

Properties of High Modulus PEEK Yarns for Aerospace Applications

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ABSTRACT: A study has been carried out on the influence of extrusion and drawing related process parameters with an object of obtaining high modulus poly ether ether ketone yarns that can be tailor made to meet critical requirements of aerospace applications. The influence of the interaction between rheological properties, spinning process variables, and drawing conditions has been given special attention to engineer a yarn that exhibit excellent structure property relationships. The wide angle X-ray diffraction results suggest that drawing carried out above glass transition temperature (T_g) influences the structure that include unit cell parameters, density, and mechanical properties. The degree of orientation characterized in terms of sonic velocity measured as

high as 3 km/s with sonic modulus of 105 gpd. With progressive increase in draw temperature, crystallinity was found to increase, and useful properties were observed at an optimum draw temperature of 200°C (may be region of maximum crystallization rate) primarily attributed to the maximum crystallization temperature and the heat setting effect. Thermal studies (TGA) indicate that these materials can be used in high temperature applications (up to 250°C) for long time exposure and 500°C for short term exposure. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2497–2510, 2009

Key words: crystallization; drawing; orientation; PEEK; sonic modulus

INTRODUCTION

The development of high performance high temperature engineering materials [poly ether ether ketone (PEEK)] for air borne vehicles and structural applications requires special consideration of spinning and drawing process parameters to meet the stringent requirements of composites. Over the last 2 decades, growing aerospace activities has created a momentum to the development of high performance composites using high performance engineering thermoplastics that satisfy functional and techno-economic aspects. Since its introduction by the Imperial chemical Industries (ICI) in 80s, PEEK material has generated lot of interest in the aerospace industry as one of the leading thermoplastic matrix candidate for use in advanced composites due to its unique properties of chemical resistance, high thermal stability (first and second order transitions), coupled with satisfactory fiber properties. PEEK is a semi crystalline, aromatic engineering thermoplastic fiber which can be used as a thermoplastic resin for critical aero space applications and advanced structural composites. There is a long history of studies on structure development in

melt spinning of fibers. The earliest published data on morphology of crystallization kinetics of poly aryl ether ketones were those of Blundell¹ and Dawson.² These authors have worked extensively on topics covering crystallinity related parameters, spherulitic structure, crystalline unit cell of PEEK. Other authors³ concentrated on rheology and morphology of PEEK and liquid crystal polymer blends.

The melt spinning of PEEK material has been well investigated.^{4–8} Important aspects including structure development, crystallinity, and orientation parameters have been dealt by above authors. Recently, this area has been reviewed by a number of research workers.^{9,10} There has not been much study on the development of high tenacity, high modulus PEEK fiber as a resin system in the advanced glass reinforced composites. Most of the studies have used Instron rheometer for extrusion, which may not simulate the industrial conditions of extrusion and drawing, whereas limited studies have been carried out using PEEK in the form of powder or film for composite applications.

The patents^{11–18} available basically describe the process of preparing hybrid fabric and composites and attention regarding resin-fiber properties and their importance is not well documented.

The present article involves a study comprising of rheological properties, spinning and drawing of

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PEEK fibers by varying process parameters and finally an evaluation of the resulting fiber structure and mechanical properties. The work has been aimed at designing a high modulus fiber that can be used along with inorganic fibers like glass and high modulus para-aramid fibers keeping in view the suitability and the end use of composite applications.

METHODS

Materials

Spinning

PEEK granules from ICI (151G) and Gharda Chemicals (Gatone 5400), Mumbai were used in the study.

The extrusion and drawing of PEEK fibers was carried out on a laboratory high temperature experimental spinning equipment developed by Bradford University. The machine works on the principle of rod spinning with cylinder and piston. The piston is driven by a screw jack which in turn is driven by a servo controlled motor. The schematic diagram of the machine is shown in Figure 1. The extrusion temperature of the polymer was maintained at 370–380°C. The RAM pressure was 750–1000 kg and the RAM speed was maintained at 7–10 mm/min. Spinnerets with mono and multiholes having 100–300 μ diameters were fitted to the heating block. The spin length

was varied from 50 to 100 cm to study the effect of distance on crystallinity.

The polymer chips were dried in a hot air oven at a temperature of 120°C for 4 h before taken for spinning.

Drawing

The fiber drawing operation was carried out using a drawing set up that was a part of extrusion equipment. The extruded filament was passed via a thread guide on to an intermediate winding unit, then to a drawing unit, and finally on to a take up package as shown in Figure 1. The extruded fibers were drawn on a drawing unit consist of two sets of rollers running at different circumferential speeds. The draw plate temperature (DT) was varied from T_g (143–145°C) to above crystallization temperature (180–210°C) to study the effect of draw temperature (DT) and draw ratio (DR) on properties of fibers. One of the samples was extruded and wound on the take up package with no velocity difference between the feed and take up rollers at ambient temperature. Another sample was prepared similar to the above sample but the draw temperature was maintained at 160°C. This is similar to heat setting of samples with lengths constrained. In addition to above samples, few melt spun fibers were also drawn with draw ratio ranging from

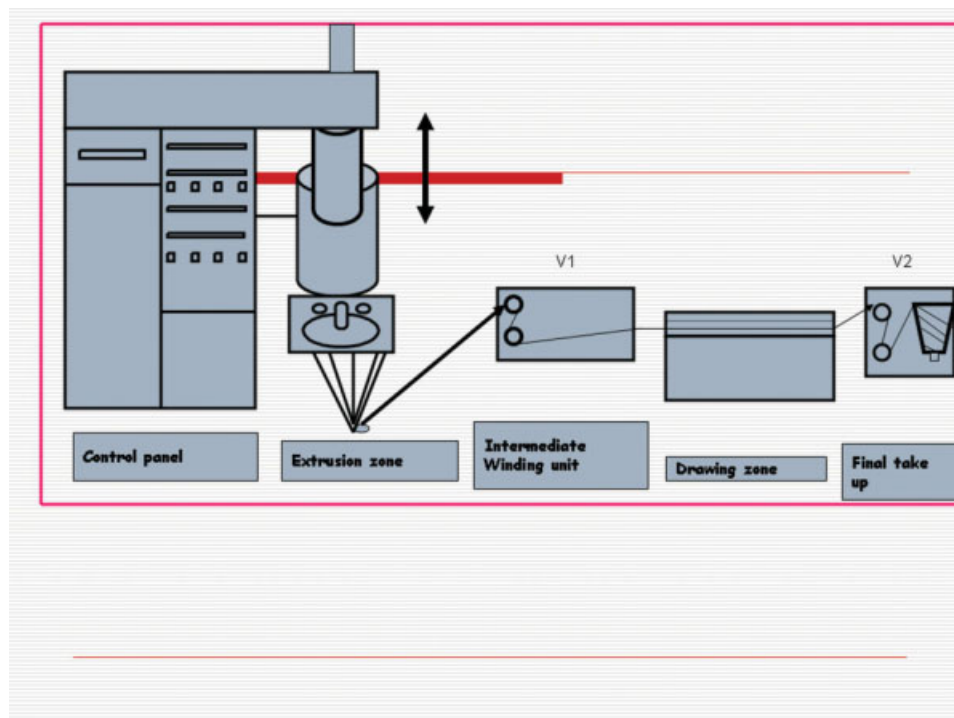


Figure 1 Melt extruder and drawing unit used for extrusion and orientation Parameters studied: (i) Distance between spinneret to intermediate winding unit (50–100 cm), (ii) variable speed between intermediate winding unit to final take up (30–100 cm), and (iii) Draw temperature (less than T_g –210°C). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

3–5 in both single and two stage process. The results of selected samples excluding some of the variables are reported for ease of understanding.

Structural characterization

The characterization of PEEK material and yarn were carried out using the following equipments.

Melt flow index (MFI)

The melt flow Index of PEEK granules was evaluated by melt flow meter at a pressure of 2.1 kg at different temperatures of 350, 360, 370, 375, 380, 385, 390, and 400°C. This was done to have prior knowledge of the volumetric flow of dope before the materials are taken for spinning.

Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction (WAXD) technique (Phillips Analytical X-ray) was used to characterize the crystallinity related parameters. With Cu as a target 40 kv and 20 mA ratings are generally used to produce sufficient intensity of characteristic X-rays. To select $\text{CuK}\alpha_1$ radiations with divergence of 0.001 Å, the nickel filter is used.

Yarn samples with a fixed weight were carefully wound parallel to one another on the glass slide. Equatorial intensity scans in the range $2\theta = 10\text{--}60^\circ$ was scanned. The technique of multiple peaks fitting using Gaussian distribution was applied on the Grazing incidence XRD curves to express the results in terms of crystallinity index (CI). The percent crystallinity was calculated using net area and peak area of the graph.

The crystal structure of PEEK was characterized using half maximum peak width and standard hkl values. The data was analyzed with the help of TA instruments software. Unit cell parameter (a) and volume was evaluated with the help of standard hkl values.

An apparent size, E , the volume average in a direction perpendicular to the diffracting planes was calculated by Scherrer's formula.¹⁹

Sonic velocity

Molecular orientation in fibers and young's modulus of elasticity were characterized based on sonic velocity measurements with a pulse propagation meter PPM-5 (5 kHz frequency). The PPM has been designed for the continuous measurement of the transit time of a pulse between two transducers coupled to a test sample. Sonic velocity (C) was calculated based on the time taken for the pulse to travel a distance of 50 cm along the specimen. The transit time of the

pulse between the spaced transducers is inversely proportional to the propagation velocity in the sample and is read directly in microseconds on the panel meter or recorder. The dynamic modulus was calculated using sonic velocity ($11.3 \times C^2$). The velocity at which the molecules move was used to relate structure property relation.

Scanning electron microscopy (SEM)

The surface morphology of the extruded fiber was studied with the help of scanning electron microscope (Jeol 35 CF with Polaron DC sputtering unit).

Birefringence (Δ_n)

Birefringence of the fibers were measured using polarizing optical microscope.

The specific index of birefringence is a measure of orientation of fiber. For all the samples studied, five specimens were considered to calculate the average birefringence. Δ_n was evaluated using the following formula

$$\Delta_n = \frac{R}{D} \quad (1)$$

where R is the retardation expressed as a function of time and speed of light in vacuum, and D is the diameter of the fiber.

TGA

TGA of the PEEK yarns under dynamic conditions were carried out on a TA instruments (2950) at a heating rate of 10°C/min under nitrogen atmosphere.

DSC

DSC of the PEEK yarns were carried out on a Du Pont (2100) at a heating rate of 10°C/min under nitrogen atmosphere.

Mechanical properties

The force elongation properties of extruded and drawn yarns were evaluated using Statimat ME (Textechno, Germany) using a load cell of 100N. At least 20 samples were tested and the average reading is reported.

RESULTS AND DISCUSSION

Extrusion of PEEK yarn

Table I shows the results of melt flow index (MFI) of PEEK. PEEK being high molecular weight aromatic polymer with molecular weight > 40,000 has high melt viscosity, and the effect of molecular weight can

TABLE I
MFI (Melt Flow Index) of PEEK Granules
at Different Temperature, g/10 min

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

be seen in the MFI values, which are significantly low when compared with the 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 36–42 was observed which was found to be ideal for satisfactory and smooth extrusion of the material. The ability of PEEK to retain its properties even at high temperature (as high as 315°C) makes it difficult to extrude at low temperatures and pressures.

The MFI values not only provide useful data to optimize the spinning process parameters (ram pressure, ram speed, spinning speed, and spinning temperature) but are also handy when it comes to conversion of hybrid fabrics into composites, wherein the thermoplastic PEEK has to undergo melting and impregnate the available surface area of reinforcement yarns. The temperature profile in conjunction with ram speed, spinning speed, and length of spinning path need to be taken into consideration to ensure that PEEK does not crosslink at high temperature in the presence of oxygen. The extrusion of the material was extremely difficult at temperature greater than 390°C, as PEEK readily crosslink with oxygen with corresponding change in melt viscosity accompanied by significant reduction in volumetric flow. The extent of crystallization that takes place during the short span of time in the quench chamber is influenced by the length of the spinning path in addi-

TABLE II
Particle Size and Unit Cell Parameters
of Various PEEK (Harris²⁰)

Lattice parameters	PEK	PEEK	PPE
<i>a</i>	7.63	7.75	8.07
<i>b</i>	5.96	5.86	5.54
<i>c</i>	10.0	10.0	10.26
Crystal density, g/cm ³	1.43	1.40	1.41
Amorphous density, g/cm ³	1.27	1.26	1.27

tion to other parameters that include temperature of crystallization maxima and the degree of cooling. The length of spinning path being independent in nature can be effectively used to develop initial morphology and orientation in PEEK fibers. Because the flow field in melt spinning process is mostly extensional except near the die exit, where transition from shear to extensional flow occurs, the crystallization behavior is accelerated due to the increased efficiency of chain orientation in this particular zone. Taking into consideration the above aspects, the PEEK filament was extruded and drawn by varying extrusion temperature, length of spinning path, draw temperature, draw ratio, and take up speed. The influence of various spinning process conditions that were investigated are scrutinized and only important variables and selected samples that have contributed to the structure development have been discussed and presented in Tables III–VIII. GATONE 5400 with very low intrinsic viscosity could not be extruded satisfactorily as evident from the low MFI values shown in Table I.

Crystal structure and crystallinity

The crystal structure of various poly aryl ether ketones summarized by Haris and Robeson²⁰ is shown in Table II. The influence of melt process parameters and subsequent drawing on orientation and crystal perfection was examined using WAXD. The crystallinity index of selected samples and their particle size is presented in Table III. It has been found that this family of polymers possesses orthorhombic unit cells and cell parameters are little

TABLE III
Particle Size and Structural Parameters of PEEK Yarn

Substrate	Particle size (Å)	Unit cell parameter (<i>a</i>)	Volume (Å ³)	Crystallinity index (%)	Draw temperature (°C)
P ₉	–	6.734	305.36	15.15	<T _g
P ₀	21.53	6.666	296.20	–	144
P ₀ (A)	46.13	6.678	297.80	28.0	144
P ₁ B	50.57	6.638	292.49	35.0	164
P ₅	62.05	6.961	337.29	36.0	190
P ₇	54.67	6.718	303.19	44.0	210

Standard JCPDS value of “*a*”: 7.747; *V*: 469.70.

affected by changes in either-ketone ratio's (decrease of mole percent ketone content along the chain backbone causes a slight decrease in b and c axes and a slight increase in a axis lengths).¹⁰ The variation in melt process parameters cause significant changes in structural parameters as evidenced in the results of particle size and crystal lattice parameter (a). The WAXD patterns of extruded and drawn samples shows that there is significant change in the half maximum peak width with variation in draw temperature and this has been reflected in both the particle size and unit cell parameter width (a). The particle size varied from 21.53 to as high as 62 suggests that the crystal lattice is rearranged according to the distance between planes. For any crystal, these planes exist in a number of different orientations each with its own d -spacing value. The WAXD patterns of samples was (Fig. 2) shown to illustrate this nature. It can be seen from the WAXD patterns that the samples with large crystal size show sharp peaks, where as samples with small crystal size exhibit broad peak width. It is further observed that samples drawn at increasing draw temperature generally show large

crystal size except for some variation observed in sample P₅ and P₇ which were drawn at 190 and 210°C, respectively. The crystal size which measured 21.5 Å near T_g temperature, measured 62 Å at 190°C, and beyond this temperature, the crystal size measured lower values. The increase in crystal size may be attributed to phase transition of small crystallites to larger crystallites. These results are consistent with the fact that increasingly well defined WAXD reflections are observed with increase in draw temperature indicating the development of change in crystal parameters with corresponding change in the development of oriented crystal structure. The principle WAXD reflection of PEEK has been found to be in 110 and 012 planes (Fig. 2). Although the crystal size observed in above samples lie in broad range between 21 and 62 Å, and the data obtained hints at possible relation between crystal structural parameters with crystallinity index and process parameters, it is felt that at this stage further investigation related to crystallization temperature and molecular diffusion is required to correlate these parameters with kinetics of crystal growth and possibly towards overall

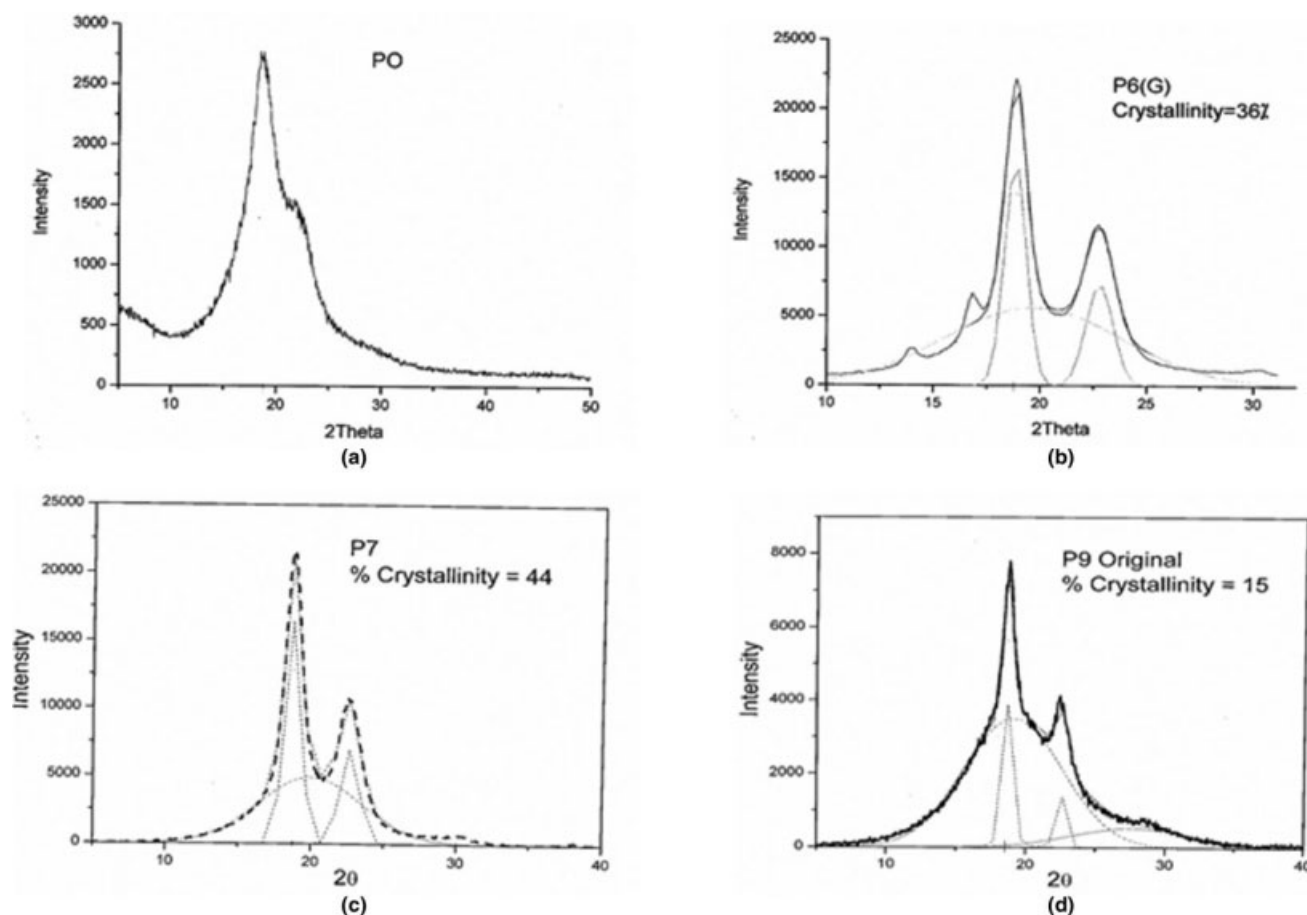


Figure 2 Wide angle X-ray diffraction photograph of PEEK filament drawn at different draw temperatures: (a) P₀ A (144°C); (b) P₆ G (200°C); (c) P₇ (210°C); (d) P₉ (< T_g).

TABLE IV
WAXD Data of Samples Drawn at a
Draw Ratio of Three

Sample	Crystallinity index (%)	Draw temperature (°C)
P ₉	15.0	<T _g
P ₂₀	–	<T _g
P ₁₈	15.2	160
P ₂₅ ^a	16.9	162
P ₂₅ RD ^b	30.7	162
P ₁ B	35.0	164
P ₃	35.0	170
P ₅	36.0	190
P ₆	36.0	200
P ₇	44.0	210

^a Draw ratio 2.

^b Draw ratio 5.

contribution to structure property relationships. Our results are consistent with the results of Wakelyn²¹ who has also reported variation in unit cell parameters with crystallization temperature.

The distance between the spinneret and the intermediate draw rollers was varied and as high as 100 cm was maintained to develop initial crystallinity in high molecular weight polymers (PEEK) which have very low crystallization rate. The WAXD patterns of selected samples are shown in Figure 2 and it can be seen that the width of peaks in particular phase pattern provide an indication of the average crystallite size. Although the peak broadening occurs as a result of variations in “*d*” spacing (Bragg’s law) caused by microstrain, the relationship between broadening and diffraction angle 2θ is different from that of crystallite size effects making it possible to differentiate between the two phenomena. The variation in the process parameters (drawing) used in the present study causes significant changes in the unit cell parameters of crystal lattice especially “*a*” which is dependent on the “*d*” spacing which in turn varies according to the nature of the material. The influence of draw temperature on structural parameters can be seen with the varying levels of crystallinity achieved, which vary from as low as 15% (P₉) to as high as 44% (P₇) (Tables III and IV and Fig. 2). From the analysis of data, it is observed that samples drawn below T_g (P₉), and at T_g, temperature exhibited crystallinity index in the range of 15–28%. This is because at temperatures lower than T_g temperature and at T_g temperature, mobility of PEEK chains is not enough to facilitate the alignment of molecules.

In one of the samples (P₂₀) (Table IV), the yarn was directly wound on to the take up device without any draw ratio and draw temperature (below T_g) to see the effect of winding speed on crystallization. Similarly, sample P₁₈ was also directly wound on to the take up device at draw temperature of

160° in the absence of the draw ratio. The idea was to study whether the temperature differential of the extruded yarn (350°C) is sufficient to cause any changes in the crystallization as is done in the case of fully oriented yarns (FOY), which are extruded and wound at high speeds without any draw ratio. The data (Table IV) show that neither of these two samples exhibit any appreciable level of crystallinity. This suggests that, on one hand in polymers exhibiting very low crystallization rates, the orientation produced by spinning at low speeds involves amorphous regions; secondly, it is the combination of time allowed to undergo initial crystallization (relaxation time) before the yarn enters the drawing zone and the optimum draw temperature-draw ratio that results in high crystallinity. The progressive increase in the crystallinity index values observed with increasing draw temperatures may be attributed to increased molecular mobility coupled with effect similar to annealing. Transition of less stable crystal phase to more stable crystal forms may take place when the as spun fiber is immediately subjected to further drawing as is done in the present case.

An analysis of the crystallization behavior of PEEK suggests that some similarity exists with conventional polyester except the local rearrangement of molecular chains and growth requires more time probably due to high melt viscosity of PEEK as a consequence of high molecular weight (>40,000). The complex melt behavior of PEEK at high temperature is not well understood (probably the oxidation of PEEK resulting in crosslinking at high temperature), which may cause other changes in the structural aspects. The volume expansion and change in specific volume of material as a function of temperature before and after extrusion may give a good indication of the possible changes in properties. The lower values of volume (Table III) observed with increase in draw temperature indicates increase in densities of the drawn fibers, resulting from crystalline orientation brought about by drawing.

The temperature dependence of viscosity during melt spinning was studied using Arrhenius relationship.

$$\eta(T) = A \exp(\Delta E/RT) \quad (2)$$

where ΔE is the activation energy of flow, R is a universal gas constant, and T is an absolute temperature.

TABLE V
TGA Analysis for Calculation of Activation Energy

Conversion level (%)	Activation energy (kJ/mole)	60 min Half life temperature (°C)
1	29.6	82.5
2.5	28.0	57.8

The value of activation energy evaluated using TGA analysis (Table V, Fig. 11) at three different heating rates (5, 10, and 15°C/min) shows value in the range 29.6 and 28.0 kJ/mol at 1 and 2.5% conversion levels, respectively. The high activation energy of flow exhibited by PEEK suggests that its viscosity is prone to rapid changes with small change or variation in temperature. Data obtained in the present case are in close agreement with those reported by previous studies,¹⁰ although a different approach has been used to (relationship between viscosity and shear stress) evaluate activation energy. Also, the characterization method used by us gives more accurate prediction. Various relationships established between parameters derived from WAXD are shown in Figures 3–5. The coefficient of correlation (r) and coefficient of determination (COD) obtained for the above parameters is summarized in Table X.

The above discussions illustrate that in the absence of stress-induced crystallization, which happens at high spinning speeds, the effect of draw temperature (at constant draw ratio) plays an important role that primarily affects the structure property relationships.

Sonic velocity

Charch and Moseley^{22,23} have shown that sonic velocity measurements which are independent of thickness can be used to quantitatively determine molecular orientation in fibers and has also been studied extensively for assessing the ballistic properties of some of the high performance fibers such as Kevlar. Further, there have been studies showing good correlation between sonic velocity and birefringence.²⁴ The sonic velocity data of PEEK and other conventional high performance fibers which have thermal properties close to that of PEEK are presented in Table VI–VII. Results of sonic modulus which is essentially a function of crystallinity are

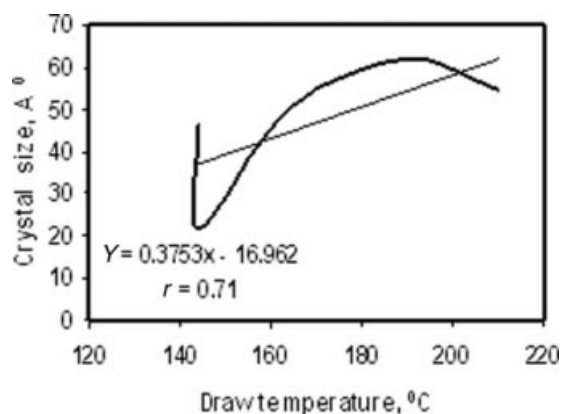


Figure 3 Correlation between draw temperature and crystal size.

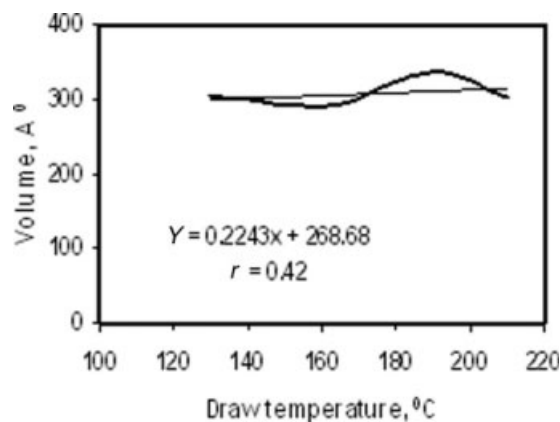


Figure 4 Correlation between draw temperature and crystal volume.

also presented in Table VI–VII. Sonic modulus (E) was evaluated using the following equation.^{25,26}

$$E = 11.3C^2 \quad (3)$$

where “ C ” is the sonic velocity in km/s. Using Moseley equation,²³ orientation factor (α) was evaluated and the results for selected samples are presented in Table VI.

$$\alpha = 1 - \frac{C_u}{C} \quad (4)$$

where C_u is the Sonic velocity for an unoriented filament and C is the Sonic velocity of the fiber under investigation.

Data presented in Table VI–VII shows the relevance of draw temperature on semi crystalline fibers like PEEK whose modulus varies with the draw temperature. Sample (P₁B) drawn near heat of distortion temperature and crystallization temperature (Fig. 12) exhibit high sonic velocity with corresponding high sonic modulus values. This can be explained in the light of higher mobility of

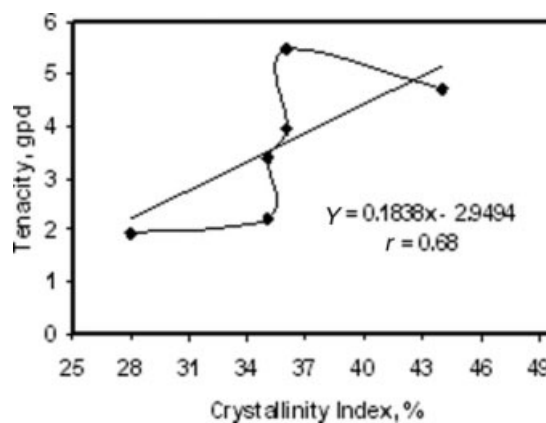


Figure 5 Correlation between crystallinity index and tenacity.

TABLE VI
Sonic Velocity Results of PEEK Fibers Drawn at a Draw Ratio (DR) of Three

Substrate	Transmit time (μs)	Sonic velocity (km/s)	Sonic modulus (gpd)	Draw temperature ($^{\circ}\text{C}$)	Mosley equation ^a (α)
P ₀	30.5	2.62	77.74	144	0.4969
P ₁ B	26.25	3.04	104.95	164	0.6273
P ₃	29.25	2.73	84.53	170	–
P ₅	30.75	2.60	76.48	190	0.4886
P ₆	28.0	2.86	92.24	200	–
P ₇	26.75	3.00	101.1	210	0.6130
P ₉	43.0	1.86	39.11	$<T_g$	–

^a Ref. 23.

molecules at this temperature which facilitates effective drawing and orientation of molecules. However, above this temperature (164°C) sonic velocity values decrease with increasing temperature up to 190°C suggests that the increased mobility of molecules might have caused some chain folding. The relative reduction in sonic velocity observed in the temperature range between 170 and 190°C appear to be due to random change in the geometrical alignment of molecules which are essentially inter molecular in nature. Beyond this temperature (190°C) samples [P₆ (DT 200°C and P₇ (DT 210°C)] approaches the value as that observed near 164°C indicating the combined effect of heat setting and drawing carried out in one process. The possible reason for the above behavior may be release of strains experienced as a result of high ram pressure applied during manufacturing and the thermal healing of voids between the fibrils. The draw temperature used is close to the temperature, where maximum rate of crystallization takes place and can be considered as optimum temperature, at which the material exhibits high degree of crystallinity. A comparison of results of the samples shown in Table VI reveals that the increased orientation is brought about by the combination of draw temperature and draw ratio that has resulted in high sonic velocity and typifies the extent of reduction in plasticity of material.

A comparison of the results of conventional high performance fibers with that of PEEK (Table VI–VII)

TABLE VII
Conventional High Performance Fibers

Substrate	Transmit time (μs)	Sonic velocity (km/s)	Sonic modulus (gpd)
High tenacity dope dyed polyester	22.5	3.56	143.21
Medium tenacity undyed polyester	25.5	3.14	111.41
High tenacity polyester undyed	21.0	3.80	163.17
Medium tenacity nylon	34.25	2.34	61.87

and Figure 6 shows that the pulse velocity and sonic modulus of PEEK are at par with the medium tenacity polyester but higher than that of nylon.

Birefringence

Birefringence data obtained for conventional fibers are shown in Table VIII. The data could not be compared with that of PEEK fibers as we could not see any fringes probably due to the property of opaqueness induced during the process of drawing. To test the possibility of the existence of relationships, we also tried to theoretically estimate birefringence values on the basis of reported literature^{27,28}. However, none of the equations exactly fit the experimental data and a strong positive deviation was observed from the calculated one. In general, the overall orientation of fibers is expected to increase with increase in draw ratio and draw temperature (up to 200°C) before leveling off to a constant value.

Figure 7 shows the relation between birefringence and sonic velocity for conventional high performance fibers. The correlation between these two parameters in the case of PEEK is also expected to be

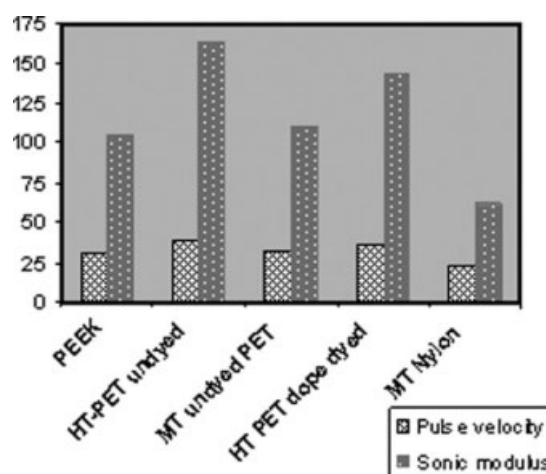


Figure 6 Sonic velocity values of PEEK and other high performance fibers.

TABLE VIII
Birefringence Data of Conventional High Performance Fibers

Substrate	Phase difference (nm)	Diameter (mm)	Birefringence (Δ_n)
High tenacity dope dyed Polyester	830	24.27	0.21
Medium tenacity undyed polyester	810	23.44	0.21
High tenacity polyester dyed	772	21.76	0.22
Medium tenacity nylon	325	26.78	0.08
PEEK	–	–	Fringes could not be seen

similar to that of polyester as the latter has a structure similar to that of PEEK. The birefringence values of the some of the high modulus yarns developed earlier measured higher values (50–57%) when compared with those reported earlier²⁵ owing to the high degree of orientation of yarns, whereas the results of medium tenacity nylon measured values to those reported earlier.

Mechanical properties

The stress–strain properties of the yarn to a large extent depends on the manner in which the chain molecules are arranged, which can be suitably reorganized to achieve enhanced strength, modulus, and thermal stability. The mechanical properties of selected samples extruded and drawn under various conditions are presented in Table IX. The force elongation curves of selected samples are shown in Figure 8(a,b). The effect of draw temperature on tenacity and modulus is shown graphically in Figures 9 and 10. The influence of higher draw temperature (170–200°C) (keeping draw ratio constant) on tensile properties was further investigated. It can be seen from Table IX that appreciable increase in tenacity can be achieved at draw temperatures above 170°C. It can be seen that at constant draw ratio of three, the effect of draw temperature appear to have a significant influence on the stress–strain properties. With the progressive increase in draw temperature from T_g , the tenacity increases with corresponding increase in modulus up to a draw temperature 200°C. The increase in tenacity observed in samples P₃–P₇ at higher draw temperatures is primarily a result of the development of crystallinity which causes densification of the structure, which in turn locks the chains tightly in the fiber structure preventing their slippage during the tensile test.

At 200°C, the tenacity shows a significant jump when compared with 190°C and then starts decreasing (210°C). The reduction in tenacity beyond 200°C may be due to the disorder in the packing of chains, which is due to misalignment of adjacent molecular chains. This indicates that to achieve superior tensile properties, high molecular weight polymers like

PEEK requires high temperature rather than high draw ratio. Although the elongation behavior of the samples is inconsistent and did not show any definite trend, it is interesting to note that the elongation which shows a progressive increase with increase in draw temperature (barring P_{Gr} sample), recorded a minimum value at 200°C. The probable reason for the above behavior may be due to the combined effect of following factors (a) crystalline orientation, (b) effect similar to heat setting, and (c) densification of structure. Our views are consistent with the fact that modulus which measured a highest value at 200°C shows reduction in modulus beyond this temperature. PEEK being very sensitive to temperature changes (very high activation energy) (Table V), the variation in temperature is bound to affect the spin line stress which in turn influences the filament denier and extension.

At low take up speeds, isolating the influence of draw temperature and draw ratio, essentially amorphous fibers are produced. Hsuing¹⁰ concludes without taking into consideration the effects of other spinning process parameters that high spinning speed results in development of crystallinity in the as spun fibers. This may be due to the high spin line tension and drag force that may partially orient the fibers. Sample P₂₀ which was wound on to the take up package (100 mpm) below T_g temperature and

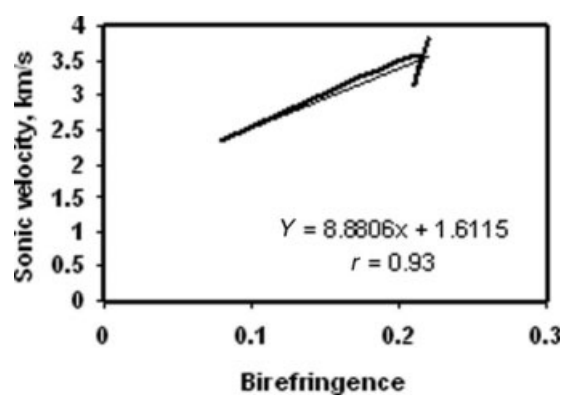


Figure 7 Correlation between birefringence and sonic velocity.

TABLE IX
Stress–Strain Data of Samples Drawn at Various Draw Temperature
(At Constant Draw Ratio of Three)

Sample	Tenacity (gpd)	Elongation (%)	Work of rupture (g cm ⁻¹)	Modulus (gpd)		Draw temp. (°C)
				0–1%	1–2%	
P ₉	1.40	86.48	15,220.1	29.95	25.53	<T _g
P ₂₀	1.70	110.0	–	–	–	<T _g
P ₀	1.93	22.47	3939.3	31.47	28.24	144
P _{Gr}	1.47	85.52	11,282.5	45.11	37.64	144
P _{1B}	2.23	26.13	6257.1	38.62	33.34	164
P ₃	3.37	29.86	6340.5	54.08	48.28	170
P ₅	3.93	33.12	6445.4	63.0	56.61	190
P ₆	5.48	17.72	2578.6	80.10	67.10	200
P ₇	4.70	25.44	5813.0	71.27	61.32	210
P ₂₅ ^a	1.0	120.0	–	–	–	162
P ₂₅ RD ^b	2.5	33.8	–	–	–	162

^a Draw ratio 2.

^b Draw ratio 5.

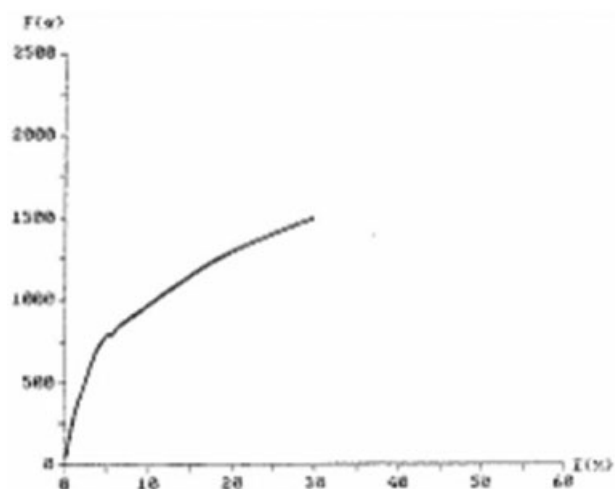
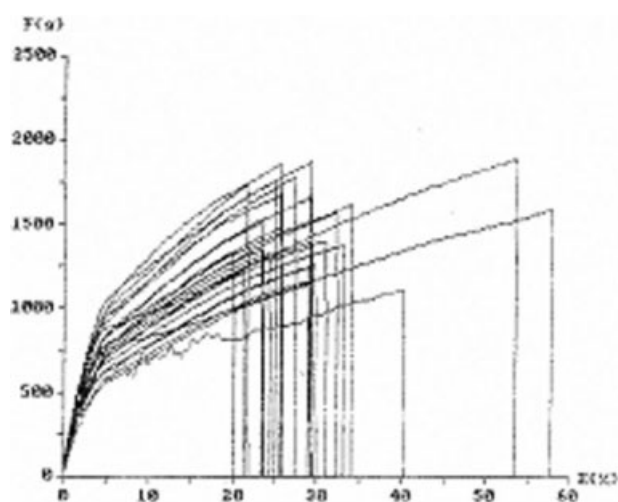


Figure 8 Force elongation curve of PEEK yarn (individual). (a) Force elongation curve of PEEK yarn (average).

with no difference in circumferential speeds between the rollers exhibited low tenacity (1.7) and very high elongation (110%), which suggests that the material is more or less amorphous. The yarn samples (P₀ and P_{Gr}) were drawn at 144°C, and the known T_g of PEEK measured very low tenacity and high elongation similar to that observed in sample P₂₀. Our results are consistent with that discussed in the previous section.

From the above discussions, it is clear that any appreciable improvement in the tenacity is possible only when the samples are drawn above T_g. Hsuing¹⁰ in his studies on PEEK material is of the view that significant improvement in the development of crystallinity is achievable in the as spun fibers that are drawn above T_g. Our results in the above case are in close agreement to the work reported by Hsuing.¹⁰

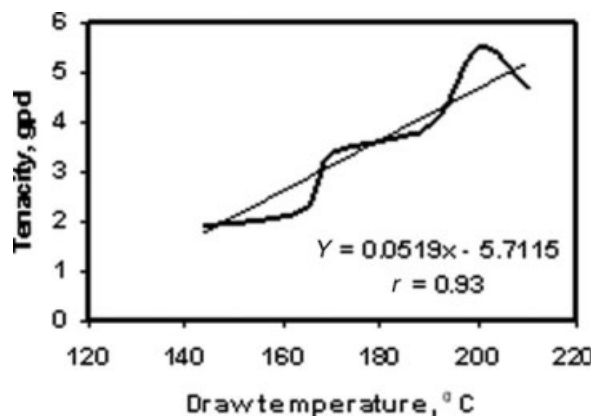


Figure 9 Correlation between draw temperature and tenacity.

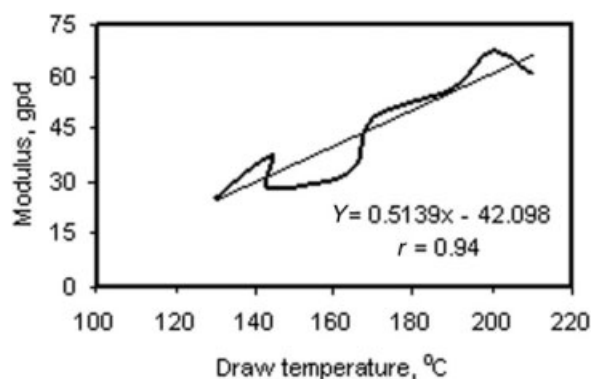


Figure 10 Correlation between draw temperature and modulus (force-elongation).

The effect of two stage drawing was investigated and it can be seen from the results (Table IX) that sample P₂₅ prepared from single stage drawing with a draw ratio of two measured very low crystallinity and tenacity. Sample P₂₅ RD, under the same process conditions as used in sample P₂₅ and redrawn in two stages with draw ratio of two and five measured higher value. This suggests that a two stage sequential process is better than the single stage process especially when the spinning speeds used are low (100 mpm). Generally speaking, orientation is observed to increase most during the first stage of drawing and continues to increase even in the second stage drawing due to the lower degree of orientation in the as spun material.

Although the mechanical properties exhibit a consistent behavior with draw temperature, a general inference in the above case is not possible because of the dependence of stress strain properties on a number of process variables that includes both spinning and drawing. From the above discussions, it is observed that the influence of draw temperature, take up speed, draw ratio contributes for the tensile properties. It is difficult to isolate the influence of a particular parameter on tenacity in the above samples studied.

Correlation properties

The various spinning parameters that have been found to influence structure property relationships

have been studied to provide a wider understanding of the relationship between these properties. The results are tabulated in Table X and graphical representation is shown in Figures 3–5, 7, 9, and 10. The relationship between various properties was measured on the basis of strength of the linear association between each pair. The correlation coefficient (r) and COD were determined with the help of regression line. It can be seen from Table X that moderate to strong correlation exists between draw temperature versus particle size, crystallinity index versus tenacity, draw temperature versus tenacity, birefringence versus sonic velocity, draw temperature versus modulus, whereas the relationship between draw temperature and crystal volume shows very poor correlation. The application of partial and multiple correlation statistical techniques is being presently worked out to identify primary parameters influencing the structure property relationships so that meaningful conclusions can be drawn.

TGA

TGA studies were carried out on the drawn samples to ascertain possible changes in the decomposition behavior. Figure 11 shows TGA curves of PEEK yarn at three heating rates of 5, 10, and 15°C/min. It can be seen that the first initiation of decomposition is observed between 513 and 537°C and completed at around 600°C. The weight loss was found to be less than 1% up to 537°C, and the total weight loss between 537 and 600°C was observed to be 22%. This indicates that PEEK can be used for short term exposure at high temperature applications up to 500°C. The different heating rates used was found to affect the onset temperature with sample scanned at 15°C showing higher transition temperature of the order of 24°C as against the sample scanned at 5°C/min.

Differential scanning calorimetry (DSC)

The DSC curves of samples drawn to achieve different levels of crystallinity are shown in Figure 12(a–c). A comparison of the samples exhibiting low crystallinity [Fig. 12(a,b)] and high crystallinity [Fig. 12(c)] reveals

TABLE X
Relationship Between Various Parameters

Parameters	Coefficient of correlation (r)	Coefficient of determination (COD)
Draw temperature vs. crystal volume	0.42	17.64
Crystallinity index vs. tenacity	0.68	46.24
Draw temperature vs. particle size	0.71	50.41
Draw temperature vs. tenacity	0.93	86.49
Birefringence vs. sonic velocity	0.93	86.49
Draw temperature vs. modulus	0.94	88.36

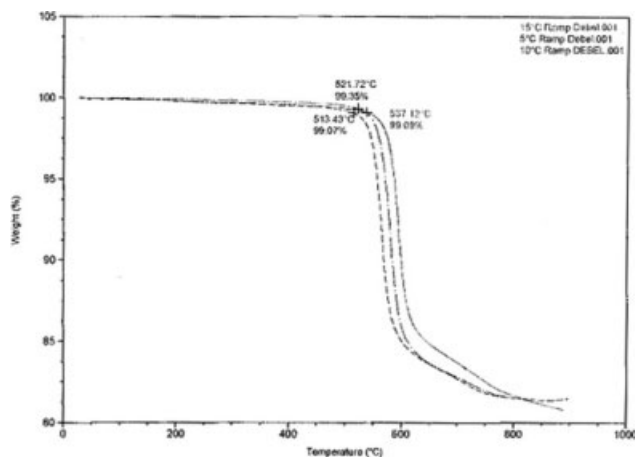


Figure 11 TGA thermogram of extruded and drawn PEEK yarn at three different heating rates.

many interesting features. DSC curve of sample shown in Figure 12(b) considered more or less amorphous exhibited onset of T_g at 139°C, Peak T_g at 142°C, cold crystallization peak at 168°C, and melting point at 340°C. The crystallization peak observed at 167°C is $\sim 40\%$ of the area under the curve of melting giving indication of the semi crystalline behavior of PEEK yarn.

Figure 12(c) shows the DSC curve of drawn sample with crystallinity index in the range of 35–40%. A comparison of the above samples shows that the sample [Fig. 12(c)] exhibits higher melting point (350°C). The cold crystallization peak which was very predominant in amorphous sample [Fig. 12(b)] has smoothed and is not present in sample shown in Figure 12(c). The double endotherm observed in amorphous sample [Fig. 12(a)] at 217°C and 287°C is found to be of a typical behavior of aromatic polycondensates that includes PPS and PET.¹⁰ Summarizing it can be concluded that PEEK yarns can be prepared that exhibit higher thermal stability (T_g and melting point) with corresponding decrease in cold crystallization temperature, which in some case may approach T_g . Hsuing¹⁰ has observed that the area under crystallization and melting peak of as spun fibers to be roughly equal and concluded that the fibers produced under the above condition are amorphous. However, the above trend was not observed in the present case probably due to the different crystallinity levels achieved as a result of the spinning variables used.

Using a value of 130 J/g^1 for 100% crystalline PEEK, we have theoretically calculated the crystalline fraction of as spun PEEK and drawn fibers under various conditions. It was observed that the average DSC crystallinity varied from 16 to 45% with multifilament PEEK yarn drawn at higher draw temperature and draw ratio of three exhibits high

degree of crystallinity. This suggests that PEEK material can be engineered to suit and meet various end use applications.

Scanning electron microscopy (SEM)

Surface behavior of drawn samples has been studied under SEM at different magnifications. Figure 13 shows the SEM photographs of extruded and drawn PEEK yarns. The filaments are cylindrical in shape with smooth surface, uniform in diameter, and transparent with no irregular striations on their surface.

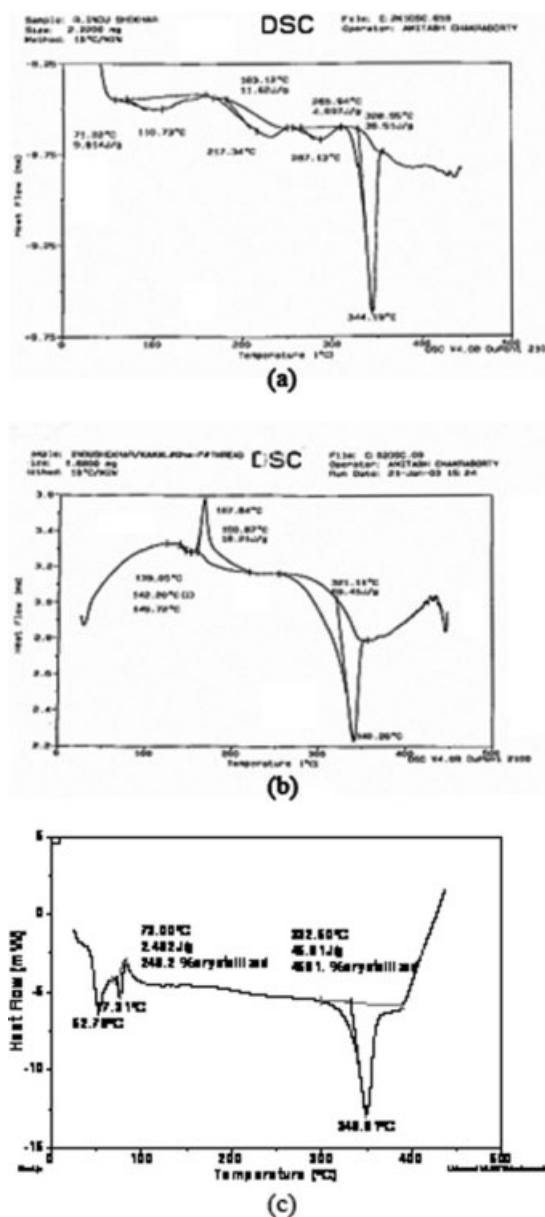


Figure 12 DSC thermogram of PEEK yarns. (a and b) Drawn samples with low crystallinity (amorphous) and (c) drawn sample with good crystallinity.

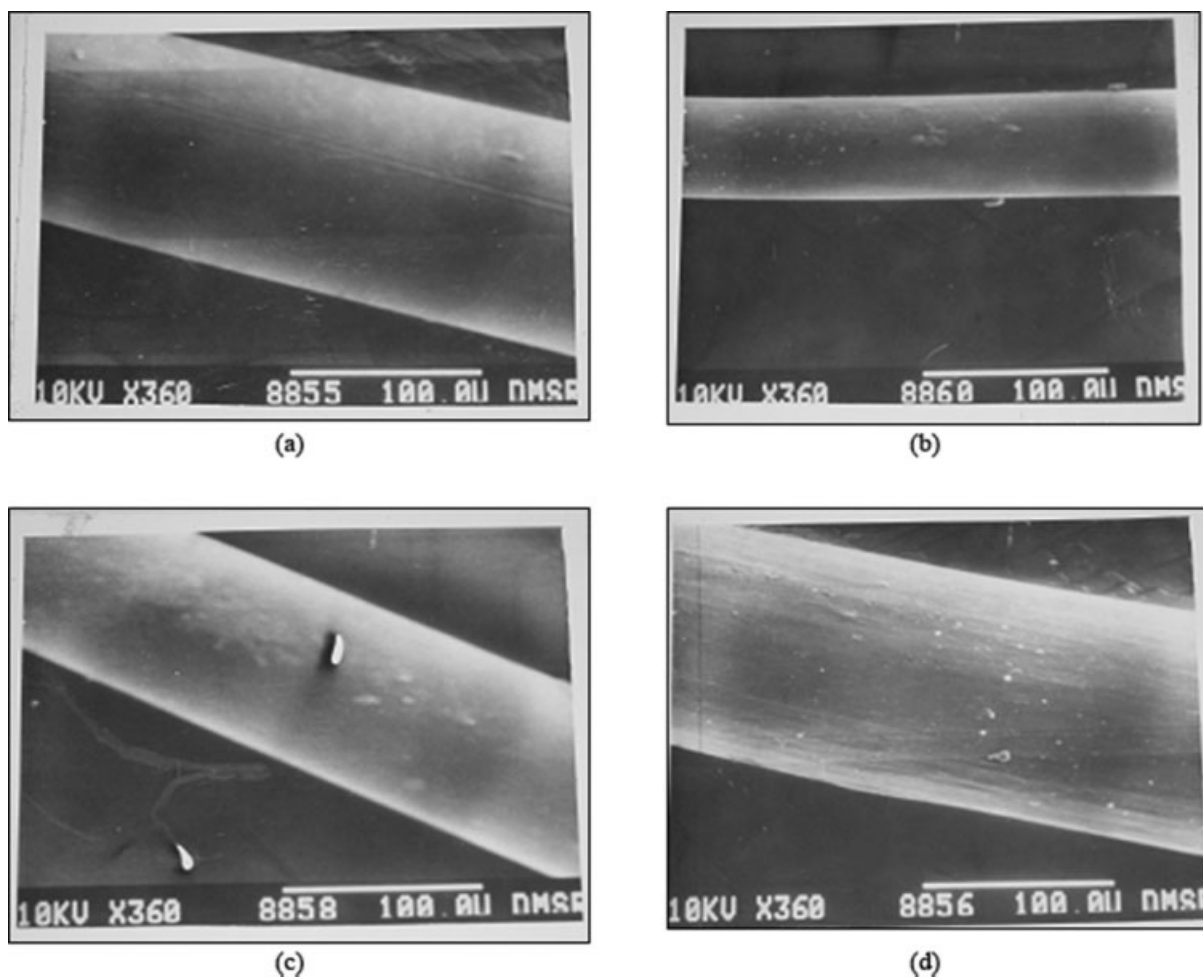


Figure 13 SEM photographs of PEEK yarns.

The photographs did not show any irregular twists or convolutions on the fiber surface.

CONCLUSIONS

- The PEEK polymer can be extruded with useful properties suitable for an array of applications that include structural components, radomes, and other aerospace applications. The fiber grade PEEK can be tailor-made with special properties during the extrusion process to produce high tenacity-high modulus yarn and can be effectively processed with reinforcing materials like glass.
- A progressive change in selected unit cell dimension and volume with crystallization temperature is observed. Crystal lattice parameters (unit cell parameter-width " a ") decreased with progressive increase in draw temperature. The implication of these changes is important as this behavior can be effectively used to prepare a wide range of fibers to correlate structure property relationship.
- The tensile strength results of PEEK filament yarn were at par with the conventional fibers. The tensile strength of oriented yarn correlates well with degree of crystallinity (30–44%). This was confirmed by WAXD.
- The sonic velocity properties of PEEK filaments are comparable to that of conventional Nylon (2.34 km/s) suggests that PEEK can be used for high temperature applications involving strength bearing structures.
- The data generated demonstrate that with progressive increase in draw temperature, crystallinity, increases. Useful properties were observed at an optimum draw temperature of 200°C (may be region of maximum crystallization rate) primarily attributed to the maximum crystallization temperature and the heat setting effect.
- The thermal stability of PEEK yarn under dynamic conditions (TGA) suggests that PEEK can be used for high temperature applications. The weight loss was less than 1% up to 537°C and increased to 22% at 600°C. This suggests that the

PEEK fiber can be used for applications up to 250–260°C (continuous usable temperature), whereas for applications that involve short term temperature exposure, it can be used up to 500°C (in nonenriched oxygen atmospheres).

- The relationships established between various parameters (draw temperature versus crystallinity index, crystallinity index versus Tenacity, draw temperature versus tenacity, birefringence versus sonic velocity, draw temperature versus Modulus) shows moderate to good correlation.

It can be concluded that the thermal characteristics established using TGA and DSC make PEEK fibers attractive components as nonconsolidated thermoplastic matrix components for designing a spectrum of reinforcement structures (KFRP, CFRP) that are adaptable to complex structures of different end use applications.

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