Hybrid Fiber Fabric Composites from Poly Ether Ether Ketone and Glass Fiber

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ABSTRACT: Poly ether ether ketone (PEEK) polymer was extruded into filaments and cowoven into unidirectional hybrid fabric with glass as reinforcement fiber. The hybrid fabrics were then converted into laminates and their properties with special reference to crystallization behavior has been studied. The composite laminates have been evaluated for mechanical properties, such as tensile strength, interlaminar shear strength (ILSS), and flexural strength. The thermal behavior of the composite laminates were analyzed using differential scanning calorimeter, thermogravimetric analyzer, dynamic mechanical analyzer (DMA), and thermomechanical analyzer (TMA). The exposure of the fabricated composite laminates to high temperature (400 and 500°C) using radiant heat source resulted in an improvement in the crystallanity. The morphological behavior and PEEK resin distribution in the composite laminates were confirmed using scanning electron microscope (SEM) and nondestructive testing (NDT). Although DMA results showed a loss in modulus above glass transition temperature (T_g), a fair retention in properties was noticed up to 300°C. The ability of the composite laminates to undergo positive thermal expansion as confirmed through TMA suggests the potential application of glass–PEEK composites in aerospace sector. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1446–1459, 2010

Key words: PEEK; orientation; crystallization; crystallinity index; enthalpy; modulus

INTRODUCTION

In recent years glass–poly ether ether ketone (PEEK) based thermoplastic hybrid composites based on coweaving and commingling are increasingly being explored for specific aerospace applications due to their high strain to failure, impact tolerance, toughness, damage tolerance, chemical resistance, mechanical properties, and drapability. The excellent drapability and flexibility of hybrid yarn fabrics can be utilized to fabricate certain complex shapes, such as Radome (radar dome, which acts as an electromagnetic window).[1–6]

As its introduction by the Imperial chemical Industries (ICI) in 80s, PEEK has generated lot of interest in the aerospace industry as the leading thermoplastic matrix candidate for use in advanced composites. PEEK is a semicrystalline, aromatic, engineering thermoplastic fiber, which can be used as a thermoplastic resin for critical aerospace applications and advanced structural composites. PEEK can be obtained in amorphous or semi crystalline form, depending on the processing conditions from the molten state. Crystallinity is an important structural parameter that plays a major role in determining many ultimate properties of composite and provides a means for understanding and controlling the structure property relationships. The anisotropic behavior of the hybrid composites due to different nature of fiber characteristics greatly complicates their analysis. However, it also provides unique opportunities for designing a tailor made composite utlizing the strength of constituent fiber components to meet specific performance requirements.

There have been a number of approaches followed by researchers to achieve high performance thermoplastic composites. PEEK in reinforced form, powder, film has been extensively tried out by researchers and a significant amount of data is available related to PEEK degradation, crystallization kinetics, and short and long term mechanical properties.[7–18] Recently melt spinning of fine and ultra fine PEEK filaments have been studied keeping in view aerospace applications.[19] Although work related to

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development of carbon-PEEK composites utilizing unidirectional hybrid yarn fabrics is well documented,[20–23] comprehensive study on the development of fiber–fiber based hybrid composites using engineered resin system inter-relating process variables of spinning, weaving, and heating cycles based on commingling and coweaving is still scanty. These process variables are found to have a significant influence on the properties of composites for specific aerospace applications. Most of the PEEK yarns used as resin system in the hybrid composites reported are extruded using laboratory capillary rheometer. The earlier technique does not simulate true industrial extrusion conditions and drawing process. Scope for varying the process variables to investigate crystallinity related aspects in the earlier technique are limited.

In this article, development of an advanced composite system using modified PEEK (high crystallinity, modulus) filament yarn as resin and e-Glass as reinforcement material has been discussed inter-relating spinning, weaving, and composite preparation to meet specific requirements of high temperature thermal stability (500°C) that the end product is expected to meet for a structural component like Radome.

The characterization techniques used include melt flow Index (MFI), differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXS), dynamic mechanical analysis (DMA), thermomechanical analysis (TMA), and air-coupled ultrasonic C–scanning [Nondestructive testing (NDT)]. Mechanical properties were also measured to provide an overview of the achievable properties for high temperature application. A brief account of the crystallization behavior of PEEK subjected to isothermal heating conditions is also reported.

METHODS

Materials

PEEK granules from ICI (Victrex 151 G), DMSRDE, Kanpur and Gharda Chemicals (GATONE 5400), Mumbai were used in the study. The polymer granules were dried in a hot air oven at 120°C for 4 h before spinning. The coweaving concept was used to obtain hybrid fabrics with glass as reinforcement fiber in warp direction. Hybrid fabrics in basket and sateen weave were woven on a rapier loom (80 picks per minute speed) at Urja Products, Ahmedabad, India. However, PEEK from DMSRDE, Kanpur and Gharada chemicals was difficult to extrude due to difficulties associated with very low melt flow Index values and associated viscosity related aspects. Hence we pursued only with ICI PEEK and all the work reported on hybrid fabrics and composites has ICI PEEK (Victrex 151 G) as fiber resin. The apparent weight average molecular weight, glass transition temperature, melting point, enthalpy of fusion, and crystallinity of neat PEEK was 39,000, 143°C, 343°C, 40 j/g, and 35% respectively.

Extrusion, drawing, and weaving

A laboratory model extrusion machine (Bradford University, UK) working on cylinder-piston principle was used to obtain the continuous PEEK filaments through melt spinning technique. Melt flow index values of PEEK granules were evaluated (Table I) and used as a base to select the extrusion temperature. PEEK being high molecular weight aromatic polymer with molecular weight >40,000 has high melt viscosity and the effect of molecular weight can be seen in the MFI values, which are significantly low compared to conventional polyester or nylon. At 350°C, which is close to its melting temperature of 334°C, there was no flow and a steady but slow increase in flow properties were observed in the temperature range of 360–380°C. Between 385 and 390°C, MFI values of 36 to 42 was observed, which was found to be ideal for satisfactory and smooth extrusion of the material.

The extrusion temperature of the polymer was maintained at 370–380°C. The RAM pressure was 7500–10000 MPa and the RAM speed was 7−10 mm/min. After extrusion, the filament was passed through a thread guide followed by an intermediate winding unit and drawing unit. The obtained filaments were doubled and twisted before subjecting it for coweaving process. The doubled and twisted PEEK yarns were coweaved with e-glass fibers to obtain unidirectional hybrid fabrics. The effect of spinning process parameters, such as extrusion temperature, draw temperature, draw ratio on the performance of PEEK fiber has been investigated. The PEEK yarn having 7 gpd (grams per denier) tenacity was obtained with an extrusion temperature of 380 to 385°C, draw ratio of 3 and draw temperature of 200°C. The obtained PEEK yarn having high tenacity was used in the coweaving process as resin fiber

TABLE I
Melt Flow Index of PEEK Granules at Different Temperature (g/10 min) (Ref. 24)

Temperature (°C)	ICI Victrex 151G	GATONE 5400
350	Did not flow	Did not flow
360	20	2.95
370	23.3	4.12
375	27.6	4.45
380	30.5	6.59
385	36.25	Did not flow
390	42.0	Did not flow
400	64.20	Did not flow

along with glass fiber. The hybrid fiber (glass and PEEK) fabrics having basket and sateen weave configuration was achieved on a Rapier loom at a speed of 80 picks per minute. The Peirce's cloth geometry was adopted to get the required proportion of PEEK (35%) in the hybrid fabric.[25]

The hybrid fiber fabrics were then converted into flat composites using compression molding technique. The heating and consolidation process was optimized with respect to pressure (250 to 300 MPa), rate of heating (5°C per minute) and soaking time (30 min at 385°C). The composites prepared using 15 layers of hybrid fiber fabric having sateen wave configuration was designated as S-9. Composite with 17 layers of hybrid fiber fabric having basket weave configuration was designated as S-11. The S-11 composite was exposed to radiant heat source (20–25 kW/m^2) for short time intervals to investigate the performance of S-11 composite. The S-11 composite sample exposed at 400°C for 1, 2, and 5 min were designated as 1A, 2A, and 5A, respectively. The S-11 composite exposed to radiant heat for 1, 2, and 5 min at 500°C were denoted as 1, 2, and 5 and then scanned in thermogravimetric analyzer (TGA) and DSC.

The effect of exposure of S-9 and S-11 composites in a ceramic furnace at 500°C for 30s on the mechanical properties has been investigated. The S-9 and S-11 composites exposed to radiant heat source were used for DSC and TGA. The unexposed S-11 samples were selected for DMA and TMA characterization.

Techniques

Melt Flow Index (MFI) of PEEK granules was carried out as per ASTM D 1238 using melt flow meter. The melt flow Index was calculated at a pressure of 21 MPa at different temperatures (350 to 400°C). Wide angle X-ray diffraction technique (Philips Analytical X-ray) was used to characterize the crystallinity using nickel filtered CuKα (1.54 Å) radiation. The technique of multiple peaks fitting using Gaussian distribution method was applied on the Grazing incidence XRD curves to express the results in terms as crystallinity index (CI). The percent crystallinity was evaluated by considering the total area under the crystalline peak area. One of the three crystallographic parameters of orthorhombic crystalline structure of PEEK (a) was obtained using half maximum peak width and standard hkl values. An apparent size and volume average in a direction perpendicular to the diffracting planes was calculated using Scherrer's formula.

The surface morphology of composites was investigated using scanning electron microscope (SEM) (JEOL JSM-35CF).

Thermal characterization

Thermal stability of the composites under dynamic and isothermal conditions was measured using TA instruments (2950) at a heating rate of 10°C /min in air and nitrogen atmosphere. The TGA profiles were recorded over a temperature range of 30 to 800°C.

The crystallinity of the PEEK fiber and its composites with glass fiber were determined and analyzed using DSC (TA instruments model 2910) in the temperature range from 50 to 450°C in nitrogen atmosphere at a heating rate of 10°C/min in nitrogen atmosphere. The maxima of the glass transition and melting endothermic peaks were taken as glass transition (T_g) and melting temperature (T_m), respectively. The thermomechanical measurements of the composites were carried out on DuPont (2100) by penetration mode on specimens at a heating rate of 10°C/min in nitrogen atmosphere. The storage modulus and related properties of composites were studied by DMA. DMA of the composites were carried out using TA-2980 and GABO instruments at a heating rate of 10°C/min in nitrogen atmosphere. The selected frequency range was 0.01 to 1 Hz and modulus range was 10^3 to 3×10^{12} Pa. The temperature-frequency sweep (three point bending) in the frequency range of 0.10 to 10 Hz was also carried out using a reference temperature of 25°C.

Nondestructive testing

QMI, USA make air-coupled ultrasonic test equipment was used in the this study. Planar/focused narrow-band piezoelectric air-coupled ultrasonic transducer probes with center frequencies of 120 kHz and 400 kHz were used for the measurements. These transducers were driven by their matching electronics provided by the SONDA 007CX pulser and receiver system. The dimensions of the piezoceramic elements ranged from 3/4″ to 1″ diameter. The settings were maintained at 60 dB gain/62 dB and 40 dB gain/60.9 dB attenuation for ultra sonic frequencies of 120 and 400 kHz, respectively.

Tensile strength, ILSS, and flexural strength of the prepared composites were carried on MTS machine USA (model No. MTS 810) as per as per ASTM -D 3039, D2344, and D 790, respectively, the details of which are well reported.

RESULTS AND DISCUSSIONS

Differential scanning calorimetric analysis

The DSC thermograms of PEEK granules (Victrex 151G), undrawn yarns and drawn yarns are shown in Figure 1(a,d). The degree of crystallinity for different yarn samples were evaluated using area under the crystallization and melting peak. To calculate the

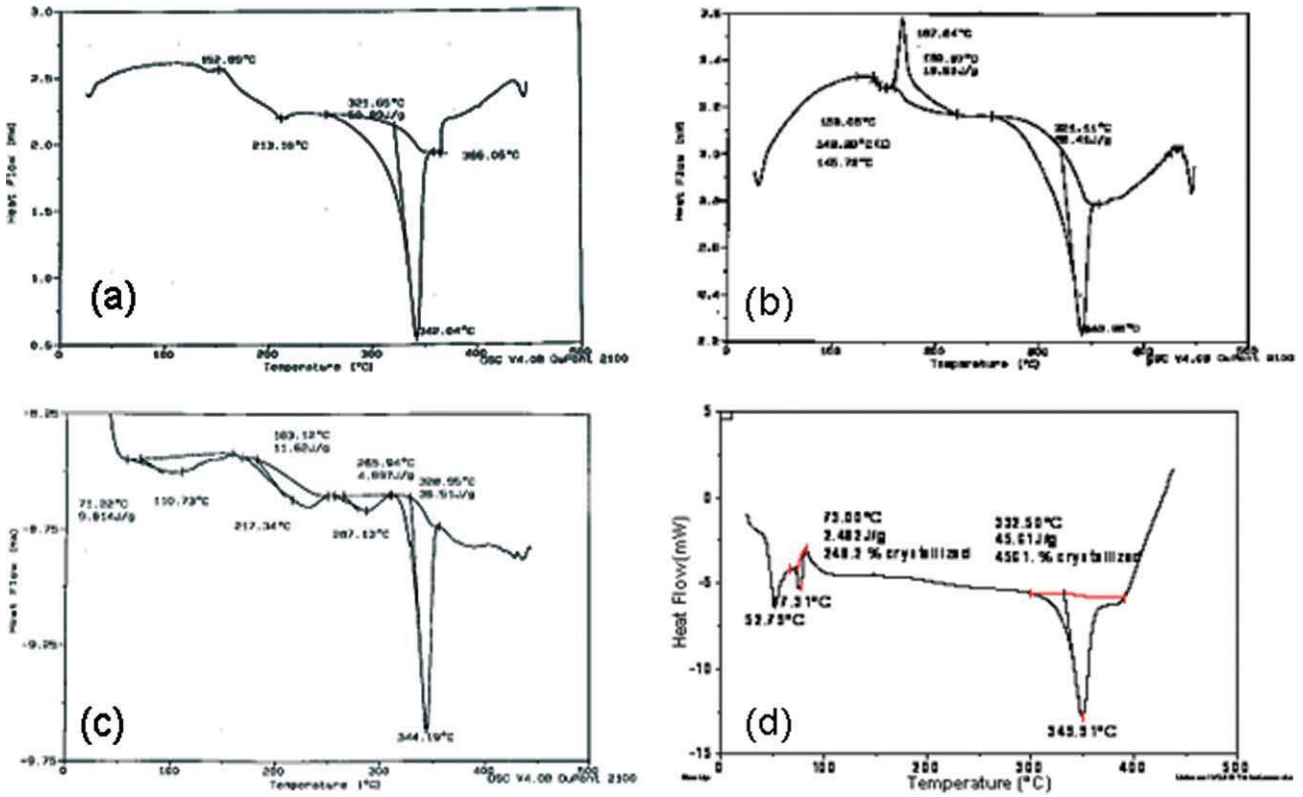

Figure 1 DSC thermograms of (a) ICI PEEK granules, (b) amorphous yarn, (c) drawn yarn 1 (crystalline), and (d) drawn yarn 2 (crystalline) (Ref. 24). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

degree of crystallinity (PEEK) from the endotherm, a heat of fusion value of 130 J/g was used.[26] The thermal transitions are expressed in terms of onset of melting temperature (T_i), melting peak temperature (T_p), and completion of melting (T_f). The DSC curve of neat PEEK [Fig. 1(a)] shows a T_g around 145°C, followed by a well defined melting endotherm at 342°C. The DSC curve of undrawn yarn [Fig. 1(b)] shows T_g at 145°C, crystallization exotherm at 167°C and melting peak at 340°C. The area under crystallization exotherm was found to decrease with increase in draw temperature up to 200°C at a constant draw ratio of 3. Figure 1(c,d)[24] did not show any traces of crystallization peak in the drawn sample. This may be due to presence of small and unstable crystals that start to melt at a much lower temperature because of which crystallization exotherm shown in Figure 1(b) gets overshadowed by the melting endotherm. The area under the crystallization peak of undrawn sample is around 40% of the melting peak of drawn sample and is an indication of the semi crystalline nature of PEEK material. The thermal transitions observed in this investigation are in close agreement with the reported range for commercial polymers reported by other research workers.[24,26,27]

The influence of orientation induced crystallization and the realization of structure property relation on enthalpy of fusion values and melting transitions have been discussed in detail in our earlier work.[28]

A comparison of the results of amorphous and crystalline yarns (Fig. 1) shows that the crystalline sample with higher enthalpy of fusion (ΔH_f) values exhibit higher crystallinity. The crystallinity index, evaluated by WAXS (Fig. 2) using relative estimation of amorphous and crystalline regions was found to be as high as 44% with samples exhibiting correspondingly high tenacity (6–7 g per denier) and modulus.[28]

Table II shows the data obtained from DSC analysis of glass–PEEK laminates [S-11] evaluated at three different heating rates of 5, 10, and 15°C/min. From the DSC thermograms, it is observed that the onset of melting is seen at around 337 to 340°C and an endothermic peak at around 347 to 349°C. The effect of different heating rates on endothermic and melting peak transition temperatures was not significant and small variations observed in the melting point of samples evaluated are attributed to morphological effects such as defects and variations in sizes of spherulites. The earlier transition temperatures, especially melting point are observed to be on the higher side compared to the data reported earlier[29] and are due to the high modulus high tensile strength of the yarn achieved as a result of improvement in crystallinity and thermal stability.

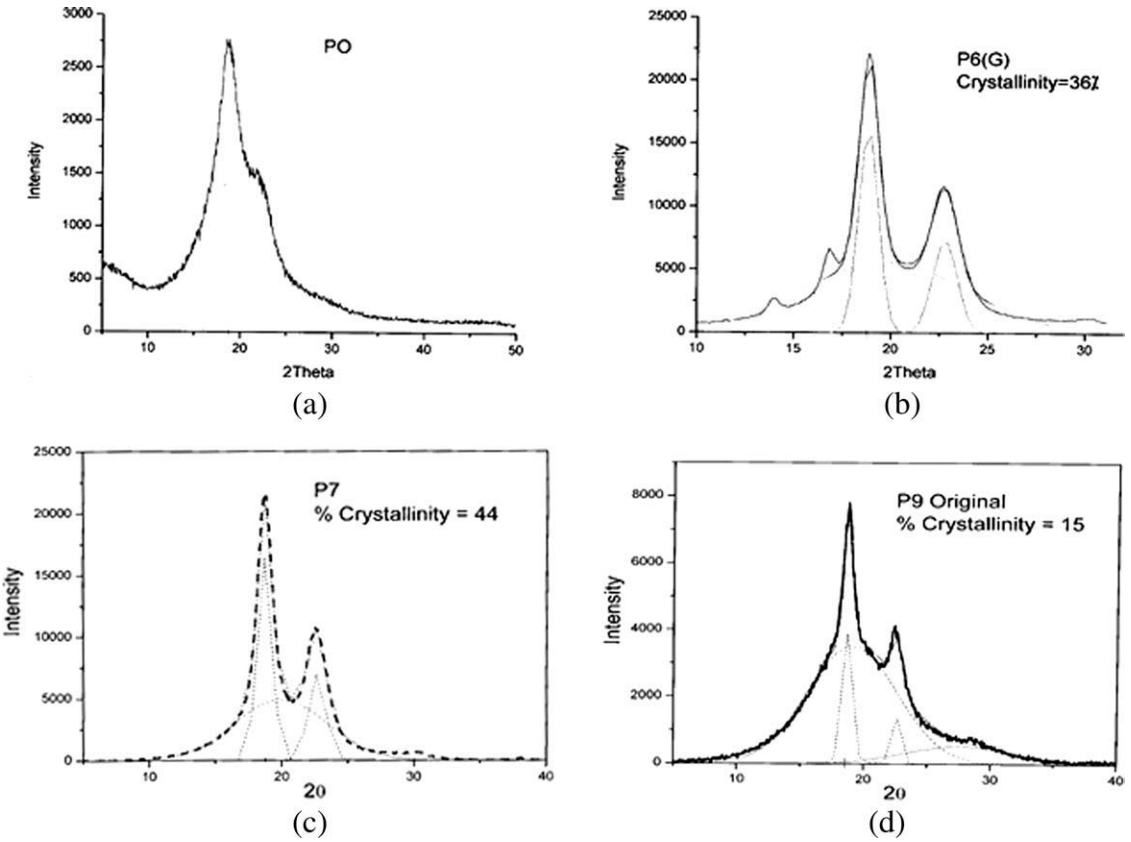

Figure 2 Wide angle X-ray diffraction spectra of PEEK yarn drawn at different draw temperatures: (a) 144°C, (b) 200°C, (c) 210°C, and (d) $<T_g$ (140°C) (Ref. 24).

The extent of crystallinity in the glass fiber–PEEK composite was calculated using the relation[30]

$$X_c = \frac{Q_m}{\Delta_w Q_c} \times 100$$

where, X_c is the degree of crystallinity, Δ_w is weight content of PEEK fiber in the composite, Q_c is the melting enthalpy of fully crystallized PEEK (130 J/g), and Q_m is melting enthalpy obtained from DSC curve.

The thermodynamic melting point of PEEK is reported at 395°C[26] and it is interesting to study the behavior of samples above this temperature to see the possible changes in crystallization and enthalpy of fusion. The effect of exposure of composites to radiant heat temperature of 400 and 500°C for time intervals of 1, 2, and 5 min is given in Table III. The thermograms and data of above samples further subjected to an isothermal temperature scan in DSC for 1, 2, and 5 min are given in Figure 3 and Table IV, respectively. On exposure to high temperature the crystallizable components get favorable conditions for crystallization and this is observed in the samples exposed to 400 and 500°C. A comparison of earlier samples show that samples exposed at 400°C exhibited higher heat of fusion values compared to samples exposed at 500°C, probably due to the temperature of former being close to equilibrium melting point, beyond which the increased mobility of chains does not contribute towards improvement in structure. Further at very high temperatures the

TABLE II
DSC Data of Glass Fiber–PEEK Composites Scanned at Three Different Heating Rates (Nitrogen Media)

Heating rate (°C)	T_i (°C)	T_p (°C)	T_f (°C)	Enthalpy of fusion (J/g)	Crystallization (DSC, %)
5	337	347	360	11.0	25.0
10	338	349	360	10.2	23.2
15	340	349	360	7.6	17.4

TABLE III
Glass Fiber–PEEK Composite Samples Exposed to Radiant Heat at 400 and 500°C (Radiant Heat) for Different Duration

Sample code	Exposed to (°C)	Time (min)	Weight loss (%)
1	500	1	Nil
2	500	2	0.114
5	500	5	0.067
1A	400	1	Nil
2A	400	2	0.183
5A	400	5	0.150

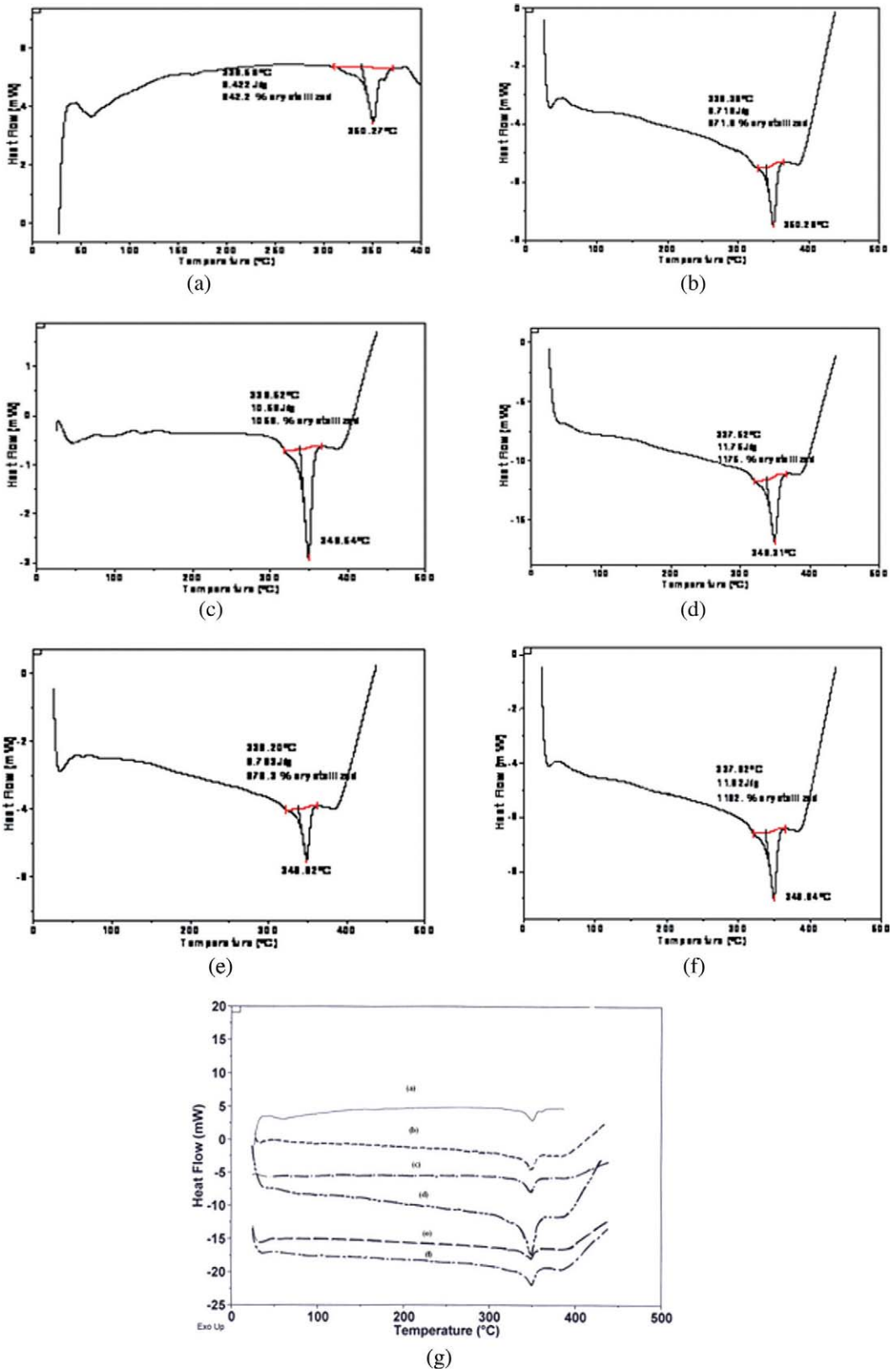

Figure 3 DSC curves of glass–PEEK laminates under isothermal conditions; (a) 1 min at 500°C, (b) 1 min at 400°C, (c) 2 min at 500°C, (d) 2 min at 400°C, (e) 5 min at 500°C, (f) 5 min at 400°C, and (g) overlay. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
DSC Data of Glass–PEEK Composite Initially Exposed to Radiant Heat at 500°C and 400°C and Scanned Under Isothermal Temperature

Sample code	Duration of exposure (min)	Isothermal temperature (°C)	Melting point (°C)	Heat of fusion (J/g)	Crystallinity (DSC, %)	Crystallinity index (WAXS, %)
1	1	500	350	8.4	19.1	21.0
2	2	500	350	10.6	23.8	17.0
5	5	500	349	9.7	22.0	19.5
1A	1	400	350	8.7	19.7	15.8
2A	2	400	349	11.7	26.5	19.1
5A	5	400	350	11.8	26.8	21.2

molecular chains gets into molted state and begins to move vigorously, with change in alignment of molecular chains resulting in the weakening of the specific interactions.[31] It is interesting to notice that a well defined sharp narrow melting endotherm is observed in all the DSC thermograms. This indicates simultaneous melting of crystals present in the material after crystallization. However, the results could not be corroborated with the data on crystal size shown in Table V. From the data generated, it is observed that the improvement in crystallinity is not much probably due to the very short durations of exposure in radiant heat followed by isothermal treatment again for short durations. This suggests that the short time intervals used in this study may not significantly influence crystallization process and the changes observed may be influenced by the surface morphology rather than the core structure of laminates. The crystallinity values measured by WAXS technique are generally found to be lower compared to the values measured by DSC and show a definite trend only in the samples subjected to radiant heat of 400°C, indicating again that temperature near equilibrium melting point is ideal for achieving useful properties. Generally, the crystallinity measured using WAXS technique is found to be lower compared to the values measured using DSC. Measurement of the degree of crystallinity by WAXS and DSC is complicated and derive different average values for the same sample.[32,33] The variation in crystallinity index of glass–PEEK composites compared to that of neat PEEK fiber (Table II) may be due to the repeated exposure of the PEEK to higher processing temperature employed during subsequent processes. The high temperature heating cycle selected during the fabrication of composites might have induced an optimum degree of crystallinity in PEEK matrix, because of which the composites show a reduced crystallization tendency during DSC heating scan.[30] The improvement in the degree of crystallinity as observed in DSC and WAXS techniques is thus not very high and because of the strong dependence of nucleation and growth related parameters on temperature, an optimum time-temperature condition need to be established to arrive at improvement in properties.[28] DSC although can be used to determine the degree of crystallinity of PEEK and its composites, due consideration must be given for allowances for melting and recrystallization, which may occur on heating during the process of evaluation itself.[32]

TABLE V
Structural Parameters of Glass–PEEK Composite Obtained from WAXS

Sample code	Particle size (t, Å)	Unit cell parameter (a)	Volume (Å^3)	Crystallinity index (%)
1	155.67	6.6326	291.78	21.0
2	136.22	6.6255	290.84	17.0
5	157.38	6.6184	289.91	19.5
1A	121.15	6.6567	294.97	15.7
2A	155.69	6.6284	291.22	19.1
5A	137.51	6.6357	292.19	21.2

From the data shown in Table IV, it is observed that the melting point of the composites remains more or less constant irrespective of the exposure of the composites to radiant heat source followed by an isothermal treatment in DSC. The minor variations noticed may be due to the difference in crystal size of PEEK yarns (Table V). Significant variations in particle size and unit cell parameter shown in Table V also gives an indication of variation that arises in estimating crystallinity and supports the validity of our argument.

Thermomechanical analysis

TMA was used to find out the thermal transitions and linear coefficient of thermal expansion (CTE) of composites. Figure 4 shows the change in CTE of composites measured parallel to the fiber direction. In a unidirectional fiber reinforced composite (FRP) composite, the CTE is controlled by the behavior of individual constituents parallel to the reinforcement direction. The temperature dependant modulus properties of the fibers to a great extent will contribute for the final expansion properties.[34]

The thermal expansion characteristics of the composites were observed between the selected temperature ranges of 100 to 250°C. The aforementioned

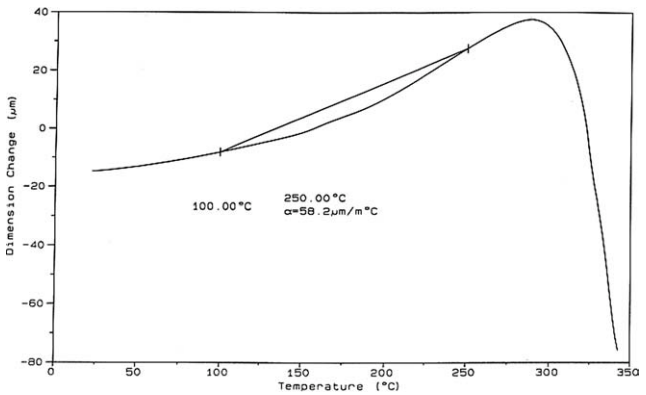

Figure 4 TMA of glass fiber–PEEK laminate.

temperature range was chosen to study the behavior of glass–PEEK composites keeping in view the continuous use temperature of 250 to 260°C. From the variation of dimensional change of composite against temperature, CTE (α) was calculated and found to be low as 58.2 μm/m-°C. The change in the dimensions of sample was very slow and gradual up to 100°C and then started to increase more rapidly. Above T_g, somewhere near heat of distortion temperature started to increase more rapidly possibly because of the of turbulent state of molecules. CTE shows a maximum value at 290°C, after which it decreases rapidly. The low value of α measured in the sample is related to the properties of fiber. The enhanced thermal stability of PEEK obtained as a result of process optimization (extrusion and drawing) has contributed to higher T_g (Fig. 5). This may be due to reorganization of the unorganized smaller crystals into a more organized large crystals resulting in better alignment of chain molecules that has resulted in reduced free volume. This in turn has contributed to rigidness of the structure and a possible increase in crystal density as observed in our earlier studies,[28] which is expected to affect the modulus and hence the thermal expansion characteristics. Thus, in general, with the increase in temperature, CTE bears a direct relation to the free volume change. At T_g, the free volume show a significant change to ease the molecular mobility which will also reflect on CTE.

Dynamic mechanical analysis

The improvement in the crystallinity of PEEK and its influence on structure property relation of composites in terms of elastic modulus, strength, and strain to failure can be explained with the help of DMA thermographs. Figure 5(a,b) shows the variation of storage modulus (E′), loss modulus (E″) and loss tangent (Tan δ) of glass–PEEK composites as a function of temperature and frequency. From the DMA thermogram [Fig. 5(a)] it can be seen that with increase in temperature, dynamic storage modulus decrease steadily and more rapidly near the T_g temperature of 145°C. The loss modulus and tan δ value shows a maximum at 185°C to 175°C, respectively and is due to the α-relaxation related to PEEK as previously reported.[35] At 185°C, storage modulus shows a steep drop, whereas the loss modulus shows a peak loss. The relative decrease in the height of tan δ peak and E″ at Tg is related to increase in the extent of crystallinity in the polymers as the transition behavior is associated with the local mobility of the polymer chains in the amorphous-region of the polymer. The maximum value of tan δ is nothing but T_g as explained by many investigators[29] is on the higher side and is probably an indication of increase in crystallinity. The effect of frequency [Fig. 5(b)] on E′, E″, and tan δ was investigated in the frequency range of 0.1 to 10 Hz using a reference temperature of 25°C. It can be seen from Figure 5(b) that major transitions are observed below a frequency of 1 Hz.

The processing conditions used for converting hybrid fabrics into composites may influence the final properties of the product. To understand the influence of fabrication conditions on the performance, a set of composites were prepared with higher soaking times at important transition temperatures of PEEK. Figure 5(c) shows the effect of heating cycle on the storage modulus of the composite. It can be observed that composites fabricated with soaking time of 20 min at major transition temperatures of 143°C (T_g), 170°C (crystallization temperature), 260°C (continuous use temperature), 350°C (melting temperature), and 385°C (processing temperature) exhibited superior dynamic mechanical properties compared to composites, which were fabricated using faster heating cycle [(without soaking time) and directly processed at 385°C for 20 min. At room temperature, the modulus which was around 6250 MPa do not show any change in modulus up to T_g. Above T_g up to 200°C and between 200 to 300°C, a loss in modulus to an extent of 35 and 38%, respectively, is observed. Even though the modulus at T_g temperature as well as the retention of properties at 300°C was observed to be significantly high in the former case, beyond 300°C the two samples underwent drastic loss in modulus and the behavior in both the samples was more or less identical. Similar trend was observed even in the case of loss modulus.

It is also observed that primary viscoelastic transition (tan δ) at low frequency (1 to 5 Hz) is observed between 150 to 170°C, whereas at higher frequency (10 Hz), the peak is observed at 180°C indicating that T_g evaluated is an apparent value that varies with frequency.

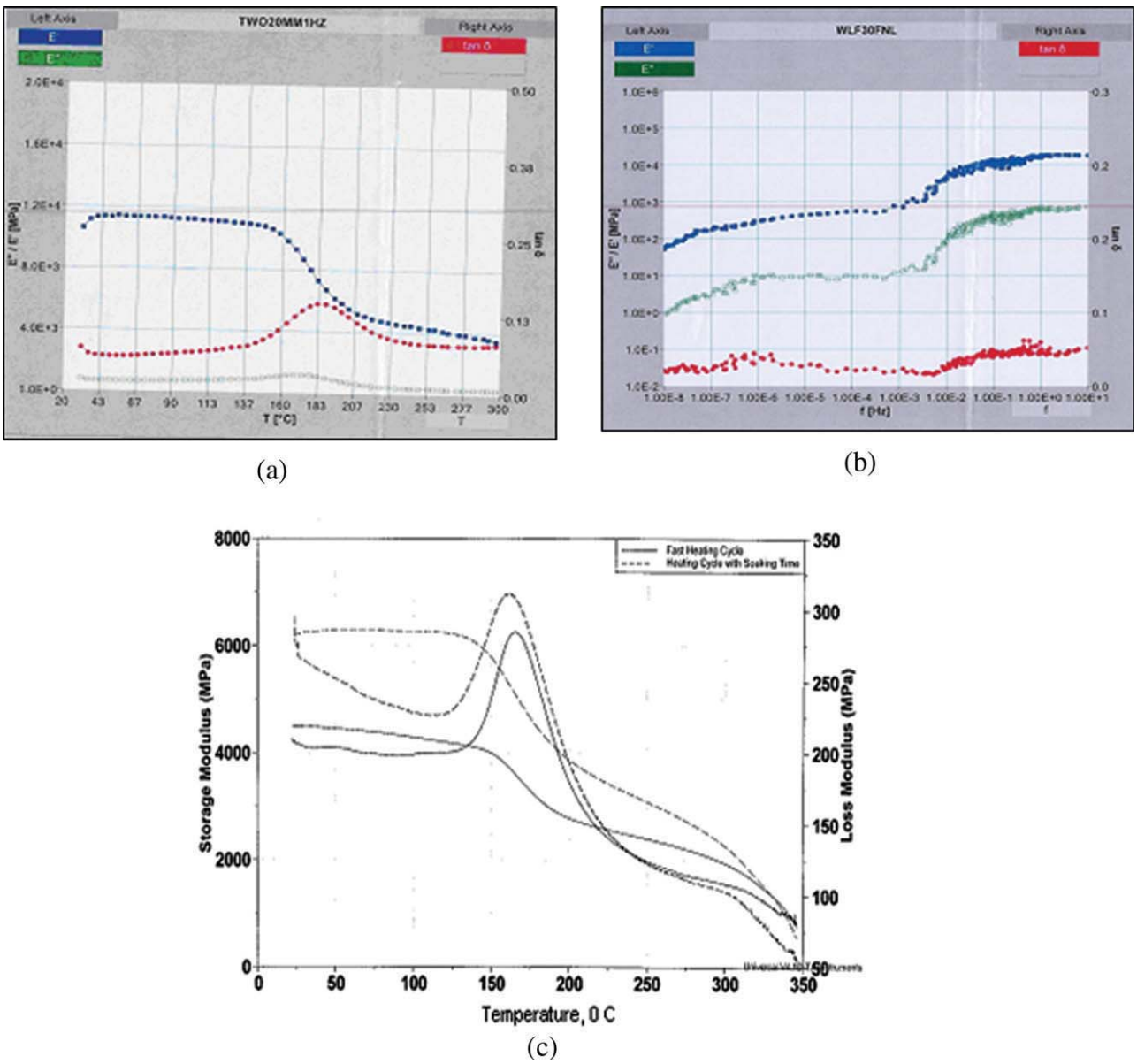

Figure 5 DMA of glass–PEEK laminates; (a) modulus Vs temperature (three point), (b) modulus Vs frequency (three point), (c) Modulus Vs temperature (dual cantilever) (effect of heating cycle). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Scanning electron microscopy

The surface morphology of glass–fiber PEEK laminates is shown in Figure 6. As flexural and interlaminar shear strength properties are dependent on the stress transfer ability of the resin, it is important to understand the distribution of PEEK, which has high melt viscosity. The effect of weave, the relative movement of yarns, role of binding points in weaves can be observed from the SEM photomicrographs. The special sateen weave (four end crow foot) having high percent maximum weavability provides high surface area for the adhesion of the PEEK resin and ensures proper impregnation of the resin onto the reinforcing glass fiber by restricting the outward and downward movement of the resin. From the Figure 6(a,b), it can be observed that though the PEEK fiber is arranged perpendicular to the direction of reinforcement fiber, the distribution of resin is uniform as evident from the nondistinct visibility of reinforcement yarns. The sateen weave used in the hybrid fiber fabric provides high tightness factor and prevents shearing and buckling of fibers.

Thermo gravimetric analyzer

The TGA data of PEEK fibers used in the fabrication of glass–PEEK composites is summarized in Table VI–VII. A comparison of the thermal stability of samples in air (Table VI) and nitrogen (Table VII)

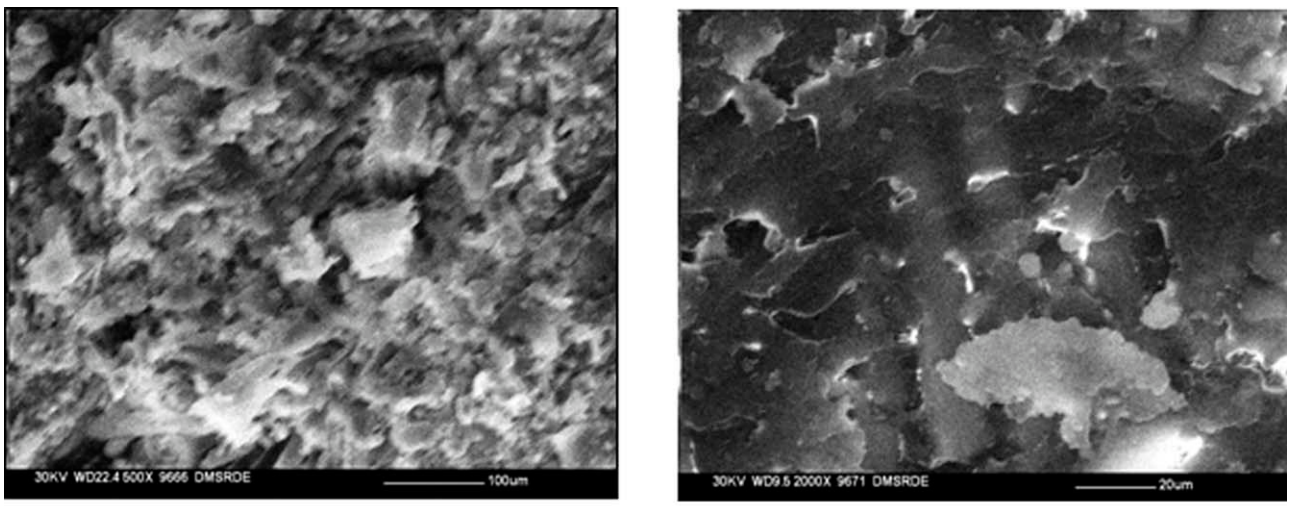

Figure 6 SEM photographs of Glass–PEEK laminates (a) 500 X, C/S of laminate, (b) 500 X middle outer layer.

shows that there is significant difference in the overall transition temperatures (onset, mid point, and end point). The onset of degradation temperatures in Nitrogen (570 to 580°C) was much higher compared to that in air (360 to 370°C). The weight loss of samples in air between 360 to 460°C varies from 6.75 to 10% compared to 37 to 48% observed in the case of nitrogen between 570 to 620°C.

The thermal transition temperatures of PEEK fibers prepared are on the higher side compared to that reported values by other workers.[27–29] The higher onset of degradation temperature for the PEEK prepared in this study may be due to the optimization of spinning process parameters such as draw temperature and draw ratio. The degradation of PEEK fiber proceeds more rapidly at around 525°C in both air and nitrogen.

The effect of heating rate on the degradation behavior of glass–PEEK composites is shown in Figure 7 and the data is summarized in Table VIII. Although variation in onset and peak temperatures was observed, the weight loss was found to be more or less constant irrespective of different heating rates. At 500°C, the weight loss was less than 1%, which suggests that these composites can be used up to 500°C for small intervals of time. However, the drop in viscoelastic properties beyond 300°C as observed in DMA thermogram (Fig. 5) needs to be taken into consideration before using the composites for high temperature aerospace applications.

Table IX shows the weight loss of glass fiber–PEEK composites exposed to isothermal temperatures for 1 min in nitrogen atmosphere. It can be seen from the data that the weight loss of the exposed samples at 500, 700, and 800°C for 1 min was less than 1.7%. To further study the thermal stability under isothermal conditions and the influence of previous history of the composites, the same samples were exposed to radiant heat at 400 and 500°C (heat flux of 20 to 25 kW/m^2) for 1, 2, and 5 min. Table X and Figure 8 show the TGA results of samples exposed to radiant heat and then subjected to scanning in TGA. It can be seen that at 500°C, the weight loss of the samples was found to decrease with increasing exposure time possibly due to the conversion of low melting crystals to high melting stable crystals. Crystals which initially melted on the low temperature side of the main endotherm

TABLE VI
TGA of Typical PEEK Yarns Spun Under Various Spinning Conditions (in Air)

Sample code	T_i (°C)	T_p (°C)	T_e (°C)	Weight loss %
A	360	439	460	8.0
B	370	438	455	6.7
C	365	438	460	9.4
D	370	440	460	7.8
E	360	439	460	10.0

A, B, C, D, and E: samples drawn at 210°C, 200°C, 190°C, 180°C, and 160°C, respectively.
T_i: initiation; T_p: Peak; and T_e: end point.

TABLE VII
TGA of Typical PEEK Yarns Spun Under Various Spinning Conditions (in Nitrogen)

Sample code	T_i (°C)	T_p (°C)	T_e (°C)	Weight loss %
P_G	577	594	625	33.4
P_{10}	580	596	680	37.1
P_6	544	562	580	45.8
P_{11}	570	597	620	41.8
P_{13}	575	595	625	48.8

P_G (Gatone): Draw ratio (DR) 3; P_{10} : DR 4; P_6 (PEEK synthesized at DMSRDE lab) : DR 3.5; P_{11} : DR 3; P_{13} : DR 4.5.

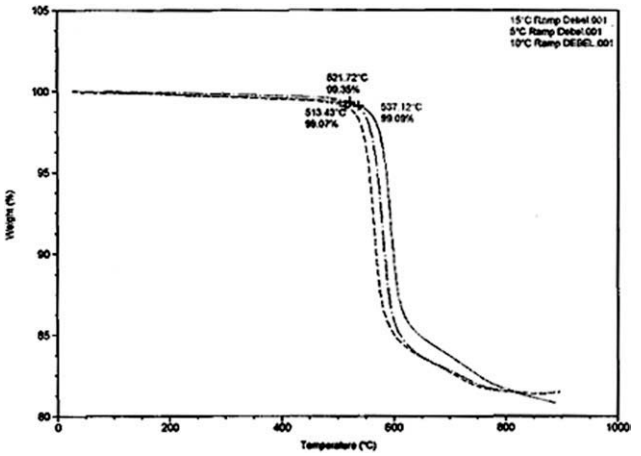

Figure 7 TGA thermogram of glass-PEEK laminate at 3 different heating rates.

[Fig. 1(c)] are perfected during successive heat treatments at higher temperature.

The kinetic parameters such as activation energy and half life temperature of glass–PEEK composites calculated using Arrhenius equation from Figure 7 are given in Table XI. The observed activation energy levels at conversion levels of 1 and 2.5% showed that PEEK is sensitive to small changes in temperature.

Nondestructive testing

In the recent past, air-coupled ultrasonic C-scanning is increasingly being used by research workers in the field of nondestructive evaluation (NDE). The advantage of this technique is that it does not rely on any external couplant media (liquids, gels, pastes, etc.). The use of lower frequencies employed in this new method ensures improved transmission characteristics of the ultrasound through materials, especially for foams and composites.[36,37]

Table XII shows the mean transmission (as obtained from inbuilt WINSPECT Software) of ultrasonic waves through glass fiber–PEEK composites scanned at 120 and 400 Hz frequencies. The percentage transmission can be read from the color index given separately for each of the frequencies.

TABLE VIII
TGA of Composites (S-11) at Three Different Heating Rates (Nitrogen)

Rate of heating (°C)	T_i (°C)	T_p (°C)	T_e (°C)	Weight loss at 500°C (%)	Weight loss between T_o to T_e (%)
5	500	560	584	0.8	14.0
10	530	574	603	0.5	14.4
15	540	592	616	0.7*	13.3

* at 512°C.

TABLE IX
TGA Data of Composites (S-11), Under Isothermal Conditions for 1 min in Nitrogen (50°C/min)

Sample	Temperature (°C)	Weight loss (%)
S-11	500	0.05
S-11	700	0.12
S-11	800	1.68

The mean transmission through the samples increased with increase in frequency in both the samples. It is also observed that sample with more number of hybrid fabric layers (thickness of 4.5 mm) exhibits slightly less uniformity in the distribution of resin and may be due to the skin core effect behavior generally observed in thicker laminates. The mean transmission of samples with less number of layers (thickness 3.3 mm) exhibited very high values suggesting that the laminates are not much influenced by the attenuation of the waves. Although short wave length waves (400 Hz) give a better representation of inhomogeneities within the structure due to the interaction with microscopic features, surprisingly the samples exhibited a behavior, which seems to be independent of the frequencies and impendence. The mean transmission through the samples increased at higher frequency (400 kHz) possibly due to the different variable gain used in the case of 120 and 400 Hz frequencies. The other reason for the earlier behavior may be the effect of resolution capability and the effective interaction with the materials at a particular frequency.

Even though C-scan images of samples show very high transmission characteristics and demonstrate the diagnostic capabilities of the method, the identifiable heterogeneities or homogeneities of the structure need to be corroborated with mechanical testing to arrive at a meaningful conclusion. This will ensure that the defects so identified truly represent the behavior of the laminates in actual use.

Mechanical properties

Table XIII shows the mechanical properties of glass–PEEK composites prepared with modified PEEK

TABLE X
TGA Data of Glass–PEEK Composite (S-11) Initially Exposed to Radiant Heat at 500 and 400°C and Then Subjected to TGA at Isothermal Temperature

Sample	Duration of exposure (min)	Isothermal temperature	Weight loss (%)
1	1	500	0.7
2	2	500	0.6
5	5	500	0.3
1A	1	400	0.2
2A	2	400	0.2
5A	5	400	0.3

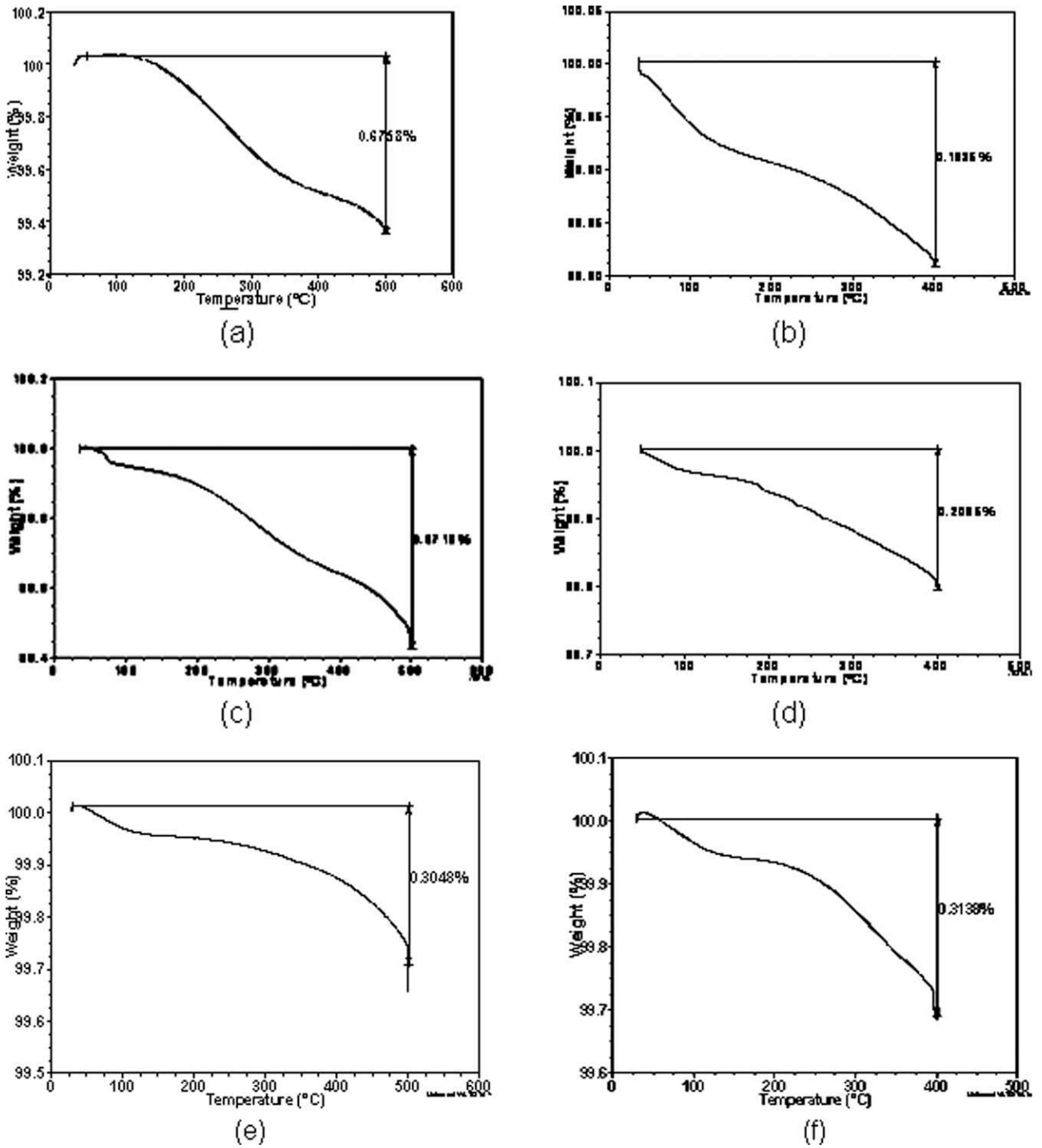

Figure 8 TGA of glass–PEEK laminate at isothermal temperature (a) 1 min at 500°C, (b) 1 min at 400°C, (c) 2 min at 500°C, (d) 2 min at 400°C, (e) 5 min at 500°C, and (f) 5 min at 400°C.

fibers in different resin proportions (30.6–34.5). The values obtained are high compared to conventional glass fiber reinforced epoxy resin composites. Our earlier experience with unidirectional glass-epoxy composites with similar resin content and thickness indicates that ILSS, flexural, and tensile strength values are higher by 30 to 40%.

The samples exposed to high temperature (at 500°C for 30s) showed increase in tensile properties, but the improvement in ILSS and flexural strength were not significant. Compared to flexural strength, ILSS properties were more consistent and did not vary much with resin content. The consistent properties achieved in ILSS also gives an indication of level

TABLE XI
TGA Analysis of Glass–PEEK Composites (S-11)–Kinetic Parameters at Different Conversion Levels

Conversion level (%)	Activation energy (kJ/mol)	Log (pre-exp factor, 1/m)	60 mins half life temperature (°C)
1	29.6	2.41	82.5
2.5	28.0	2.49	57.8
5.0	3.0	−2.11	−1159.5
10.0	0.6	−2.43	−335.5
20.0	7.6	−1.05	174.9

of anisotropy, which was supported by the morphological characteristics as discussed in earlier SEM and NDT section. The uniformity in the distribution of resin between various layers of laminate is expected to play a major role and have a dominant impact on the mechanical properties of composites for aerospace applications. The high ductile values generally observed in glass–PEEK systems[5] is expected to act as a non crack growth center as initially the stress moves through the high modulus resin before reaching the fiber, which is the primary member that bears the load.

CONCLUSIONS

The PEEK fiber used as resin fiber in the hybrid fabric was spun by optimizing the spinning process parameters. It was found that PEEK spun at 385°C and drawn at 200 to 210°C with a draw ratio of 3 exhibited crystallinity that resulted in strength as high as 6 to 7 gpd.

Hybrid fabric cowoven using e-glass as reinforcement material and PEEK as fiber resin in basket weave and sateen weave was converted into composites using compression molding machine. The time, temperature, and pressure cycle for converting the hybrid fabric into laminates was optimized. It was found that laminates prepared with higher soaking times at important transition temperatures of PEEK exhibited superior dynamic mechanical properties compared to the composites fabricated using faster heating cycle (without soaking time) and directly processed at 385°C for 20 min.

The improved orientation and modulus of the PEEK fiber contributed for the superior properties

TABLE XII
NDT Transmission Data of Glass Fiber–PEEK Laminates (S-11)

Sample	Transmission (%)	
	120 Hz	400 Hz
Laminate with 15 layers of hybrid fabric, thickness, 3.3 mm	83	100
Laminate with 17 layers of hybrid fabric, thickness, 4.5 mm	47	67

TABLE XIII
Mechanical Properties of Glass Fiber–PEEK Woven Composites [Thickness 4 mm]

Sample code	Resin content (%)	Tensile strength (MPa)	Flexural strength (MPa)	ILSS (MPa)
S-9 Unexposed	30.8	294.9	490.1	50.94
S-9 exposed to, 500°C, 30 s	30.6	332.8	431.9	54.34
S-10 Unexposed	33.1	280.8	323.9	54.50
S-10 exposed to 500°C, 30 s	33.0	317.2	467.5	55.90
S-11 Unexposed	34.5	291.8	435.1	50.69
S-11 exposed to 500°C, 30 s	34.4	340.7	436.8	52.46

ILSS: Interlaminar shear strength

(ILSS, tensile, and flexural strength) of the composites generally not observed in Glass–epoxy systems.

The influence of radiant heat on development of relative crystallinity with respect to time above equilibrium crystallization temperature was investigated. It was found that small intervals of exposure time do not affect the properties related to crystallinity.

DMA studies carried out suggests that a reasonable retention of modulus even at high temperatures (300°C). TMA analysis carried out shows low positive CTE that was well within the engineering limits for fabrication using match mold techniques.

The surface morphology studies carried out on laminates using SEM and air-coupled ultrasonic C-scan technique indicate uniform distribution of thermoplastic fiber resin that contributed for uniform stress distribution resulting in superior ILSS.

Summarizing, hybrid fabric based glass–PEEK laminates exhibit excellent thermal stability (up to 300°C) and can be used for high temperature aerospace applications. These resin systems offer advantages in terms of easy processability, shapability, uniformity, and consistency in properties over their counterpart systems.

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