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SMC-TR-93-29

AEROSPACE REPORT NO
TR-93(3935)-10

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Crystallinity and Dielectric Properties of PEEK, a Thermoplastic Poly(ether ether ketone)

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1 May 1993

Prepared for

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P.O. Box 92960
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Contract No. F04701-88-C-0089

Engineering and Technology Group

THE AEROSPACE CORPORATION
El Segundo, California

93-13954



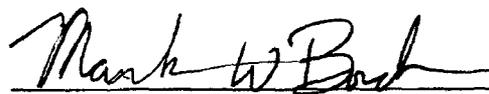
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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-88-C-0089 with the Space and Missile Systems Center, P. O. Box 92960, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by R. W. Fillers, Principal Director, Mechanics and Materials Technology Center. Captain Borden was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.


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 26 MAY 93
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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				
1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) TR-93 (3935)-10		5. MONITORING ORGANIZATION REPORT NUMBER(S) SMC-TR-93-29		
6a. NAME OF PERFORMING ORGANIZATION The Aerospace Corporation Technology Operations	6b. OFFICE SYMBOL <i>(If applicable)</i>	7a. NAME OF MONITORING ORGANIZATION Space and Missile Systems Center		
6c. ADDRESS (City, State, and ZIP Code) El Segundo, CA 90245-4691		7b. ADDRESS (City, State, and ZIP Code) Los Angeles Air Force Base Los Angeles, CA 90009-2960		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL <i>(If applicable)</i>	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F04701-88-C-0089		
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
				WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Crystallinity and Dielectric Properties of PEEK, a Thermoplastic Poly(ether ether ketone)				
12. PERSONAL AUTHOR(S) Giants, Thomas W.				
13a. TYPE OF REPORT	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) 1 May 1993	15. PAGE COUNT 35	
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Insulation Conductivity Crystallinity Breakdown Strength	
FIELD	GROUP	SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The overall objective of this study was to investigate the interdependence of specific dielectric properties of polymers on their fundamental molecular parameters in order to optimize the application of these polymeric materials in critical SMC systems. SMC systems utilize polymeric materials in applications involving high voltage (HV) insulation in systems aboard DSCS, Milstar, and several classified spacecraft. Studies of polymer dielectrics have shown that changes in polymer morphology can influence fundamental electrical properties leading to premature breakdown. This investigation focused on the effect of polymer morphology on the electrical characteristics of PEEK, a high temperature insulating thermoplastic, as part of an effort in understanding the causes of dielectric breakdown. This amorphous material was thermally annealed to produce a range of crystallinities. The results of this effort showed that as the crystalline/amorphous ratio of the polymer increases, the dielectric breakdown strength is reduced. Electrical conductivity of the material was also shown to decrease. When translated to resins, blends.				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL	

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE (Continued)

and advanced composites where environmental aging or thermal cycling can influence the morphology of the material, any reliance on the maintenance of stable electrical properties may have to be carefully considered. The introduction of advanced materials with tailored properties that involve different families of polymers will require a sophisticated understanding of the morphology of materials and the processes by which it varies. This will not only be important for enhancing mechanical properties of materials but also for recognizing the subtle influences that affect electrical properties of materials.

PREFACE

The author wishes to thank Robert Castaneda for materials preparation, density gradient, thermal and dielectric property measurements, Paul Adams for the x-ray data and interpretation, and Dr. Frank Hai for insightful discussions on the dielectric measurement techniques.

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INTRODUCTION

The objective of this work was to investigate and understand the causes of electrical breakdown in high voltage (HV) insulation systems aboard SMC spacecraft and to identify changes in HV configuration and/or materials that will postpone or eliminate such breakdown.

The original hypothesis for this work was that charge trapping is a key parameter in dielectrics and that structural disorder is the basis for trap formation. This disorder can include crosslinks, free volume holes, impurities, partial charges on chemical groups, and disorder at the crystalline/amorphous interface. Two-dimensional surfaces arising from phase separation are expected to provide key locations for electron trapping. Phase boundary networks help prevent an uninterrupted electron path parallel to an applied field, thereby reducing chances for impact ionization. Strong trapping is also expected to limit overall current (i.e., dc conductivity) as well as impact the ultimate dielectric breakdown properties. Phase-separated polymer microstructures are hypothesized to force breakdown paths to assume more tortuous routes around trap-rich two-dimensional phase boundaries, compared to polymers in which there are only "point defects" (free volume holes and crosslinks).

Our approach was to assess the effect of polymer morphology on the dielectric properties of insulating materials with a focus on elucidating the interrelationship between the crystalline/amorphous nature of the polymer and its effect on dielectric breakdown strength.

Our specific objectives were to monitor thermal aging effects on materials and to study the interrelation of conductivity, permittivity, and dielectric breakdown strength during aging. In order to accomplish this, a polymer system was chosen which minimized contributions from other parameters and focused on the specific crystalline/amorphous morphology.

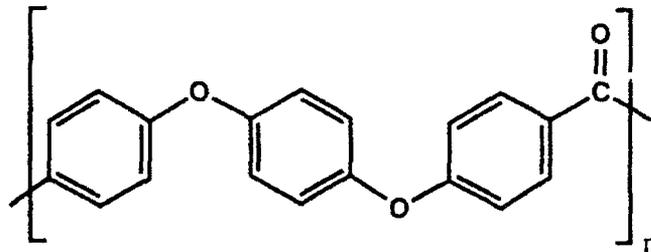
BACKGROUND

Historically, significant electrical property data have been obtained from studies involving the polyalkylenes, particularly polyethylene and polypropylene, where the degree of crystallinity can be varied easily without changing any other fundamental parameter.^{1,2}

For spacecraft applications, however, property requirements other than electrical characteristics often drive the choice of material and exceed those where polyalkylenes are useful. Advanced materials and composites with increased performance capability are more complex and must be evaluated in order to be able to predict both their long-term mechanical and electrical behavior.³ Long-term aging, thermal cycling, etc. can cause deterioration in mechanical properties and is a primary concern for both neat and composite materials.⁴⁻¹⁰

The case for the polyalkylenes is rather elegant in that the annealing conditions change only the crystalline/amorphous nature of the polymer and allow an unambiguous evaluation of the relationship between morphology and electrical characteristics. Since many of the high temperature polymers desired for their insulating characteristics are rather complex molecules, they do not lend themselves well to an evaluation of this kind. However, one high temperature thermoplastic, a poly(ether ether ketone), can be thermally annealed to produce varying degrees of crystallinity. This can be accomplished without the attendant chemical changes that can interfere with a fundamental study of this kind. This is a common problem with polymers whose aging characteristics can result in a variety of changes affecting ultimate properties during an annealing process and therefore contribute some ambiguity to the concept under study.¹¹ A review of the factors affecting the electrical strength of polymers and the problems associated with understanding breakdown processes have been presented from the standpoint of their inherent properties, such as chemical structure, etc.¹²

The material chosen for this study, PEEK, is produced by ICI Americas. This material is a high molecular weight thermoplastic with good thermal stability whose chemical structure is essentially unchanged when exposed to thermal cycling or annealing. The only change exhibited by this material when the amorphous form is subjected to annealing is in its physical morphology.¹³ Thus our study of the dielectric properties of this material will not be confused by other parameters, such as chemical degradation or incomplete cure.



Repeat unit of a poly(ether ether ketone) (PEEK)

The PEEK material used in this work was supplied in an unoriented amorphous film form with a nominal thickness of ~ 10 mils. According to the manufacturer the PEEK film is considered to be less than 1% crystalline in the amorphous form. Crystallinity in this material can be induced either by thermal annealing above its glass transition temperature or by cooling from the melt. The useful mechanical properties of the film are said to be maintained to a crystallinity value of approximately 30%, beyond which the material becomes too brittle for useful application. In order to avoid batch to batch property variations due to manufacturer's processing, comparable measurements were made on separate single sheets of annealed material.

Our approach has been to vary the crystalline/amorphous ratio in PEEK by selective annealing of the film in an inert atmosphere. The resultant samples were characterized by thermal analysis, density gradient, and x-ray crystallographic techniques. The electrical conductivity, dielectric constant, and dielectric breakdown strength of the annealed samples were measured and the relationship between the morphological nature of PEEK and its effect on the electrical properties were examined. The experimental details of this work will be described and the property relationships compared.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used as a guide in assessing the annealing conditions which would produce the widest range of crystallinities. DSC curves were obtained with a Mettler TA 3000 differential scanning calorimeter. This capability was also used to understand how PEEK behaves under a variety of thermal conditions.

Thermal Annealing

The amorphous as-received PEEK was subjected to thermal annealing under an atmosphere of argon in a convection oven using a variety of time/temperature parameters designed to provide a range of useful crystalline/amorphous ratios. Sample strips of PEEK film taken from a single sheet were placed between clean glass plates to maintain planarity and the temperature was monitored with thermocouples placed in close proximity to the film. Samples were annealed in a manner designed to produce the widest variation in density without affecting the integrity of the material. Useful crystallinity values up to approximately 40% can be attained in this way. A wide variety of annealing conditions were examined, including a range of cooling conditions. The material undergoes rapid crystallization above its glass transition temperature and conditions must be controlled carefully in order that suitable samples be obtained. On completion of the annealing process, the samples were cooled to room temperature at a constant rate and stored.

Crystallinity Determination

The most precise determination of the degree of crystallinity was made by measuring the density of the samples and relating the values obtained to the measured density of amorphous PEEK and the calculated density for fully crystalline PEEK. A Technic density gradient column meeting the temperature and dimensional requirements of ASTM D1505-60T was used to determine the density of the annealed PEEK samples prepared for this study. An aqueous sodium bromide solution was selected to encompass the range of densities expected for the amorphous/crystalline range of the material. Calibrated density standards were introduced into the column and allowed to descend slowly until they reached the level where the density of the liquid was equal to the density of the standard. The PEEK sample densities could then be determined from a graph of height versus density.

X-ray Diffraction

X-ray diffraction (XRD) studies were also performed to gain additional information on polymer morphology and to obtain an independent estimate of the crystalline/amorphous ratio. Unfortunately, the more accurate methods require the measurement of completely amorphous and crystalline samples. Since the 100% crystalline form of PEEK can not be obtained, a peak intensity approximation technique was used. Theta two-theta scans were recorded with copper radiation using a computer-controlled Philips Electronics Instruments APD3720 vertical powder diffractometer equipped with a theta compensating slit and a scintillation detector. Samples were cut to 5 mm × 5 mm and mounted to a zero background plate consisting of single crystal quartz cut 6° off the c-axis. This plate has no XRD reflections in θ - 2θ scans and produces very little background scatter. Scans were recorded from 2° to 60° with a step size of 0.02° 2θ and a count time of 1 second. In order to measure the percent crystallinity of the PEEK samples, the XRD pattern of a completely amorphous PEEK specimen was superimposed on the pattern of a semicrystalline specimen. An intensity scaling factor was applied to the amorphous pattern so that it best approximated the intensity of the amorphous component in the semicrystalline sample. This was performed so that the discrimination of the amorphous and crystalline contributions to the XRD patterns would be as reproducible as possible. On a hardcopy plot, a baseline was then drawn underneath the amorphous pattern and the amorphous and crystalline contributions were then cut out and weighed on an analytical balance in order to measure the percent crystallinity. For the measurement of the full width at half maximum (FWHM) of the crystalline reflections, the pattern of an amorphous pattern was similarly fitted to the amorphous component of a mixture and digitally subtracted to produce the XRD pattern of the crystalline component. The results from the density gradient method were compared with those from the XRD method.

Conductivity Measurements

The electrical conductivity of a sheet material is calculated using the expression $\sigma = (L/A)(I/V)$ where L is the thickness of the sheet, A is the cross-sectional area conducting current I, and V is the voltage applied across the sheet. Therefore, the conductivity of PEEK was measured by monitoring I as a function of V. These current versus voltage studies were performed on 7.5 cm square samples of PEEK having a nominal thickness of 10 mils. Each sample was prepared for test by sputter depositing a gold film on the bottom surface and a similar film in the form of a 5-cm diameter spot enclosed by a guard ring on the top surface. The sample was inserted in the test fixture, with the bottom surface in contact with the flat surface electrode at high voltage and the circular spot and guard ring in contact with the spherical electrodes at ground potential. The entire assembly was placed under vacuum in a chamber with feedthroughs to accommodate the electrical inputs and outputs.

For measurements of I at various values of V between 0 and 500 V (or stress from 0 to 20 kV/cm), each sample was conditioned and tested as follows: For the lowest voltage V_1 , the voltage from the dc power supply (Electronic Measurement Inc. TCR 600 SI) was set at 50 V above this value and applied to the sample for one hour. The voltage was then reduced to V_1 , producing a change in the current (monitored with a Keithley 610C electrometer) that decreased with time. Current I_1 corresponding to voltage V_1 was recorded only after the current had stabilized. This sequence was repeated for several values of V up to and including 500 V. Conductivity for each sample of known crystallinity was calculated at each value of V to indicate how σ varied with voltage (or electrical stress) and with percentage crystallinity.

Dielectric Constant Measurements

The dielectric constant for each sample is calculated using the expression $\epsilon = (C/\epsilon_0)(L/A)$. The value $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of space and C is the capacitance measured at 1 kHz and 23°C, using an Andeen-Hagerling Model 2500A capacitance bridge.

Dielectric Strength Measurements

The dielectric strength measurements were performed using a breakdown test fixture consisting of two 1-in. diameter brass cylindrical rod electrodes with rounded edges. Each sample sheet was placed between the two electrodes and immersed in a dielectric fluid (Fluorinert FC 77). A 60 Hz ac voltage increasing at a constant rate was applied to the top electrode using a Biddle 40 kV breakdown test supply with automated ramp capability. The bottom electrode was tied to ground potential. During test, the Biddle test voltage was monitored as a function of time using an XY recorder, generating a straight line with constant slope up to the breakdown point. At breakdown of the sample, a drop in Biddle voltage occurs and is recorded on the plot, giving precisely the breakdown voltage. In these breakdown studies, a minimum of 10 breakdown measurements per sample was obtained.

RESULTS

This differential scanning calorimetry curve for the as-received amorphous PEEK shows its behavior as the temperature is raised from ambient through its melting temperature (see Figure 1).

An endotherm is observed in the region of 153°C defining the glass transition temperature (T_g) of PEEK. With increasing temperature, a crystallization exotherm is observed at approximately 185°C. As the temperature increases further, a point is reached where the crystalline material melts, as shown by the endotherm peaking at 340°C.

By thermal annealing the sample for different lengths of time at selected temperatures, amorphous PEEK can be converted into a material with varying degrees of crystallinity. The behavior of the material resulting from four different annealing processing conditions is seen in the DSC scans in Figure 2.

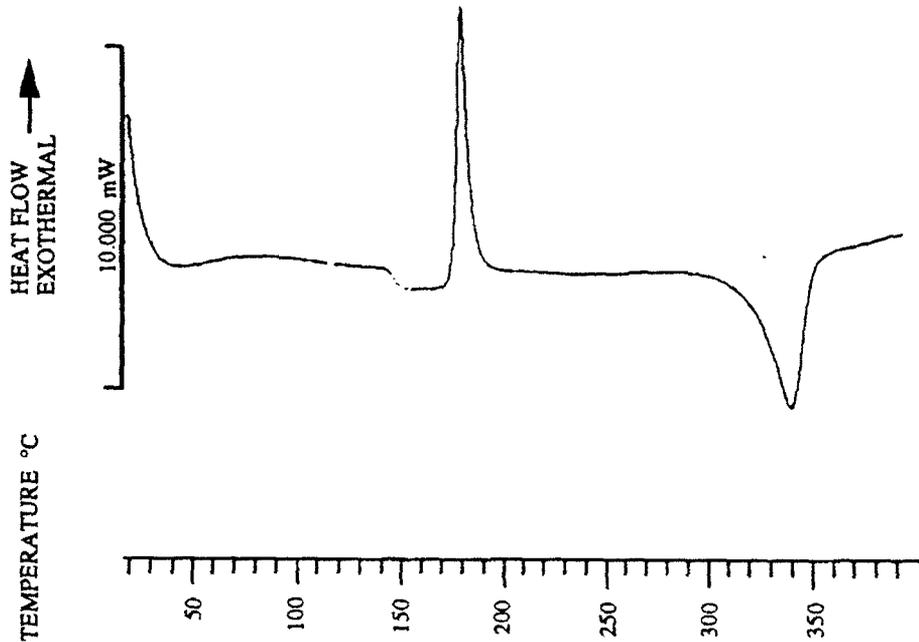


Figure 1. Differential scanning calorimetry curve at 20°C/min of unoriented amorphous PEEK.

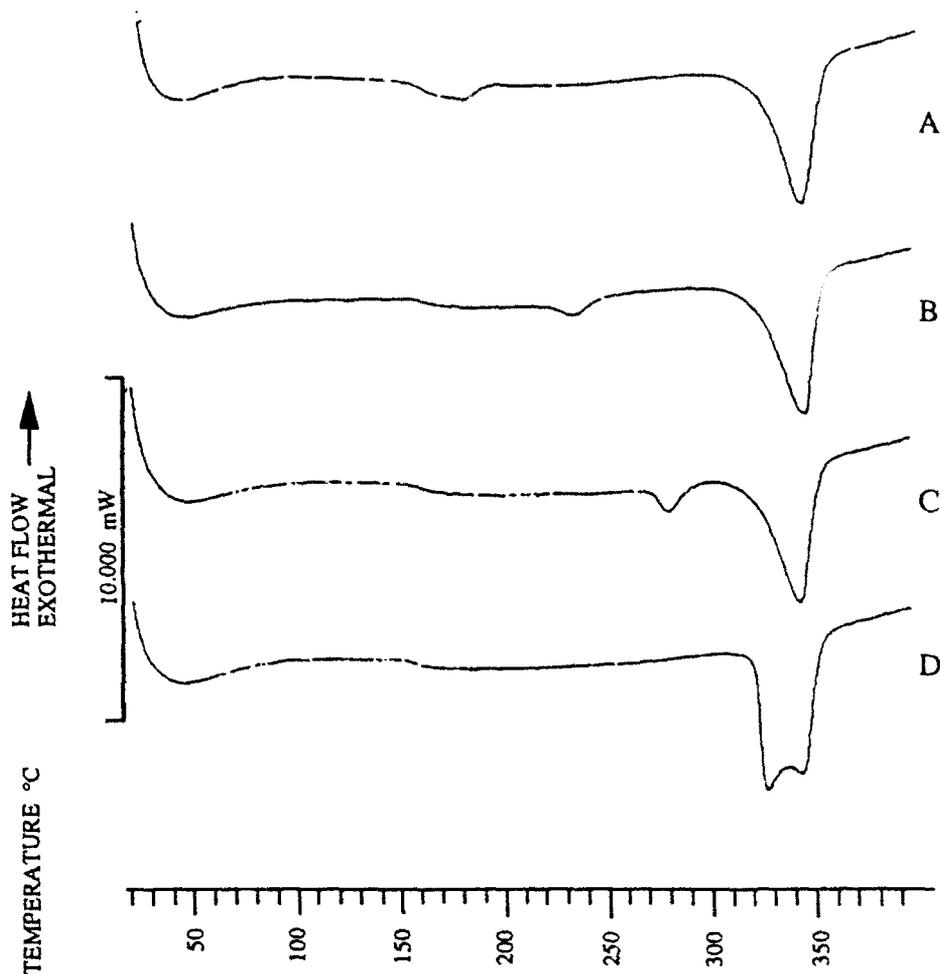


Figure 2. Differential scanning calorimetry curve at 20°C/min of annealed PEEK: crystallized isothermally at 160°C for 1 hr (A); 210°C for 1 hr (B); 260°C for 1 hr (C); 310°C for 1 hr (D).

In these examples the material has been isothermally crystallized at different temperatures and then cooled to room temperature. All scans in Figure 2 exhibit a similar T_g at 153°C as that seen in Figure 1. In scans A through D, in addition to the melt endotherm at 340°C, a lower temperature endotherm is also observed. The lower temperature endotherms that occur in these DSC scans represent melting of the crystals formed during the annealing process. In each instance the lower melting endotherm occurs at a temperature slightly higher than the annealing temperature. As the isothermal annealing temperature is increased, it appears that the polymer experiences increasing crystalline perfection culminating in a higher melting endotherm.^{14,15}

Using the results from Figure 2, the annealing process was varied in order to produce a wide range of crystallinities consistent with the integrity of the material. A separate set of film samples was processed uniformly by heating to predetermined temperatures, the hold times were varied, and the samples cooled to room temperature at the same rate, all in an argon atmosphere. The

crystallinity of these samples was initially determined by the density gradient method.¹⁶ The calibration curve for the aqueous sodium bromide density gradient column is shown in Figure 3.

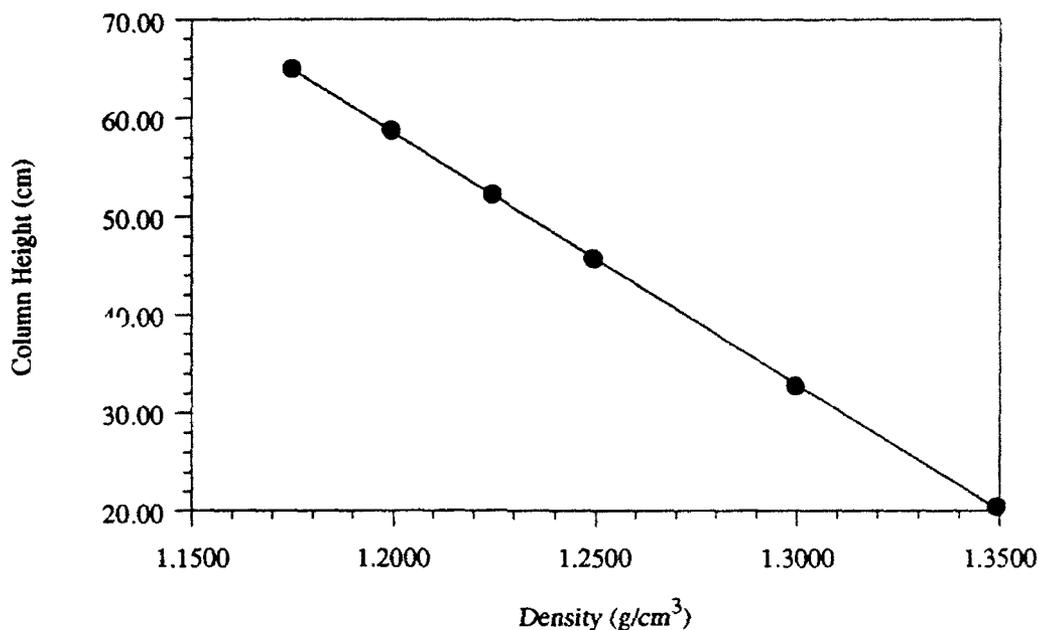


Figure 3. Calibration curve for aqueous sodium bromide density gradient column at 24.9°C.

Preliminary x-ray data for the as-received PEEK shows no indication of the presence of a crystalline phase. This is in agreement with the amorphous nature of the material. Samples were first annealed at 210°C and 310°C, utilizing previous literature process conditions, and complemented with annealing temperatures of 160°C and 260°C. Their densities were compared with the as-received material. Utilizing the calibration curve from Figure 3, the densities of the annealed PEEK samples were determined. The results are shown in Table 1.

Table 1. Density of PEEK Samples Obtained from Varying Annealing Conditions

Annealing Temp (°C)	Time (hr)	Density (g/cm ³)
Amorphous	-	1.2649
Amorphous	-	1.2685
Amorphous	-	1.2732
160	1	1.2879
160	1	1.2898
210	1	1.2957
210	1	1.2994
210	2	1.2950
210	2	1.2982
260	1	1.3036
260	2	1.3012
310	1	1.3025
310	1	1.3084
310	2	1.3073

It was found from the annealing experiments that little change occurred to the morphology of PEEK when annealed below its T_g for any length of time. Above the T_g crystallization occurs rather rapidly to reach an equilibrium condition.¹⁷ This is indicated from the small variations in crystallinity observed for different times at the same temperature. It has also been noted by this work and that of previous authors that by annealing above the T_g but below the melting temperature, it is extremely difficult to produce a low degree of crystallinity. However, three low density values were obtained from different batches of as-received PEEK, and these are included in Table 1. A calibration curve of percent crystallinity versus density for amorphous and crystalline PEEK is shown in Figure 4. The measured density of the amorphous, as-received PEEK is taken to be 1.2642 g/cm³ and that for a 100% crystalline sample has been calculated to be 1.378 g/cm³.¹⁸

X-ray crystallographic studies were also performed on the annealed PEEK samples in order to compare their crystallinity values with those obtained from the density data. Although differential scanning calorimetry would be expected to provide useful data for percent crystallinity, the nature of the PEEK material is such that further annealing would occur during the measurement and the results can not be considered reliable. The x-ray technique is not invasive but was somewhat handicapped by the unavailability of a 100% crystalline sample for comparative analysis. However, it was felt that this exercise would be instructive as a comparative study with the density gradient method. Examples of x-ray diffraction curves for annealed and unannealed PEEK samples are shown in Figure 5. Estimates of crystallinity were obtained by scaling an amorphous curve under the diffraction peaks.^{1,18} The ratio of the areas of the

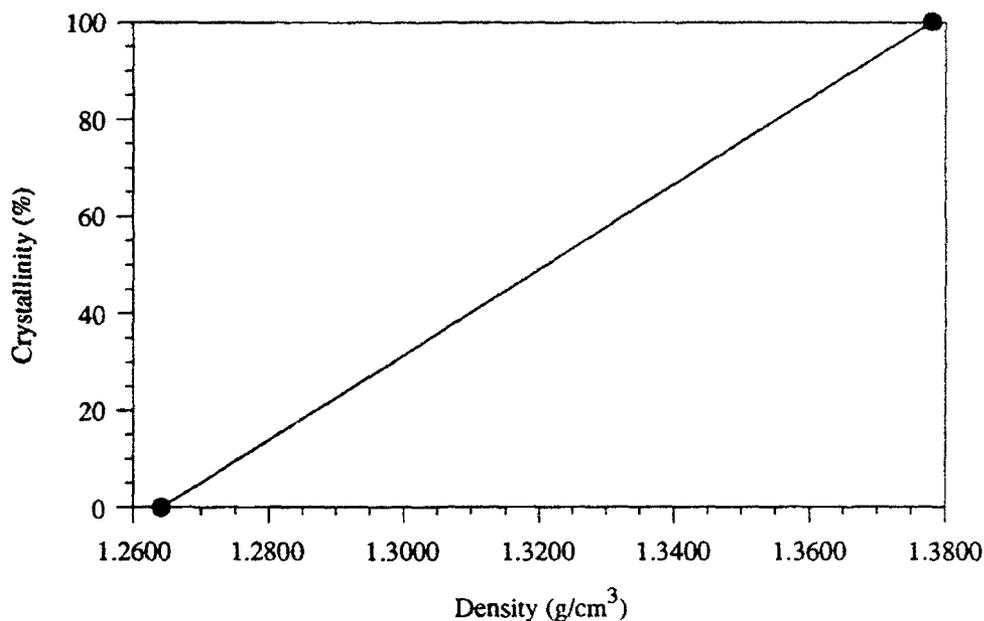


Figure 4. Calibration curve of crystallinity vs. density for amorphous (0%) and crystalline (100%) forms of PEEK.

crystalline peaks to the total area was taken as a weight fraction index for the x-ray crystallinity. Compared with the crystallinity values derived from the density measurements, the x-ray data appear to be acceptable given the limitations of the approximations described.

From the calibration curve in Figure 4 and the density data from Table 1, the crystallinity of samples annealed from the same film batch of controlled thickness is compared with that from the x-ray data and shown in Table 2. Unfortunately, a limited supply of material of controlled thickness prevented a broader range of crystallinities from being generated for this work.

Table 2. Percent Crystallinity of PEEK from Density and X-ray Data

Density (g/cm ³)	Crystallinity (%) (from density data)	Crystallinity (%) (from X-ray data)
1.2649	0.62	0.0
1.2685	3.7	0.0
1.2732	7.91	0.0
1.2827	16.26	19.8
1.2967	28.56	24.6
1.2982	29.88	33.8
1.2994	30.93	26.4
1.3025	33.65	38.2
1.3036	34.62	32.7
1.3084	38.84	40.5

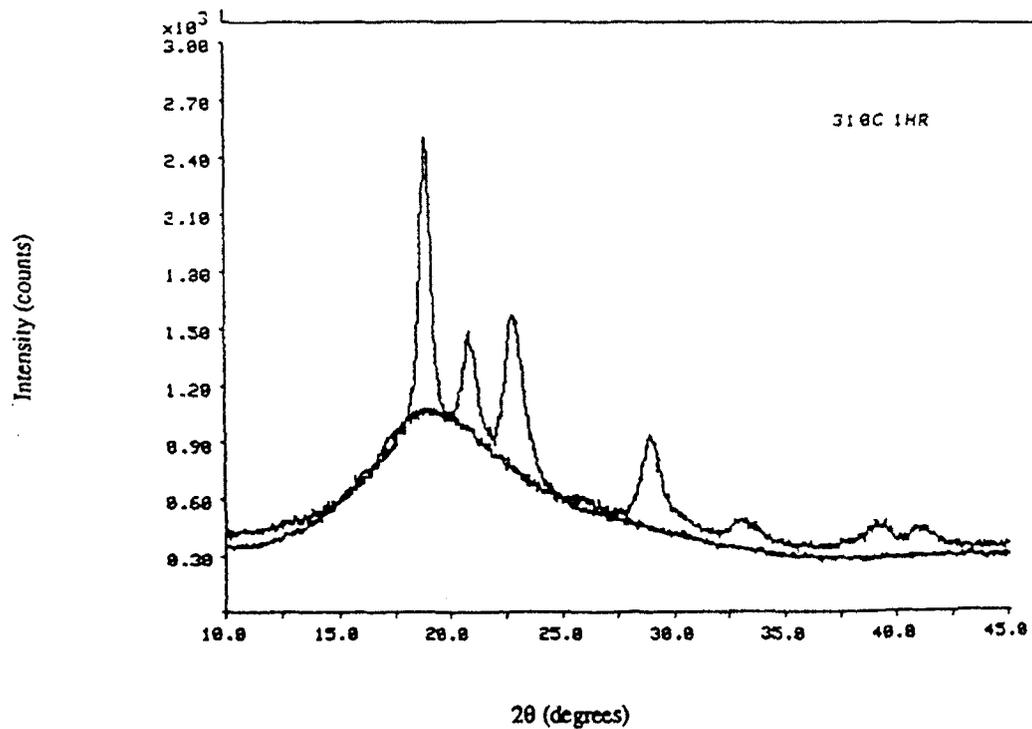
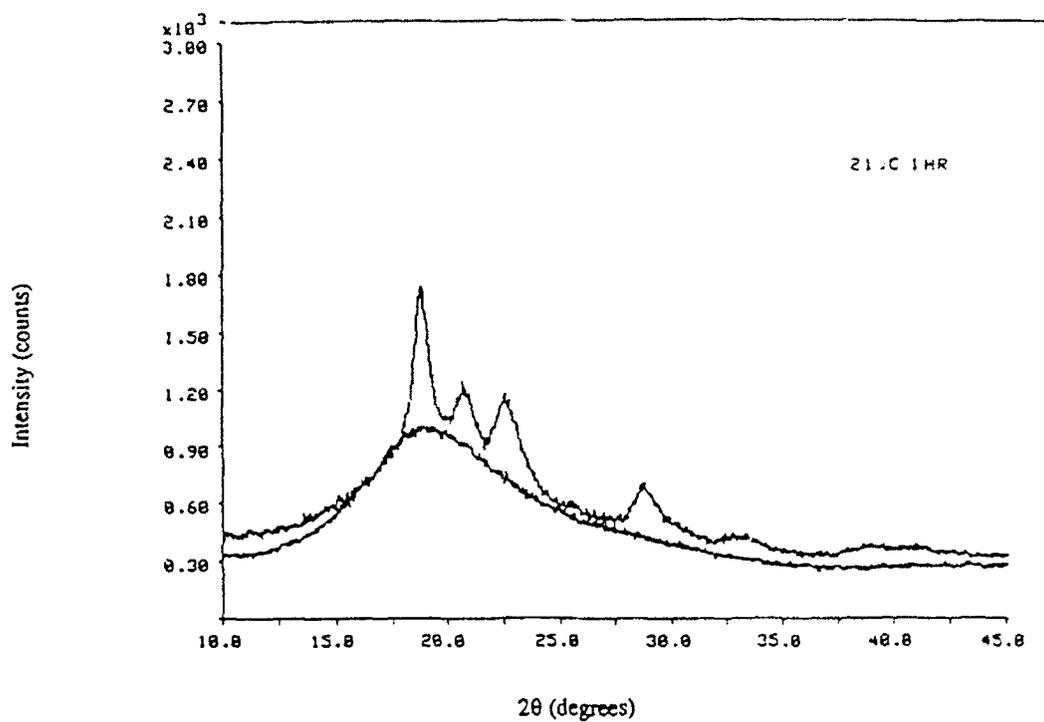


Figure 5. X-ray data for PEEK annealed at 210°C (upper graph) and 310°C (lower graph), normalized to amorphous PEEK.

A graphical comparison of crystallinities determined by the x-ray method and by the density gradient method is shown in Figure 6. Given the relative deficiencies in the analytical techniques used to establish the extent of crystallinity in polymeric thin film samples of this kind, the results are in fairly good agreement.

In the conductivity study, current/voltage measurements were obtained under ambient temperature conditions for nominally 10-mil thick PEEK samples. These samples were obtained from the same material batch processed for the density measurements. Each sample was placed under vacuum for 24 hours prior to application of voltage for the conductivity experiments. The results of these experiments were in agreement with the hypothesis that increased charge trapping at the crystalline/amorphous interface results in decreased conductivity. This was indeed observed. Conductivity versus crystallinity determined from density data is shown in Figure 7, while conductivity versus crystallinity determined from x-ray data is shown in Figure 8. Since the x-ray experiments were insensitive to low crystallinity values for unannealed PEEK, a value of zero percent crystallinity was assigned.

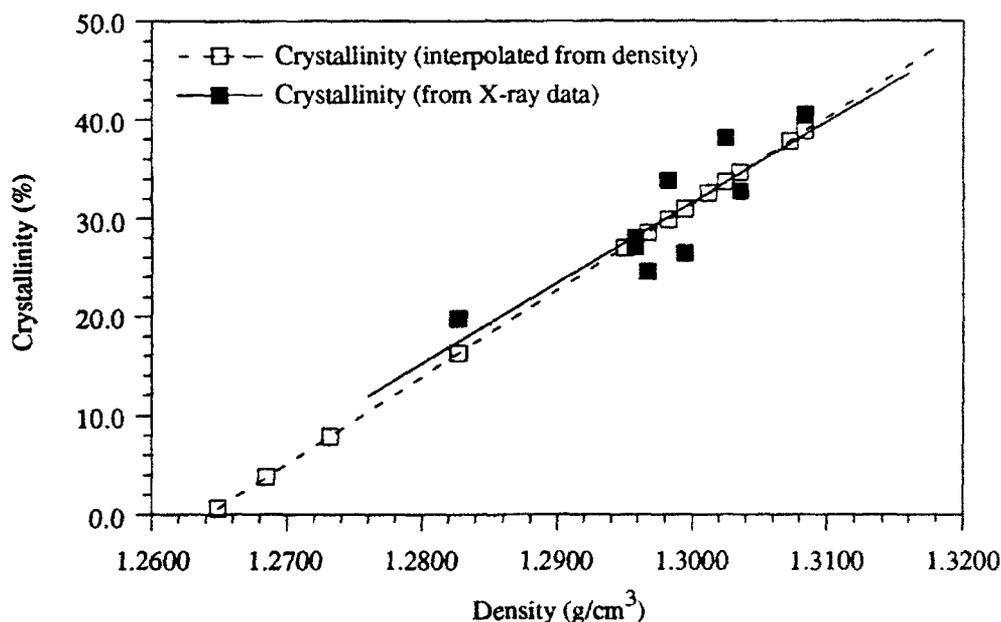


Figure 6. Comparison of percent crystallinity of PEEK determined from density and x-ray diffraction data.

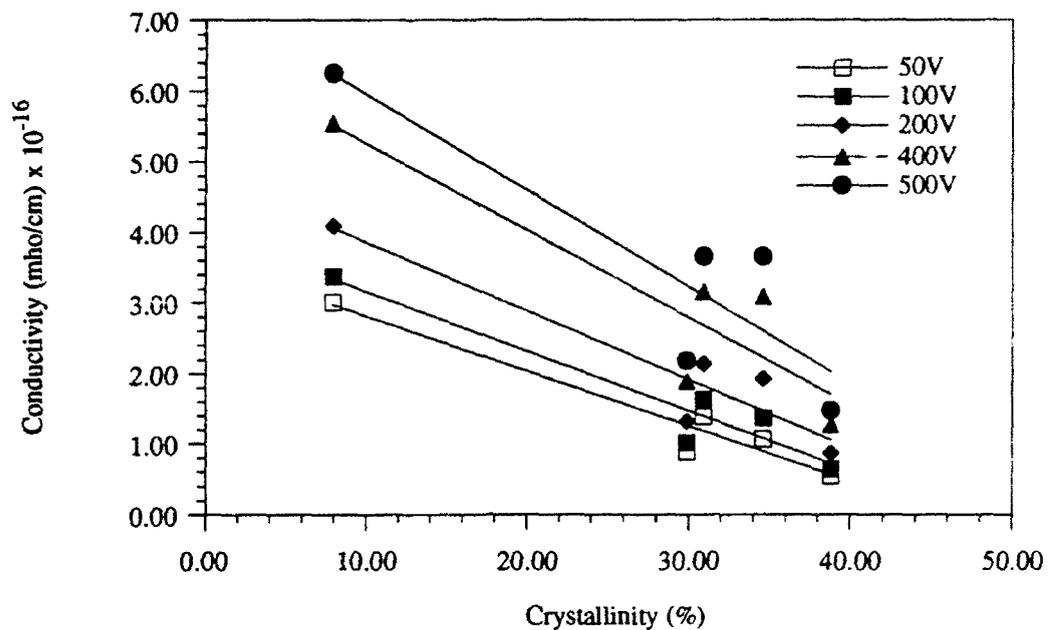


Figure 7. Conductivity vs crystallinity for annealed PEEK (from density data).

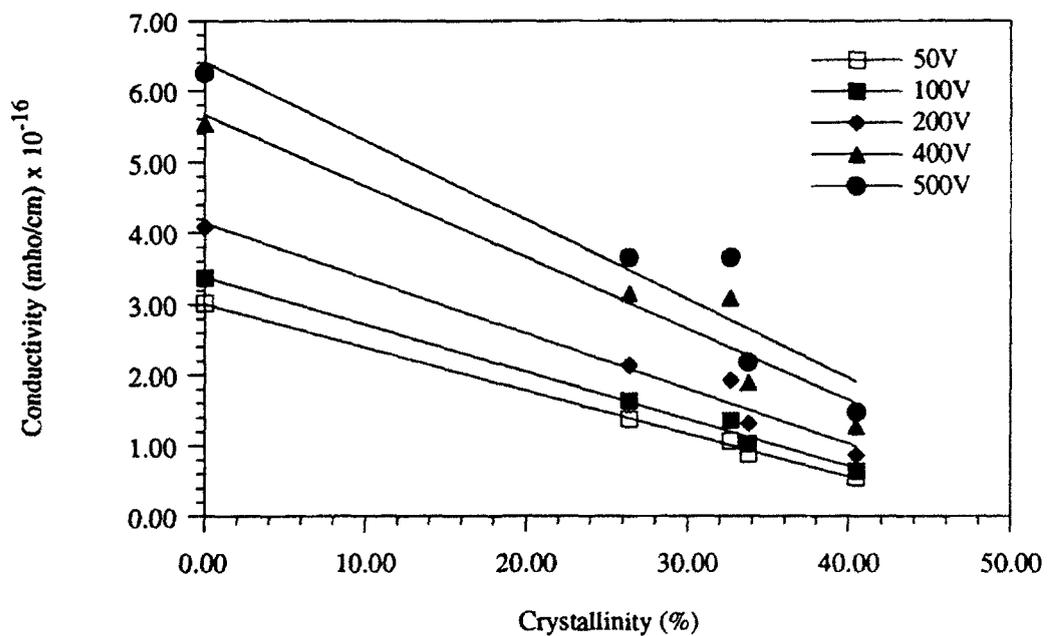


Figure 8. Conductivity vs crystallinity for annealed PEEK (from x-ray data).

Although the extent of crystallinity for the annealed PEEK samples differs depending on the methodology used, the trend of the results shown in Figures 7 and 8 appears to confirm the technique. Increasing crystallinity at the expense of the amorphous phase presents restrictions to pathways for the transport of charge. With the exception of the result for 30% crystallinity in Figure 7, which we attribute to a faulty density determination, the data are consistent with the increased trapping hypothesis.¹⁹ Unfortunately, the sensitivity of amorphous PEEK to annealing temperature made it difficult to obtain sufficient samples with controlled crystallinity below 25%.

The effect of crystallinity on the dielectric constant proved to be inconclusive. With film thicknesses in the range of the as-received PEEK samples, there was difficulty in obtaining accurate thickness values with which to calculate the dielectric constant from the measured capacitance values. However, the average of a set of values obtained from micrometer measurements of thickness was compared with that obtained utilizing sample densities.²⁰ The results are shown in Figure 9. The set of values obtained using micrometer-measured thickness is comparable to those obtained from calculated values of sample thickness. However, the measured values are displaced from those values reported for commercial PEEK, which are in the range exhibited for the values calculated from sample density. A number of similar measurements made on a variety of samples of varying crystallinity also showed no particular trend. The overall results are seen in Figure 10. Thus the dielectric constant obtained by this technique did not reflect the results of the conductivity experiments and was not a sufficient predictor of the effect of crystallinity on ultimate breakdown properties.

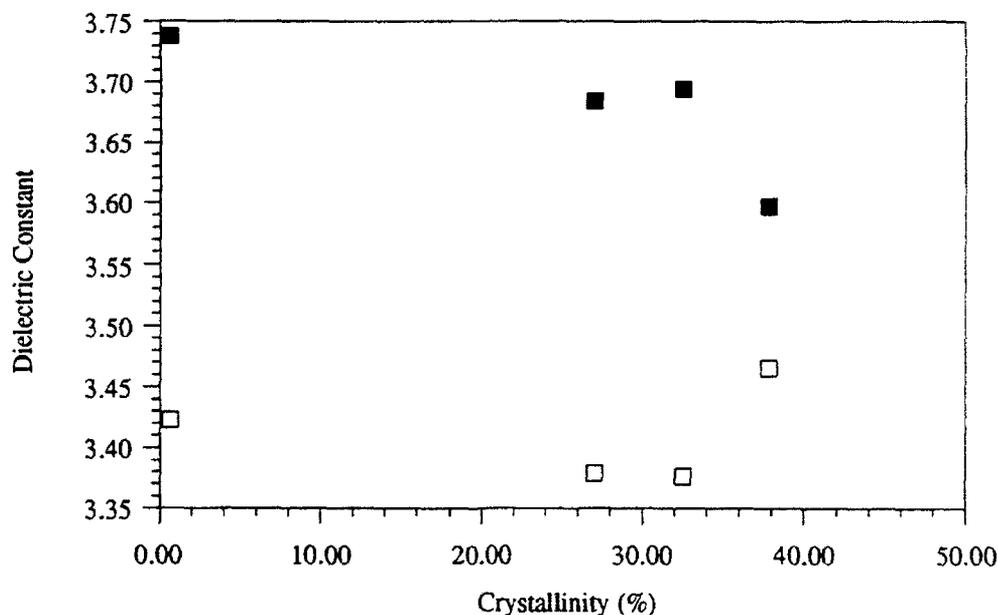


Figure 9. Dielectric constant from capacitance measurements vs crystallinity (from density) for annealed PEEK samples: (■ - measured thickness; □ - calculated thickness).

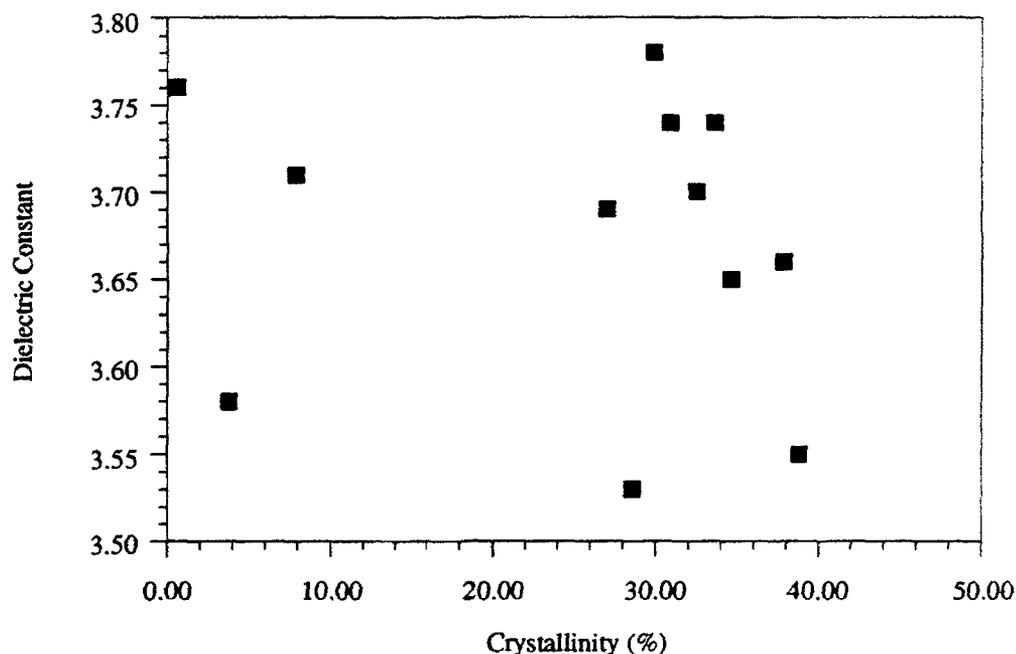


Figure 10. Dielectric constant from capacitance measurements (measured thickness) vs crystallinity (from density) for annealed PEEK samples.

Dielectric breakdown studies were performed on a selected sheet of as-received PEEK, which provided the lowest thickness variability. In general the dielectric breakdown strength decreases with increasing sample thickness. This has usually been ascribed to increasing level of defects in materials providing sites for the propagation of a breakdown route. Recent studies have attempted to correlate the relationship between film thickness, and dielectric breakdown and the causes of breakdown in polymers.²¹⁻²³ It was deemed essential to minimize this variation for the sample under study. The sheet was cut into strips and annealed under similar conditions at different temperatures to provide a broad range of crystallinities. After annealing, the samples were subjected to breakdown conditions described previously. The results are shown in Figure 11.

The results in Figure 11 distinctly show a deterioration in dielectric breakdown strength as one proceeds from an amorphous to a crystalline morphology for PEEK. Attempting to narrow the number of variables that contribute to breakdown was a major emphasis of this work and one of the reasons for choosing PEEK. The wide error limits displayed are indicative of the difficulty in obtaining a uniformly flat film, and a large number of measurements were made to provide statistical significance to the data. In addition, the data obtained were limited by other factors. First, the annealing conditions that were used did not allow precise control of crystallinity in the region between zero and 25%.

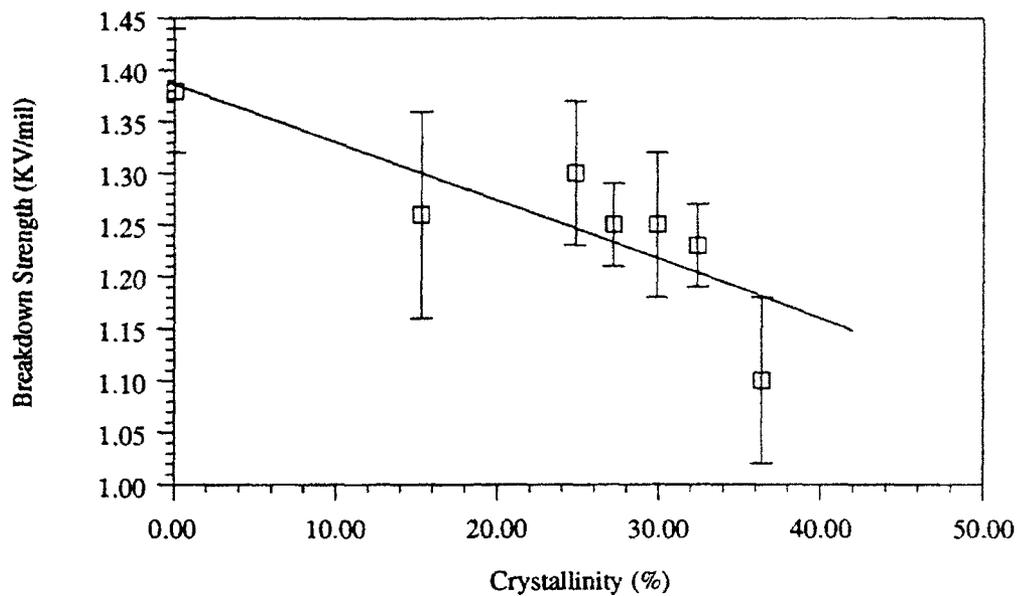


Figure 11. Dielectric breakdown strength vs crystallinity (from density) for annealed PEEK.

Secondly, as the percent crystallinity exceeds 35%, the film becomes quite brittle and begins to deviate from planarity, thereby introducing large errors in thickness measurements. Therefore, for the purposes of this investigation, these limitations prevented a more thorough analysis of the effect of crystallinity on electrical properties.

DISCUSSION

The morphology of PEEK for crystallization temperatures up to about 300°C is said to be in the form of spherulites consisting of narrow lath-like lamellae which adopt an edge-on orientation in thin films. At higher crystallization temperatures, the lamellae have greater thickness and are more perfectly ordered.²⁴ These samples were also said to exhibit much higher electron densities in the center of the spherulites than in their periphery.²⁵ It has been mentioned previously that the samples annealed at 310°C tended to be more brittle as the percent crystallinity exceeded ca. 30%. If the description of the morphology developed above and below 300°C is as described, there appears to be little effect on the trend of the conductivity observed in Figures 7 and 8. This is consistent with a gradual nucleation and growth of spherulites and of increasing crystallite size, where the crystalline/amorphous interface dominates the conductivity. These morphology differences also show little effect on the dielectric constants seen in Figures 9 and 10. Studies of chain dynamics of PEEK indicate that most of the aromatic rings are essentially immobile in the amorphous and crystalline phases.²⁶ This evidence supports a frozen morphology after annealing where locked-in polarizable groups might explain the variation in dielectric constants observed. The conductivity results are consistent with the original hypothesis, but the corollary relationship with the dielectric constant is not supported by these data.

On inspecting the dielectric breakdown data shown in Figure 11, the value for the sample annealed at 310°C is noticeably lower on the curve than the samples annealed at temperatures below 300°C. A study of isothermal crystallization of PEEK for annealing times in excess of 20 minutes has shown that the relative fractional free volume remains constant.²⁷ Since free volume holes have been mentioned as providing a breakdown pathway, these data argue for an alternate breakdown pathway. Assuming nominal average sample thickness, the lower breakdown strength observed at 310°C may be due to defects arising from the different morphologies said to be generated above and below 300°C. Support for this view derives from the controversy regarding the origin of the multiple endothermic behavior of PEEK and related materials (refer to Figure 2). Two models have been proposed to explain this endothermic behavior. One model describes the initial formation of low melting crystals that are then transformed to a higher melting form during annealing.¹³ The other describes the double melting endotherm as arising from separate populations of crystals.¹⁵ Additional reports have added to the controversy by giving supporting evidence for each of the models presented.^{28,29} Each model, however, provides an opportunity for the formation of an increasing population of defect sites during annealing. The dielectric breakdown strength appears to decrease with increasing crystallinity, indicating that changing morphology introduces breakdown pathways not present in the amorphous material. The relationship between decreasing breakdown strength and decreasing conductivity as morphology changes does not appear to be consistent with the original hypothesis.

Recent reports on the electrical properties of polyethylene provide some insight to understanding breakdown mechanisms and the relationship of these results to the study of PEEK. In a report on polyethylene cable insulation, the breakdown strength was found to vary either directly or inversely with the degree of crystallinity, depending on the aging process used.³⁰ It is important to note that the various aging processes used also introduced additional structural changes in the polymer. As described previously, different structural changes in the material affect the breakdown process in different ways leading to ambiguous results. Similarly, a report on partial discharge experiments involving polyethylene blends concluded that thermally induced

mechanical stresses can introduce cracking in materials with increased crystallinity and thereby shorten the life of the polymer.³¹ Although the binary blends were designed to introduce varying degrees of crystallinity, a change in the molecular weight distribution of the various blends was an inherent part of the process. This introduces an additional molecular parameter, which has the potential for compromising the degradation mechanism.

In a report that minimizes structural variations in polyethylene and is most closely related to the experimental approach taken in our study of PEEK it was found that the breakdown strength decreases with increasing crystallinity.³² The report describes annealing of vapor-deposited polyethylene films to varying degrees of crystallinity in an inert atmosphere, thereby avoiding the introduction of chemical changes which can affect the breakdown mechanism. Further study of these films also found that the mean-free-path of injected electrons was longer in the samples with increased crystallinity and that these energetic electrons were responsible for the reduced dielectric strength of the polymer. The implication is that the electron transport is more favorable with increasing crystalline content.

CONCLUSIONS

It is difficult to assess which of the subtle effects of changes in morphology are responsible for changes in electrical properties. Both free volume holes and imperfections at the crystalline/amorphous interface are potential contributors to breakdown. The relationship of crystallite size on electrical breakdown has been discussed by others and has been considered here. A gradual nucleation and growth of a large number of crystalline sites are in keeping with the annealing conditions used. The consistency of the annealing process is not believed to have introduced variation that would have influenced the results from the standpoint of crystallite size. However, experiments that can introduce variation in crystallite size while simultaneously maintaining the same degree of crystallinity would clarify this relationship. The resolution of the controversy regarding the origin of the melting endotherms may also be of considerable importance to the understanding of defect structure and its relationship to dielectric properties.

This work has attempted to limit impurity variations and the introduction of decomposition products by choosing a thermoplastic material of high thermal and chemical stability. This was to ensure that any effect on breakdown strength can be limited to the aforementioned parameters and a more fundamental relationship can be examined. In this study it was found that, in the absence of other processing variables, there is a reduction in the dielectric breakdown strength as the morphology of the material changes from a purely amorphous nature to one of increasing crystallinity. This result is in agreement with that for annealed polyethylene described as the result of increased electron transport in the crystalline phase. The precise source of the reduction in dielectric strength with increasing crystallinity is still open to question as the results of the detailed morphological characterization of PEEK and the more recent studies with polyethylene have indicated.

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