal conductivity (200–320 W/m K), low CTE (4×10^{-6}/°C), low dielectric constant (8.7) and excellent mechanical properties [28,29].

As far as our knowledge goes, no report has been published on the behavior of high temperature thermoplastic polymer composites specially PEEK as matrix and AlN as reinforcement. With this perspective in mind, in the present work, a systematic investigation has been made on effect of AlN particles on the density, melting, crystallization, thermooxidative stability, and hardness of the various compositions of AlN/PEEK composite prepared by solution blending method followed by hot pressing.

2. Experimental

2.1. Materials

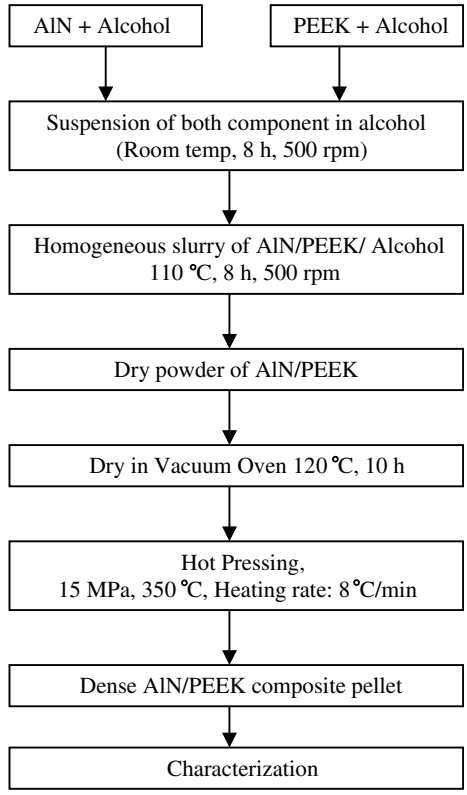
The commercial poly(ether–ether–ketone), grade 5300PF donated by Gharda Chemicals Ltd. Panoli, Gujarat, India under the trade name GATONE™ PEEK was used as matrix. It has a reported inherent viscosity of 0.87 dl/g measured at a concentration of 0.5 g/dl in

H_2SO_4. The particulate used in the preparation of composites was AlN powder with particle size < 10 μm and density 3.26 g/cm^3. It was used as supplied by Aldrich Chemical Company. Fig. 1a and b are typical scanning electron microscope (SEM) micrographs of AlN and PEEK powder. As received ethanol of Merck grade was used for homogenizing the AlN and PEEK mixture. Particle size distribution for the PEEK and AlN were determined on a GALAI CIS-1 laser particle size analyzer. The particle size of PEEK powder ranges from 4 to 49 μm and of AlN from 1.5 to 9.6 μm. The mean diameter of the PEEK particle was 25 μm and of the AlN was 4.77 μm.

2.2. Sample preparation

The procedure for preparation of pure PEEK and AlN/PEEK composite pellets is shown in a flowchart illustrated in Scheme 1. Both AlN and PEEK powders were dried overnight at 150 °C prior to hot pressing. The filler was premixed with ethanol for 10 h to improve its dispersion capacity. This premix was added very slowly into PEEK suspension with concurrent stirring. The suspension was stirred continuously with the help of a digital magnetic stirrer [Model: Heidolph MR 3001 K] in alcohol for 8 h at 500 rpm, which results in homogeneous slurry of AlN/PEEK. Then the slurry was further stirred with simultaneous heating at 110 °C for 8 h to evaporate alcohol and moisture (if present). The resultant powder was further dried in oven at 120 °C for 10 h and then hot pressed.

A laboratory hot press was used to fabricate the circular disk in a cylindrical chamber made of tool steel. The dried mixed powder of controlled PEEK and AlN/PEEK were filled in three pieces die. A mould release agent was used to prevent the PEEK melt from sticking to the die surface. The die was heated at an average heating rate of 8 °C/min to a maximum temperature of 350 °C. The pressure of 15 MPa was kept constant at 350 °C for 10 min and then, naturally cooled to below glass transition temperature of PEEK in a mould at an average cooling rate of 3 °C/min. Finally, the pellets were ejected out from the mold cavity. The



Scheme 1. Flowchart for preparation of novel high performance AlN/PEEK composite.

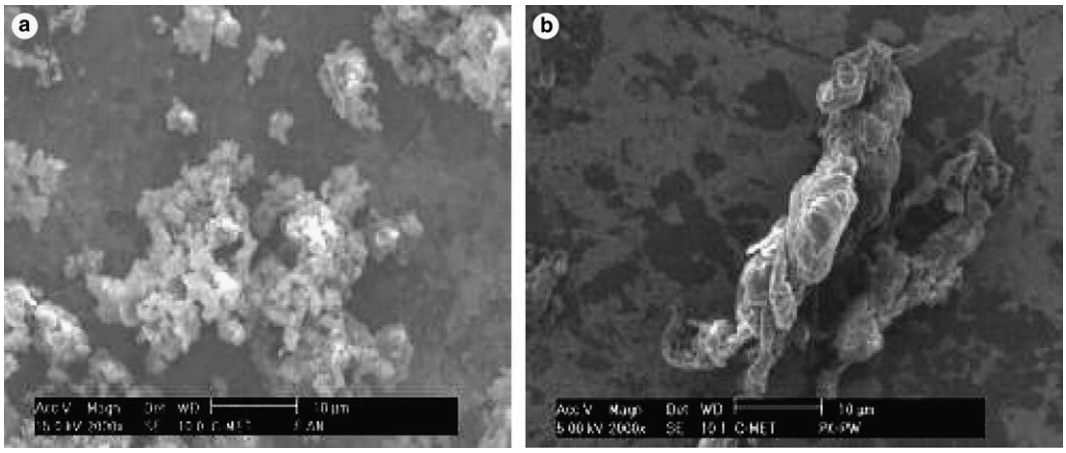


Fig. 1. SEM micrographs of (a) aluminum nitride (b) PEEK powder.

Table 1
Actual weight fraction of AlN, degradation temperature of composites at 10 wt.%, 30 wt.% and 50 wt.% loss, and char yield determined by TGA

Sample code	Wt.% of AlN in PEEK		Theoretical vol.%	Degradation temperature (°C)			Char yield % at 900 °C
	Theoretical	Actual		T_{10}	T_{30}	T_{50}	
PKAN-0	0	0	0	570	595	640	48
PKAN-5	5	5.2	2.05	575	610	655	52.40
PKAN-10	10	9	4.24	575	620	665	51.3
PKAN-20	20	21	9.06	580	630	655	58.40
PKAN-30	30	31	14.60	580	635	665	65.30
PKAN-50	50	48	28.50	580	637	670	73.75

size of molded disks was about 25 mm in diameter and 2 ± 0.2 mm in thickness. These pellets were finished by abrading with emery papers and cleaned with acetone and dried. Six different compositions containing 0–50 wt.% AlN in PEEK matrix were prepared. Samples were coded by PK–AN–X, where PK, AN and X denotes PEEK, AlN and wt.% of AlN, respectively. Small pieces of composites were cut from the compression molded disks and then used for thermogravimetric analyzer (TGA) and DSC analysis. The actual filler incorporated in the composite samples after processing was determined by TGA (shown in Table 1) in air atmosphere.

3. Characterization

3.1. Density

Theoretical density of the samples was calculated by rule of mixture (ROM) using the density of AlN 3.26 g/cm^3 and of PEEK 1.29 g/cm^3 for 20% crystalline powder. Experimental density of the filled PEEK samples prepared by hot pressing was measured by Archimedes' principles, where the volume is measured by the buoyancy in a immersing medium with known density. The weight and volume is measured in air and immersing medium, i.e. absolute alcohol respectively at room temperature.

3.2. Thermogravimetric analysis (TGA)

Actual filler content and thermooxidative stability of the pure PEEK and AlN/PEEK composites were performed on a TGA using Mettler-Toledo 851. Approximately 8–10 mg sample was taken in Alumina pan. The samples were heated from room temperature to 1000 °C at the heating rate of 10 °C/min in air atmosphere with flow rate of 50 ml/min. Wt.% of char yield was determined by heating samples in a nitrogen atmosphere at a heating rate of 10 °C/min.

3.3. Differential scanning calorimetry (DSC)

Heat of fusion and hot crystallization temperature of PEEK and AlN/PEEK composites were determined by using a Du Pont Instruments 910 DSC. A nitrogen flow rate of 50 ml/min was used. Approximately 20–25 mg samples placed in aluminum pan were first heated from 30 °C to 400 °C at a heating rate of 10 °C/min and soaked isothermally at 400 °C for 1 min to allow complete melting of the polymer. The samples were then cooled to 30 °C at a cooling rate of 10 °C/min. Each sample was subjected to single heating and cooling cycles under a dry nitrogen purge, and data were recorded during the heating and cooling cycle.

3.4. X-ray diffraction measurements

XRD pattern of as molded pure PEEK and AlN/PEEK composite was recorded on Philips X'Pert PANalytical PW 3040/60 to qualitatively investigate the development of crystallinity. XRD data were obtained by using CuK radiation of wavelength 1.54 Å at 40 kV and 30 mA. All the experiments were carried out with 2θ varying between 15° and 35° at room temperature.

3.5. Microstructure analysis

Morphology of pure PEEK and AlN/PEEK composite samples was studied using SEM (Philips XL-30) with an accelerating voltage of 10–20 kV. The distribution and the particle size of the filler particle in PEEK matrix were also investigated. Before observation, they were cleaned with acetone, dried and coated with gold by using a gold sputter coater [Polaron SC 7610].

3.6. Microhardness testing

Resistance to plastic flow for pure PEEK and AlN/PEEK samples were measured using microhardness tester (Model: DVK-2S, Matsuzawa Seiki Co. Ltd. Tokyo) with a Vickers diamond pyramidal indenter having a

square base and pyramidal angle of 136°. A constant load of 300 g (2.94 N) was applied for a dwell time of 15 s on all polished samples. Average values of three readings were reported as the Vickers hardness of the samples.

4. Results and discussion

Various compositions of novel high performance PEEK composites prepared by hot pressing are characterized and discussed in details in this section.

4.1. Density

From Fig. 2 it can be seen that the experimental density of composites is higher as compared to theoretical density. This higher density might be an indication of the increased crystallinity as a result of the AlN addition. However, the experimental density of the composite reinforced with 50 wt.% AlN is lesser than theoretical density, which suggests that at higher filler content there is some void formation. This is well known that the infiltration of melt polymer resin become more difficult with increasing filler loading.

4.2. Thermogravimetric analysis (TGA)

TGA measurement was carried out to obtain actual incorporated filler and thermooxidative stability of the pure PEEK and AlN/PEEK composites. The temperature at 10 wt.% loss (T_{10}) was taken as the onset of the degradation process and the temperature at 30 wt.% loss (T_{30}) and 50 wt.% loss (T_{50}) for polymer and composites are tabulated in Table 1.

The percentage of original weight remaining and the derivative curve are shown as a function of the temperature in Figs. 3 and 4 respectively. When major weight loss begins, there is a sharp increase in the derivative, which then reaches a maximum rate of weight loss. After the maximum, the derivative curves tend to level off somewhat. The pure PEEK shows an onset of thermal degradation at 570 °C, which corresponds to the decomposition of PEEK. It is fully decomposed before 700 °C. It is observed that as the percentage of AlN increases in PEEK the thermal stability of composite increases. The onset for the PKAN-50 composite was 580 °C. Temperature for 50% weight loss was increased from 640 to 670 °C. The temperature of maximum derivative weight loss was increased by 40–50 °C for composites. Therefore, the incorporation of aluminum nitride in polymer matrix improved the thermal stability of the composites. The increase in thermal stability could be due to strong interaction and/or interfacial bonding between the polymer matrix and the AlN particles, which hindered the segmented movement of the PEEK. Liu et al. reported similar type of trend of high thermal stability for PS/clay composites [32]. The TGA residue above 800 °C representing the weight of the AlN filler are summarized in

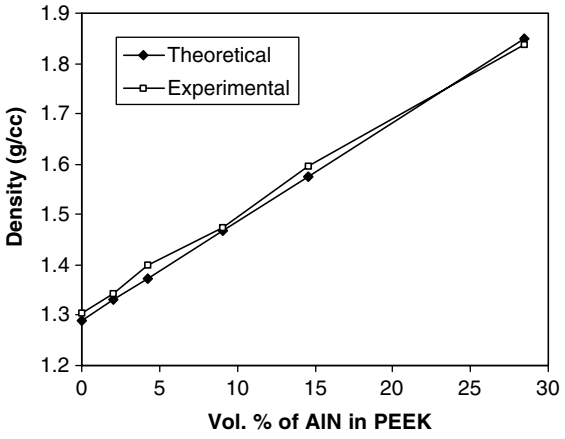


Fig. 2. Density of pure PEEK and PEEK composites.

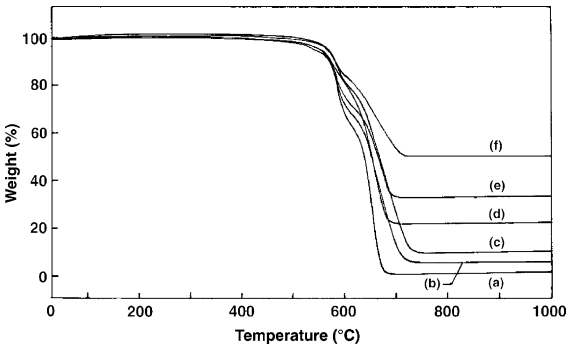


Fig. 3. TGA curves of pure PEEK and AlN/PEEK composites (a) PKAN-0, (b) PKAN-5, (c) PKAN-10, (d) PKAN-20, (e) PKAN-30, (f) PKAN-50.

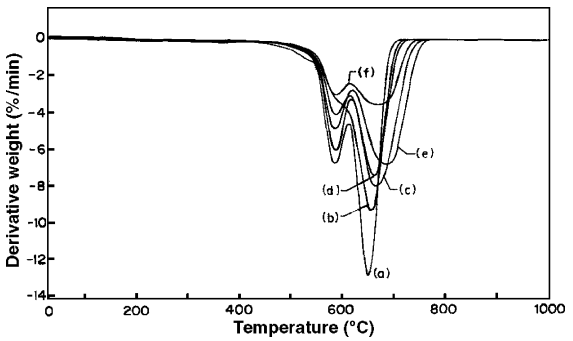


Fig. 4. DTG curves of pure PEEK and AlN/PEEK composites (a) PKAN-0, (b) PKAN-5, (c) PKAN-10, (d) PKAN-20, (e) PKAN-30, (f) PKAN-50.

Table 1, which was close to the percentage of the incorporated filler. Some difference in theoretical and actual weight of AlN determined by TGA may be due to loss of a little quantity of AlN or PEEK powder during the composite mixing process. It can be seen from Table 1 that the weight of residue in nitrogen atmosphere at 900 °C increases from 48 to 73.75 wt.% as the AlN content increases. This enhancement of the char formation is due to the good heat resistance of the AlN.

4.3. Differential scanning calorimetry (DSC)

DSC measurements were carried out to determine the heat of fusion and hot crystallization temperature of PEEK and AlN/PEEK composites. The DSC heating and cooling curves are shown in Figs. 5 and 6 for PEEK and AlN/PEEK composite respectively. From the recorded heating and cooling curves, thermal properties such as crystallization temperature (T_c), melting temperature (T_m), starting crystallization temperature (T_{on}), heat of crystallization (H_c), heat of fusion (H_f), and degree of crystallinity were calculated and tabulated in Tables 2a and 2b. Degree of crystallinity were obtained by integrating the area under the melting peak and crystallization peak during heating and cooling cycle respectively and normalized to the actual weight fraction of polymer and then divided the area by the heat of fusion of 100% crystalline PEEK (130 J/g). The crystallinity of

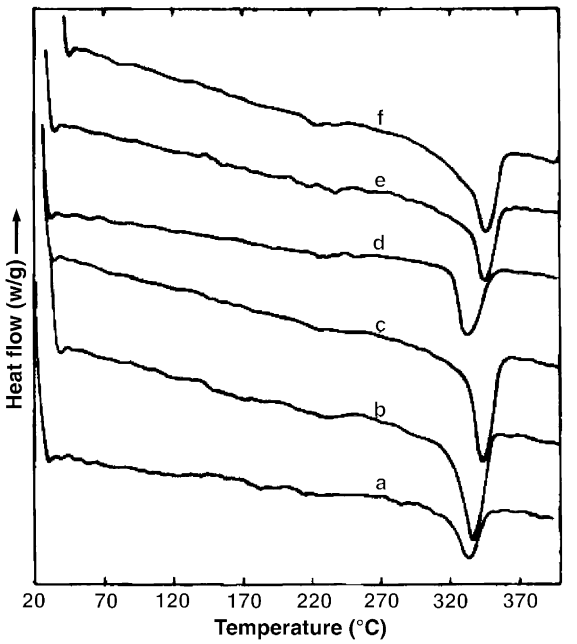


Fig. 5. DSC heating curves of pure PEEK and AlN/PEEK composites (a) PKAN-0, (b) PKAN-5, (c) PKAN-10, (d) PKAN-20, (e) PKAN-30, (f) PKAN-50.

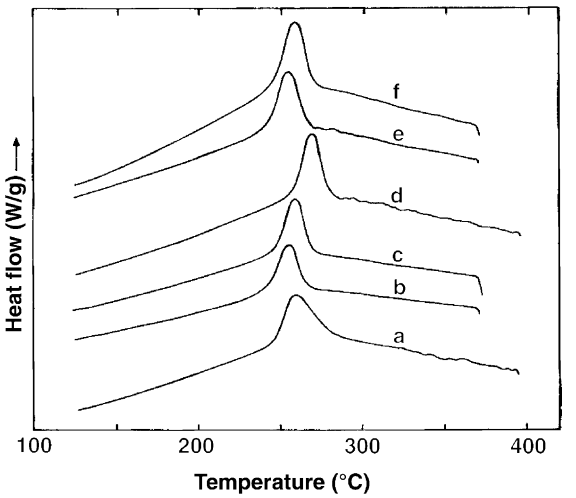


Fig. 6. DSC cooling curves of pure PEEK and AlN/PEEK composites (a) PKAN-0, (b) PKAN-5, (c) PKAN-10, (d) PKAN-20, (e) PKAN-30, (f) PKAN-50.

PEEK constituent in composite was determined by Eq. (1) [27]

$$\chi_c(\%\ \text{Crystallinity}) = \Delta H_f \times 100/(\Delta H_f^0 w) \quad (1)$$

where ΔH_f^0 is the heat of fusion for 100% crystalline PEEK; ΔH_f is the heat of fusion of PEEK; w is the mass fraction of PEEK in the composite.

It can be seen from the curves 6a–f, that addition of AlN content significantly shifts the position of hot crystallization temperature (T_c). For a given cooling rate, T_c of composite was shifted by 15 °C than pure PEEK, indicating that the addition of AlN into PEEK enhanced the rate of PEEK crystallization [33,34]. The crystallization enthalpy (ΔH_c) except PKAN-10 decreases as the AlN in composite increases but normalized crystallization enthalpy (ΔH_c^*) increases as the AlN content increases. Thus, crystallization of AlN/PEEK composites become more perfect than pure PEEK. The increase in perfection or crystallinity is due to the enhanced crystal nucleation in the region surrounding the reinforced particles [35].

It is interesting to find that the appearance of two distinct endothermic peaks corresponding to a low temperature peak ($T_{m,1}$ = 212.54 °C) and a high temperature peak ($T_{m,2}$ = 333.74 °C) for pure PEEK as shown in Fig. 5a–f and Table 2a. This double melting phenomenon of the PEEK has been well reported in the literature [36]. It is seen that the low temperature melting peak is increased by 15 °C for PKAN-30 composite. The high temperature melting point (T_m) is increased by 11 °C from 334 °C for pure PEEK to 345 °C for AlN/PEEK (50/50). Pingping et al. reported that in PET/$CaCO_3$ composites the addition of $CaCO_3$ particles does not have significant effect on melting point of composites

Table 2a
Thermal properties of composites during heating cycles

Compositions	$T_{m,1}$ (°C)	$T_{m,2}$ (°C)	ΔH_f (J/g)	ΔH_f (J/g)[a]	$\chi_{c,DSC}$
PKAN-0	212.54	333.74	26.07	26.07	20.05
PKAN-5	205.77	335.74	38.44	40.46	31.12
PKAN-10	211.14	342.48	39.92	44.36	34.12
PKAN-20	220.68	334.14	37.78	48.95	37.65
PKAN-30	227.58	343.97	24.83	35.47	27.28
PKAN-50	214.61	344.76	20.33	40.66	31.28

[a] Normalized heat of fusion of PEEK constituent in AlN/PEEK composite.

Table 2b
Thermal properties of composites during cooling cycles

Compositions	T_c (°C)	T_{on} (°C)	ΔH_c (J/g)	ΔH_c (J/g)[a]	$\chi_{c,dsc}$	$t_{1/2}$ (min)	ΔT (°C)
PKAN-0	259.65	280.11	39.76	39.76	30.58	2.05	74
PKAN-5	269.87	281.34	38.25	40.26	30.96	1.15	66
PKAN-10	274.21	285.02	43.41	48.23	37.10	1.08	68
PKAN-20	269.44	282.02	32.86	47.01	36.16	1.07	64
PKAN-30	269.07	282.01	28.69	40.99	31.53	1.29	75
PKAN-50	272.91	285.43	22.84	45.68	35.14	1.25	72

[a] Normalized heat of crystallization of PEEK constituent in AlN/PEEK composite.

[37]. However, in our case increase in melting temperature could be due to well dispersion of AlN particles and thus, good interaction between the polymer and AlN particles. The resultant interaction makes the PEEK segmental motion more perfectible crystalline, as confirmed by XRD, during the crystallization. Liu et al. [32] have reported 18 °C increase in melting temperature in PET/SiO_2 (97.5/2.5) nanocomposite.

The half time ($t_{1/2}$) of nonisothermal crystallization temperature of pure PEEK and AlN/PEEK can be determined by using the equation [$t_{1/2} = (T_{on} - T_c)$/rate of cooling]. Table 2b shows that $t_{1/2}$ value of composite decreases with the loading of AlN content compared to pure PEEK. Thus, AlN particles accelerate the crystallization process of pure PEEK. For the same rate of cooling, there is enough time for the molecular chains of PEEK to pack into a closer arrangement and because of the increase in onset temperature the mobility of the PEEK molecular chains are increased so that the molecular chains are organized in an orderly fashion. Khare et al. [38] have reported that $CaCO_3$ particles of 6 μm reduced the crystallization half time significantly.

4.4. X-ray diffraction measurements

The angular position in the range of $2\theta = 15$–$35°$ of major crystallographic reflection for the PEEK and AlN/PEEK composite sample are shown in Fig. 7. Wide angle X-ray diffraction pattern in Fig. 7 showed that pure PEEK and its composites crystallizes primarily in the orthorhombic form showing diffraction peaks corresponding to Miller indices (1 1 0), (1 1 1), (2 0 0) and (2 1 1). It can be seen that AlN shows diffraction peak above 30°. Here we have shown one diffraction peak only for AlN exhibiting at $2\theta = 33.19°$.

It can be seen from Table 3 that there is a displacement of each reflection towards a higher angular position as compared to pure PEEK with increasing AlN content. The inter-planer spacing, d_{hkl} of different crystalline planes (hkl = 1 1 0, 1 1 1, 2 0 0, 2 1 1) are the highest for the pure PEEK, but decreases as the AlN content increases in PEEK. A smaller d_{hkl} for composite may be attributed to perfection of crystals. A remarkable decrease in d_{110}, d_{111}, d_{200}, and d_{211} were observed in direction perpendicular to plane (1 1 0), (1 1 1), (2 0 0) and (2 1 1) respectively. Table 3 showed total decrease in d_{hkl} of about 0.09, 0.07, 0.04 and 0.05 Å for the (1 1 0), (1 1 1), (2 0 0) and (2 1 1) planes respectively. Because of the decrease of d-spacing, the dimensions of crystalline units decreases as the AlN content increases and thus, improve the crystallinity of bulk composite. This type of effect was reported for the pure PEEK as the annealing time or temperature of crystallization was increased [39]. The quantitative increase in crystallinity was confirmed by DSC technique.

4.5. Scanning electron microscope

The morphological and particles distribution in polymer matrix was studied using SEM. Fig. 1a and b showed micrographs of AlN and pure PEEK powder. Size of the AlN particles ranged from 1 to 10 μm. AlN particles is irregular in shape. PEEK powders are in the form of rods of length varied 10–50 μm. Fig. 8a

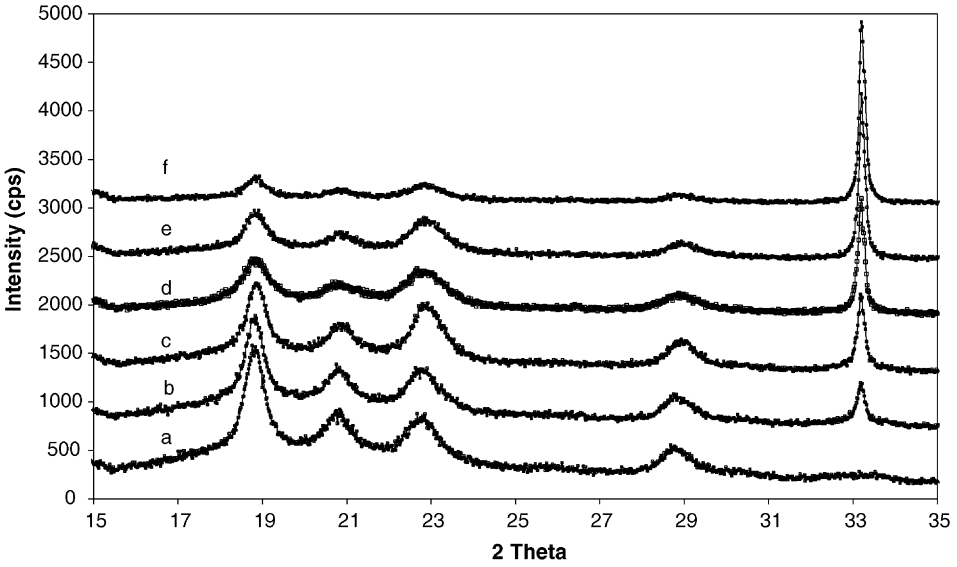


Fig. 7. WAXD pattern of pure PEEK and AlN/PEEK composites (a) PKAN-0, (b) PKAN-5, (c) PKAN-10, (d) PKAN-20, (e) PKAN-30, (f) PKAN-50. For clarity, scans for sample b, c, d, e and f have been displaced upward by 600, 1200, 1800, 2400 and 3000 counts per second (cps) respectively.

Table 3
Angular position and inter-planer distance of composites determined by WAXD

Compositions	2θ (°)				Inter-planer spacing d_{hkl} (nm)			
	$2\theta_{110}$	$2\theta_{111}$	$2\theta_{200}$	$2\theta_{211}$	d_{110}	d_{111}	d_{200}	d_{211}
PKAN-0	18.525	20.564	22.573	28.489	0.4790	0.4319	0.3939	0.3133
PKAN-5	18.789	20.782	22.916	28.744	0.4719	0.4271	0.3878	0.3103
PKAN-10	18.854	20.733	22.783	28.954	0.4703	0.4281	0.3900	0.3081
PKAN-20	18.838	20.596	22.658	28.920	0.4707	0.4309	0.3921	0.3085
PKAN-30	18.839	20.834	22.732	28.969	0.4707	0.4260	0.3909	0.3080
PKAN-50	18.827	20.885	22.736	28.859	0.4710	0.4250	0.3908	0.3091

and b showed SEM micrographs for fractured PEEK and PKAN-30 composite. Fig. 8b showed that the AlN particles are uniformly dispersed in the PEEK matrix containing 30 wt.% AlN and any aggregates of AlN particles are not seen, which is expected due to good processing condition during the sample preparation. Fig. 9a–d showed the morphology of pure PEEK, PKAN-5, PKAN-20, and PKAN-50 composite samples. Before observation, samples were polished by successive emery papers followed by etching using a 2% w/v solution of potassium permanganate in a mixture of 4 volumes of orthophosphoric acid and 1 volume of water. Samples were etched for 150 min. Some spherulites were seen in pure PEEK matrix but they were absent in composite. It was observed that samples were over etched, which result excessive pittings. The severity of pitting decreases as the AlN content increases. AlN particles were uniformly distributed without any agglomerates except PKAN-50. As the inter-particle distance between reinforced particles is decreased, they have tendency to attract each other and form aggregates.

4.6. Microhardness measurement

Hardness test, because of its simplicity and nondestructive technique, has been employed widely as a useful tool for determining the mechanical properties of materials. Samples were polished by emery paper to ensure a smooth sample surface. The average hardness of three readings was taken using average diagonal length of the residual indentation mark on the composite sample. Indentation image was displayed on the projected screen through objective lenses at magnification 100×. Vickers hardness number can be calculated by using Eq. (2).

$$H_V = 1.8544(F/d^2) \quad (2)$$

where F is load (kg) and d is the average diagonal length (mm).

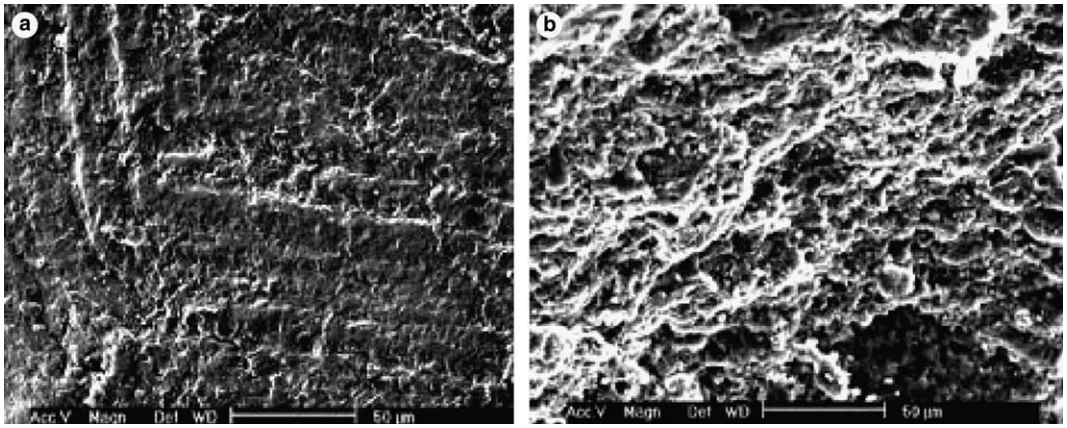


Fig. 8. SEM micrographs of compacted (a) PKAN-0, (b) PKAN-30 composite after fracture.

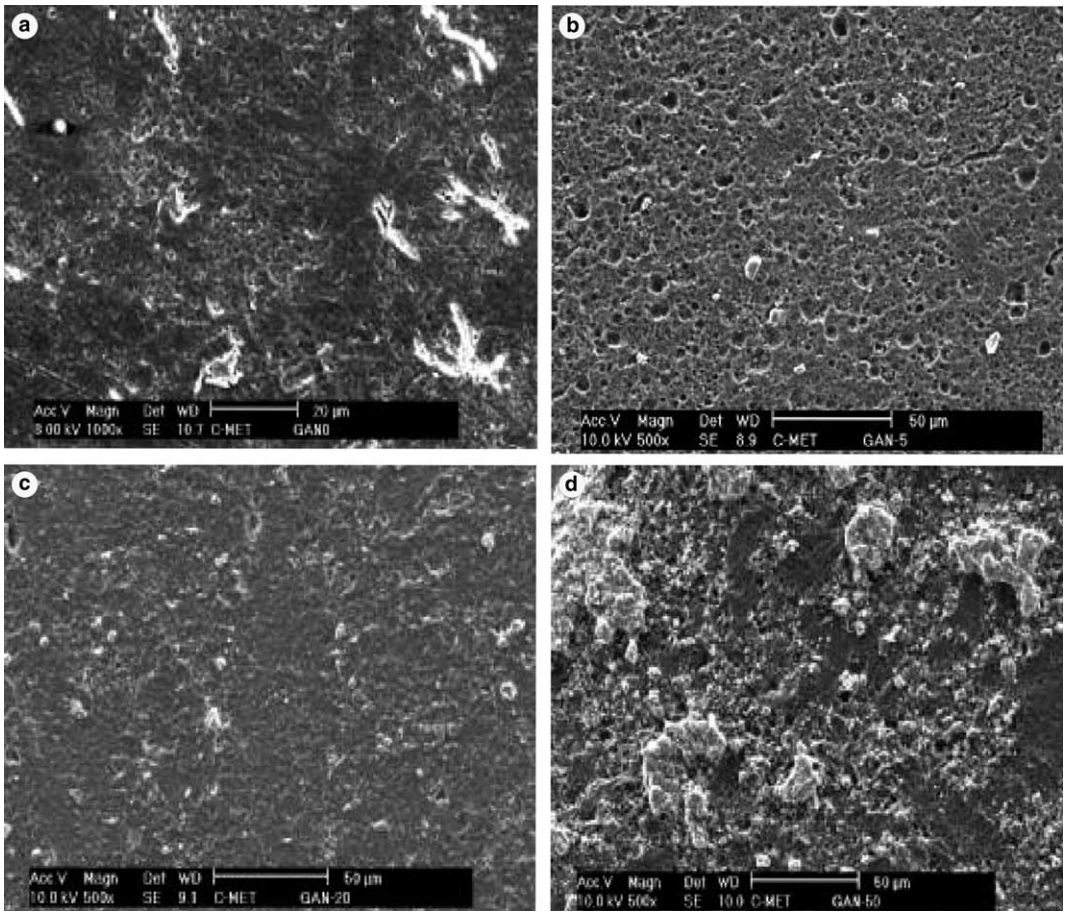


Fig. 9. SEM micrographs after etching of (a) PKAN-0, (b) PKAN-5, (c) PKAN-20, (d) PKAN-50 composites.

Fig. 10 showed the Vickers hardness of pure PEEK and composites at various wt.% of filler. Diagonal length of the impressed square is reduced as the percentage of filler is increased to 50 wt.%. It is observed that the hardness of composites nonlinearly increases from 24 for the pure PEEK to 35 for PKAN-50

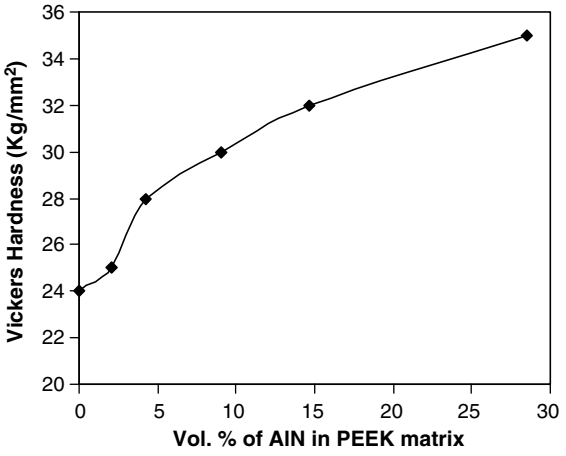


Fig. 10. Vickers hardness of pure PEEK and PEEK composites.

composite, i.e. addition of AlN showed a marked increase in hardness of around 46% at 50 wt.%. Therefore, the hardness of the composites may be increased due to (i) increase in crystallinity of the PEEK fraction in composite as confirmed by density, XRD and DSC. Stuart reported that scratch hardness of crystalline PEEK is higher than amorphous PEEK [26], (ii) resistance of the deformation by hard ceramic particles. Thus uniformly distribution of particles improved the stiffness of PEEK polymer. Presence of these stiff ceramic particles and entanglement of polymer chains made the composite harder. Chen reported similar type of trend for AlN/Polyimide nanocomposite. The Vickers hardness of a polyimide nanocomposite containing 25 vol.% AlN was approximately doubled of the pure polyimide sample [29].

5. Conclusions

We have prepared the dense new high performance PEEK matrix composites incorporating AlN up to 50 wt.% by solution blending method followed by hot pressing. Their thermal stability and char yield is increased as determined by TGA. Vickers hardness of the composites was found to increase from 24 to 35 kg/mm^2 for pure PEEK to PKAN-50 which results in increasing the load carrying capacity of composites. The degree of crystallinity, melting point, and hot crystallization temperature of the composites were also increased. We can conclude that there is good interfacial adhesion between AlN particles and polymer matrix, which results in improved properties. These futuristic composite materials are promising candidates for the materials requiring good thermal conductivity and low coefficient of thermal expansion.

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