

**A STUDY OF THE DAMAGE ACCUMULATION PROCESS IN
POLY(ARYL ETHER KETONE KETONE) AND IT'S AS4
CARBON FIBER REINFORCED COMPOSITES.**

by

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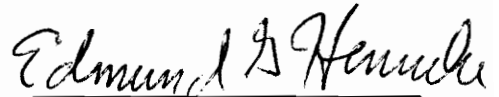
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Abstract

This thesis presents the results of a study done on the damage accumulation process in poly(ether ketone ketone) and its AS4 carbon fiber reinforced composites. The damage accumulation process was studied as a function of applied heat treatment. This study is the result of a project funded by duPont and was done in part to explain the dramatic change in fatigue properties observed at duPont as the applied heat treatment is changed.

The mechanical properties were characterized using a battery of tests. The quenched composite systems have lower moduli, but higher toughness and elongations. The quenched systems also have the best fatigue performance and therefore, it can be concluded that the quenched composite systems have the best potential as far as industrial applications are concerned. Quenching has other advantages in industrial applications. These include decreased chances of operator error, and decreased processing times.

The damage accumulation process was characterized using the acoustic emission method and also the drop in stiffness during flexure testing. It has been observed that the ultimate mechanical properties show a weak dependence on the applied heat treatment, whereas the damage accumulation process changes dramatically. A model has been developed to simulate the damage accumulation process. This model has then been used to predict the fatigue S-N curve in stress control and to qualitatively relate it to the available fatigue data in stress control.

To,

The hand that rocks the world and the hand that rules the cradle.

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Let me thank all my friends in Blacksburg, and specially all my friends in room 200 in Hancock Hall, and also all those in Holden Hall for the very enlightening discussions I had with them.

Let me end this long list with the most important acknowledgements. I am what I am because of the encouragement and support provided by my parents and my sister. They have always encouraged me to aim for the best and, although with time I have learned to settle for much less, I cannot thank them in words for it.

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1. Introduction

Poly(aryl ether ketone ketone), PEKK, is a relatively new high temperature, high performance thermoplastic polymer being developed by DuPont^{1,6-10,14,15}. It is currently being used commercially as DECLARTM flame resistant thermoplastic sheets¹⁴, and has numerous potential composite applications¹⁴⁻¹⁵. It belongs to the same family of poly(aryl ether ketones) as ICI's poly(aryl ether ether ketone), PEEK. The crystallization kinetics, crystal morphology, and chemical structure of poly(ether ketones) have been extensively reported in the literature^{2-5,18,19}. PEKK differs from PEEK in that it has a higher percentage of keto units (67%) and contains both para and meta linked keto units, while PEEK has a lower percentage of keto units (33%) and contains only para linked keto units¹. The higher percentage of stiffer keto

units in PEKK results in (among other things) higher glass transition and melting temperatures, slower crystallization rates and a higher modulus^{12,1}.

PEKK crystallizes more slowly than PEEK, and the crystallization kinetics of PEKK can be manipulated by changing the percentage of the meta linked keto units. The crystallization rates can be increased or decreased to afford more control over the crystallization process¹. The morphology and thus the mechanical properties of PEKK can be controlled by changing the heat treatment. As mentioned before, PEKK has numerous potential applications as a matrix material in composites. The properties of such composites will be a function of, among other things, the heat treatment applied on the PEKK matrix. This phenomena can be exploited to develop property specific processing windows. However, the effect of heat treatment on the mechanical properties of PEKK has not been thoroughly investigated. Until this is done, PEKK cannot be fully exploited in industrial applications.

In order to fully characterize the mechanical properties of any material, a battery of tests is required, as the properties measured in one testing configuration cannot be easily correlated with the properties measured in other configurations. This battery typically includes fatigue testing, which can be expensive and cumbersome, specially at low stress values. This is because fatigue life has a semi-log relationship with stress level, and at low stress values, a material may typically take a million cycles or more to fail. In addition, mechanical testing gives us ultimate mechanical properties in a special uniaxial testing configuration. In real applications, structural parts are rarely loaded in a manner which can be simulated in the laboratory. Actual loading

might be some complex combination of simple uniaxial loading configurations. Hence, models which can be used to simulate the damage accumulation process have significant potential application.

Fatigue loadings in practical applications can be simulated by fatigue testing at multi-stress levels. Models are available which can predict the fatigue life in a multi-stress cyclic fatigue loading situation if the fatigue Stress - Number of Cycles (S-N) curve is experimentally determined³⁵⁻⁴⁰. Very few authors have proposed models to predict the fatigue S-N curve, and to date, reliable and easy to use models for predicting fatigue S-N curves are not available³⁵. Hence, there is significant practical applications for a simple model which can predict the fatigue S-N curve.

In this study, the effect of heat treatment on the mechanical properties of PEKK and carbon fiber reinforced PEKK composites has been investigated. A battery of tests were performed to characterize the mechanical properties. In addition, the damage accumulation process during quasi static three point bend loading and during fatigue loading has been measured using the Acoustic Emission Method. The Acoustic Emission Method²⁰⁻³⁴ involves converting the mechanical energy of the acoustic waves released by damage events into electrical signals and analyzing the waveforms to obtain information on the type and amount of damage. Models have also been developed to simulate the damage accumulation process during quasi static three point bend loading. These models have been extended to simulate the damage accumulation process in fatigue testing and to qualitatively explain the fatigue S-N curve.

2. Literature Survey

2.1 Poly(ether ketones)

Poly(ether ketones) are an important class of thermoplastic polymers with numerous industrial applications¹⁴. This family of materials includes poly(ether ether ketone) PEEK and poly(ether ketone ketone) PEKK. Poly(ether ketone ketone) is a unique member of the poly(ether ketone) family^{1,6-10,14,15}.

The structures of various poly(ether ketones) are given in Figure 2.1¹. Note that PEEK has two ether units for every keto unit. Also, all the bonds in PEEK are para linked. Unlike PEEK, PEKK has one ether bond for every two keto bonds. Since keto units have a relatively higher rotational conformation energy barrier¹², they are stiffer than ether units. Hence, PEKK has a higher glass transition temperature (T_g)^{1,13} and melting temperature (T_m)^{1,2}, and

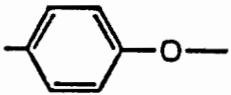
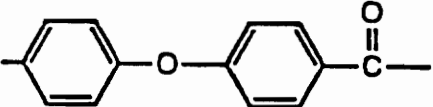
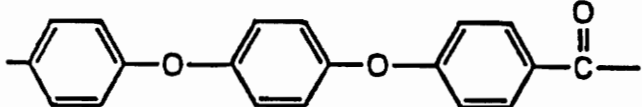
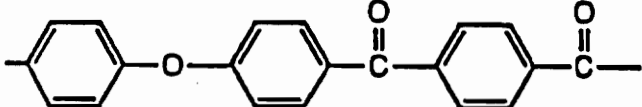
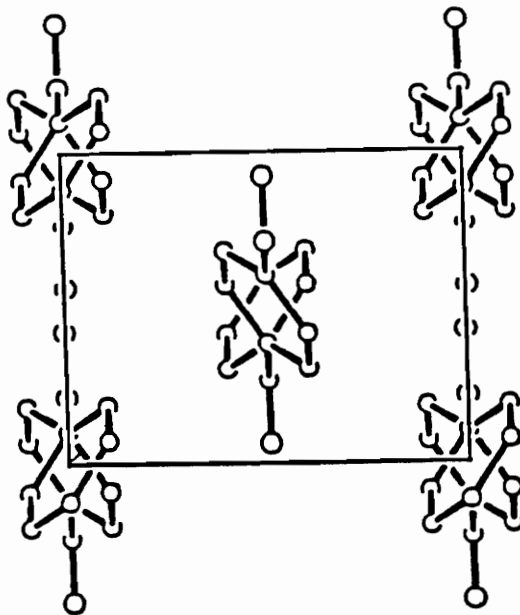
		% KETONE
	PPO	0%
	PEK	50%
	PEEK	33%
	PEKK	67%

Figure 2.1 Structures of various poly(aryl ether ketones)¹.

slower crystallization rates than PEEK²⁻⁵. The crystalline structure of poly(ether ketones) has been extensively studied¹⁻⁵. PEKK is unique in the family of poly(ether ketones) in that it shows two crystal structures¹. These two structures have been labelled form 1 and form 2 by Gardner et al. Figure 2.2 shows the two proposed crystal structures of PEKK¹. The effect of changing the percentage of keto units on the structure^{1,5,16,17}, thermal properties^{1,2,15} and crystallization behavior^{2-5,18,19} of poly(ether ketones) has been investigated. Figure 2.3 summarizes the effect of changing the percentage of keto units on the unit cell parameters of poly(ether ketones), and Figure 2.4 summarizes the effect of changing the percentage of keto units on the T_g and the T_m of poly(ether ketones)¹. Increasing the percentage of stiffer¹² keto units results in increasing T_g 's and T_m 's as expected.

The structure of the PEKK chain is given in Figure 2.5¹. PEKK is typically prepared by the condensation reaction of diphenyl ether (DPE), terephthalic acid (T) and isophthalic acid (I)¹¹. Figure 2.6 depicts a hypothetical synthesis route for PEKK^{1,11}. Because of this synthetic route, PEKK can be thought of as copolymers of the 'diads' containing DPE-T-DPE-T (TT) and DPE-T-DPE-I (TI). From Figure 2.5, it can be seen that PEKK has some meta linked keto units in addition to the para linked keto units found in PEEK. The ratio of the number of the TT diads to the TI diads (TT/TI ratio) can be controlled by changing the ratio of terephthalic acid to isophthalic acid (T/I ratio) used in the synthesis. The effect of changing the T/I ratio on the T-T/T-I ratio is outlined in Table 2.1¹. Each TT diad has two para linked keto units while each TI diad has one para linked keto unit and one meta linked keto unit.

FORM 1
(Edge to Face Phenyl Packing)



FORM 2
(Face to Face Phenyl Packing)

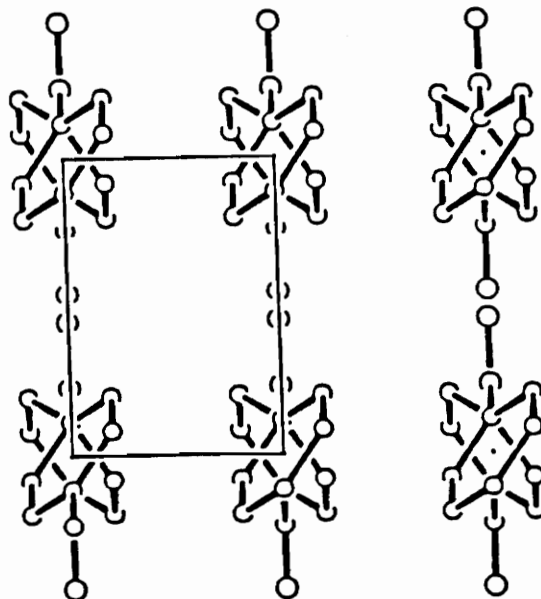


Figure 2.2 : The two crystal structure of Poly(aryl ether ketone ketone) PEKK1.

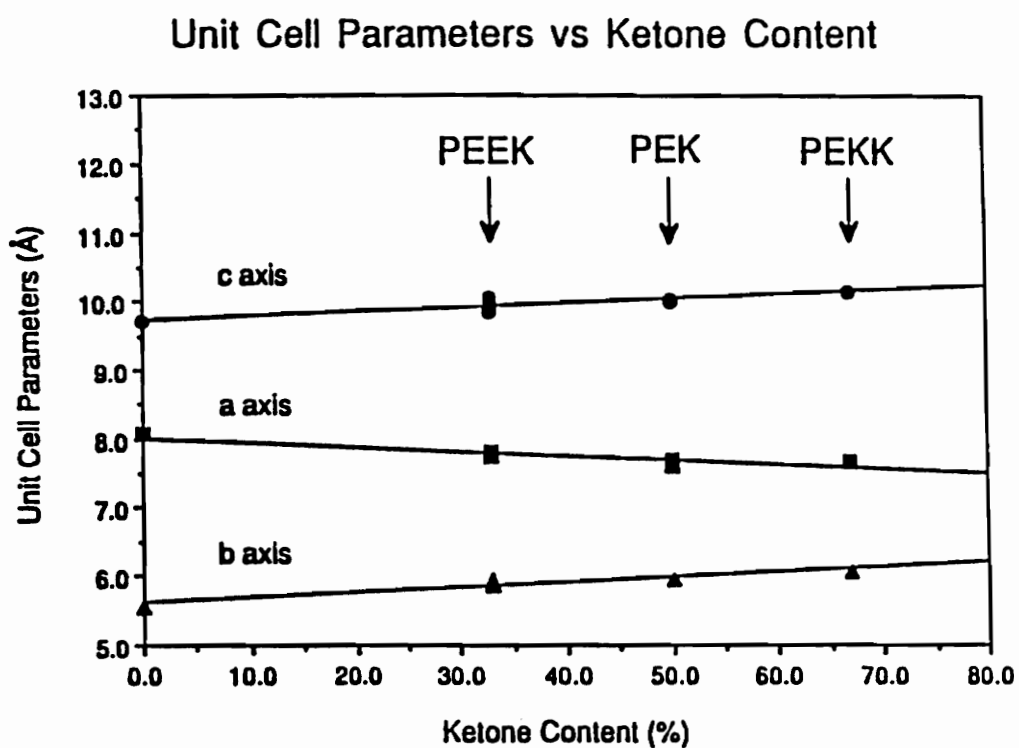


Figure 2.3 Effect of ketone content on the unit cell parameters of poly(aryl ether ketones)¹.

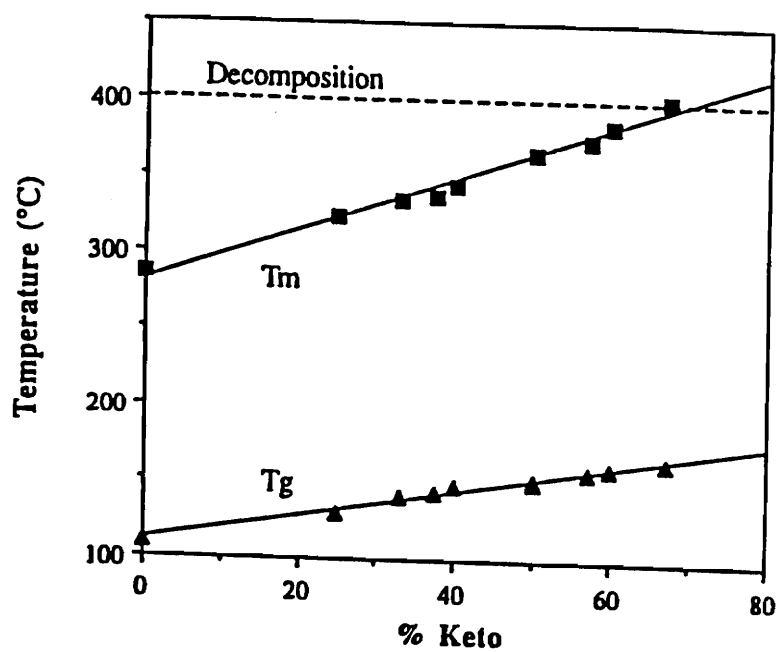


Figure 2.4 Effect of ketone content on the melting temperature (T_m) and glass transition temperatures (T_g) of poly(aryl ether ketones)¹.

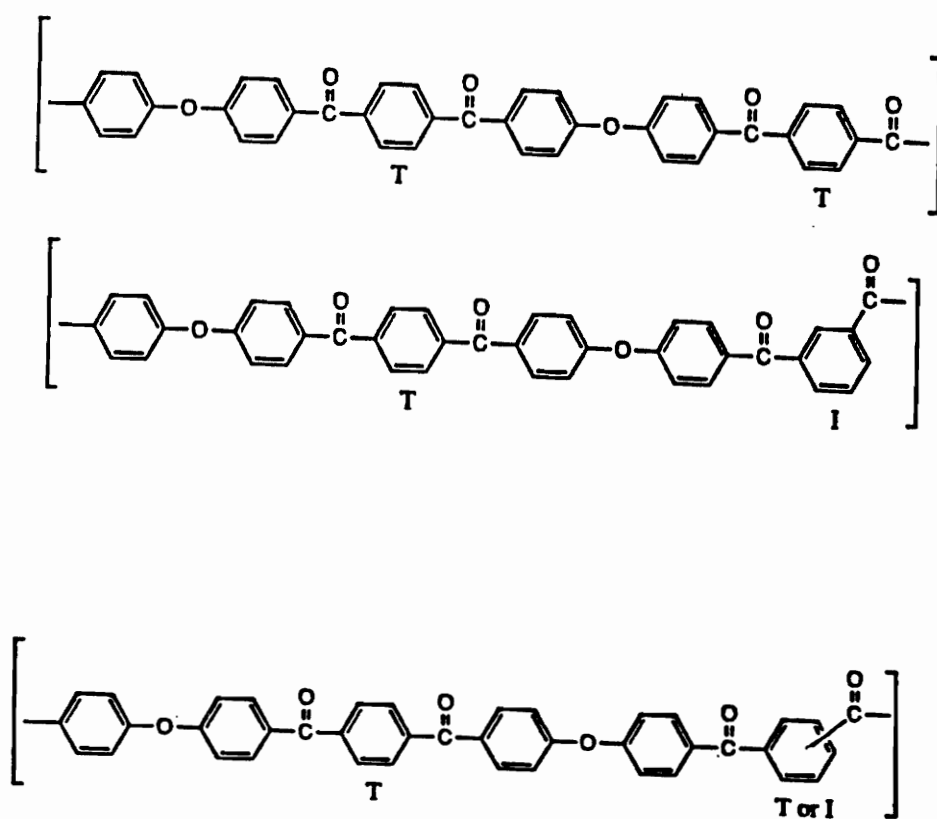
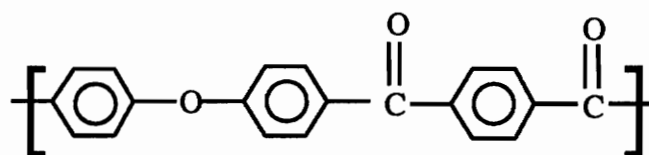
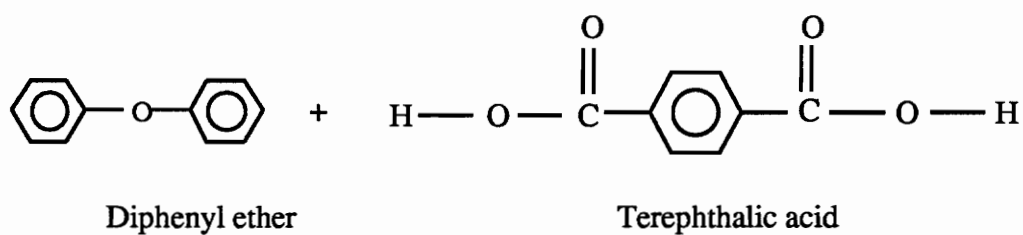
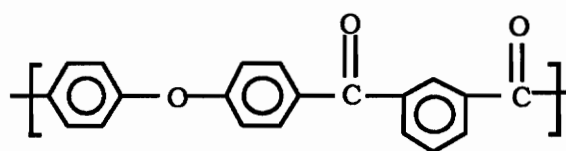
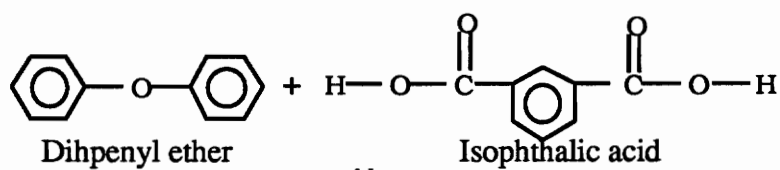


Figure 2.5 Structure of poly(aryl ether ketone ketone) PEKK chain¹.



The DPE-T repeat unit



The DPE-I repeat unit

Figure 2.6: Hypothetical synthesis route for PEKK¹¹.

Table 2.1: Effect of changing T/I ratios on the TT/TI ratio in poly(aryl ether ketone ketone)¹.

T/I Ratio	T-T/T-I ratio
100/0	100/0
80/20	60/40
70/30	40/60
60/40	20/80
50/50	0/100

Changing the TT/TI ratio will also affect the thermal and mechanical properties of PEKK¹. The crystallization kinetics of PEKK has been studied by Gardner et. al for various T/I ratios and their results are summarized in Figure 2.7¹. Gardner et al. explained the observed crystallization kinetics in terms of the chain architecture of PEKK. PEKK with T/I ratios of 100/0 and 50/50 (T-T/T-I ratios of 100/0 and 0/100 respectively) are homopolymers while PEKK with other T/I ratios are copolymers of the diads TT and TI¹. Increasing the number of meta linked keto units slows the rate of crystallization by introducing a kink in the PEKK chain. However, PEKK with a T/I ratio of 50/50 has a slightly faster rate of crystallization than PEKK with a T/I ratio of 60/40 because 50/50 PEKK is a homopolymer¹.

The effect of changing the T/I ratio on the melting temperature (T_m) and glass transition temperature (T_g) of poly(aryl ether ketone ketone) PEKK has been studied by Gardner et al¹. Figure 2.8 summarizes the results of these authors. Increasing the percentage of the terephthalic acid used (%T) in the synthesis increases T_m while T_g remains essentially unchanged. In Figure 2.4, the melting temperature reported for PEKK is the melting temperature for PEKK with a T/I ratio of 100/0.

The effect of processing on the microstructure of 60/40 PEKK has been studied.¹¹ The center to center distance of the spherulites has been reported and is listed in Table 2.2¹¹. Table 2.2 shows that the spherulitic diameters and center to center distances decrease as the crystallization temperature is decreased. This is expected because crystallization at lower temperatures results in more nuclei, which therefore have less room to grow.

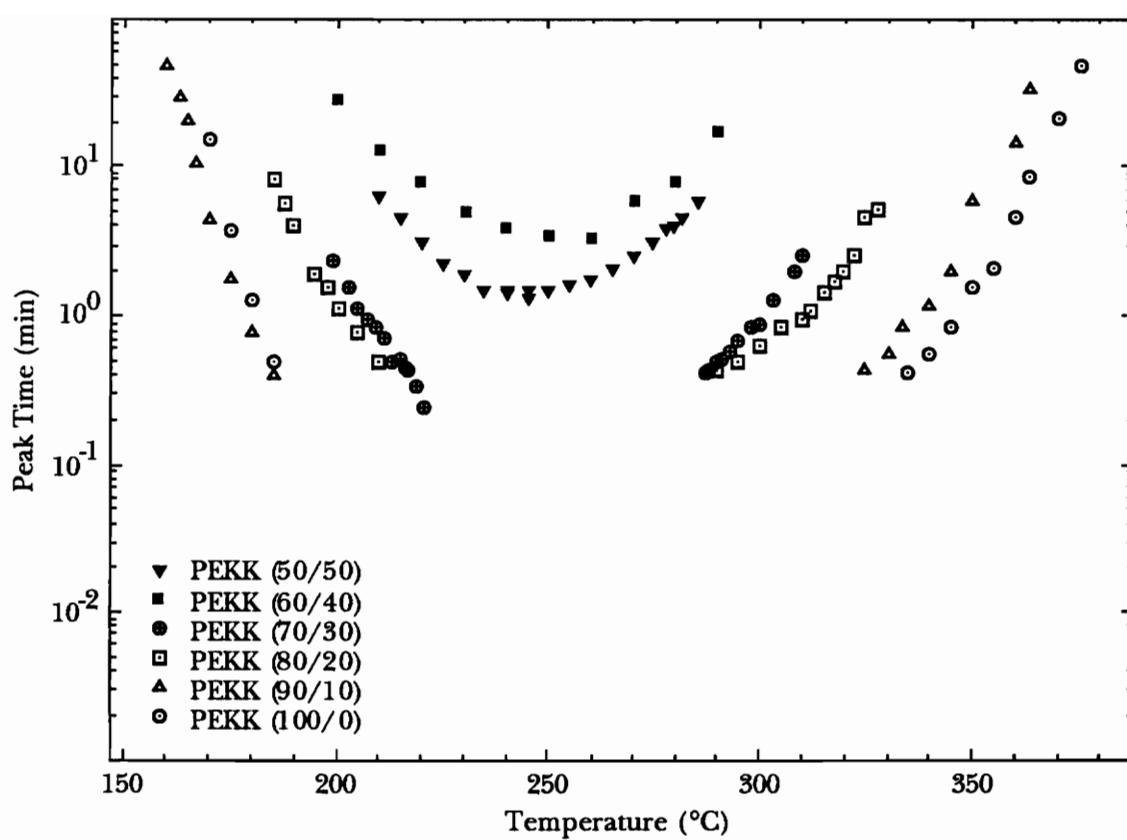


Figure 2.7 Effect of changing T/I ratios on the crystallization kinetics of PEKK¹.

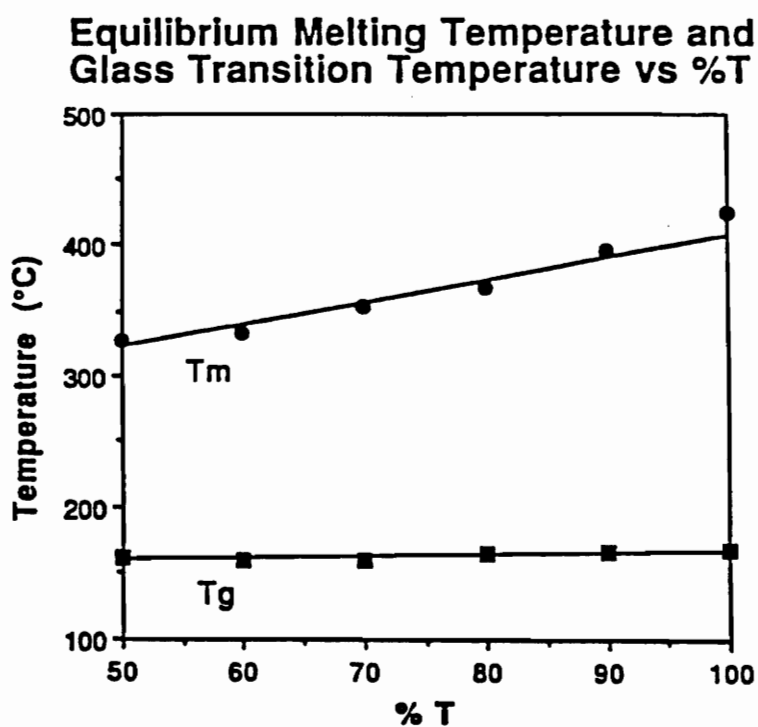


Figure 2.8 Effect changing the T/I ratio on the melting temperature (T_m) and glass transition temperature (T_g) of poly(aryl ether ketone) PEKK¹.

Table 2.2 : Effect of changing the crystallization temperature on the center-to-center distance of the spherulites in poly(aryl ether ketone)¹¹.

Treatment	Center to Center distance (nm)	Spherulite diameter (mm)
280 °C, 2hr	31	---
250 °C, 2hr	24	11
210 °C, 2hr	15	10
2 °C/min cool	19	13
10 °C/min cool	23	9

The fatigue life of carbon fiber reinforced PEKK has been measured at about 65% of the failure stress by Croman⁴⁴⁻⁴⁵. He has measured the fatigue life for both the 60/40⁴⁴ and the 70/30⁴⁵ composites as a function of processing. His results for the Carbon fiber reinforced 60/40 PEKK composite systems are summarized in Figure 2.9.

Croman's fatigue tests were performed in stress control with a maximum stress of 170 kpsi. According to his tensile test results⁴⁴, this stress level corresponds to about 65% of the failure stress. It can be concluded from Croman's results that the quenched AS4 carbon fiber reinforced PEKK 60/40 has the lowest fatigue life and the sample crystallized at 280° C had the highest fatigue life when tested in stress control with a maximum stress of 170 ksi (the slow cooled sample is not a part of this study and is therefore ignored). Croman's data suggests that either there is a substantial change in the static mechanical properties or in the damage accumulation process as a function of processing. In this study, both the damage accumulation process and the ultimate mechanical properties have been studied and attempts have been made to qualitatively explain Croman's data.

The fracture toughness in mode I has been studied for AS4 carbon fiber reinforced PEKK 60/40 and 70/30 composite systems¹¹ by Kander et al. Table 2.3 summarizes their results. From Table 2.3, it can be seen that the quenched composite systems have a higher toughness in mode I as opposed to the crystallized systems.

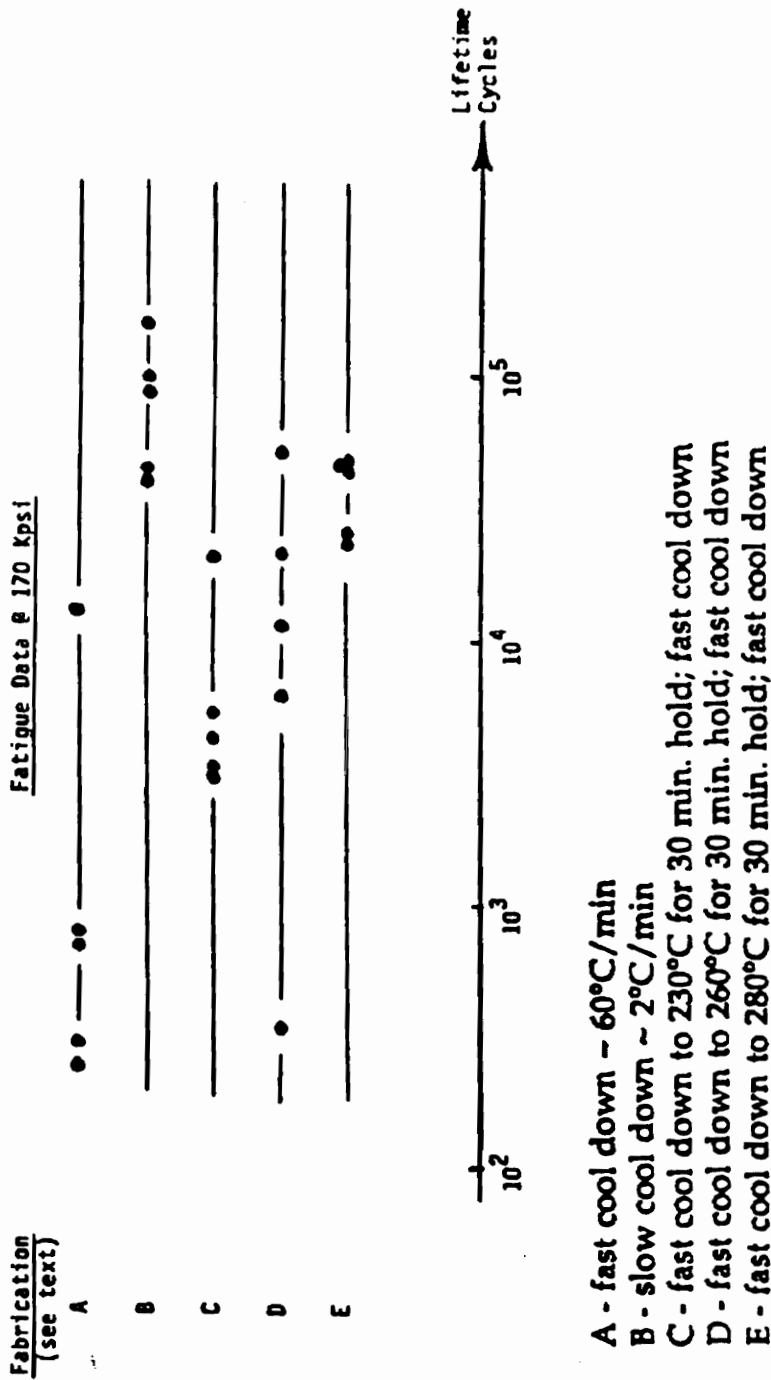


Figure 2.9 Fatigue lives of AS4 Carbon fiber reinforced PEKK 60/40. Fatigue testing done at 170 ksi in stress control. 170 ksi corresponds to approximately 65% of failure stress⁴⁵.

Table 2.3 DCB results for AS 4 carbon fiber reinforced PEKK composites as a function of heat treatment¹¹.

(60/40) Carbon/PEKK

Treatment	K _{1c} (kJ/m ²)
Quenched	1.610/0.246
280 °C, quench	0.648/0.115
260 °C, quench	0.708/0.052
230 °C, quench	0.866/0.092

(70/30) Carbon/PEKK

Treatment	K _{1c} (kJ/m ²)
Quenched	1.468/0.080
300 °C, quench	0.808/0.173
260 °C, quench	0.908/0.160
220 °C, quench	0.762/0.018

2.2 Acoustic Emission Testing

Acoustic emission testing²⁰⁻³⁴ (AET) involves a number of piezoelectric crystals acoustically coupled to the material being tested. Damage "events" in the material release acoustic waves, which propagate in the material and reach the piezoelectric crystals, creating a "hit" on the piezoelectric sensor. The mechanical energy in the acoustic waves is then converted by the piezoelectric crystals to electrical signals, which are then amplified and analyzed to obtain information on the damage events. Figure 2.10 outlines a typical acoustic emission test setup. The setup includes a test frame for mechanical loading, piezoelectric sensors for converting mechanical energy to electrical signals, preamplifiers and amplifiers (in the acoustics unit) to amplify the electrical signals and a PC to analyze acoustic waveforms and store characteristic parameters (amplitude, duration, risetime etc.)

AET is an important tool in the study of the damage accumulation process in composite materials²⁰⁻³⁴. AET offers a real time record of damage initiation and progression. Acoustic waves are generated by the rapid release of stored energy during a damage event in the composite itself. These events include fiber fracture, interfacial debonding and delamination, and matrix cracking. A number of authors have simultaneously monitored Acoustic Emission (AE) signals and Scanning Electron Microscope (SEM) images of composite materials while the system was subject to some kind of loading^{20,28}. They have observed a definite correlation between the type of damage events and the amplitude of the AE signals caused by such damage events. Different types of damage events have been monitored by

SCHEMATIC OF EXPERIMENTAL EQUIPMENT

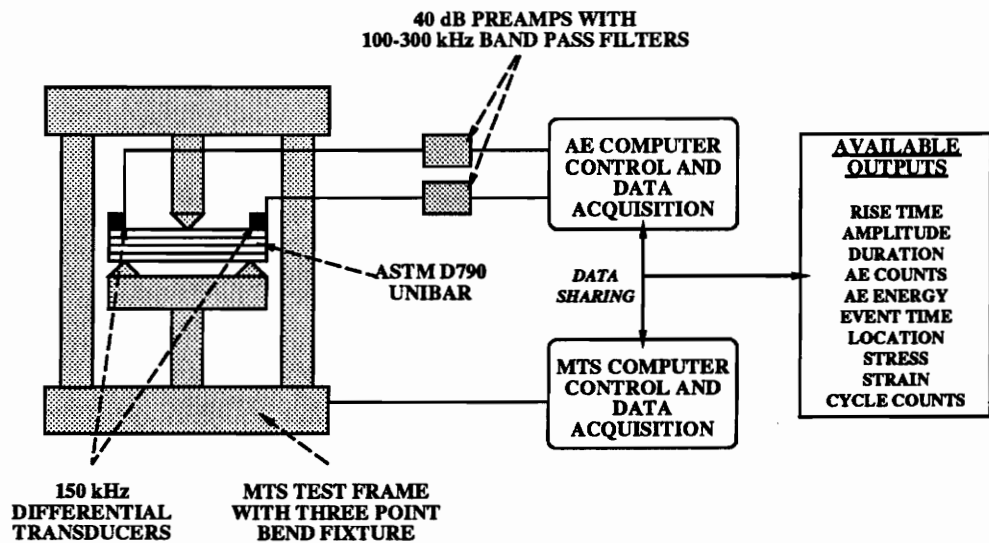


Figure 2.10 A typical Acoustic Emission Test Setup

these authors. Their work demonstrates that there is a definite correlation between the extent and type of damage events and the AE activity. The acoustic parameters monitored by these authors include the acoustic energy release rate, the event rate, the hit rate, and the amplitude of the hits. Several authors^{20-25,31} have used the amplitude of the acoustic hits to obtain information on the nature of the damage events, and the number of hits have been used to measure the extent of damage. The work done by these authors is summarized below:

Faundree et al. monitored the acoustic signature while loading a short fiber bulk molding compound (BMC) composite in tension to study the fracture process²⁰. Additional polished samples were also damaged in three point bend in an SEM and the morphology of the damaged areas identified. During tensile deformation, the initial damage process observed in the SEM was the formation of small cracks at filler particles and glass fibers. This type of damage was identified with acoustic activity in the 40 dB amplitude range. Onset of this damage mechanism occurred at very low strains, and damage continued to accumulate until fracture. At higher strains the smaller cracks were observed to coalesce and form larger cracks spanned by pulled out fibers. Formation of the larger cracks was identified with a burst of acoustic activity in the 70dB amplitude range just prior to fracture.

Koenczoel et al. studied crazing and fracture in polystyrene using acoustic emission²¹. They coupled AET with slow crack propagation experiments in polystyrene to probe the mechanism of damage and fracture. They conclude that the single AE active mechanism recorded during slow crack growth is caused by the failure of the crazed fibrils in the craze zone at the

propagating crack tip. The AE event rate and the AE energy release rate varied linearly with the crack speed indicating that the AE depends only on the amount of fracture surface created independent of the crack speed. Since the total duration of crack growth was less than 1% of the total time of experiment, they concluded that crack propagation is discontinuous.

Kander studied the damage accumulation process in unidirectional glass reinforced composites by monitoring the AE during three point bend loading²². He correlated the acoustic behavior with the mechanical stress strain response and with visual observations of the damage events. He showed that the failure process initiated with cohesive matrix damage, propagated with interfacial debonding and ended with fiber breakage near catastrophic failure. He associated three different classes of damage events with three modes of AE amplitude distribution: matrix damage at low amplitudes, fiber debonding and delamination at intermediate amplitudes and fiber breakage at high amplitudes. Kander has also studied the damage accumulation process during a load controlled fatigue test in unidirectional glass reinforced composites using acoustic emission²². His results indicate that during a fatigue test, the same three classes of acoustic events (with the same characteristic amplitudes as recorded during a quasi-static break test) are recorded. The low amplitude signals were recorded first, followed by the intermediate amplitude signals, and then the high amplitude signals. The occurrence of the high amplitude signal corresponded with observation of fiber breakage on the tensile side of the three point bend sample. Kander's results also indicated that the fatigue limit corresponds with the point at which the low amplitude signals initiate during a quasi-static three point bend test.

Kau et al.²³ studied the damage accumulation process in reinforced and unreinforced reaction injection molded polyurethanes during three point bend testing. They correlated the AE amplitude distribution with observed deformation mechanisms. They found that the initiation of microcracking in the unreinforced resin produced acoustic activity at 43 dB. Composite systems exhibited additional peaks in the amplitude distribution at 50 and 65 dB. They associated these peaks with microcracking at the well bonded interface and fiber fracture respectively.

Siegmann and Kander²⁴ studied the effect of varying span to depth ratios on the failure mechanisms and the acoustic signatures. They have observed that the failure mechanism changes with increasing span to depth ratios from a shear dominated mode to a tension/compression dominated mode. They have also shown that the AE signatures can be correlated with the change in failure modes. Kander and Siegmann²⁵ also studied the effect of changing strain rates on the damage mechanism of an orthotropic glass/polypropylene composite during uniaxial tensile testing. They have shown that the "apparent" fiber matrix interface properties and the acoustic signatures change with strain rate. The mechanical response, the acoustic signature, and the micrographs all show a strain rate dependent transition in failure mechanism.

Falchi and Gracia³¹ observed the effect of reducing span to depth ratios on the acoustic response for a carbon epoxy laminate. They found that reducing the span to depth ratio changed the failure mode from tensile to tensile/compressive to compressive/shear. They also observed a correlation between the AE signatures and the failure mode.

2.3 Damage Accumulation Theories

Fatigue loadings in practical applications can be simulated by fatigue at multi stress levels. A number of studies have been made to model the damage accumulation process during multi stress fatigue testing. Hwang and Han³⁵ have provided an excellent review of these damage models, some of which are listed below.

The damage during cyclic loading of any material will depend on the applied stress (or strain) level, the number of cycles, frequency, temperature, moisture content, shape, etc²⁵. This can be represented mathematically by the equation :

$$D = F(n, r, f, T, M. . .)$$

where,

D: the extent of damage

n: number of applied fatigue cycles

r: applied stress level

f: frequency of the fatigue loading

T: temperature

M: Moisture content

Most of the existing damage models consider the applied stress (or strain) level, and the number of cycles only. The damage function is assumed to vary from 0 at the beginning of the fatigue test to 1 at fatigue failure.

Palmgren and Miner^{36,37} proposed a linear, stress independent cumulative damage rule. This model defined damage as the ratio of the number of cycles of operation (n) to the number of cycles at failure (N).

$$D = n/N$$

This rule is widely used even today because of its simplicity. However, the Palmgren-Miner model does not predict the effect of load history. For example, it has been experimentally observed that the damage function, as predicted by the Palmgren Miner model, equals greater than one for a combination of fatigue at low stress levels followed by fatigue at high stress levels, and less than one for fatigue at high levels followed by fatigue at lower levels³⁵.

Leve³⁸ proposed a modified form of the Palmgren-Miner rule to account for the above discrepancy. His model is given below

$$D = (n/N)^C$$

where C is a constant, independent of the applied stress level. Leve³⁸ found that the constant C is greater than 1. Marco and Starkey³⁹ proposed a similar model, but they proposed that the constant C depends on the applied stress level and increases to 1 as the applied stress level increases.

Henry⁴⁰ proposed a different form of the damage accumulation model. His final equation is given below:

$$D = x/[1 + (1-x)/q]$$

where, x is the cycle ratio (n/N) and q is the ratio of the fatigue life after damage and the fatigue life of the undamaged material.

All the above damage models make use of the fatigue S-N curve to predict the damage accumulation process in a multistress fatigue problem. To date, accurate and reliable models to *a priori* predict the fatigue S-N curve are not available. Several authors⁴¹⁻⁴³ have proposed empirical models which predict the fatigue life. However, these models are unreliable, cumbersome and difficult to use because the parameters used by these models are difficult to obtain experimentally³⁵. Some of these empirical models are discussed below.

Wang and Chim⁴¹ started with an equation which relates the experimentally observed rate of fatigue modulus degradation with the number of cycles and the applied stress level.

$$\frac{\partial D}{\partial N} = A(D) N^B \quad (2.1)$$

where D is the damage variable relating the initial modulus (E_o) with the modulus after N cycles (E) in stress controlled fatigue by the relation

$$E = E_o(1-D) \quad (2.2)$$

A is a function of D and B is the slope of the line in the log log plot of $\partial D/\partial N$ vs N . Wang and Chim experimentally determined the relation between B and the maximum stress level to be of the form

$$B = b_0 + b_1\sigma_{\max} + b_2\sigma_{\max}^2 + b_3\sigma_{\max}^3 + \dots \quad (2.3)$$

Integrating equation 2.1 led Wang and Chim to the following equation which relates the fatigue life to the parameters used by their model.

$$N_f = \left\{ \int_0^{D_f} \frac{(B+1)}{A} dD \right\}^{\frac{1}{B+1}} \quad (2.4)$$

Note that in equation 2.4, the parameter B is a function of the maximum stress level (see equation 2.3) and that the function A has not been defined. This model requires a large number of experiments to determine the constants (b_0 , b_1 , b_2 etc) in equation 2.3 and also to determine the form of the function A.

Hwang and Han⁴² started with an equation of the form

$$\frac{dF}{dn} = -A c n^{c-1} \quad (2.5)$$

where F is the fatigue modulus, dF/dn is the fatigue modulus degradation rate, A and c are material constants and n is the number of cycles. Hwang and Han integrated the above expression which led to an equation relating the number of cycles to failure (N) and the two material constants

$$N = [B(1 - F_f/F_o)]^{1/c} \quad (2.6)$$

where F_o is the undamaged modulus and $B = F_o/A$.

Hwang and Han have not provided a theoretical basis for their model. In fact, their model, like the one proposed by Wang and Chim, has been constructed by curve-fitting the experimental data. Moreover, they have used

3. Experimental:

3.1 Materials and Sample Preparation:

The PEKK resin used in this study is of developmental grade, with an approximate number average molecular weight of 10,000 and a weight average molecular weight of 30,000. Unreinforced PEKK and carbon/PEKK composite samples were supplied by DuPont as molded test bars which were already annealed at various crystallization temperatures. Hercules AS-4 carbon fibers were used as the reinforcement. A typical sample preparation schedule (as followed in the DuPont laboratory) is described below.

A molded plaque (unreinforced PEKK or carbon/PEKK composite) is placed in a compression mold which, in turn, is placed in a hydraulic platen press. The mold assembly is first heated to 320 °C with an applied platen pressure of 416 psi. At this point, pressure is reduced to minimum contact

pressure and the assembly is heated to 380 °C. Temperature is held at 380 °C for 30 minutes to insure complete melting. After the 30 minute hold, the mold assembly is rapidly quenched to the desired crystallization temperature using chilled water lines in the press platens. The cooling rate of this quench is approximately 60 °C/minute. The mold assembly is then held at the desired crystallization temperature for a predetermined amount of time to insure complete crystallization (typically ~2 hours). The mold assembly is then cooled at a fixed rate to room temperature. The rate of this final cooling step was varied from slow (2-10 °C/minute) to rapid quench (approximately 60 °C/minute). Additional samples were also prepared by directly cooling from 380 °C to room temperature at a predefined rate without stopping at an intermediate crystallization temperature. These direct-cooled samples were prepared over the same range of cooling rates described above.

In this thesis, the effect of crystallization temperature on static and dynamic mechanical performance and damage accumulation mechanisms has been investigated for PEKK and its carbon fiber reinforced composites. Unreinforced PEKK samples with T/I ratios of 60/40 and 70/30 are studied, along with unidirectional carbon fiber reinforced composites manufactured from the same matrix resins. PEKK with a T/I ratio of 60/40 (hereafter referred to as PEKK 60/40) is the system on which most of the analysis has been performed. PEKK with a T/I ratio of 70/30 (hereafter referred to as PEKK 70/30) is used as a comparison where necessary. The 60/40 and 70/30 composites were chosen because they are the two composites systems with the slowest crystallization kinetics (see Figure 2.7).

Composite samples are nominally 60% carbon fiber by volume. Three different crystallization temperature ranges are chosen based on the kinetics data shown in Figure 2.7. Specifically, crystallization is performed at kinetics-controlled conditions (280-300 °C), at diffusion-controlled conditions (210-220 °C), and at the peak crystallization temperature (250-260 °C). All crystalline samples are assumed to have the same final degree of crystallinity, X_c . This is ensured by holding the samples at the chosen crystallization temperature long enough to ensure complete crystallization (typically 2 hours). Samples which are cooled slowly from the melt (~ 2 °C/min) are also assumed to be completely crystallized.

Note that the cooling rates used in the quenching treatment (60° C/min) will result in a largely amorphous structure. However, a certain amount of crystallinity will probably be introduced in the “amorphous” systems because the cooling rates are finite and the rate of crystallization is relatively fast (see Figure 2.7).

3.2 Acoustic Emission Characterization:

The damage accumulation process was monitored using the acoustic emission method. A "Spartan-AT" acoustic emission unit, manufactured by Physical Acoustics Corporation, combined with an Everex 386 IBM Compatible PC were used for this purpose. Piezoelectric sensors having a frequency response of 100-1000 kHz were used in conjunction with preamplifiers and band-pass filters having a frequency range of 100-1200 kHz. The total signal amplitude gains used have been reported along with the experimental results.

Two piezoelectric sensors were coupled to the sample by means of a high viscosity vacuum grease, and were symmetrically located 35 mm from the loading nose.

Damage events in the composite sample release acoustic waves which travel through the material and reach the piezoelectric sensor. The piezoelectric sensor converts the mechanical energy of the acoustic waves into electrical signals. When the incoming signal exceeds a preset threshold value, one "count" is recorded by the acoustic unit. Acoustic waves generated by the damage events typically result in multiple counts. Figure 3.1 depicts a typical waveform generated by a damage event.

It is desired that each damage event result in one *hit* in the acoustic unit. The parameters which can be varied to recognize hits from the acoustic waveforms are the Peak Definition Time (PDT), the Hit Definition Time (HDT) and the Hit Lag Time (HLT). The function of the PDT is to enable determination of the time of the true peak of the AE waveform. The PDT circuitry is triggered by new signal maxima. The main requirement for a correct PDT value is to avoid false measurements being made on a low amplitude precursor of the actual signal maxima. Subject to this condition, the PDT was set as short as possible. Figure 3.2 depicts the correct and incorrect values of PDT. If the PDT is too short, then the peak is defined prematurely, resulting in a lower characteristic amplitude of the waveform. The PDT should be long enough to span the time interval between two signal maxima in the acoustic wave.

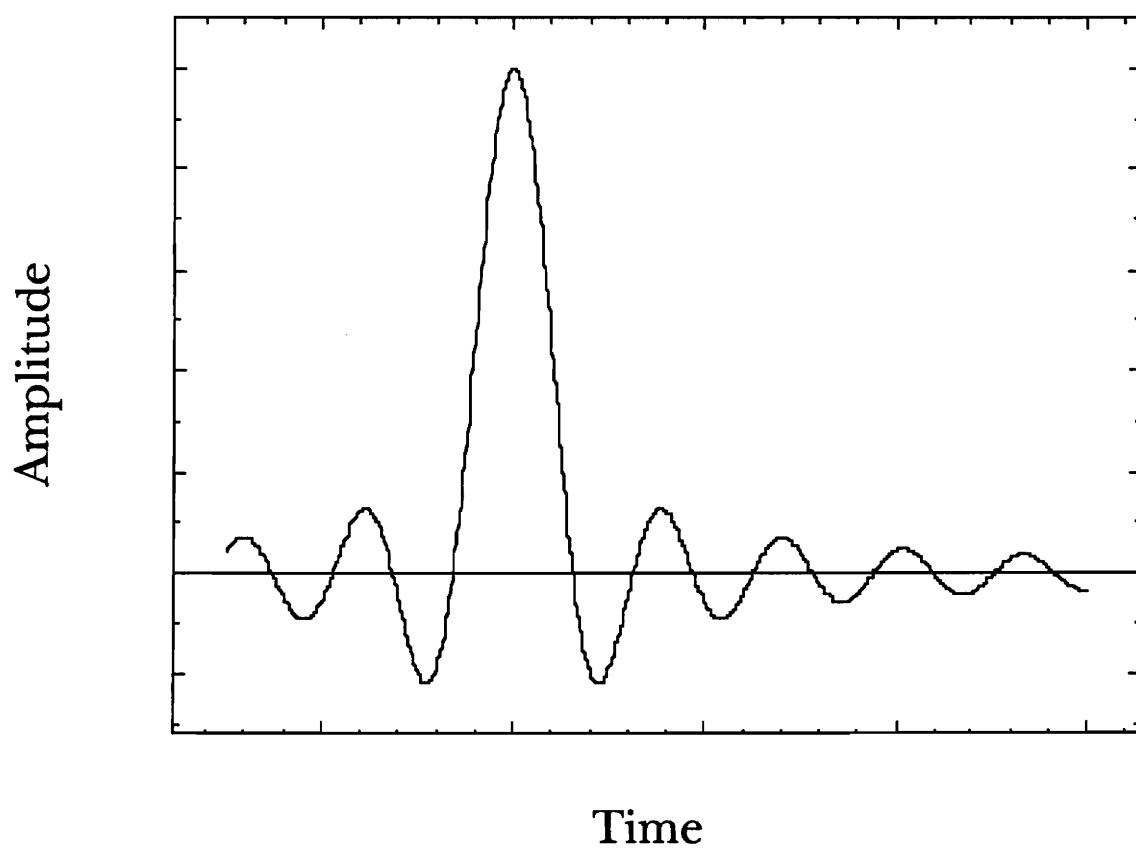


Figure 3.1 A schematic of a typical acoustic waveform

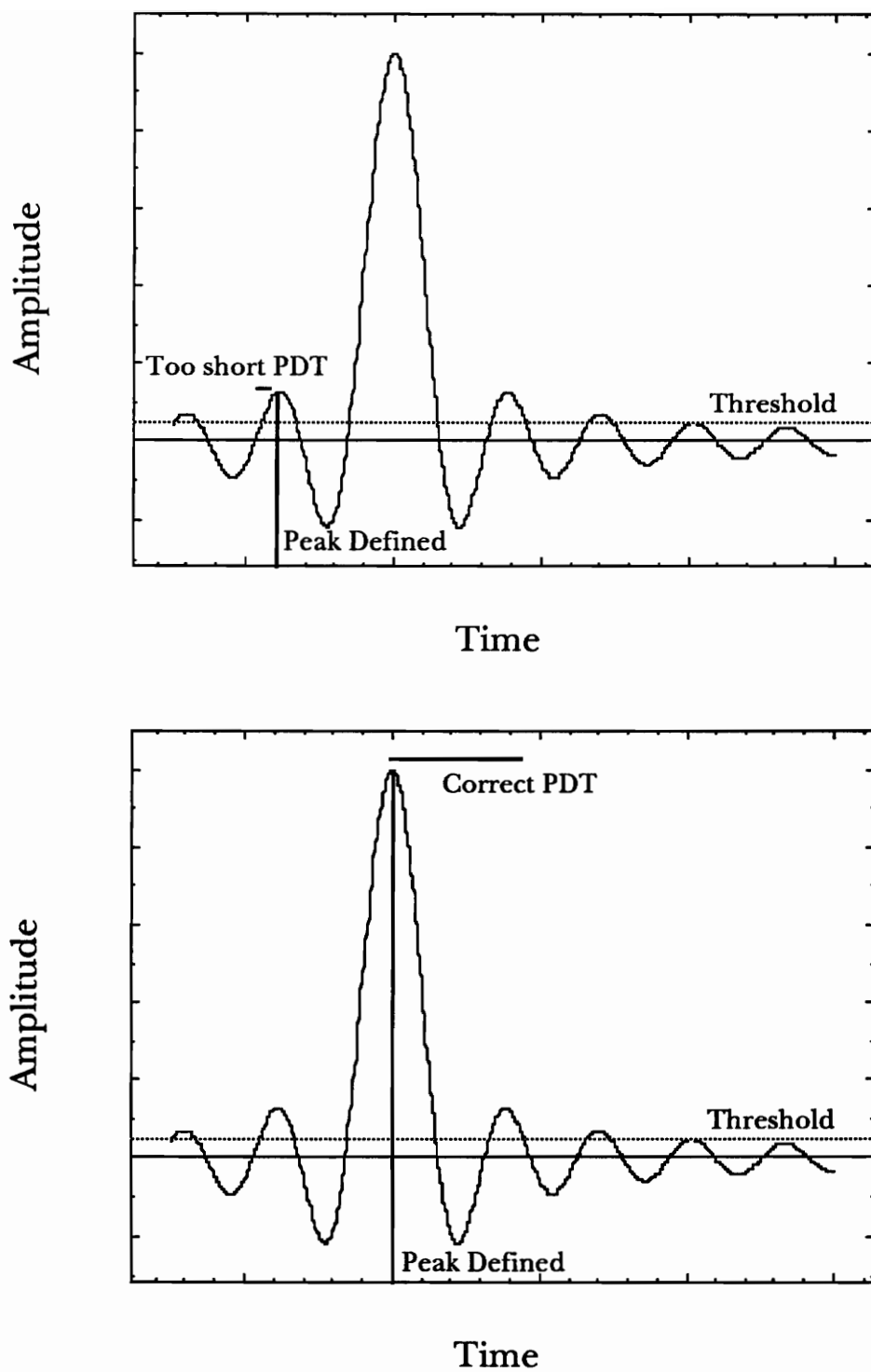


Figure 3.2 Correct and Incorrect values of the Peak Definition Time (PDT).

The function of the HDT is to enable the system to determine the time at the end of the hit, close out the measurement processes and store the measured attributes of the signal. The HDT circuitry is triggered when the signal decreases below threshold level. The main function of HDT is to identify and describe hits realistically. The HDT must be long enough to span over intervals in which the signal to be measured falls below the threshold value. Subject to this condition, the HDT is set as short as possible. Figure 3.3 outlines the correct settings for the HDT. If the HDT is set too low, then the time at the end of the hit is defined prematurely, resulting in lower counts, energy, duration, and also opening the possibility of the acoustic setup recording multiple hits from the same waveform.

The HLT is used to lock out any signal after a hit. It should be set as short as possible in order to ensure that a second hit is not locked out, but at the same time, it should be long enough to ensure that reflections from the main wave are not recorded as separate hits. Figure 3.4 illustrates the correct and incorrect settings of the HLT. If the HLT is set too low, the setup might record multiple hits from the same waveform. If the HLT is set too high, the system might lock out waveforms generated by new damage events. For the given geometry of the test samples, reflections from the main wave are typically overlapped with the main wave hence, the HLT was set as short as possible. The PDT, the HDT and the HLT have been reported along with the results.

The acoustic velocity in the composite samples was experimentally determined to be 8.7 km/sec. This compares well with the velocities of the longitudinal waves calculated using the equation relating the acoustic velocity

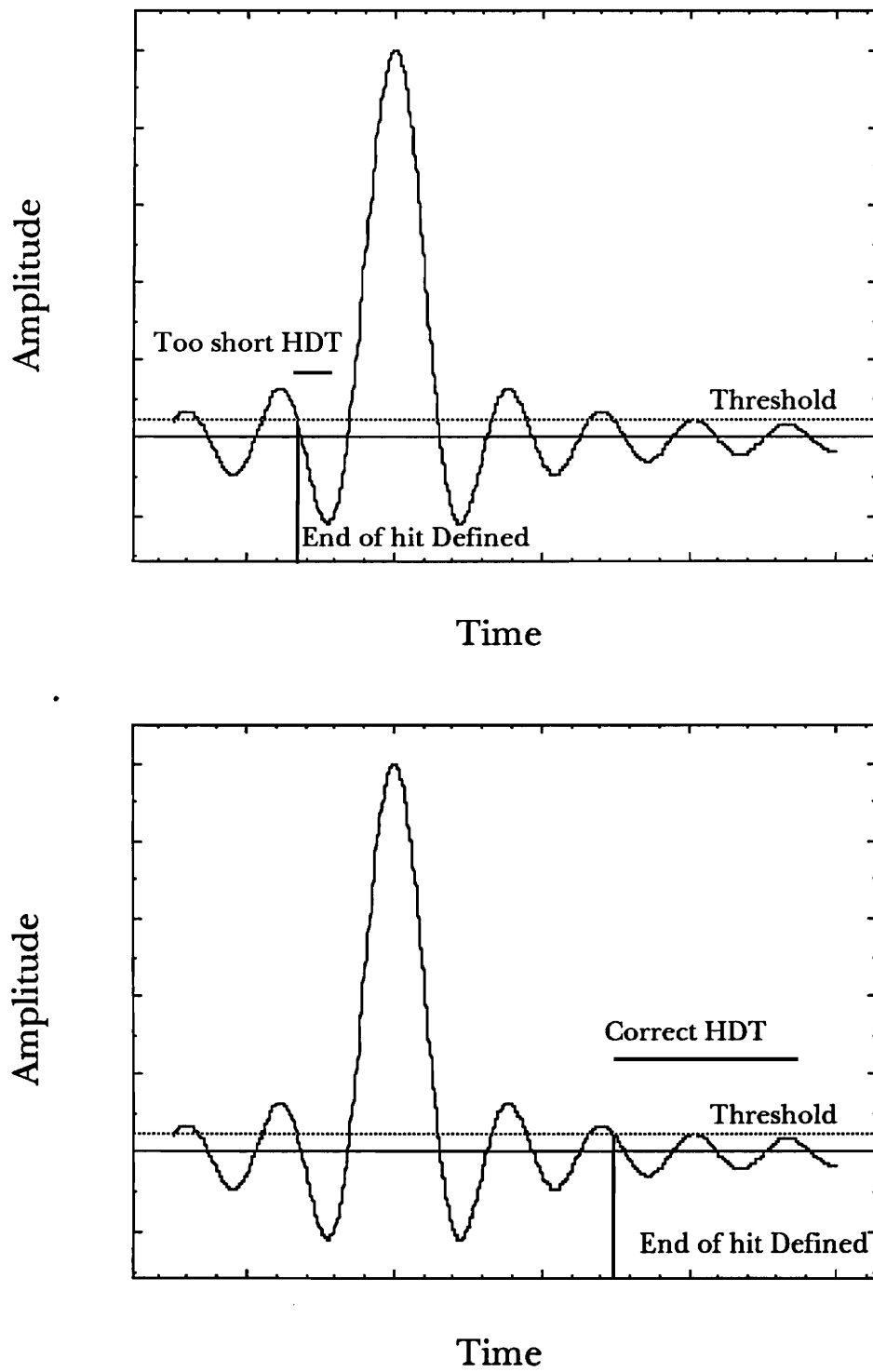


Figure 3.3 Correct and Incorrect values of the Hit Definition Time (HDT).

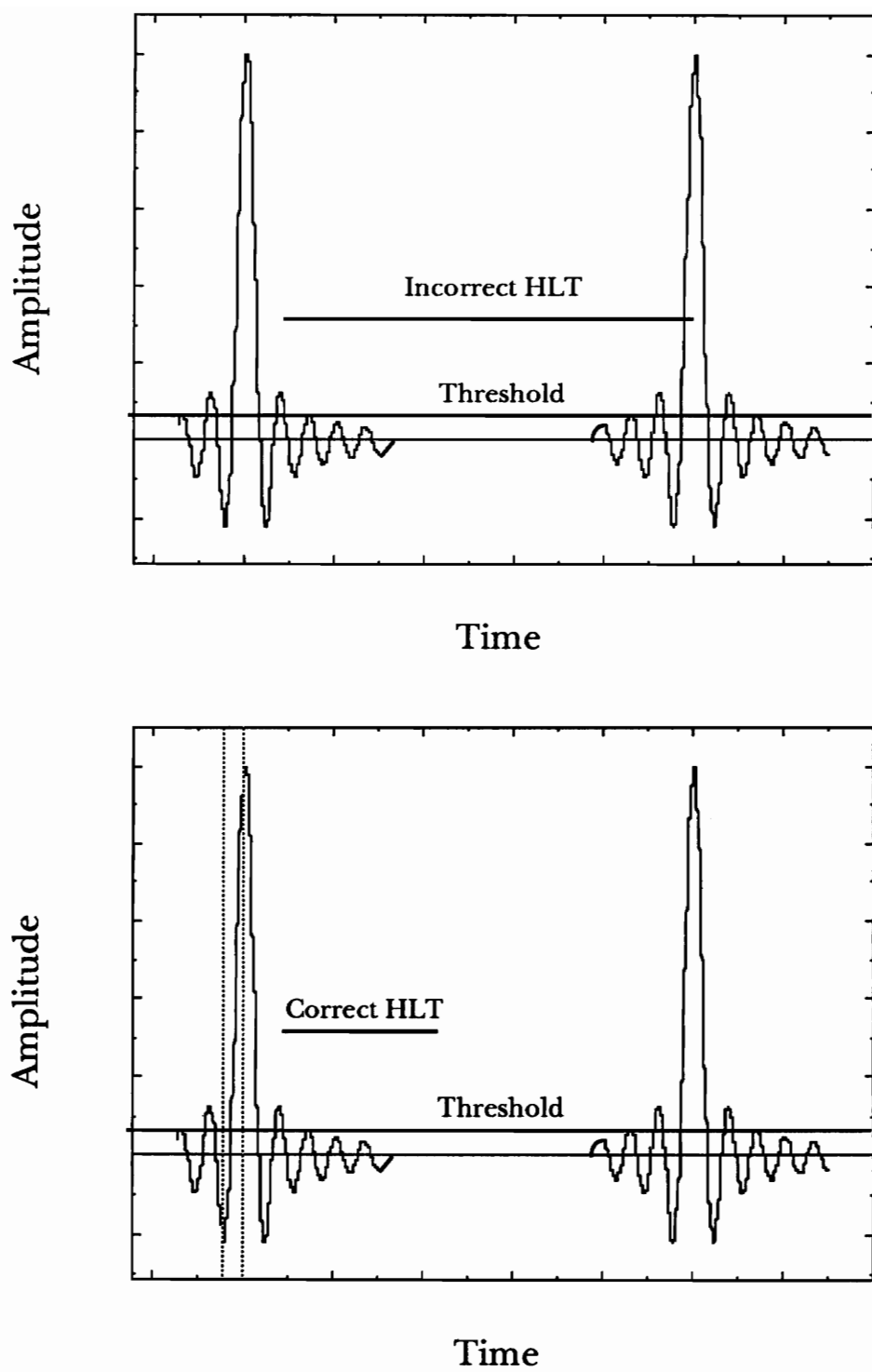
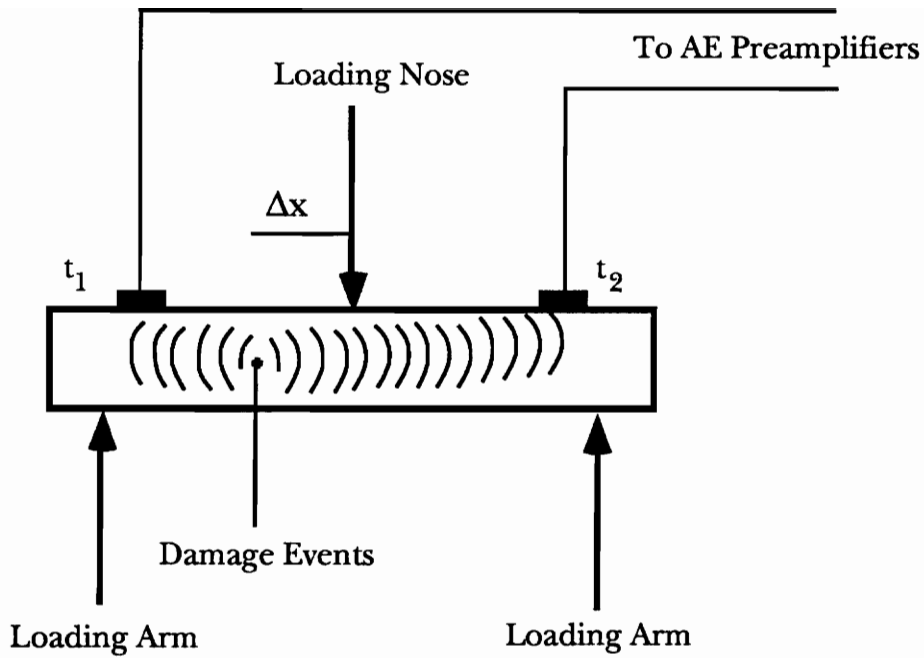


Figure 3.4 Correct and Incorrect Values of the Hit Lag Time.

to the density and modulus of the medium ($V = (E/\rho)^{1/2}$, where V is the acoustic velocity, E is the modulus and ρ is the density of the medium). Based on the reported⁴⁶ values of modulus and densities of the AS4 Carbon fiber (231 GPa and 1780 kg/m³ respectively), the predicted acoustic velocity is 11.391 km/sec. Also, based on the experimentally determined modulus and density of the composite samples (88.2 GPa and 1562 kg/m³ respectively for the quenched AS4 carbon fiber reinforced PEKK 60/40 system), the predicted acoustic velocity is 7.512 km/sec. The actual acoustic velocity lies between the predicted velocities of the longitudinal waves in the composite material and the carbon fibers.

Acoustic waveforms typically hit the two sensors at different times. Based on the acoustic velocity, the location of the two sensors, and the difference between the time of hits at the two sensors, the locations of the individual acoustic events have been calculated. The calculation of the locations of the acoustic events is illustrated in Figure 3.5.

In order to filter out unwanted noise signals, a “count filter” was used. Acoustic waveforms typically generate multiple counts, while noise signals (probably generated in the electronic circuitry of the acoustic unit) have lower counts. Hence, all acoustic hits with the number of counts less than a preset “count filter” were filtered out. The value of the count filters used have been reported along with the results.



the location of the acoustic event can be calculated from

$$\Delta x = \frac{(t_2 - t_1)V}{2}$$

where, t_1 is the time of hit at sensor 1

t_2 is the time of hits at sensor 2

V is velocity of the acoustic wave

Figure 3.5 Schematic outlining the calculation of the location of the individual acoustic events.

3.3 Mechanical Characterization:

Unless otherwise mentioned, all mechanical properties were measured using a hydraulic Materials Test Systems (MTS) test frame. Loads were monitored using a load-cell with a maximum range of 20,000 lbs. The full scale load range used for the quasi-static flexure tests of the composite samples was 2,000 lbs. All three point bend samples had nominal dimensions of 2.5 x 12.7 x 150 mm. Stroke controlled quasi-static flexure tests were performed on the three point bend bars with a span to depth ratio (S/D ratio) of 16. A ramp rate of 0.1 inch/minute was used for this purpose. Some of the flexure tests on the unreinforced resin systems were performed using a 110 lb load cell and some were performed using the 20,000 lbs load cell with the full scale range of 2,000 and with a voltage multiplier of 10 attached to the load cell output for an effective full scale range of 200 lbs. Reported stresses and strains have been calculated from the loads and stroke using first order linear beam theory with no additional correction terms (see Appendix A).

Fatigue tests were performed on the composite systems using an S/D ratio of 16, and a stroke controlled haversine waveform with the minimum in the stroke cycle being set close to zero. Care was taken to ensure that the load never drops to zero. Within this limit, the minimum in the stroke cycle was set as close to zero as possible. The frequency of the haversine waveform used was 0.1 Hz

Impact tests were performed on a Tinius Olsen impact testing machine with a fully instrumented Dynatup load cell. Samples were impacted with a

pendulum type weight of 25.07 kg at an impact velocity of 2.31 m/s. Samples used for the impact tests had nominal dimensions of 2.5 x 12.7 x 75 mm, and were tested at a span-to-depth ratio of 16. Complete load versus time curves were recorded and numerically integrated to determine impact energy absorption. Impact strength, impact modulus, and failure strain were then calculated using linear beam theory.

4. Results and Discussion

4.1 Mechanical Properties

4.1.1 Quasi-Static Flexural Properties:

The results of unreinforced resin flexural tests are given in Table 4.1. Note that tests were performed on PEKK 60/40 as well as PEKK 70/30 . The "strains" reported in Table 4.1 refer to the strain at maximum stress, and not to the strain at failure. In fact, the samples marked "ductile" in this column did not break during the flexural test, and were able to sustain very high strains without exhibiting macroscopic fracture. These data show that, in both PEKK 60/40 and PEKK 70/30, modulus is higher for the crystallized samples and strain to failure is higher for the amorphous samples. Measured strengths in both systems follow the order (from strongest to weakest): 280 °C, Quenched, 230 °C, @ 2 °C/minute. This can be explained in terms of the morphology generated by the applied heat treatments. Quenching will give rise to a nearly

Table 4.1 Results of unreinforced resin flexure tests.

PEKK 60/40

Treatment	Modulus (Msi)	Strength (ksi)	Failure Strain (%)
Quenched	0.88	28.8	4.68-ductile
280 °C	1.31	32.6	2.34
230 °C	1.06	24.9	2.34
@ 2 °C/min	1.02	23.0	2.34

PEKK 70/30

Treatment	Modulus (Msi)	Strength (ksi)	Failure Strain (%)
Quenched	1.08	36.0	5.15-ductile
280 °C	1.08	45.0	4.21
230 °C	1.31	30.7	2.34
@ 2 °C/min	1.66	28.0	1.88

homogeneous amorphous structure and hence the strain to failure is higher, while the other heat treatments give rise to greater degrees of crystallinity and thus higher moduli. The results of carbon/PEKK composite flexural tests are given in Table 4.2. Static properties are largely as expected for these composite systems. Failure strain is primarily controlled by tensile failure of the carbon fibers (about 1.5-2.0 %). Composite modulus is slightly lower than that predicted from the modulus of the carbon fibers by a simple rule of mixtures. A rule of mixtures calculation assuming a carbon fiber modulus of ~32 Msi and a fiber volume fraction of 60% predicts a composite modulus of approximately 19-20 Msi. Note that all composite systems reported in Table 4.2 have moduli lower than this prediction. This may be due to lower fiber loadings than anticipated (ca. 45%), inefficient shear load transfer at the fiber-matrix interface, or shear deformation which is not accounted for in the linear beam analysis. Note also that the amorphous sample has the lowest reported modulus. This drop in amorphous composite modulus is too large to be accounted for by the modulus decrease in the unreinforced resin. This suggests other contributing factors such as even less efficient shear load transfer at the fiber-matrix interface, larger residual stresses in the amorphous (quenched) sample, or process-induced internal damage.

Table 4.2 Results of carbon/PEKK composite flexure tests.

Carbon/PEKK 60/40

Treatment	Modulus (Msi)	Strength (ksi)	Failure Strain (%)
Quenched	12.28	216	1.75
280 °C	14.75	252	1.4
260 °C	14.75	302	1.4
230 °C	12.90	249	1.75

Carbon/PEKK 70/30

Treatment	Modulus (Msi)	Strength (ksi)	Strain (%)
Quenched	13.1	230	1.8
300 °C	15.7	220	1.75
260 °C	16.7	235	1.75
220 °C	15.3	144	1.75
@ 2 °C/min	16.0	230	0.96

4.1.2 Impact Properties:

The results of impact tests performed on unreinforced PEKK resins and on carbon/PEKK composites are listed in Tables 4.3 & 4.4. "Failure Strain" in these tables refers to the strain at maximum stress, while "Max Strain" refers to the final strain at which the sample either failed catastrophically or stopped absorbing impact energy. It should be noted that the quenched PEKK 60/40 and PEKK 70/30 samples did not catastrophically fail during these tests. Therefore, the actual energy absorption capability of these samples is higher than that reported in Table 4.3. All other samples failed catastrophically at the reported "Max Strain". Finally, there was a large amount of data scatter in the impact properties of the slow cooled PEKK 70/30 sample. This extreme scatter made it impossible to report a significant average value. Hence in Table 4.3 the extreme values of the measured impact properties are reported.

In Table 4.4, the carbon/PEKK composite failure modes are labeled as "T/C" for cases where a single tension/compression type failure is observed. Note that both the quenched samples are labeled "D + T/C" to indicate that delamination was first observed, with both delaminated layers then failing in tension/compression. This suggests that either the interfacial shear strength is not as high in the amorphous (quenched) composite systems as compared with the crystallized composite systems, or a higher residual stress is introduced at the fiber matrix interface during the quenching treatment. This reinforces conclusions made previously from results of quasi-static tests.

Table 4.3 Results of unreinforced resin instrumented impact tests.

PEKK 60/40					
Treatment	Max Stress (ksi/MPa)	Failure strain (%)	Max Strain (%)	Energy absorbed (J)	Impact modulus (ksi/GPa)
Quenched	21.8/147	6.73	>8.00	>0.08	>317/2.19
280 °C	19.5/134	3.08	3.21	0.02	634/4.37
230 °C	22.6/156	3.40	3.45	0.035	660/4.59
@ 2 °C/min	18.3/126	2.44	2.88	0.0018	750/5.18
PEKK 70/30					
Treatment	Max Stress (ksi/MPa)	Failure strain (%)	Max Strain (%)	Energy absorbed (J)	Impact modulus (ksi/GPa)
Quenched	30.2/20.8	5.48	>5.59	>0.08	>551/3.80
280 °C	27.0/18.6	4.83	5.06	0.07	558/3.85
@2 °C/min	119/81.8	1.5	1.603	0.9	791/5.46
@2 °C/min	1/0.62	1.34	1.415	0.00045	6.6/0.046

Table 4.4 Results of carbon/PEKK composite instrumented impact tests.

Carbon/PEKK 60/40						
Treat- ment	Max Stress (ksi/GPa)	Failure strain (%)	Max Strain (%)	Energy absorbed (J)	Impact modulus (Msi/GPa)	Failure mode
Quench	221/1.53	1.73	2.81	5.60	12.8/88.2	D + T/C
280 °C	240/1.66	1.97	2.72	6.50	12.2/84.0	T/C
260 °C	266/1.84	2.06	4.41	8.50	12.9/89.0	T/C
230 °C	248/1.71	1.92	6.56	5.70	13.0/89.0	T/C
Carbon/PEKK 70/30						
Treat- ment	Max Stress (ksi/GPa)	Failure strain (%)	Max Strain (%)	Energy absorbed (J)	Impact modulus (Msi/GPa)	Failure mode
Quench	232/1.60	2.10	3.00	2.90	11.7/80.35	D + T/C
300 °C	253/1.75	2.10	2.47	2.85	12.5/86.05	T/C
260 °C	253/1.75	2.35	2.59	3.30	10.8/74.55	T/C
220 °C	271/1.87	2.20	2.62	3.00	12.9/89.10	T/C
2 °C/min	262/1.81	2.30	2.70	3.90	11.4/78.65	T/C

In the unreinforced resin systems, the amorphous samples have higher elongations in impact, absorb more energy, and have lower moduli (see Table 4.3). Note also that the failure stresses of the amorphous and crystallized samples are not significantly different from one another. Compare this with the carbon fiber reinforced composite systems, where the impact moduli are not significantly different from one another and the failure stresses and failure strains are slightly lower in the amorphous systems (see Table 4.4). The amorphous composite samples absorb less energy than the crystallized samples and delaminate before the tension/compression failure. This observation is surprising in light of Table 2.3 which indicated that the amorphous composite systems are tougher than the crystallized composite systems. This apparent anomaly is probably caused by the fact that in impact loadings, the matrix does not have time to deform, therefore the toughness of the matrix is not a factor. Also, the interface is probably weaker in the quenched composite systems, giving rise to the lower energy absorptions. This reinforces the conclusion made previously that the interface is weaker or a higher residual stress is introduced in the amorphous composite systems as compared with the crystallized composite systems.

By comparing the data in Table 4.3 with that in Table 4.1, it can be seen that the apparent modulus of the unreinforced resin systems decreases substantially with increasing strain rate. For example, the crystallized PEKK 60/40 samples have quasi-static flexural moduli ranging from 1.0-1.3 Msi. These values drop to the range of 0.63-0.75 Msi when measured at impact speeds. This trend is contrary to traditional viscoelastic theory, and may

indicate substantial changes in the mechanisms of damage accumulation as a function of testing rate.

Although composite stiffnesses are dominated by the fiber properties, this decrease in unreinforced resin modulus is often reflected in a slight decrease in the composite modulus. This can be seen by comparing the data in Table 4.4 with that in Table 4.2. For example, the (60/40) carbon/PEKK composites have flexural moduli that either remain essentially unchanged or decrease by about 10-20% in comparing quasi-static results with impact results.

4.2 Acoustic Emission Testing

4.2.1 Composite systems

Damage initiation and progression during three point bend testing of the unreinforced PEKK 60/40 and 70/30 systems and their carbon fiber reinforced composites were studied by AE monitoring. The results of these tests are given in Figures 4.1 through 4.13.

Figures 4.1 through 4.4 summarize the results of acoustic monitoring of damage in quasi-static three point bend loading of the carbon fiber reinforced PEKK 60/40 composite systems. These figures include a plot of the load vs the applied stroke (plot A), a plot of the number of hits recorded during the flexure test vs the amplitude of these hits (plot B), a point plot of the amplitude of the individual acoustic hits recorded during the flexure test vs. the stroke at which they take place (plot C), and a plot of the number of acoustic hits recorded vs the applied stroke (plot D). The acoustic monitoring was performed using a total amplitude gain of 65 dB, a threshold amplitude of 45 dB, a count filter of 10, a

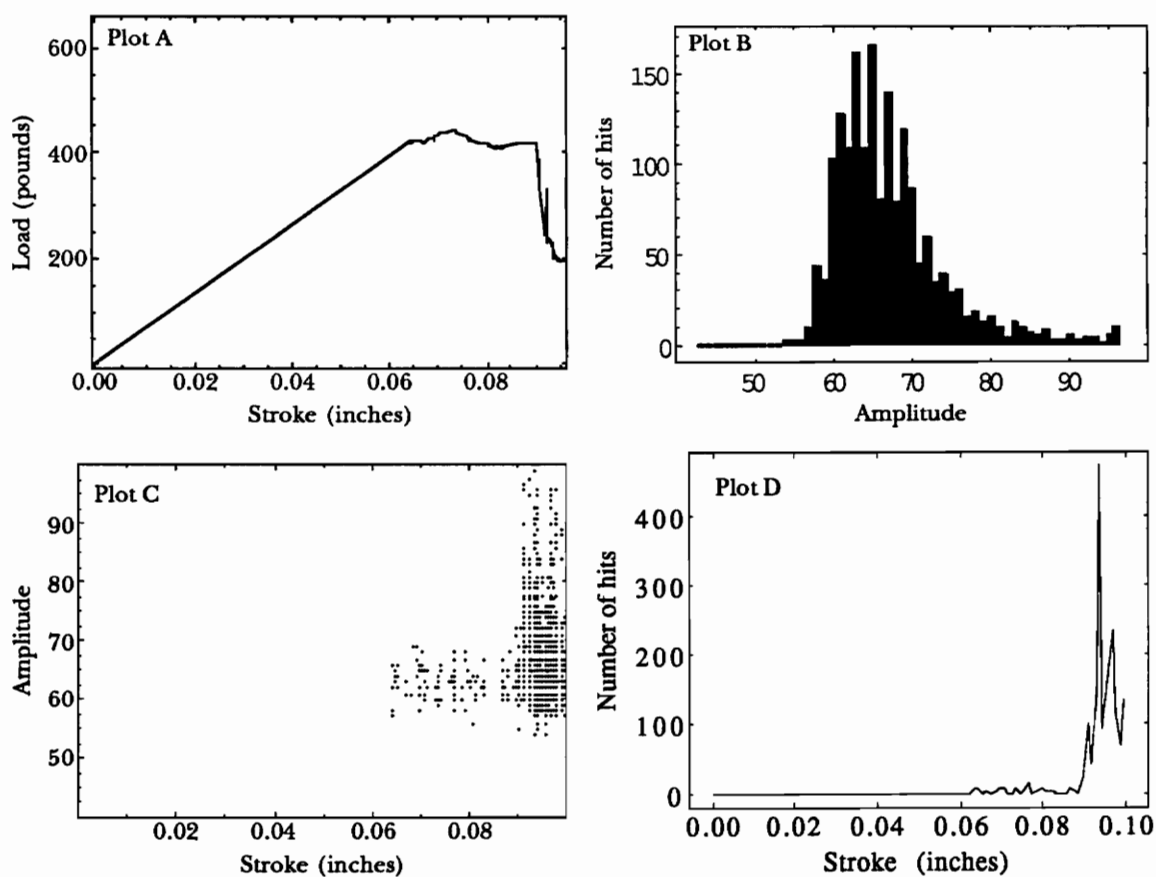


Figure 4.1 : Results of acoustic monitoring of damage accumulation in the quenched carbon fiber reinforced PEKK 60/40 system using an amplitude gain of 65 dB.

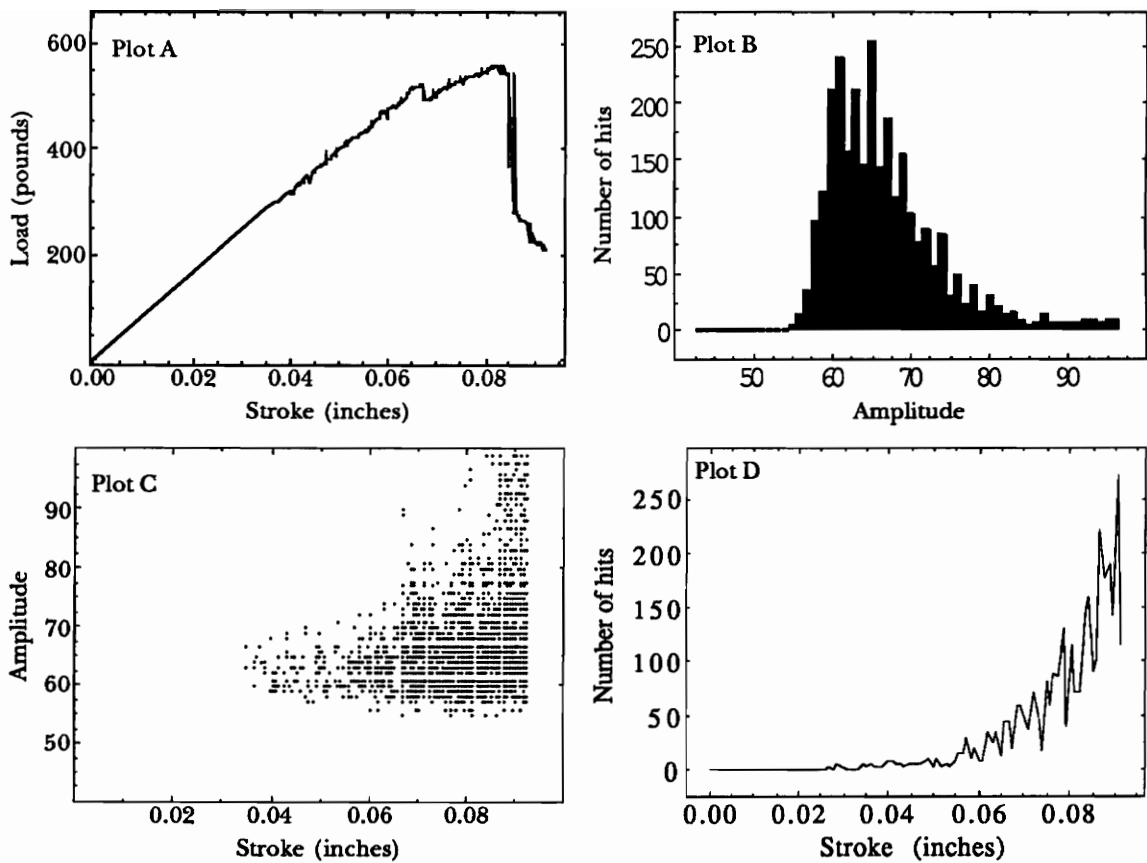


Figure 4.2 : Results of acoustic monitoring of damage accumulation in the carbon fiber reinforced PEKK 60/40 crystallized at 280° C using an amplitude gain of 65 dB.

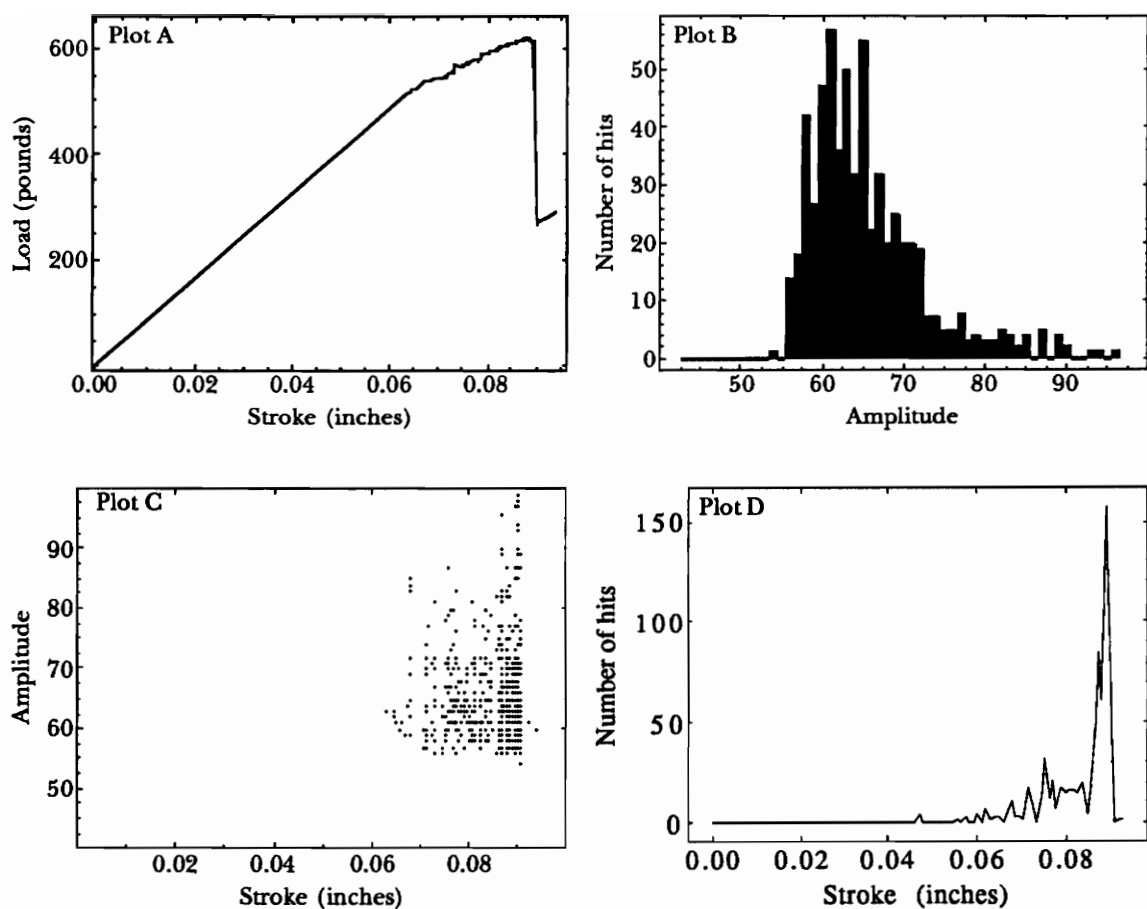


Figure 4.3 : Results of acoustic monitoring of damage accumulation in the carbon fiber reinforced PEKK 60/40 crystallized at 260° C using an amplitude gain of 65 dB.

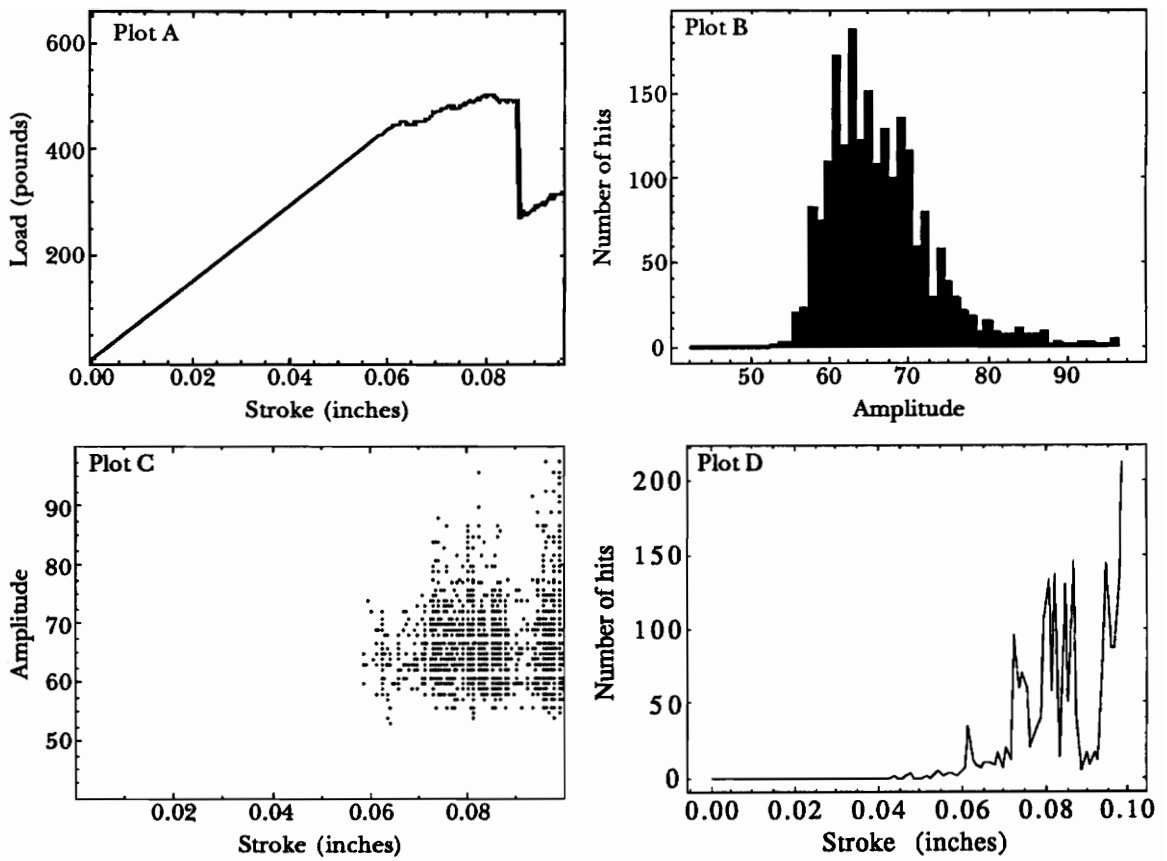


Figure 4.4 : Results of acoustic monitoring of damage accumulation in the carbon fiber reinforced PEKK 60/40 crystallized at 230° C using an amplitude gain of 65 dB.

PDT of 50, an HDT of 120 and an HLT of 300 (see section 3.2 for an explanation of these parameters). Based on the work done by previous authors²⁰⁻³⁴ using total amplitude gains in the range of 60-65 dB, the amplitude of the individual acoustic hits can be used to obtain information on the nature of the damage events. The amplitude distribution has been divided by these authors^{20-25,31} into three distributions generated by matrix cracking, interfacial failure and fiber fracture. Based on the work done by these authors and work previously done in our lab on short glass fiber reinforced polystyrene composite systems it is assumed that:

- In the carbon fiber reinforced composites, matrix cracking releases acoustic waves which have amplitudes in the range of 55-70 dB, interfacial failures release acoustic waves which have amplitudes in the range of 65-80 dB, and fiber fractures release acoustic waves having amplitudes greater than 80 dB.
- In the unreinforced resin, plastic deformation of the matrix and matrix cracking are the only damage modes, and they release acoustic waves in the range of 45-60 dB.

Figure 4.1 summarizes the results of acoustic monitoring of damage during a quasi-static three point bend test of a quenched carbon fiber reinforced PEKK 60/40 system. The amplitude distribution (plot B) has a prominent peak in the 55-70 dB range and a shoulder in the 70-90 dB range. From plot C in Figure 4.1, it can be seen that AE hits in the 60-70 dB range are initiated at a stroke of 0.06 inches. Also, since AE hits with these amplitudes have been assigned to matrix cracking, it can be concluded from plot C (based on the

assumptions made regarding the amplitude distributions) that matrix cracking initiates at a stroke of 0.06 inches in the amorphous sample. Before this point, there is little deviation from linear load/stroke behavior as seen in plot A. Plot C also indicates that the 80-100 dB hits initiate at a stroke of 0.088 inches. Since amplitudes in this range have been assigned to fiber failure, it can be concluded (based on the assumptions made regarding the amplitude distributions) that fiber failure initiates at a stroke of 0.088 inches in this system, which is the point where a substantial drop in load occurs. From plot C, it can also be seen that hits with amplitudes in the range of 65-80 dB do not initiate before 0.088 inches. Since this amplitude range has been assigned to interfacial failure, it can be concluded (based on the assumptions made regarding the amplitude distributions) that either very little energy is released due to interfacial failures taking place before 0.088 inches or interfacial failures do not initiate before 0.088 inches.

In section 4.1, results of a series of mechanical tests were presented. These results indicate that the modulus in quasi-static flexure and the modulus and energy absorbed in impact are lower in the quenched composites when compared to the crystallized samples. It was also observed that a substantial amount of delamination takes place in the quenched samples. From these experimental results, it was concluded that either the interface is weaker or the residual stress is higher in the amorphous composite systems.

On comparing the conclusions made from the acoustic monitoring of the quenched composite and the conclusions made from the mechanical properties of all the composite systems (as discussed above), it can be concluded

that the interface in the quenched carbon fiber reinforced PEKK 60/40 is weak and does not release substantial energy on failure. This conclusion is also supported by the fact that interfacial failures initiate well below 0.088 inches in the other composite systems as discussed subsequently in this section.

Figure 4.2 summarizes the AE results for samples crystallized at 280 °C. The amplitude distribution for this system (plot B) shows a prominent peak in the 55-70 dB range, with an overlapping shoulder in the 65-80 dB range, and a few hits in the 80-100 dB range. From plot C, it can be seen that the 55-70 dB hits initiate at a stroke of 0.03 inches. Since hits in this amplitude range have been assigned to matrix cracking, it can be concluded that in this system, matrix cracking initiates at a stroke of about 0.03 inches. From plot A, it can be seen that at this point the load/stroke behavior begins to deviate from linearity. Also, from plot C, it can be seen that hits in the 65-80 dB amplitude range initiate at a stroke of about 0.06 inches. Since hits in this amplitude range have previously been assigned to interfacial failure events, it can be concluded that interfacial failure events initiate at a stroke of about 0.06 inches, at which point the load-stroke response exhibits a slight drop in load and an increased deviation from linearity. From plot C, it can be seen that hits with amplitudes greater than 80 dB initiate at 0.085 inches. Since hits in this range have been assigned to fiber fracture, it can be concluded that fiber failure initiates at a stroke of about 0.08 inches, and from plot A, it can be seen that at this point the load drops by more than 50%.

Figure 4.3 summarizes the AE results for samples crystallized at 260 °C. From plot B, it can be seen that in this system, there is a prominent peak in the

55-65 dB range, with a very prominent shoulder in the 65-80 dB range. From plot C, it can be seen that the 55-65 dB hits initiate at 0.06 inches and the 65-80 dB hits initiate at 0.07 inches. Since hits with these amplitudes have been assigned to matrix cracking and interfacial failure respectively, it can be concluded that in this system, matrix cracking initiates at 0.06 inches and interfacial failures initiate at 0.07 inches. From plot C, it can also be seen that hits with amplitudes greater than 80 dB initiates at 0.085 inches. Since these hits have been assigned to fiber fractures, it can be concluded that fiber fracture start at a stroke of about 0.085.

Finally, Figure 4.4 summarizes the AE results for samples crystallized at 230 °C. In this system, there is a peak between 55 and 65 dB, a prominent shoulder between 65 and 80 dB and a small peak between 80 and 95 dB. From plot C, it can be seen that hits in the 55-70 dB range initiate at 0.055 inches, hits in the 65-80 dB range initiate at 0.065 inches and hits with amplitudes higher than 80 dB initiate at 0.09 inches. Since hits in these ranges have previously been assigned to matrix cracking, interfacial failures and fiber fracture respectively, it can be concluded that matrix cracking initiates at a stroke of 0.055 inches, interfacial failures initiate at 0.065 inches and fiber fracture initiate at 0.09 inches. From plot A, it can be seen that there is very little deviation from the linear load-stroke behavior before 0.055 inches. The load-stroke plot shows an additional deviation at 0.065 inches, corresponding to the point at which interfacial failure initiates. It is interesting to note from plots A and C, that most of the 80-100 dB hits take place after a catastrophic failure has taken place. This indicates that the catastrophic failure mode in this system is

not fiber fracture in tension. In fact, a visual examination of the damaged sample indicates a compressive buckling failure mode.

It is important to note that the absence of AE events associated with interfacial failure in the amorphous system might indicate very weak interfaces in the amorphous composites. This is consistent with the conclusions made from the flexural and impact experiments discussed earlier. Table 4.5 summarizes the points of initiation of matrix cracking, interfacial failure and fiber fracture for the four different 60/40 composite systems investigated.

Table 4.5 : Points of initiation of matrix cracking, interfacial failure and fiber failure for 4 different 60/40 composite systems investigated (as obtained from acoustic emission using an amplitude gain of 65 dB).

Treatment	Matrix Cracking (inches)	Interfacial Failure (inches)	Fiber Fracture (inches)
Quenched	0.06		0.088
280° C	0.03	0.06	0.08
260° C	0.06	0.07	0.085
220° C	0.055	0.065	0.09 (after sharp load drop)

It should be pointed out that the conclusions made in this section are based upon a set of assumptions regarding the amplitude distributions. While these assumptions have not been physically verified, they have been made on the basis of work done by previous authors and as such, seem reasonable.

Also, the conclusions made in this section for the four composite systems should be qualified with the remark that acoustic emission is not an absolute technique. Points of initiation of the various damage modes, as obtained from acoustic emission, need not correspond to the actual points of initiation. For example, for the quenched composite systems, it was concluded from plot C in Figure 4.1 that the absence of hits in the 65-80 dB range implies that either the interface is weak and therefore interfacial failure does not release acoustic energy or interfacial failure is not taking place at all. There can be one additional explanation: interfacial failures are taking place, but do not result in any hits in the 65-80 dB amplitude range. Hence the points of initiation for the various damage modes should be considered relative at best. This is specially true for matrix cracking. Matrix cracking events typically give rise to low amplitude signals. Hence the absence of hits in the 55-70 dB amplitude range below 0.06 inches in the quenched system might indicate that the energy released by matrix cracking events at low strokes is not high enough to cross the count filter (see section 3.2). In section 5, additional work is presented which pinpoints the initiation of the various damage modes with greater accuracy. Also, in order to obtain additional information on the damage accumulation process, acoustic monitoring of damage during quasi-static three point bend testing was performed using higher amplitude gains. Figures 4.5

through 4.12 summarize the results of acoustic monitoring of damage using a total amplitude gain of 85 dB, a threshold amplitude of 45 dB and a count filter of 4. The PDT, HDT and HLT used in these tests were 50, 120 and 300 respectively.

Figures 4.5 through 4.8 summarize the results of acoustic monitoring of damage in the four carbon fiber reinforced PEKK 60/40 composite systems. As before, the figures include a load-stroke plot (plot A), an amplitude distribution (plot B), a point plot of the amplitude of the individual acoustic hits vs. the stroke (plot C) and a plot of the number of hits vs. the stroke (plot D).

Plot C and plot D in the four figures depict an unusual initial acoustic activity in the 45-60 dB amplitude range at very low strokes. From plot C and, more clearly, from plot D in the four figures, it can be seen that this initial acoustic activity decreases substantially as the stroke is increased. From a literature search, it was concluded that this unusual initial AE activity has not been reported by any author. This unusual initial acoustic activity is referred to in subsequent sections as being caused by type 1 damage events. It can be seen from plots A and C that occurrence of type 1 events (as manifested by hits in the 45-55 dB amplitude range in plot C) is accompanied by negligible deviation from a linear load stroke behavior, and hence it can be assumed that type 1 events do not result in any significant damage to the composite material. From plots C in Figures 4.5, 4.7, and 4.8 it can be seen that the amplitude of these type 1 events increases initially as the stroke is increased. In the sample crystallized at 280° C (Figure 4.6), it can be seen that hits in the 45-55 dB amplitude range occur even at high strokes and that they are overlapped by hits with higher

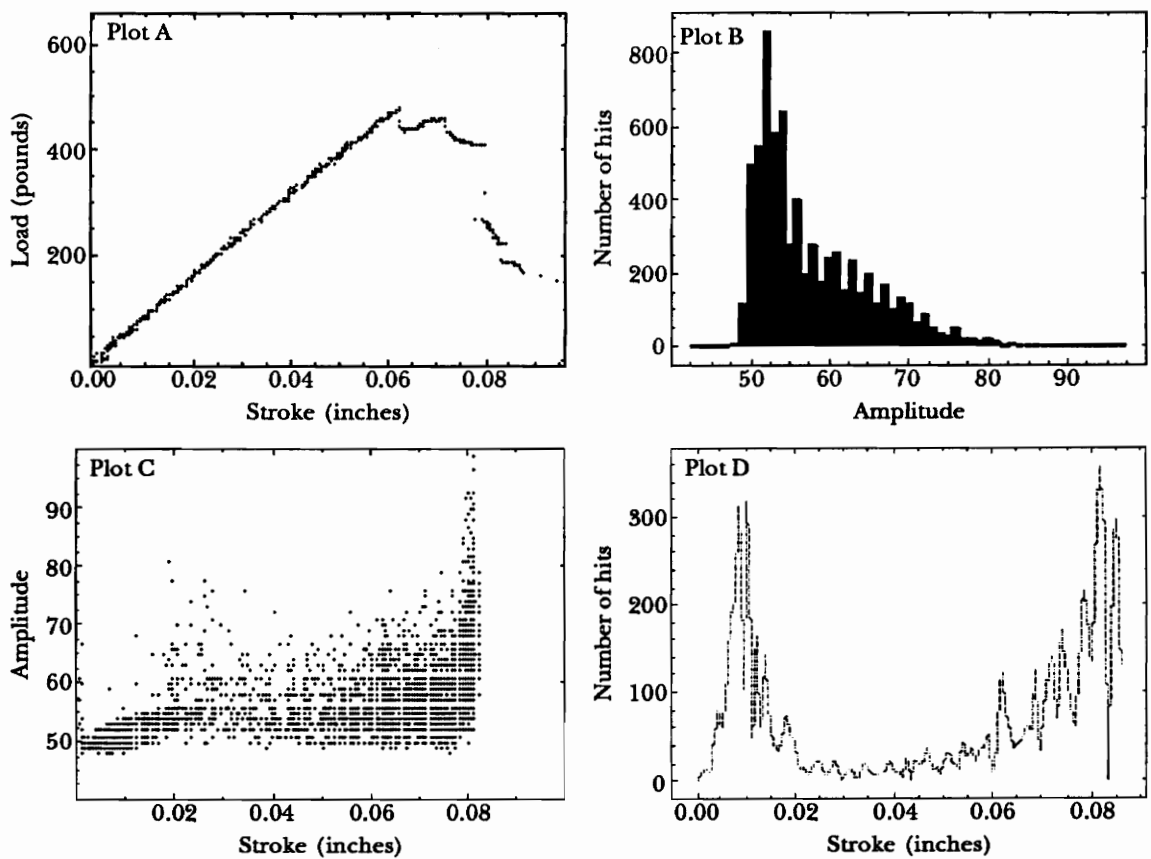


Figure 4.5 Results of acoustic monitoring of damage accumulation in the amorphous carbon fiber reinforced PEKK 60/40 using an amplitude gain of 85 dB.

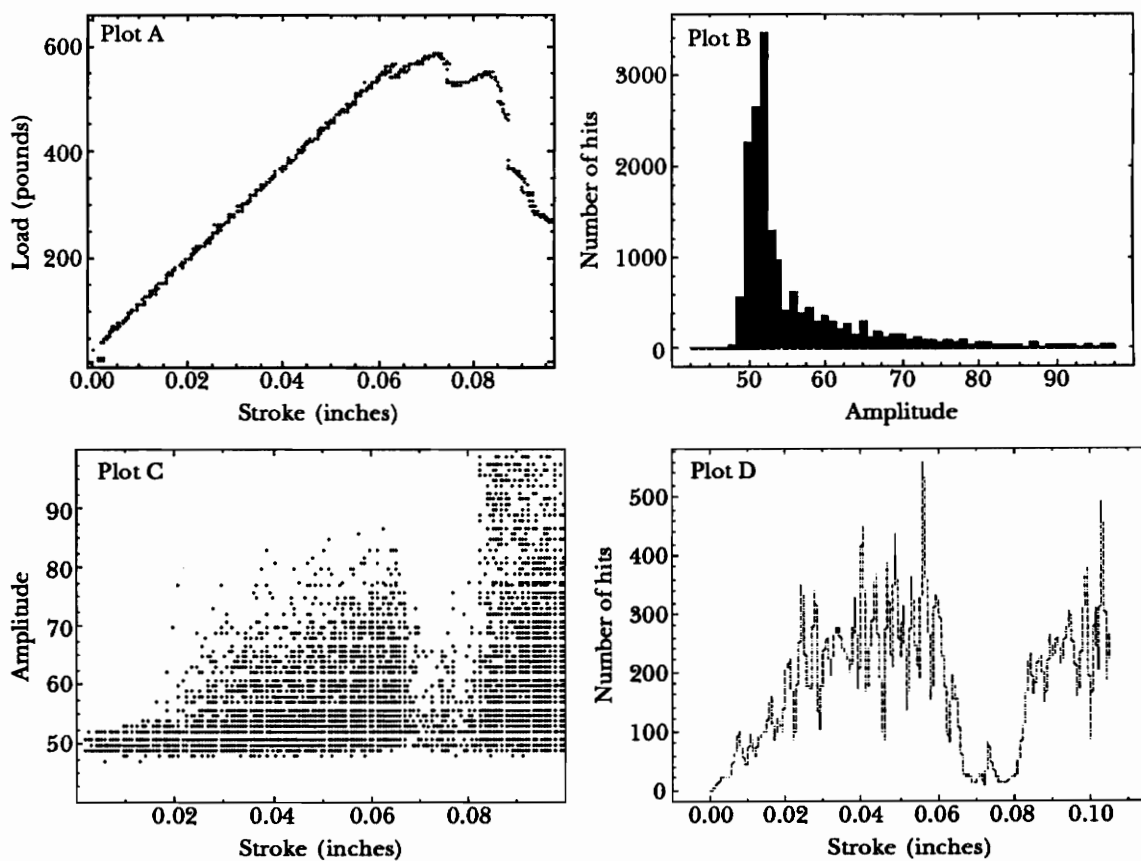


Figure 4.6 Results of acoustic monitoring of damage accumulation in the carbon fiber reinforced PEKK 60/40 crystallized at 280° C using an amplitude gain of 85 dB.

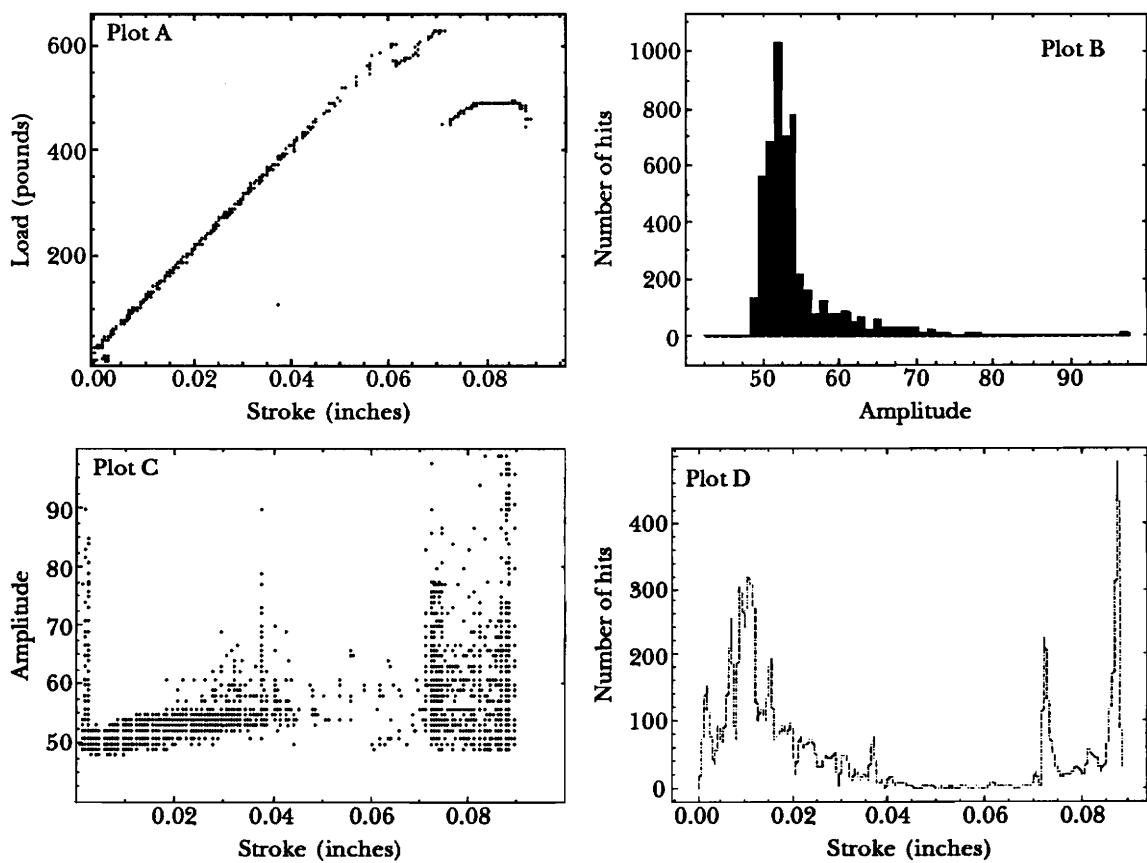


Figure 4.7 Results of acoustic monitoring of damage accumulation in the carbon fiber reinforced PEKK 60/40 crystallized at 260° C using an amplitude gain of 85 dB.

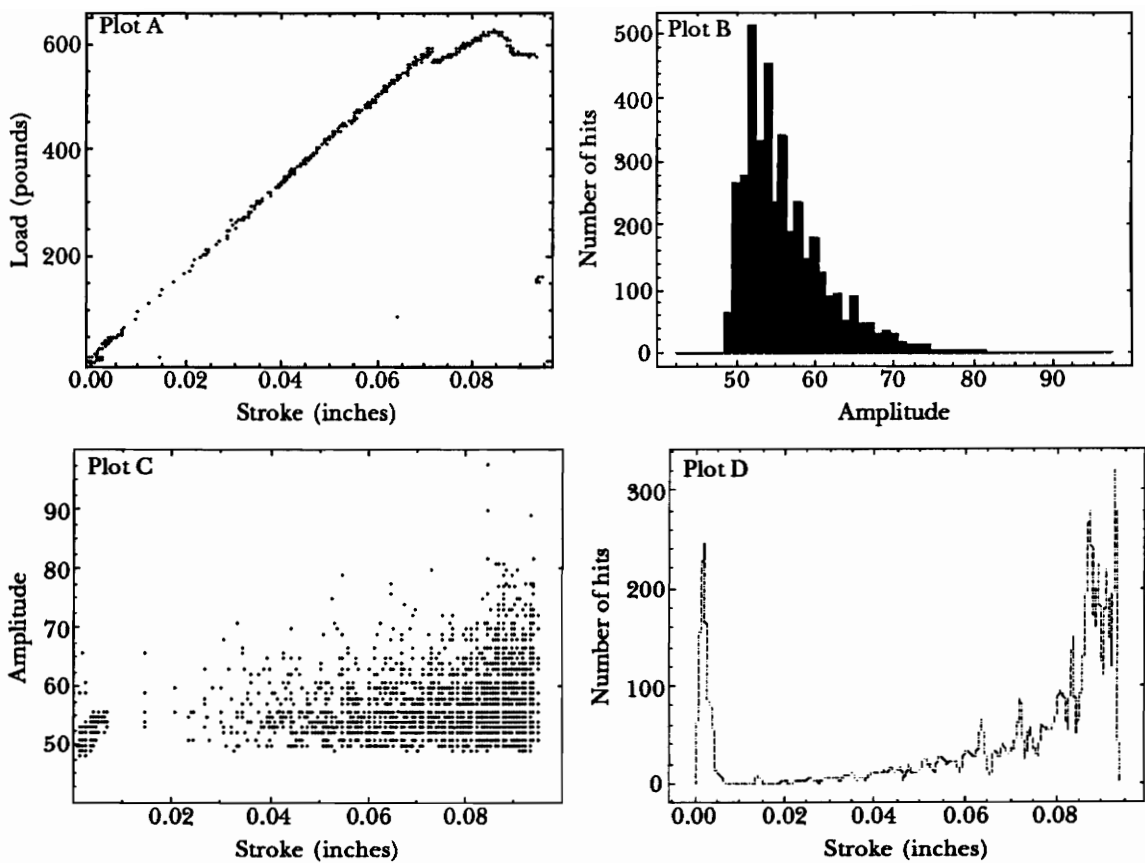


Figure 4.8 Results of acoustic monitoring of damage accumulation in the carbon fiber reinforced PEKK 60/40 crystallized at 230° C using an amplitude gain of 85 dB.

amplitudes. Hence a similar observation (increasing amplitudes of the type 1 events with increasing stroke) could not be made in this system.

In order to identify the nature of the type 1 events, carbon fiber reinforced PEKK 70/30 composite systems were loaded in three point bend and the damage accumulation process monitored using the same conditions as described for Figures 4.5 through 4.8. Figures 4.9 through 4.12 summarizes the results of such acoustic monitoring tests on four different carbon fiber reinforced PEKK 70/30 composite systems. The figures include a load-stroke plot (plot A), a plot of the amplitude distribution (plot B), a plot of the amplitude of the individual acoustic events vs. the stroke (plot C) and a plot of the number of hits vs. the stroke (plot D). Under the described acoustic setup, hits with amplitude in the 45-55 dB range were previously assigned to type 1 damage events in the PEKK 60/40 composite systems. A comparison of plot C in Figures 4.9 through 4.13 with plot C in Figures 4.5 through 4.8 indicates that the type 1 events (as manifest by the 45-55 dB hits) in the PEKK 70/30 composite systems are dramatically different from the type 1 events in the PEKK 60/40 composite systems. In fact, the initial burst of acoustic activity observed in the PEKK 60/40 composite systems is not observed in any of the PEKK 70/30 composite systems investigated. However, there are a substantial number of hits in the 45-55 dB range in these composite systems also (see plots B and C in Figures 4.9 through 12) and for the quenched system (Figure 4.9), there is a distinct peak in the amplitude distribution in the 45-50 dB range (as seen from plot B) which initiates at very low strokes and ceases at 0.06 inches (as seen from plot C). The fact that the only differences between the two series of composite systems is the

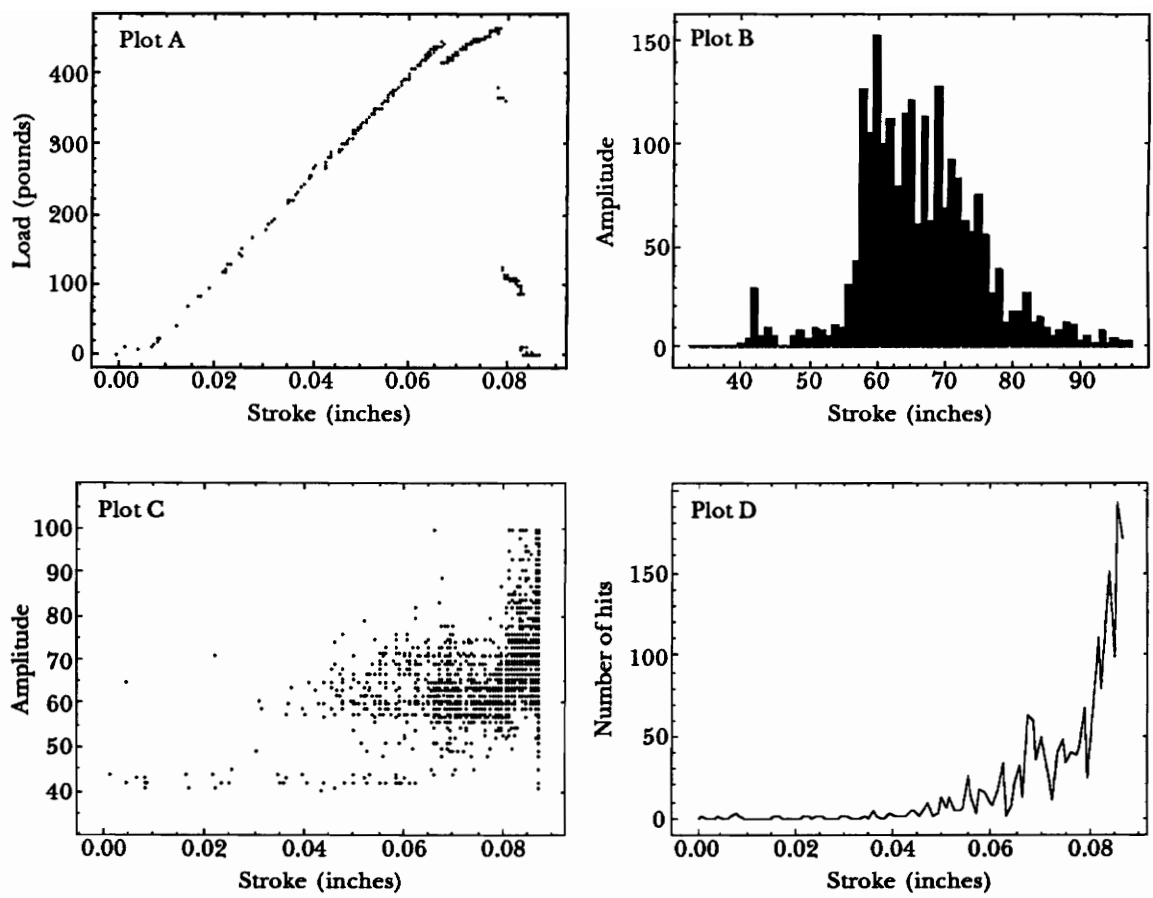


Figure 4.9 Results of acoustic monitoring of damage accumulation in the AS4 carbon fiber reinforced quenched PEKK 70/30 using an amplitude gain of 85 dB.

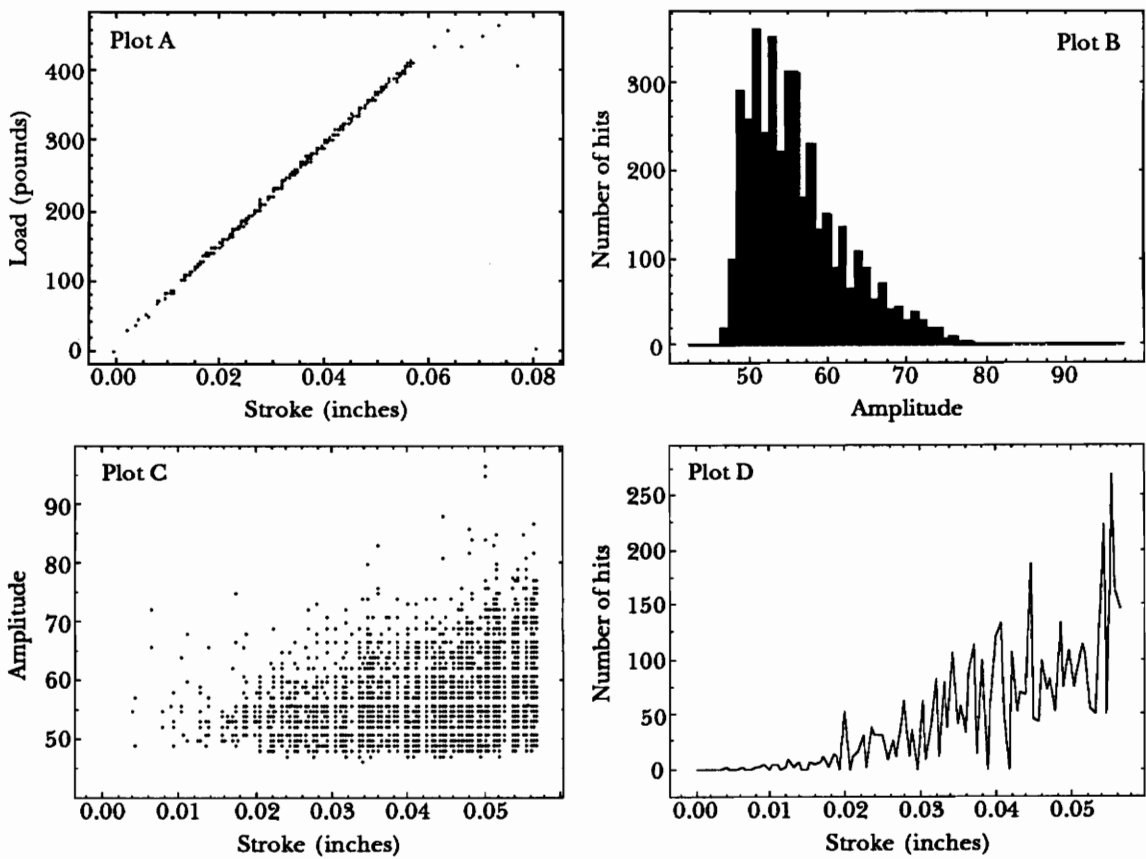


Figure 4.10 Results of acoustic monitoring of damage accumulation in the AS4 carbon fiber reinforced PEKK 70/30 crystallized at 300° C using an amplitude gain of 85 dB.

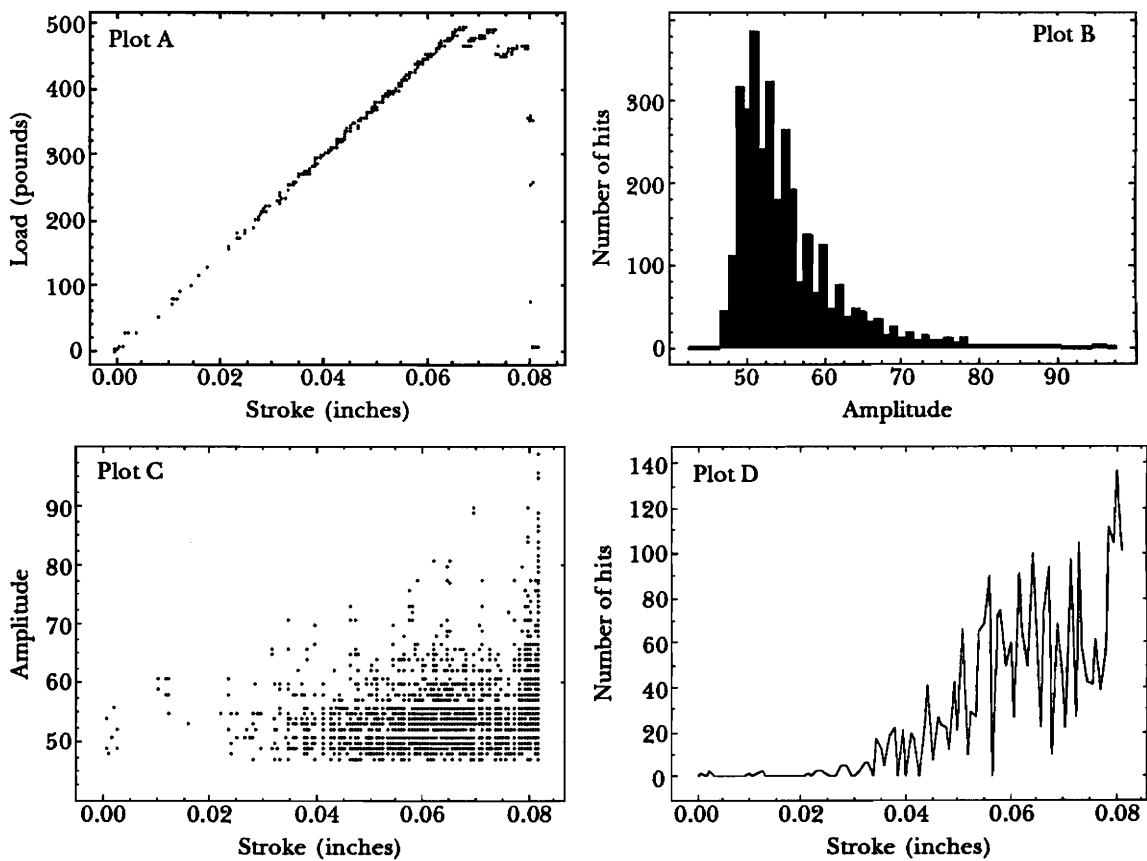


Figure 4.11 Results of acoustic monitoring of damage accumulation in the AS4 carbon fiber reinforced quenched PEKK 70/30 crystallized at 220° C using an amplitude gain of 85 dB.

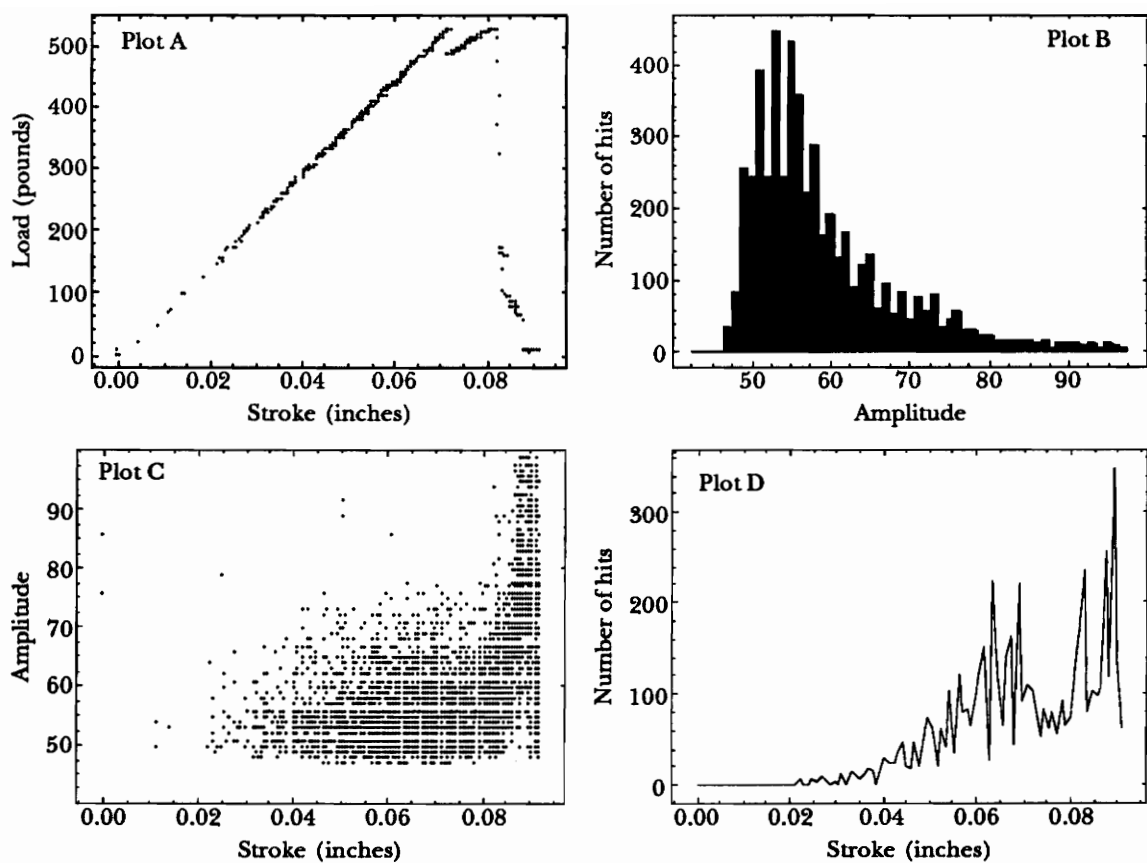


Figure 4.12 Results of acoustic monitoring of damage accumulation in the AS4 carbon fiber reinforced PEKK 70/30 cooled from the melt at 2° C/min using an amplitude gain of 85 dB.

nature of the matrix and the nature of the interface strongly suggests that type 1 acoustic events are generated by damage events in the matrix or the interface. Also, the fact that "conventional" interfacial debonding and fiber pull-out events have previously been identified as occurring at higher strokes, suggests that these type 1 events are most probably generated by damage in the matrix.

4.2.2 Unreinforced systems.

In order to confirm that type 1 events are generated by damage in the matrix, the damage accumulation process in unreinforced 60/40 PEKK test bars was monitored using identical conditions. Figures 4.13 through 4.16 summarize the results of such tests. The figures include a load-stroke plot (plot A), an amplitude distribution (plot B), a plot of the amplitude of the individual hits vs. the stroke (plot C) and a plot of the number of hits vs. the stroke (plot D). It can be seen from Figures 4.13 through 4.16 that almost all the acoustic activity is in the 45-60 dB range, which is the range previously assigned to type 1 events in the composite systems. The total attenuation in the unreinforced PEKK samples was in the range of 5-7 dB and 2-3 dB in the carbon fiber reinforced PEKK composite systems (both measured over 70 mm). Therefore, the absolute values of the amplitudes of the acoustic hits in the unreinforced test bars can be quantitatively compared with the absolute amplitudes in the composite test bars.

It can therefore be concluded that these type 1 events are generated by damage events in the matrix and that they do not cause any appreciable damage to the composite system. These type 1 events were not observed at lower amplitude gains. Previous authors²⁰⁻³⁴ who have used the AET method to

monitor the damage accumulation process probably used lower amplitude gains (most authors do not mention the total amplitude gains used in their testing). It is likely that these type 1 events can also be observed in other composite systems if the acoustic parameters (PDT, HDT, HLT, amplitude gains and threshold values, count filter etc.) are correctly adjusted. Definite assignment of these type 1 events to a specific damage mode has not been made in this work and is included in the recommendations for future work.

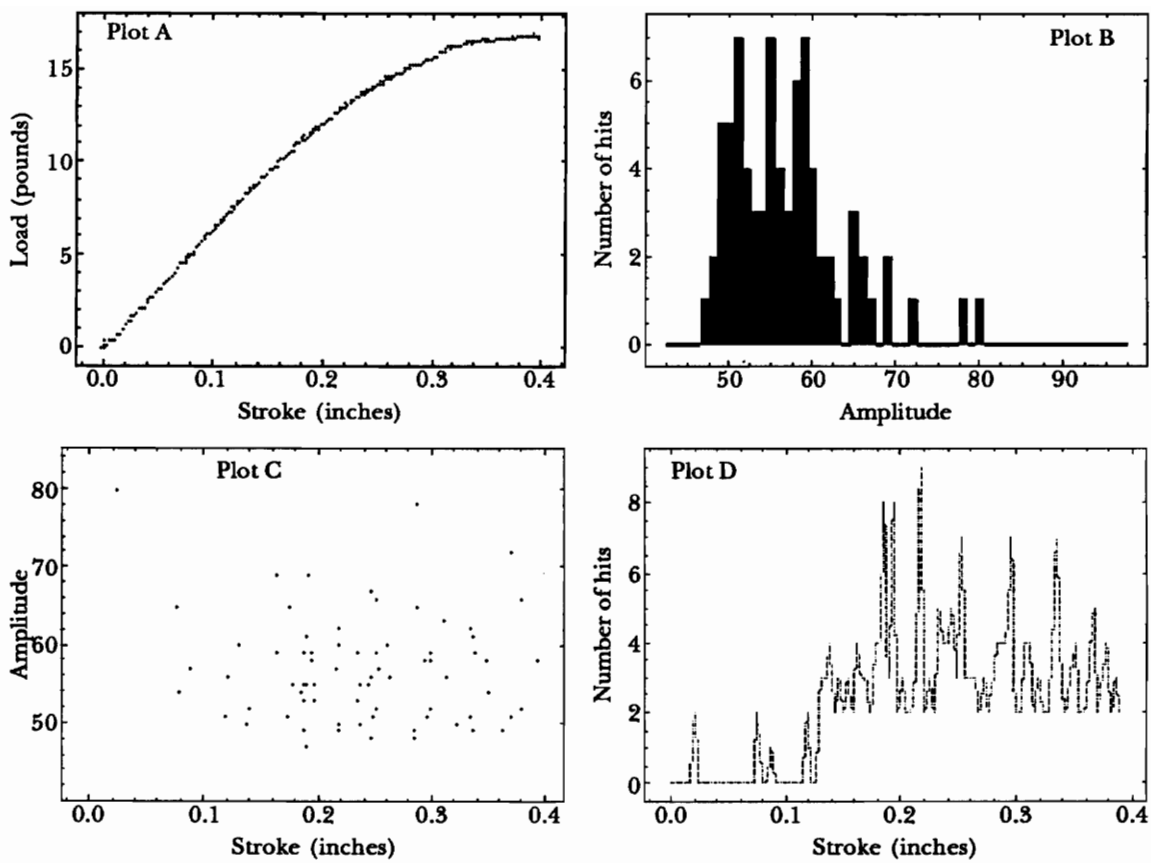


Figure 4.13 : Results of acoustic monitoring of damage accumulation in the amorphous unreinforced PEKK 60/40 using an amplitude gain of 85 dB.

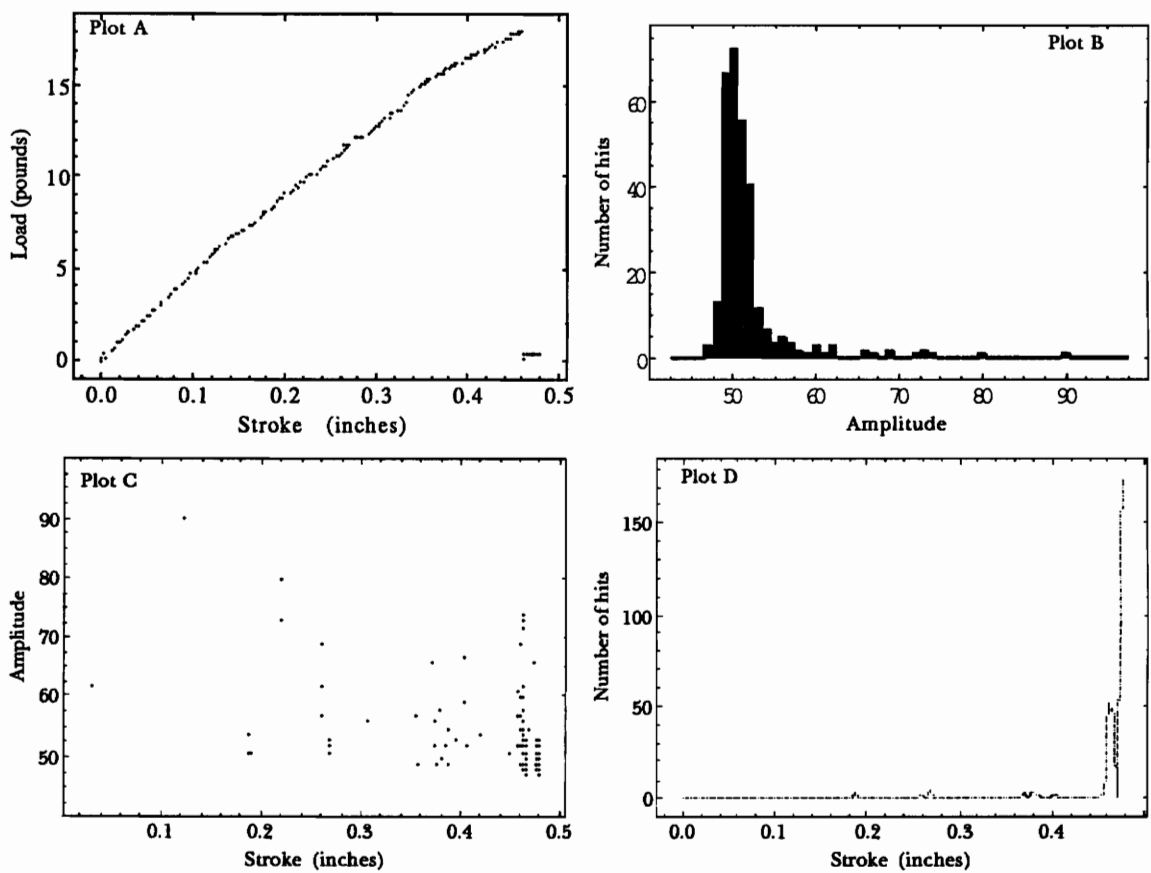


Figure 4.14 : Results of acoustic monitoring of damage accumulation in the unreinforced PEKK 60/40 crystallized at 280° C using an amplitude gain of 85 dB.

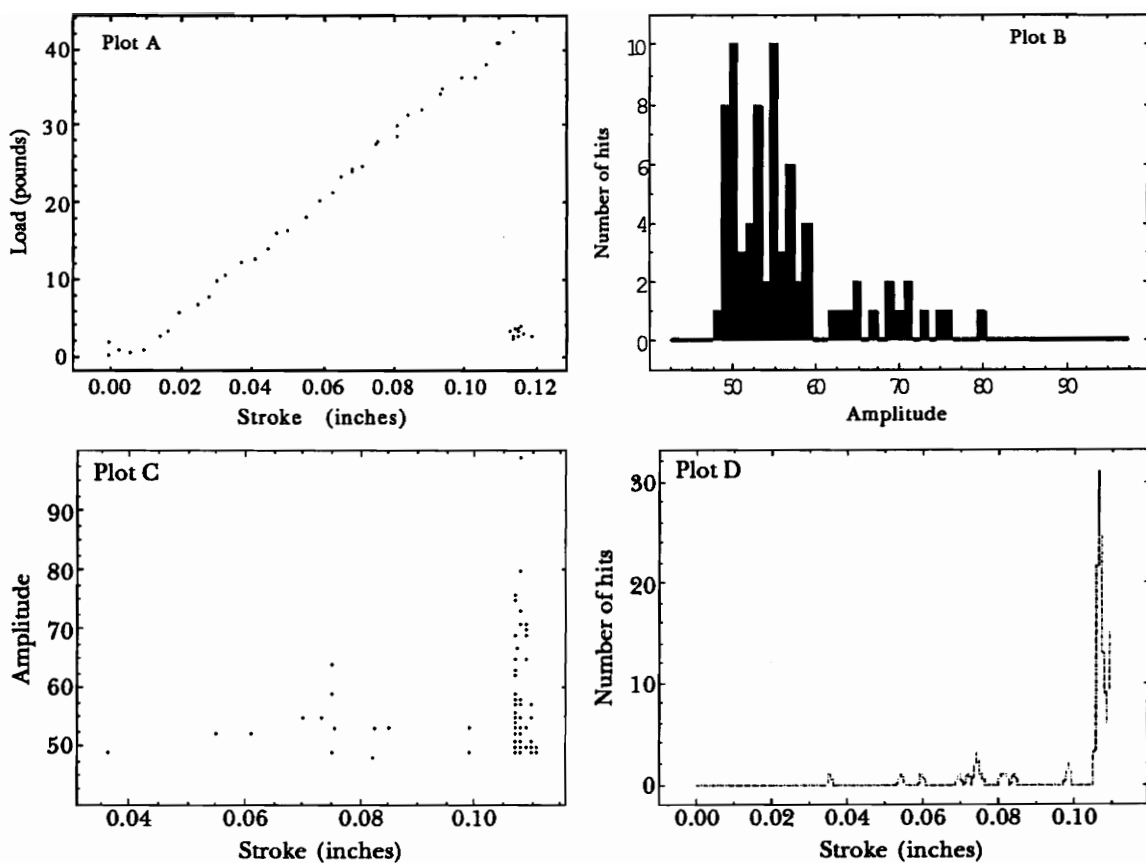


Figure 4.15 : Results of acoustic monitoring of damage accumulation in the unreinforced PEKK 60/40 crystallized at 250° C using an amplitude gain of 85 dB.

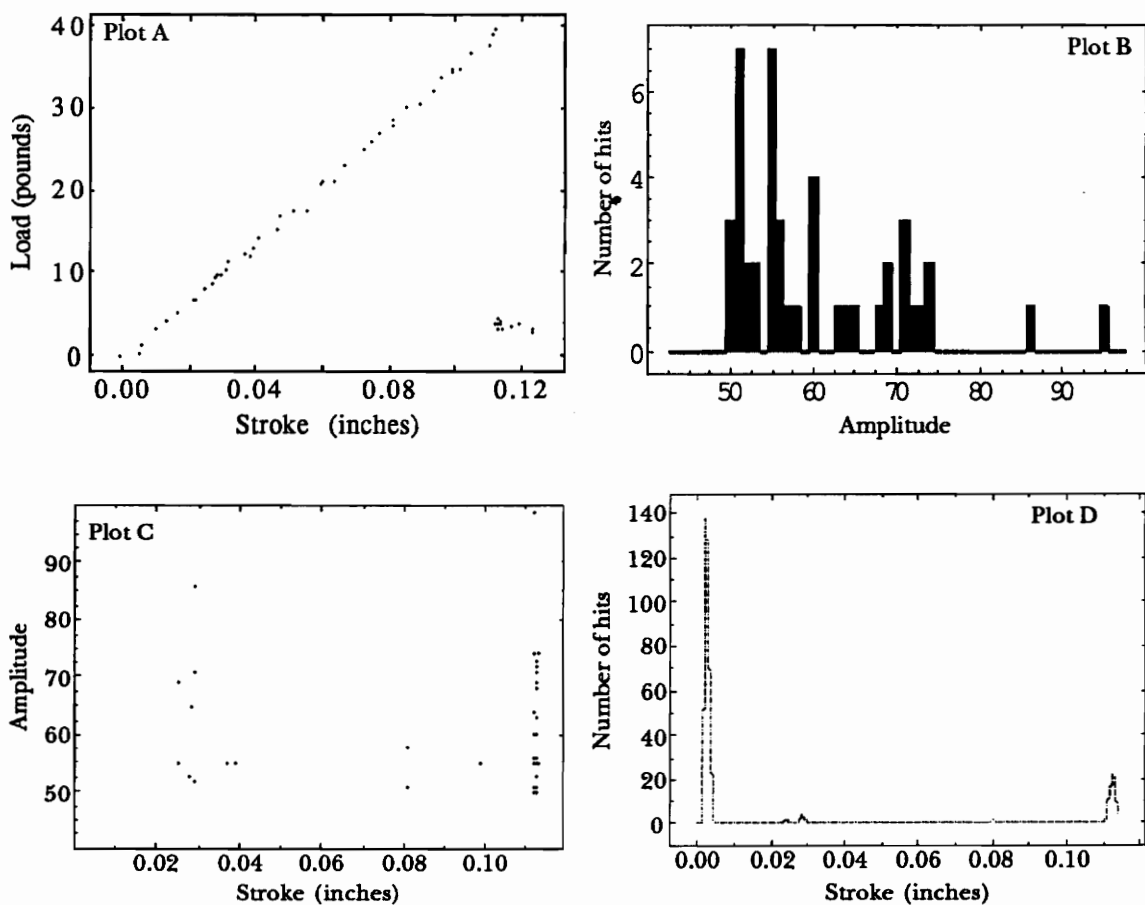


Figure 4.16 : Results of acoustic monitoring of damage accumulation in the unreinforced PEKK 60/40 crystallized at 230° C using an amplitude gain of 85 dB.

4.3 Acoustic Monitoring of Stroke Controlled Fatigue Tests

The damage accumulation process during stroke controlled fatigue of different AS-4 carbon fiber reinforced PEKK 60/40 composite systems was also monitored using AE. A haversine waveform with a frequency of 0.1 Hz, a maximum stroke of 0.075 inches and minimum stroke of zero was used for the fatigue testing. (Care was taken to ensure that the loads never dropped to zero. Within this limit, the minimum stroke was set as close to zero as possible.) Results of these tests are given in Figure 4.17 through 20. The figures include plots of the load vs stroke (plot A), load vs the number of cycles (plot B), number of hits vs stroke (plot C), and cumulative number of hits vs time (plot D). Each point on plots A & B was collected when an actual hit was detected by the piezoelectric sensors. Therefore, plots A and B have points which are not uniformly distributed, and represent the instantaneous values of the applied load, stroke, and time recorded at each acoustic hit. Plot A (load vs stroke plot) summarizes the cyclic load response to the applied cyclic stroke for the entire fatigue test. Plot B (load vs time) summarizes the cyclic load response as a function of number of cycles (or time) for the entire fatigue test. Also, it can be seen from plot C in the four figures that a large proportion of the hits are generated at low strokes (presumably caused by friction of preexisting damaged areas and not the

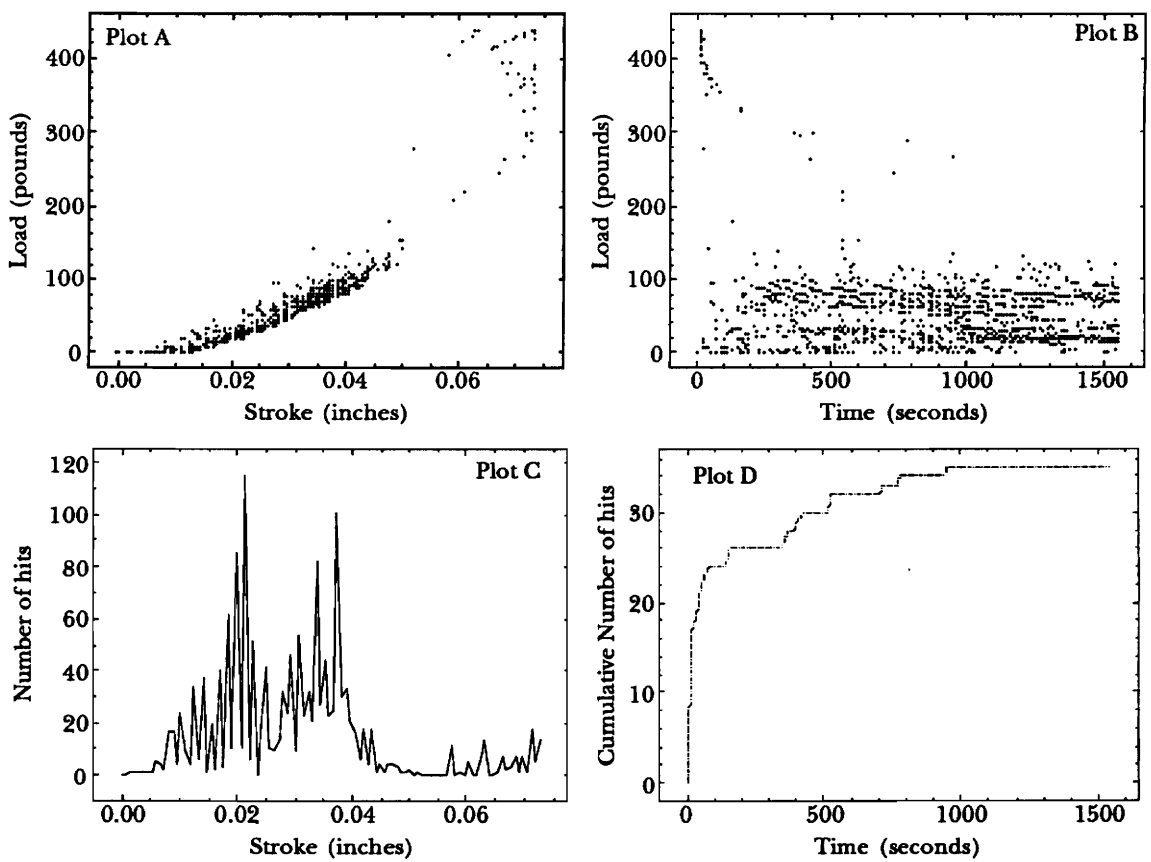


Figure 4.17 Results of acoustic monitoring of damage accumulation in the quenched AS4 carbon fiber reinforced PEKK 60/40 during a stroke controlled fatigue test.

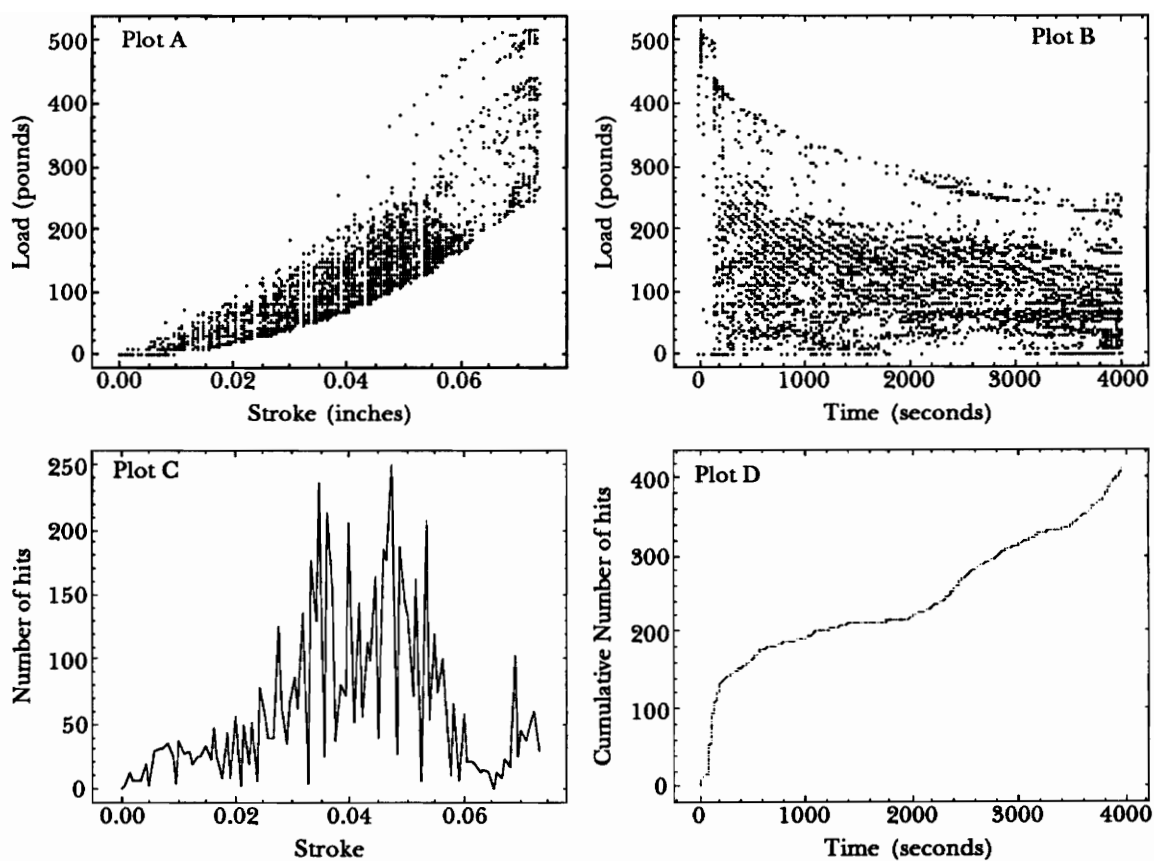


Figure 4.18 Results of acoustic monitoring of damage accumulation in the AS4 carbon fiber reinforced PEKK 60/40 crystallized at 280° C during a stroke controlled fatigue test.

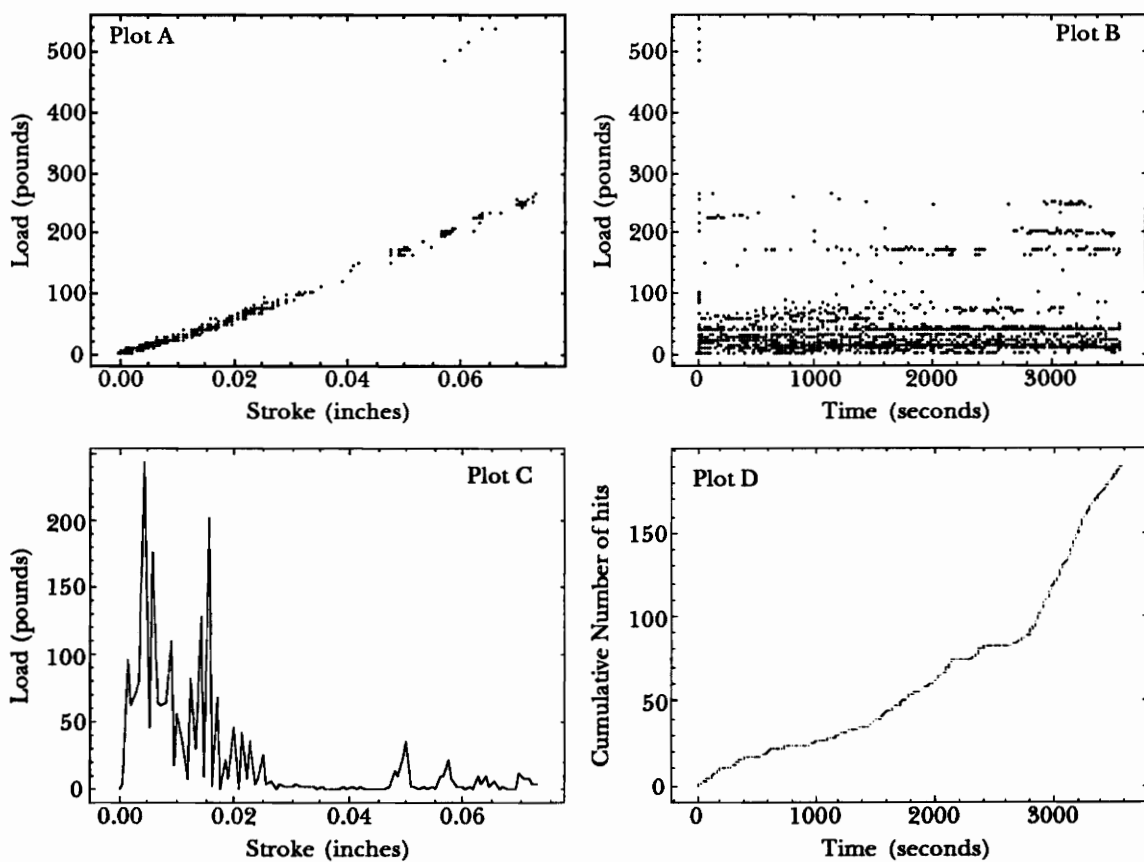


Figure 4.19 Results of acoustic monitoring of damage accumulation in the AS4 carbon fiber reinforced PEKK 60/40 crystallized at 260° C during a stroke controlled fatigue test.

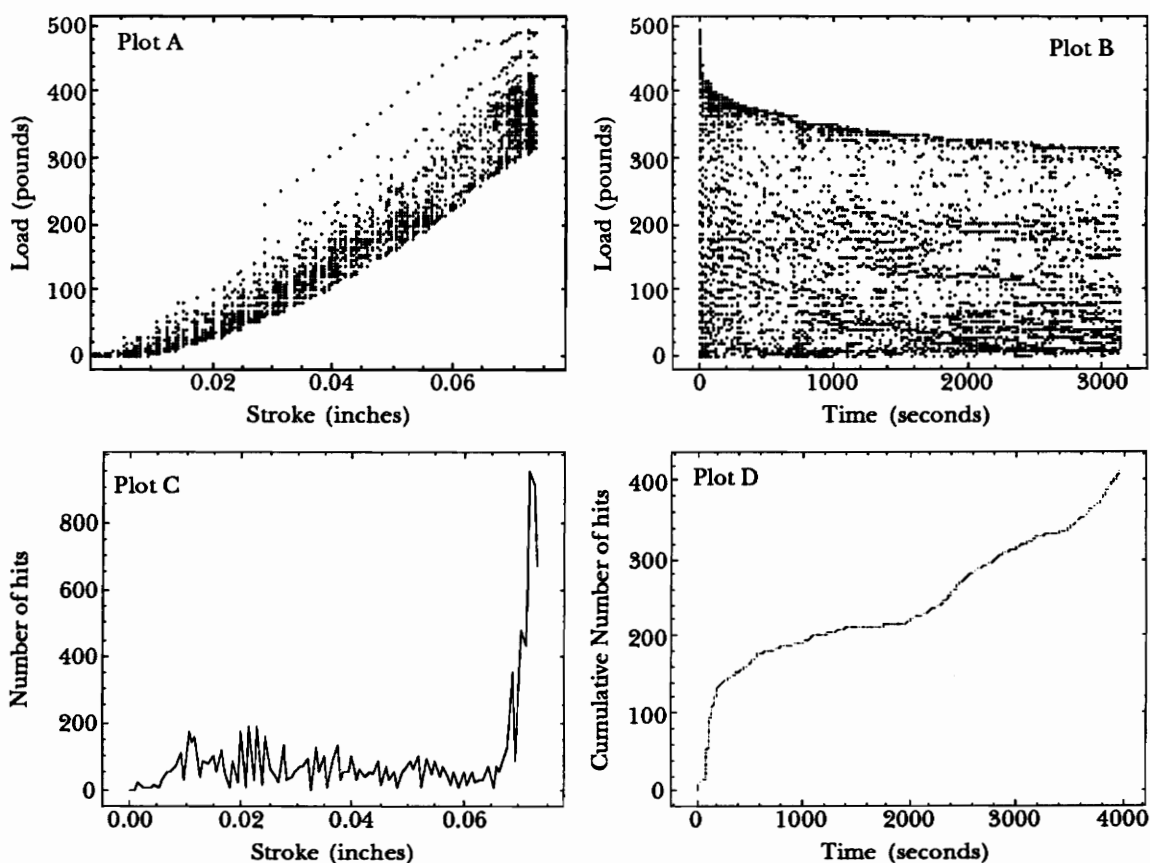


Figure 4.20 Results of acoustic monitoring of damage accumulation in the AS4 carbon fiber reinforced PEKK 60/40 crystallized at 230° C during a stroke controlled fatigue test.

creation of new damage). These “low stroke hits” have been filtered out in plot C, which is therefore a plot of the cumulative number of hits which take place at higher strokes vs time. Hence plot D in the four figures can be taken as a measure of the amount of damage induced with the loading cycles. It can be seen from plot D in the four figures that the rate of damage accumulation decreases as the fatigue test proceeds. This observation is consistent with the fact that the load at maximum stroke decreases at a higher rate initially and that the rate of decrease in the load at maximum stroke decreases in all four composite systems as the fatigue test proceeds (see plot A in Figures 4.17 through 4.20). This observation is also consistent with work done by previous authors⁴¹⁻⁴³ who have found that in the initial stages of the fatigue test, there is a greater rate of damage accumulation because of the growth of preexisting cracks and the formation of new ones at stress concentrators. As the test proceeds, the growing cracks are arrested and new ones are not formed, hence the damage accumulation rate decreases as the test proceeds.

On comparing plot C in Figures 4.17 through 20, it can be observed that the damage accumulation process during fatigue in the four composite systems differs substantially. As a result, one can qualitatively expect to observe substantial differences in the fatigue properties although the quasi-static mechanical properties are similar. This qualitative observation is quantified in subsequent sections of this thesis.

4.4 Discussion

The quenched composite systems have higher toughness in mode I and lower moduli as compared to the crystallized samples. This is expected because quenching will give rise to a nearly amorphous morphology, which in turn will have higher toughness and lower moduli. However, the quenched composite systems have a lower energy absorption in impact and this is probably caused by the fact that the interface is weaker in the quenched composite systems as opposed to the crystallized systems.

From the mechanical data available, the quenched composite systems have the best potential as far as industrial applications are concerned. The quenched systems have the best fatigue performance (see figure 2.10) as well as higher toughness in mode I (see Table 2.3). Also, in industrial applications, quenching heat treatments afford better control over the heat treatment schedule compared to isothermal crystallization heat treatments. However, quenching resulted in lower energy absorptions in impact (see Tables 4.2 and 4.4) and also slightly lower moduli as compared to the crystallized samples. Therefore, for specific applications, different heat treatments might have to be used.

From the results presented in section 4.2, it can be concluded that the damage accumulation process in the carbon fiber reinforced PEKK 60/40 composite systems change dramatically as a function of heat treatment. However, from the results presented in section 4.1, it can be concluded that the quasi-static mechanical properties remain essentially unchanged. Since the

ultimate mechanical properties are unchanged, and the reported fatigue properties in stress control (see Figure 2.10) change dramatically as a function of heat treatment, it can be concluded that the latter two phenomena are probably related. In subsequent sections of this thesis, an attempt has been made to quantitatively predict the fatigue S-N curve in stroke control from the damage accumulation process during flexure and to qualitatively relate the predicted fatigue S-N curve in stroke control to the reported fatigue properties in stress control.

5. Modelling and Discussion:

5.1 Damage Model for a Quasi Static Flexure Test

The damage model used in this analysis is a modified form of the Kachanov equation originally developed for fatigue. The original Kachanov model is given in equation 5.1

$$\frac{\partial D}{\partial N} = \frac{A\sigma^\alpha}{[1-D]^\beta} \quad (5.1)$$

where, A , α and β are material constants, D is the preexisting damage level, and ∂D is the damage induced in ∂N fatigue cycles.

The damage variable D relates the instantaneous secant modulus E to the initial (zero damage) modulus E_0 according to equation 5.2 and has absolute values ranging from 0 to 1.

$$E = E_0[1-D] \quad (5.2)$$

The original Kachanov equation has been modified to model the damage accumulation process during a quasi static three point bend test. The modified Kachanov equation is given in equation 5.3.

$$\partial D \equiv \left(\frac{\epsilon}{\epsilon_c} \right)^\alpha D^\beta \frac{\partial \epsilon}{\epsilon_c} \quad (5.3)$$

where α and β are material constants, ϵ is the instantaneous strain, $d\epsilon$ is the instantaneous change in strain, and ϵ_c is a critical strain.

Note that the original model has been modified such that damage varies with the change in strain instead of number of cycles. Also, the stress used in Kachanov's equation has been replaced by strain. This is because in a three point bend flexure test, the strains can be assumed to vary linearly along the depth and the span of the sample (linear beam theory). Hence, the strain at any point in the flexure sample can be calculated for any given applied stroke. However, the loads (or the strains) cannot be directly converted to stresses unless the damage function is known.

Equation 5.3 can be integrated to give an equation which relates the damage at any point in the flexure sample to the applied strain.

$$\int_{D_0}^D D^{-\beta} \partial D = \int_{\epsilon_0}^{\epsilon} \frac{\epsilon^\alpha \partial \epsilon}{\epsilon_c^{\alpha+1}}$$

$$\frac{D^{1-\beta} - D_0^{1-\beta}}{1-\beta} = \frac{\varepsilon^{\alpha+1} - \varepsilon_0^{\alpha+1}}{\alpha+1} \frac{1}{\varepsilon_c^{\alpha+1}}$$

Assuming that $D_0 = 0$ at $\varepsilon_0 = 0$, we have a relation between the damage state and the applied strain.

$$\frac{D^{1-\beta}}{1-\beta} = \frac{\varepsilon^{\alpha+1}}{\alpha+1} \frac{1}{\varepsilon_c^{\alpha+1}} \quad (5.4)$$

Assuming that the strains vary linearly with the distance from the neutral axis and the distance from the loading arm, it can be shown that the strain is related to the stroke by equation 5.5

$$\varepsilon \equiv Bxy \quad (5.5)$$

where x is the distance from the loading arm, y is the distance from the neutral axis and B is a constant related to the stroke by equation 5.6

$$B = 24 \frac{V}{S^3} \quad (5.6)$$

where V is the applied stroke, and S is the span.

Therefore, the desired relation between the damage variable and the applied stroke is obtained by substituting equation 5.6 into equation 5.4.

$$D = \left[\frac{1-\beta}{\alpha+1} B^{\alpha+1} \left(\frac{xy}{\varepsilon_c} \right)^{\alpha+1} \right]^{1/(1-\beta)} \quad (5.7)$$

Equation 5.7 relates the damage variable in a three point bend bar undergoing quasi-static loading to the stroke and the location in the sample. Some of the characteristics of this damage relation are listed below:

- the damage varies with the applied stroke raised to the power λ where λ is defined as

$$\lambda \equiv \frac{\alpha+1}{1-\beta} \quad (5.8)$$

- the damage varies with the distance from the loading arms raised to the power λ .

Note that λ is determined by α and β only. Assuming that the damage generated in the beam is proportional to the level of acoustic activity, the damage versus stroke relation developed in equation 5.7 can be related to the cumulative number of hits vs. stroke relation obtained from acoustic emission testing. Alternatively, the damage variable can be used to predict the secant modulus and thus simulate the load-stroke plot. This approach is discussed in greater detail in section 5.3

5.2 Extension to fatigue

The damage models developed for the three point bend tests can be extended to low stroke fatigue tests for the composite materials. This can be done by modifying the limits of integration of equation 5.3 for a stroke controlled fatigue loading situation.

As in a quasi-static three point bend test, the strain at any point in the fatigue test sample can be calculated assuming linear beam theory. For a cyclic stroke, the strain is given by equations 5.5 and 5.6, where B can be expressed as

$$B = B_m + B_a \sin \theta$$

where B_m is related to the mean stroke and B_a is related to the amplitude of the cyclic stroke by equation 5.6.

Equation 5.3 can now be expressed as

$$\partial D = [B_m + B_a \sin \theta]^\alpha \left[\frac{xy}{\epsilon_c} \right]^{\alpha+1} B_a \cos \theta D^\beta \partial \theta \quad (5.9)$$

Equation 5.9 can be integrated with respect to θ in order to obtain a relation between the damage induced in one cycle and the cyclic stroke profile.

$$\int_{D_{n-1}}^{D_n} D^{-\beta} \partial D = \left[\frac{xy}{\epsilon_c} \right]^{\alpha+1} \int_{-90}^{90} [B_m + B_a \sin \theta]^\alpha B_a \cos \theta \partial \theta$$

In setting the limits for the above integration, it has been assumed that damage is induced in the loading half of the stroke cycle only. Integrating this expression leads to

$$D_n^{1-\beta} = [1-\beta] \left[\frac{xy}{\epsilon_c} \right]^{\alpha+1} \frac{[B_m + B_a]^\alpha}{\alpha+1} \left[1 - \frac{1}{R^{\alpha+1}} \right] + D_{n-1}^{1-\beta}$$

where R is defined as

$$R = \frac{B_m + B_a}{B_m - B_a}$$

Summing from 1 to n,

$$D_n^{1-\beta} = n[1-\beta] \left[\frac{xy}{\epsilon_c} \right]^{\alpha+1} \frac{[B_m + B_a]^{\alpha+1}}{\alpha+1} \left[1 - \frac{1}{R^{\alpha+1}} \right] + D_o^{1-\beta}$$

$$D_n = \left[n[1-\beta] \left[\frac{xy}{\epsilon_c} \right]^{\alpha+1} \frac{[B_m + B_a]^{\alpha+1}}{\alpha+1} \left[1 - \frac{1}{R^{\alpha+1}} \right] \right]^{1/(1-\beta)} \quad (5.10)$$

This damage relation (equation 5.10) has several interesting characteristics. These are listed below:

- damage varies with the number of cycles raised to the power γ where γ is defined by

$$\gamma = \frac{1}{1-\beta} \quad (5.11)$$

- damage varies with the maximum stroke level $(B_m + B_a)$ raised to the power λ , where λ is defined by equation 5.8
- damage varies with the R ratio as given below

$$D_n \propto \left[1 - \frac{1}{R^{\alpha+1}} \right]^{1/(1-\beta)}$$

- damage varies with the distance from the loading arm raised to the power λ

Assuming that the fatigue S-N curves represent points of equal damage, equation 5.10 can be used to predict the fatigue S-N curve. (Alternatively, equation 5.10 can be used to model the secant modulus. Hence, the load at

maximum stroke can be related to the number of fatigue cycles and the fatigue S-N curve can be predicted in a more rigorous manner. This approach has been discussed in greater detail in section 5.3.2) If the fatigue S-N curve represents points of equal damage, and if the R ratio is held constant, then from equation 5.10 it follows that:

$$n^{1/(1-\beta)} [B_m + B_a]^{(\alpha+1)/(1-\beta)} = \text{Constant}$$

$$\therefore \left(\frac{1}{1-\beta} \right) \log n + \left(\frac{\alpha+1}{1-\beta} \right) \log [B_m + B_a] = \text{Constant}$$

$$\therefore \log n + (\alpha+1) \log [B_m + B_a] = \text{Constant}$$

However, when $B_m + B_a = B_{uts}$, (where B_{uts} is related to the failure stroke in a quasi-static three point bend test) the bar breaks after one half cycle. Therefore,

$$\log n + (\alpha+1) \log [B_m + B_a] = \log [B_{uts}] + \log \left(\frac{1}{2} \right)$$

or

$$\log n = (\alpha+1) \log \left(\frac{B_{uts}}{B_m + B_a} \right) + \log \left(\frac{1}{2} \right) \quad (5.12)$$

Note that the proposed fatigue model qualitatively matches models developed from experimental data by several authors⁴¹⁻⁴³. Equation 5.12 can be used to predict the fatigue S-N curve for a given material if the value of α is known. Equation 5.10 predicts that damage varies with the number of cycles raised to the power $1/(1-\beta)$ for any given cyclic loading. Hence β can be easily determined by monitoring the cumulative AE hits vs. the number of cycles for

any fatigue test. Alternatively, the secant modulus, which is related to the level of damage accumulation, can be used to determine the value of β .

5.3 The load-stroke relationship

5.3.1 Quasi-static three point bend

As pointed out in section 5.1, the damage variable D relates the instantaneous secant modulus to the original zero damage modulus according to equation 5.2.

$$E = E_o(1-D)$$

The secant modulus relates the applied strain (given by equations 5.5 and 5.6) to the stress as given below:

$$D = \left[\frac{1-\beta}{\alpha+1} B^{\alpha+1} \left(\frac{xy}{\epsilon_c} \right)^{\alpha+1} \right]^{1/(1-\beta)}$$

$$\sigma = E_o \left[1 - \left[\frac{1-\beta}{\alpha+1} B^{\alpha+1} \left(\frac{xy}{\epsilon_c} \right)^{\alpha+1} \right]^{1/(1-\beta)} \right] B_{xy}$$

The stresses can then be converted to an applied load using the criterion that the sum of all moments (ΣM_x) should be zero under the loading nose (moment balance),

$$\Sigma M_x = 0$$

$$\frac{P_x}{2} = 2 \int_0^{d/2} E_o B W \left[1 - \left[\frac{1-\beta}{\alpha+1} B^{\alpha+1} \left(\frac{xy}{\epsilon_c} \right)^{\alpha+1} \right]^{1/(1-\beta)} \right] x y^2 dy$$

where x is the distance from the loading arm, W is the width of the sample, d is the sample thickness (or depth) and P is the load.

Note that according to the proposed model, the loads calculated using the moment balance condition will be a function of the value of x used in the above equation. This apparent discrepancy probably arises from the fact that as any location in the composite damages, stress is transferred to neighboring locations via shear load transfer. Hence locations near a damaged area will damage faster. This synergistic effect of damage has been ignored in the proposed model. In other words, the model represents a first order perturbation in the linear stress-strain relation. The actual stress-strain relation is probably better described using a series of higher order terms which are not incorporated in the proposed model. Also, note that this apparent discrepancy will not be a problem if (xy/ϵ_c) is independent of x .

Substituting $x = S/2$ in the above equation leads to

$$\frac{PS}{8} = E_o BW \frac{S}{2} \int_0^{d/2} \left[y^2 - y^{2+\lambda} \left\{ \frac{1-\beta}{\alpha+1} B^{\alpha+1} \left(\frac{S}{2\epsilon_c} \right)^{\alpha+1} \right\}^{1/(1-\beta)} \right] dy$$

Integrating the above equation between the given limits leads to an expression relating the variable B and the load.

$$\frac{PS}{8} = E_o BW \frac{S}{2} \left[\frac{(d/2)^3}{3} - \frac{(d/2)^{3+\lambda}}{3+\lambda} \left\{ \frac{1-\beta}{\alpha+1} B^{\alpha+1} \left(\frac{S}{2\epsilon_c} \right)^{\alpha+1} \right\}^{1/(1-\beta)} \right]$$

Substituting equation 5.6 into the above equation leads to an equation relating the load to the applied stroke.

$$P = 4 E_o V \frac{Wd^3}{S^3} \left[1 - \frac{3}{3+\lambda} \left(\frac{1-\beta}{\alpha+1} \left(\frac{B S d}{4\epsilon_c} \right)^{\alpha+1} \right)^{1/(1-\beta)} \right] \quad (5.13)$$

Note that the first term in the bracket represents the linear beam theory load for the applied stroke. The second term represents a first order perturbation term for the deviation of the load from the linear load-stroke behavior predicted from linear beam theory. According to the proposed model, the deviation of the load from the linear beam theory load is proportional to the applied stroke raised to the power λ , where λ is defined in equation 5.8. The absolute values of the deviation of the load from the linear load-stroke behavior (hereafter referred to as the “load deviation”) is determined by the applied stroke, and the constants α , β and ϵ_c . In section 5.1, one approach to measure the value of λ , had been outlined, where the damage variable was assumed to be related to the number of hits recorded using acoustic emission. The value of λ can also be determined by plotting the load deviations against the applied stroke on a log-log scale. The slope of this plot should equal λ . Both approaches have advantages and disadvantages which are discussed in greater detail in section 5.4

ϵ_c can be determined quantitatively from the load deviations if the value of α and β are known. In section 5.1, one relation between α and β was outlined. In order to obtain the second relation between α and β , additional testing in other configurations needs to be done. The second relation has been

obtained in a fatigue testing configuration and is discussed in detail in section 5.3.2

5.3.2 Fatigue

The damage variable derived in section 5.2 for a cyclic fatigue test (equation 5.10) can be used to model the load-stroke relationship in fatigue.

$$D = \left[\frac{n}{\lambda} (B_m + B_a)^{1+\alpha} \left\{ 1 - \left(\frac{1}{R} \right)^{1+\alpha} \right\} \left(\frac{xy}{\epsilon_c} \right)^{1+\alpha} \right]^\gamma$$

or

$$D = \left[\frac{n}{\lambda} \left\{ 1 - \left(\frac{1}{R} \right)^{1+\alpha} \right\} \left(\frac{(B_m + B_a)xy}{\epsilon_c} \right)^{1+\alpha} \right]^\gamma$$

$$D = \left[\frac{n}{\lambda} \left\{ 1 - \left(\frac{1}{R} \right)^{1+\alpha} \right\} \frac{(xyB')^{1+\alpha}}{\epsilon_c} \right]^\gamma$$

where $B' = B_m + B_a$ and is related to the maximum stroke by equation 5.6.

Using the stress-strain relation,

$$\sigma' = E_o \left[1 - \left[\frac{n}{\lambda} \left\{ 1 - \left(\frac{1}{R} \right)^{1+\alpha} \right\} \left(\frac{xyB'}{\epsilon_c} \right)^{1+\alpha} \right]^\gamma \right] B'_{xy}$$

where σ' is the stress at maximum stroke and B'_{xy} is the strain at maximum stroke at any given location.

Using a moment balance criterion similar to the one used for a static test,

$$\Sigma M_x = 0$$

$$\frac{P'x}{2} = E_o \times B'W 2 \int_0^{d/2} \left[1 - \left[\frac{n}{\lambda} \left\{ 1 - \left(\frac{1}{R} \right)^{1+\alpha} \right\} \left(\frac{B'x}{\epsilon_c} \right)^{1+\alpha} \right]^\gamma y^\lambda \right] y^2 dy$$

where P' is the load at maximum stroke and γ is given by equation 5.11.

Substituting $x = S/2$ in the above equation leads to

$$\frac{P'S}{4} = E_o \frac{S}{2} B'W 2 \int_0^{d/2} \left[1 - \left[\frac{n}{\lambda} \left\{ 1 - \left(\frac{1}{R} \right)^{1+\alpha} \right\} \left(\frac{SB'}{2\epsilon_c} \right)^{1+\alpha} \right]^\gamma y^\lambda \right] y^2 dy$$

Integrating the above equation between the given limits leads to an equation relating the load at maximum stroke (P') with the number of cycles. This relation is given in equation 5.14 below

$$P' = 4V' \frac{Wd^3}{S^3} \left[1 - \frac{3}{\lambda+3} \left\{ \frac{n}{\lambda} \left(1 - \frac{1}{R^{\alpha+1}} \right) \right\}^{1/(1-\beta)} \left(\frac{SdB'}{4\epsilon_c} \right)^\lambda \right] \quad (5.14)$$

where V' is the maximum stroke in the fatigue cycle.

The first term in the bracket represents the linear beam theory load at maximum stroke, while the second term represents a first order perturbation term for the load deviation. Note that according to equation 5.14, the load at maximum stroke will decrease from the linear beam theory load (first term in the bracket) at a rate which is proportional to the number of cycles raised to the power γ , where γ was defined in equation 5.11.

In section 5.2, it was proposed that the value of γ could be determined by monitoring the number of hits recorded during the fatigue test. The number of hits was correlated to the amount of damage and hence it was proposed that the

number of hits is proportional to the number of cycles raised to the power γ . Equation 5.14 suggests an alternative method to determine the value of γ is to monitor the drop in load at maximum stroke as a function of the number of fatigue cycles. The two methods are compared in section 5.4

Also, in section 5.2 it was proposed that the fatigue life can be predicted by assuming that the fatigue S-N curve represents points of equal damage. A more rigorous approach, which results in a similar solution, can be obtained by using equation 5.14. Fatigue failure in stroke control can be defined as the point where the load at maximum stroke decreases by a certain fraction of its value in the first cycle. If the fatigue failure point is defined as the point where the load at maximum stroke is $(1-k)$ times the load at maximum stroke in the first cycle, then equation 5.14 yields

$$\frac{3}{\lambda+3} \left(\frac{n}{\lambda} \left(1 - \frac{1}{R^{\alpha+1}} \right) \right)^{1/(1-\beta)} \left(\frac{SdB'}{4\epsilon_c} \right)^\lambda = k$$

The above equation (which predicts failure in stroke controlled fatigue) can be rewritten as

$$\log \left(\frac{3}{3+\lambda} \right) + \gamma \log \left(\frac{n}{\lambda} \right) + \gamma \log \left(1 - \frac{1}{R^{\alpha+1}} \right) + \lambda \log \left(\frac{SdB'}{4\epsilon_c} \right) = \log k$$

$$\gamma \log \left(\frac{n}{\lambda} \right) + \lambda \log \left(\frac{SdB'}{4\epsilon_c} \right) = k'$$

$$\log n + (\alpha+1) \log (B') = k'' \quad (5.15)$$

where k' and k'' are new constants related to k by

$$k' = \log k - \log \frac{3}{3+\lambda} - \gamma \log \left(1 - \frac{1}{R^{\alpha+1}} \right)$$

$$k'' = k' + \gamma \log \lambda + \lambda \log \left(\frac{4\epsilon_c}{S_d} \right)$$

Note that this more rigorous approach gives an equation for the fatigue S-N curve which is similar in form to the one obtained in section 5.2 (equation 5.12). Also note that the absolute values of the load at maximum stroke are determined by the values of the critical strain ϵ_c in addition to the values of α and β . The value of ϵ_c can therefore be determined if α and β are known.

5.4 Calculations

5.4.1 Static tests of Unreinforced 60-40 PEKK

Figures 5.1 through 5.3. depict the deviation of the loads from the linear beam theory load as a function of the applied stroke on a log-log scale for different unreinforced 60-40 PEKK samples quasi-statically loaded in stroke control at a ramp rate of 0.1 inches/min. The three plots in all three figures summarize the results of calculations performed on three different samples with the same heat treatment. The three plots are depicted in order to demonstrate the sample to sample variation (or its absence) in all three unreinforced resin systems.

Figure 5.1 depicts the results for a quenched unreinforced PEKK sample. According to the proposed model, the drop in load is some power law function of the applied stroke. Hence a log-log plot of the load deviation should yield a straight line, which is what is observed in most of the amorphous samples tested. In some of the amorphous samples, there was a kink in the log-log plot suggesting that there were two damage mechanisms involved. This might be

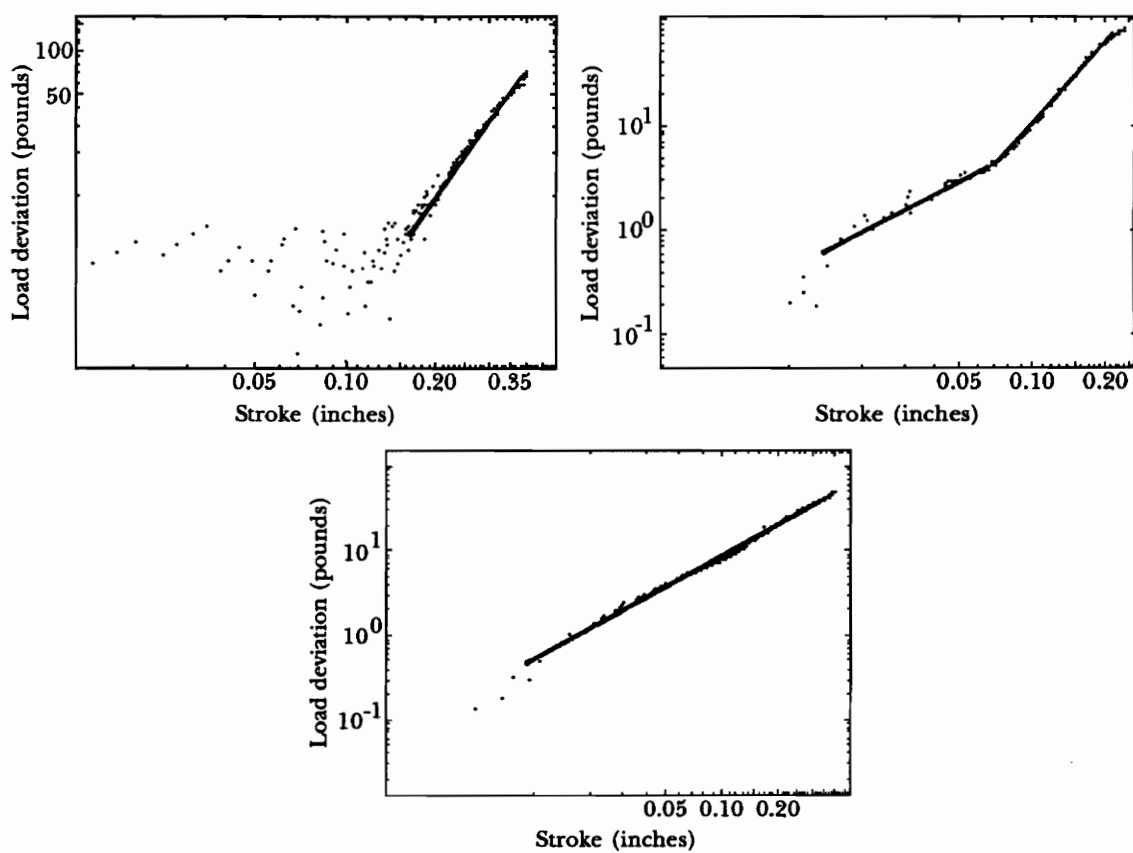


Figure 5.1 The deviation in load from the linear beam theory load plotted for three different samples on a log-log scale against the applied stroke for the quenched unreinforced 60-40 PEKK sample.

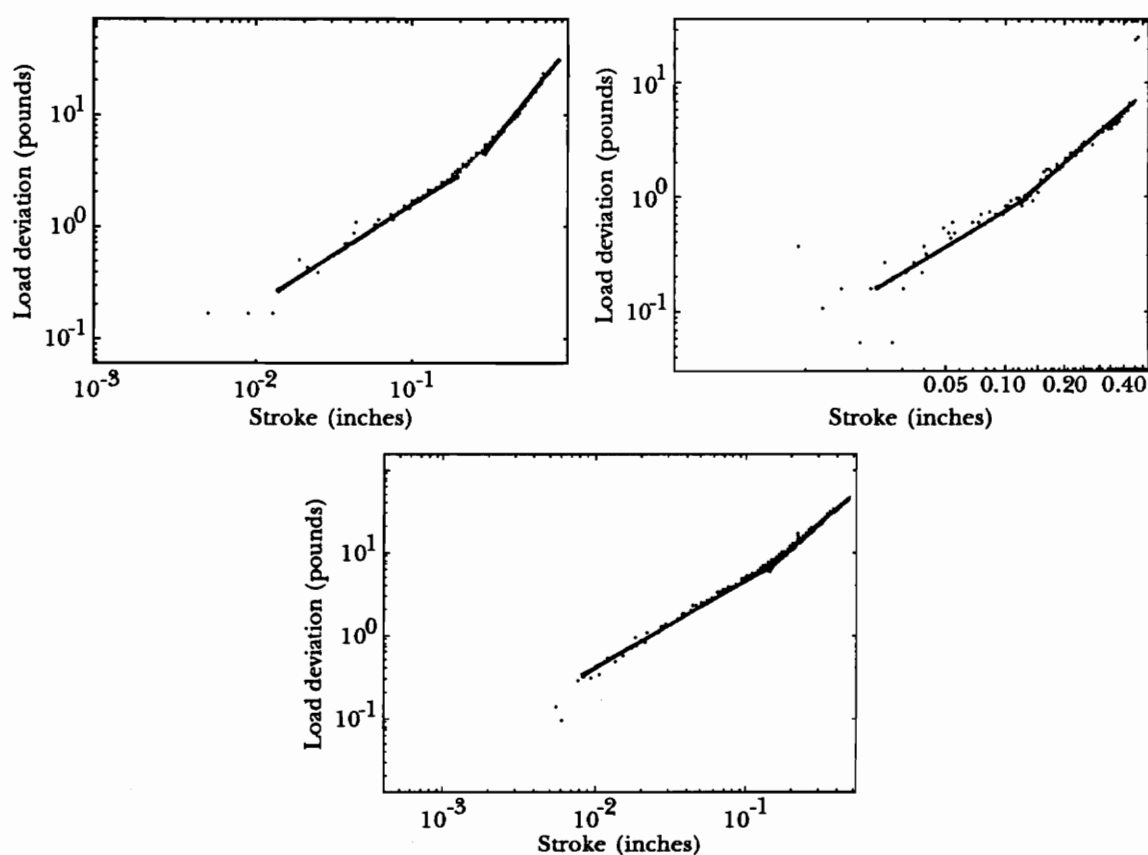


Figure 5.2 The deviation in load from the linear beam theory load plotted for three different samples on a log-log scale against the applied stroke for the unreinforced 60-40 PEKK sample crystallized at 280° C.

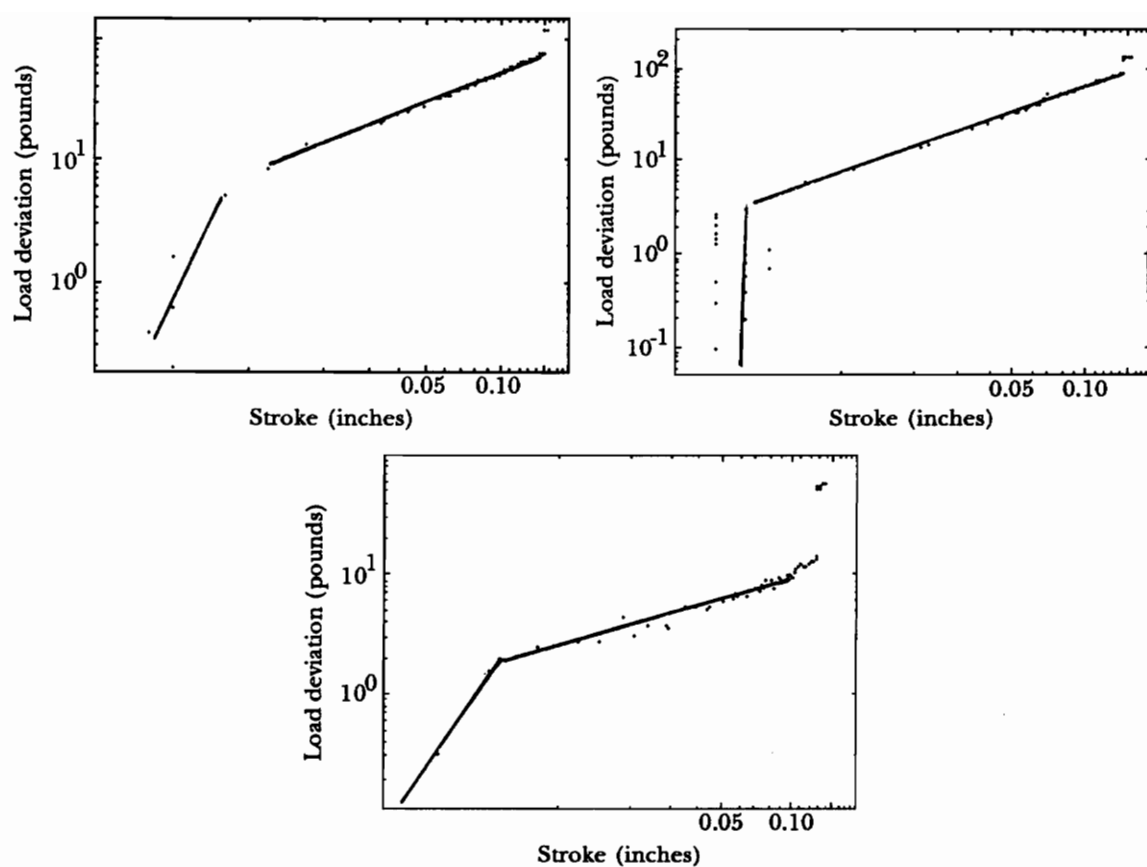


Figure 5.3 The deviation in load from the linear beam theory load plotted for three different samples on a log-log scale against the applied stroke for the unreinforced 60-40 PEKK sample crystallized at 210° C.

due to some amount of crystallinity in the “amorphous” samples. This is not entirely unexpected given the fact that PEKK 60/40 has relatively high rates of crystallization and that the quenching rates are finite (about 60° C/min). Since the half times for crystallization (see Figure 2.7) is relatively low in these systems (about 3 minutes at 260° C) and the systems were quenched from 360° C, it is likely that a certain amount of crystallinity is introduced even in the “amorphous” systems.

A semi-crystalline material should have two distinct damage mechanisms for the amorphous and crystalline parts. Hence it is expected that a log-log plot similar to the one shown in Figure 5.1 will show a kink for the semi-crystalline systems. Figure 5.2 depicts the deviation of the loads from a linear load-stroke behavior for the sample crystallized at 280° C. Figure 5.3 depicts the similar relation for the sample crystallized at 210° C. As expected, there are kinks in these plots indicating a change in the damage mechanism. This treatment gives direct proof that there are two distinct damage mechanisms in the semi-crystalline material. Presumably, these are associated with the crystalline and amorphous domains in the sample.

One inherehnt difficulty in plotting the deviation in load from the linear beam theory load is obtaining accurate values of the modulus. The errors in the load deviations, which are small at low strokes, are magnified when plotted on a log-log scale. Because of this inherent difficulty, the small load-deviations for the unreinforced PEKK crystallized at 260° C could not be plotted accurately.

The values of λ calculated from these drops in loads are summarized in Table 5.1 for the different regimes in the 3 samples. From Table 5.1 it can be seen that the value of λ in regime 1 for the quenched system is close to that in regime 1 for the sample crystallized at 280° C and that in regime 2 in the sample crystallized at 210° C. Hence, it can be concluded that in the PEKK samples crystallized at 280° C initial damage (regime 1) is concentrated in the amorphous region, while in the sample crystallized at 210° C, initial damage is concentrated in the crystalline region.

Table 5.1: Values of l in the different damage regimes and the point of initiation of regime 2 in the unreinforced 60-40 PEKK. The asterisk indicates that regime 2 was observed in only one of the amorphous samples.

Treatment	λ in Regime 1	Pt of initiation of Regime 2	λ in Regime 2
Quenched	1.14	0.06 inches*	2.39*
280° C	1.09	0.1 inches	1.5
210° C	high	0.005 inches	0.9036

Potentially, the number of AE hits recorded during the static test of these materials can also be used to determine the value of λ . If the number of hits is assumed to be proportional to the amount of damage, then according to the proposed model, the number of hits plotted on a log-log scale versus stroke should also give a straight line with a slope of λ . These plots are depicted in Figures 5.4 through 5.7 for the four different 60-40 PEKK samples. The inherent difficulty in using the number of hits as a measure of damage in these unreinforced resin systems is that very few hits are recorded even at very high acoustic amplitude gains (80 dB in this case). Therefore, the signal to noise ratio is very low, and in these tests determinations of λ cannot be made with a large degree of accuracy from the hits vs stroke plot of the unreinforced resin systems. In subsequent sections, the number of hits vs stroke relation has been used to determine the value of λ in the carbon fiber reinforced composite systems where the signal to noise ratio is higher. However, the hits vs stroke relation has not been used to determine the value of λ in the unreinforced resin systems.

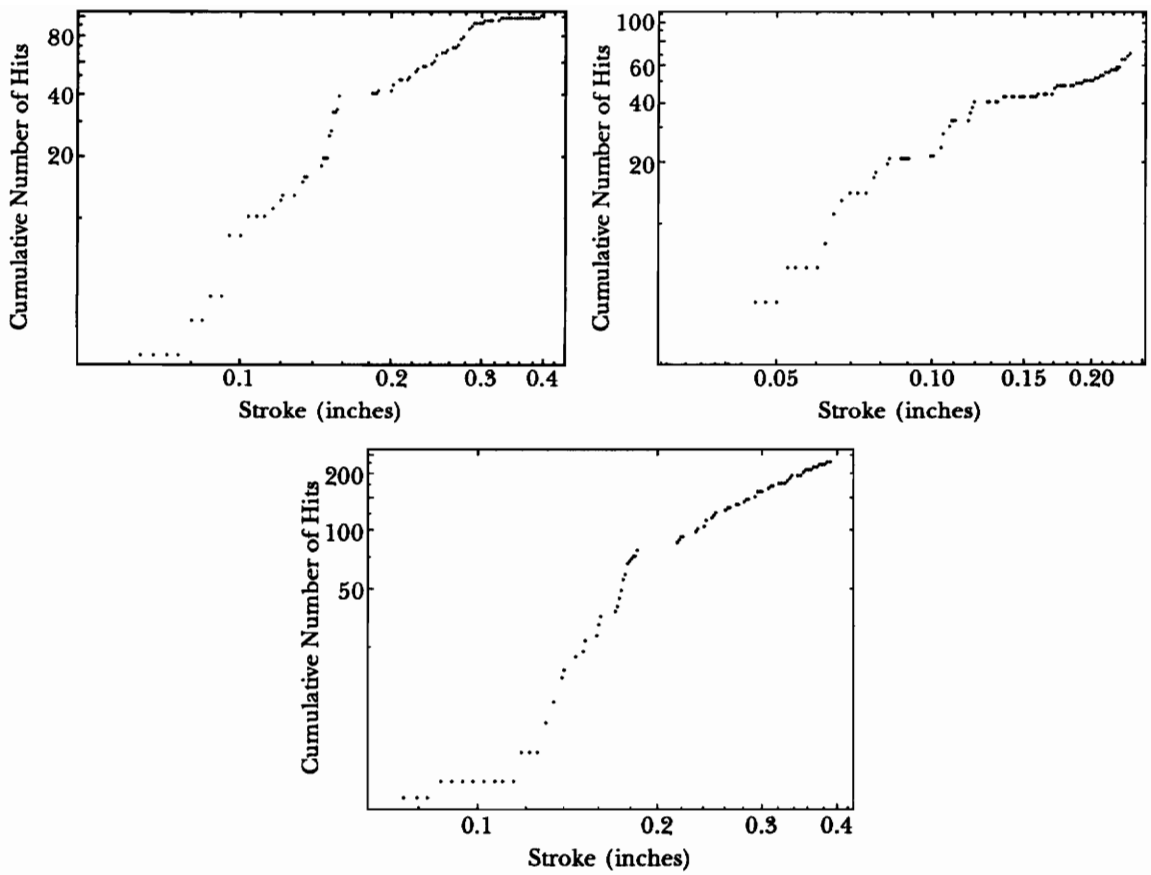


Figure 5.4 The cumulative number of hits obtained from acoustic monitoring of damage in static three point bend using an amplitude gain of 80 dB plotted for three different samples on a log-log scale against the applied stroke for the quenched unreinforced 60-40 PEKK sample.

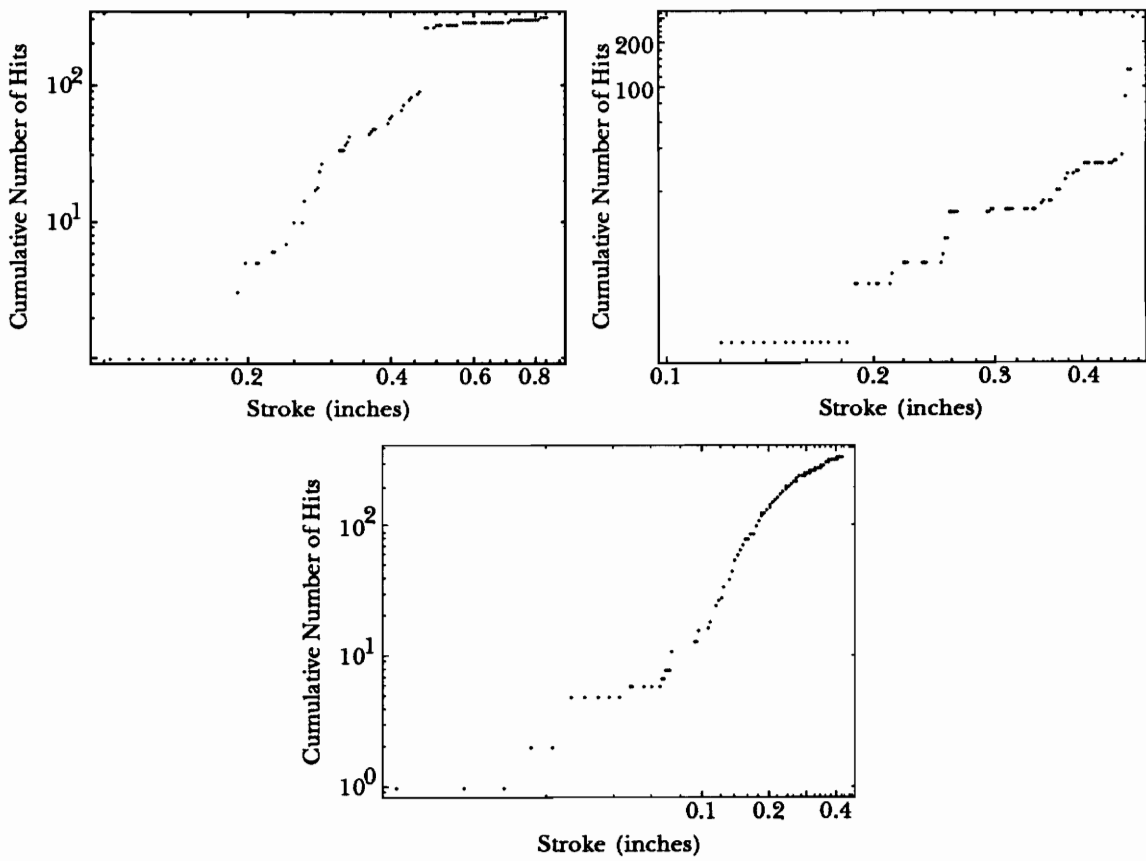


Figure 5.5 The cumulative number of hits obtained from acoustic monitoring of damage in static three point bend using an amplitude gain of 80 dB plotted for three different samples on a log-log scale against the applied stroke for the unreinforced 60-40 PEKK sample crystallized at 280° C.

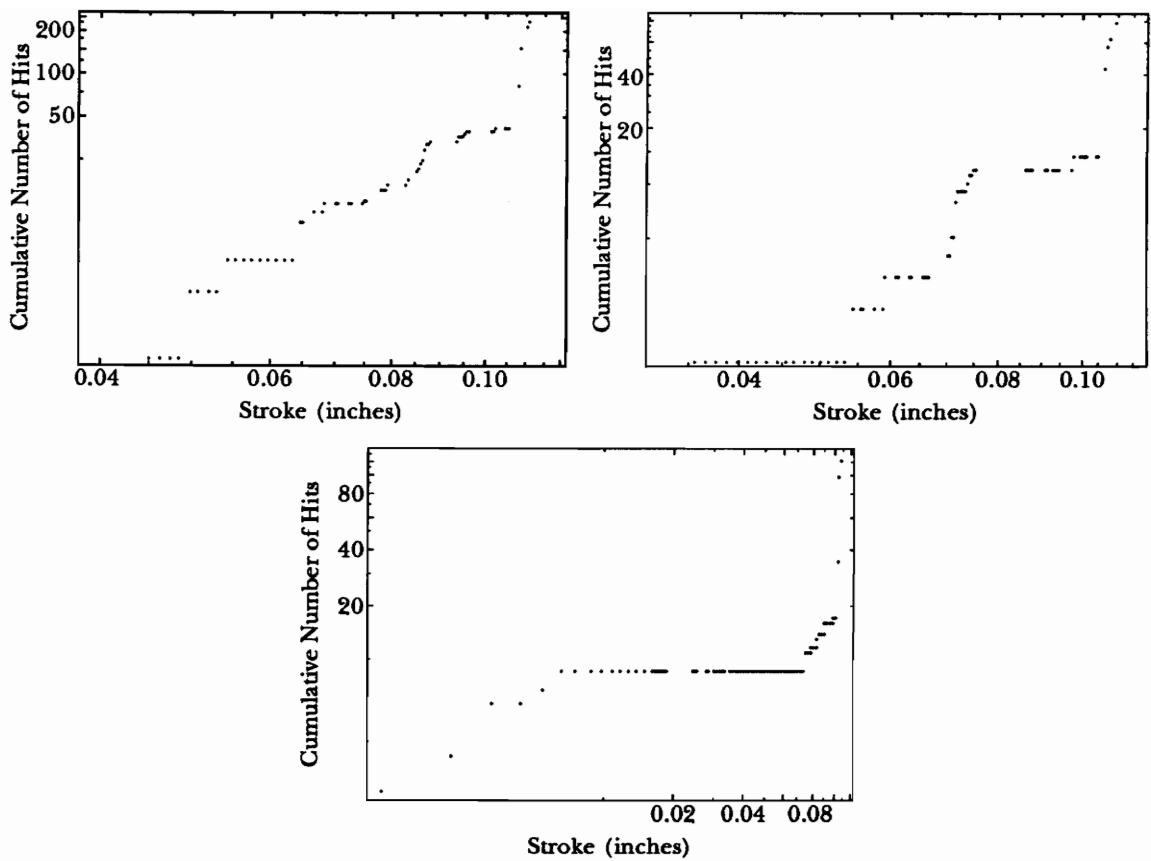


Figure 5.6 The cumulative number of hits obtained from acoustic monitoring of damage in static three point bend using an amplitude gain of 80 dB plotted for three different samples on a log-log scale against the applied stroke for the unreinforced 60-40 PEKK sample crystallized at 250° C.

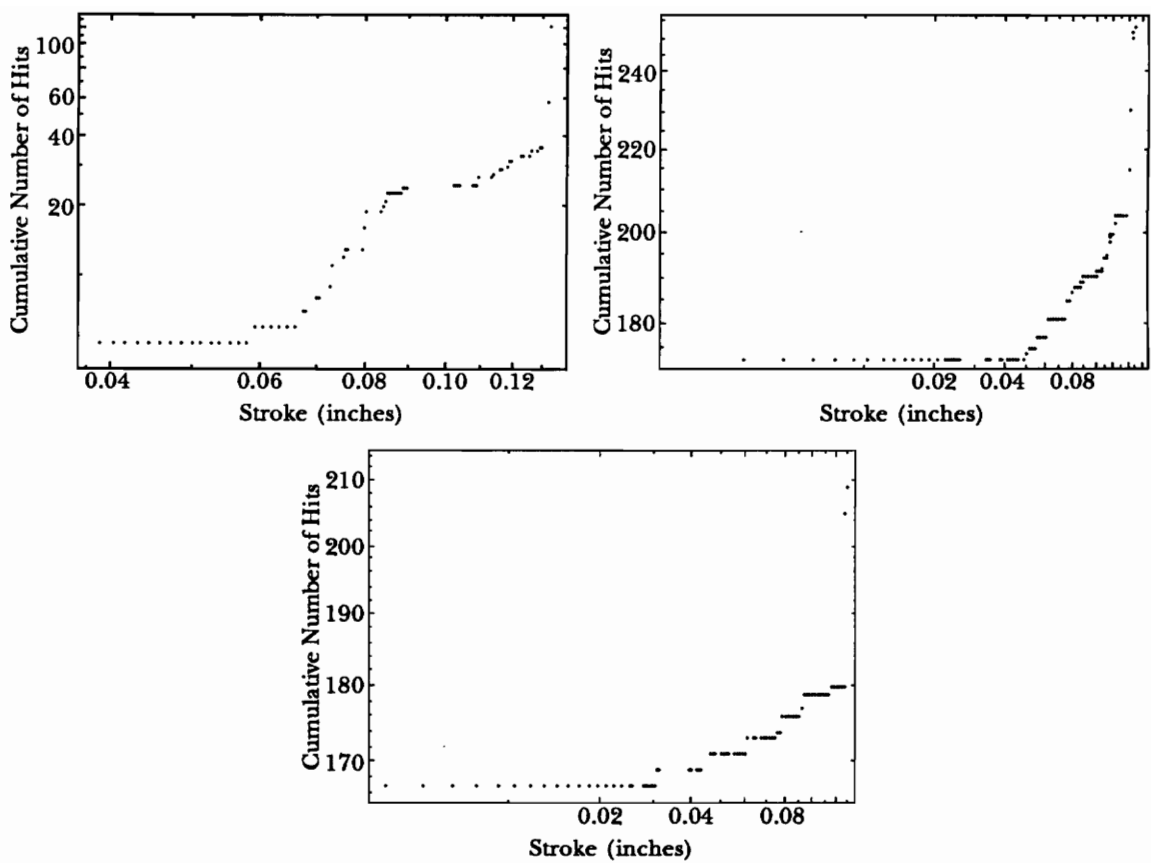


Figure 5.7 The cumulative number of hits obtained from acoustic monitoring of damage in static three point bend using an amplitude gain of 80 dB plotted for three different samples on a log-log scale against the applied stroke for the unreinforced 60-40 PEKK sample crystallized at 210° C.

5.4.2 Static tests of AS-4 Carbon fiber reinforced 60-40 PEKK

The deviation in loads from the linear beam theory load plotted on a log scale as a function of the applied stroke for the four carbon fiber reinforced 60/40 PEKK composite systems investigated are depicted in Figures 5.8 through 5.11. The figures show three distinct regimes of straight line behavior. The point where the kinks in the plots occur have previously been identified using acoustic emission as points of initiation of new damage mechanisms (see Table 4.5). For example, the kink at around 0.06 inches has been identified to be the point where interfacial failure starts. The slopes of the straight lines (λ) in the four composite systems for the different damage regimes are tabulated in Table 5.2. The table also includes the points where the damage regimes initiate. By comparing Table 5.2 with Table 4.5, it can be seen that the points of initiation of new damage mechanisms as determined from Figures 5.8 through 5.11 compare well with those determined by monitoring the amplitude of the acoustic hits.

The value of λ in regime 1 for the sample crystallized at 280° C could not be computed because of the high amount of data scatter in that region. However, from Figure 5.9, it can be seen that the value of λ in regime 1 for this sample is of the same order of magnitude as in the other samples. Since the value of λ in regimes 1, 2 and 3 are distinct from one another, it can be concluded that they represent different damage modes. From the results of acoustic monitoring of damage, it was concluded that the three different damage modes are matrix cracking, interfacial failure and fiber fracture, which are represented in Table 5.2 by regimes 1, 2 and 3 respectively.

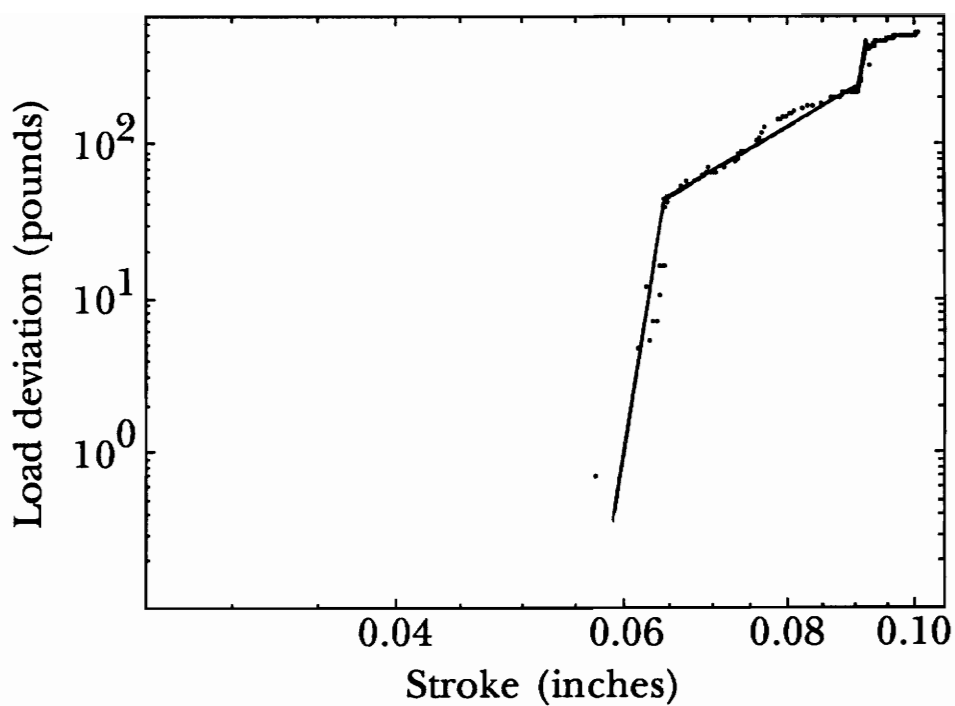


Figure 5.8 The deviation of the loads from the linear beam theory load plotted on a log log scale against the applied stroke for the quenched AS4 carbon fiber reinforced 60-40 PEKK.

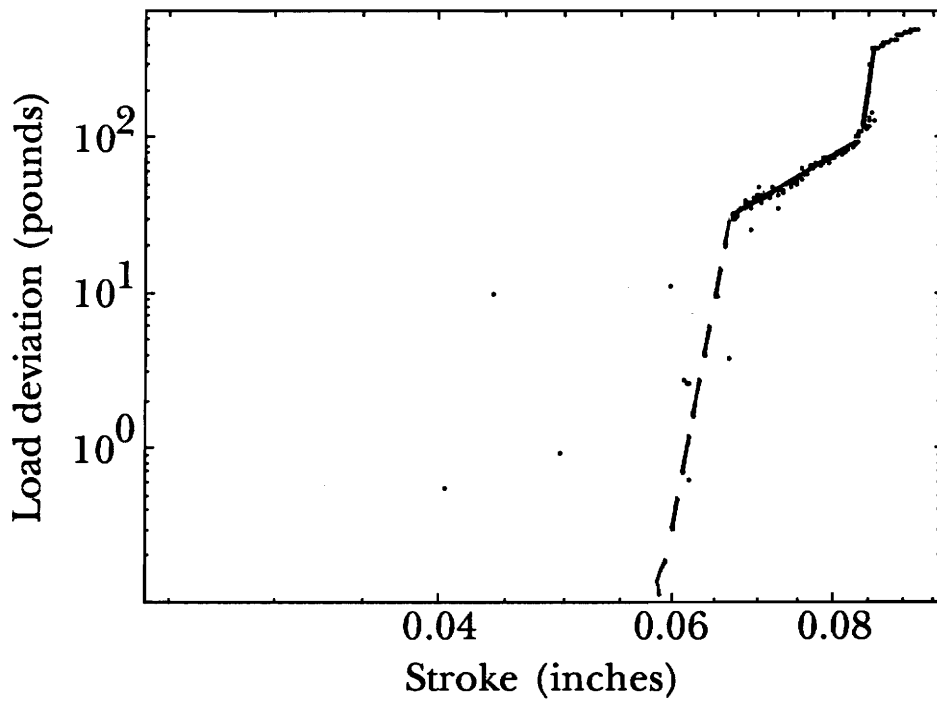


Figure 5.9 The deviation of the loads from the linear beam theory load plotted on a log log scale against the applied stroke for the AS4 carbon fiber reinforced 60-40 PEKK crystalized at 280° C.

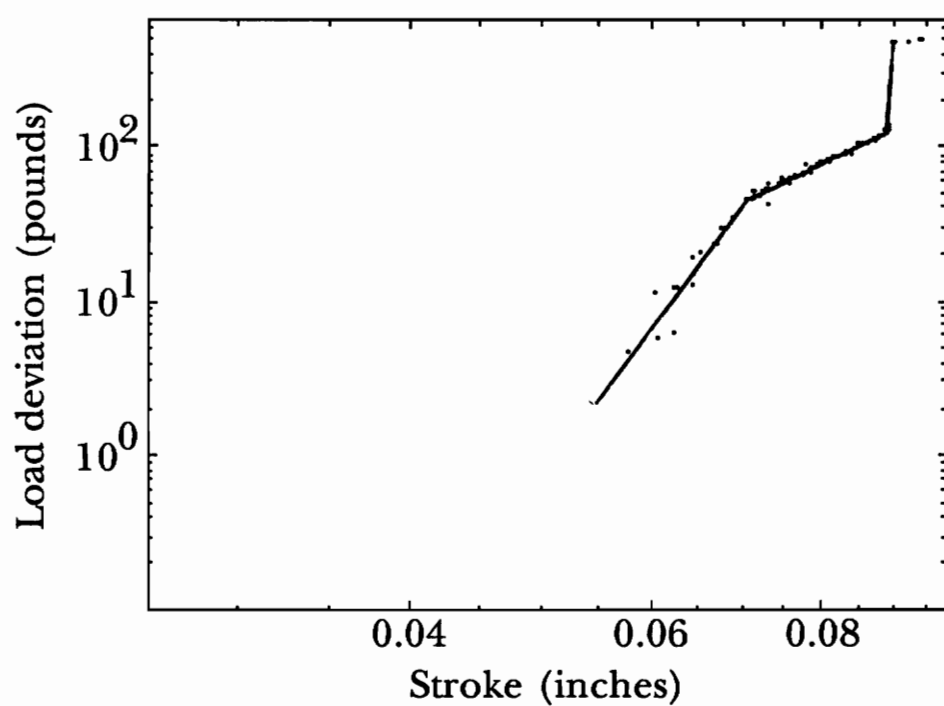


Figure 5.10 The deviation of the loads from the linear beam theory load plotted on a log log scale against the applied stroke for the AS4 carbon fiber reinforced 60-40 PEKK crystalized at 260° C.

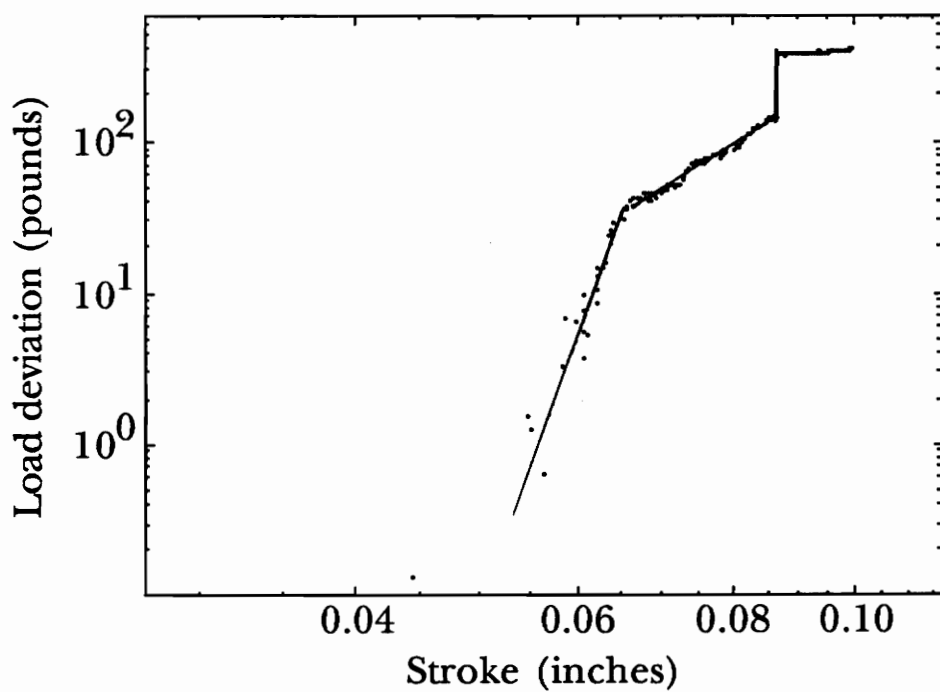


Figure 5.11 The deviation of the loads from the linear beam theory load plotted on a log log scale against the applied stroke for the AS4 carbon fiber reinforced 60-40 PEKK crystalized at 230° C.

Table 5.2 : Values of λ in the different damage regimes and their points of initiation in AS4 Carbon fiber reinforced PEKK composite systems undergoing a quasi-static stroke controlled three point bend loading.

Treatment	λ in Regime 1	Initiation of Regime 2	λ in Regime 2	Initiation of Regime 3	λ of Regime 3
		inches		inches	
Quenched	8.49	0.064	2.2	0.09	high
280° C	—	0.06	2.71	0.085	high
260° C	12.97	0.07	4.12	0.09	high
230° C	20	0.065	2.4	0.087	high

In fact on comparing Tables 5.2 and 4.5, it can be seen that the correspondence between the points of initiation of new damage mechanisms as determined from acoustic emission and as determined from the model is very quantitative (within $\pm 10\%$). This correspondence provides additional support in favour of the proposed model.

The cumulative number of hits plotted on a log-log scale versus the applied stroke is depicted in Figures 5.12 through 5.15 for the four AS4 carbon fiber reinforced 60-40 PEKK composite systems investigated. These hits were recorded using amplitude gains of 65 dB. As pointed out before, accurate determinations of the value of λ cannot be performed using the number of hits as a measure of damage for the unreinforced systems as the signal to noise ratio is low. In the carbon fiber reinforced systems the signal to noise ratio is higher. However, a one to one correspondence between the number of hits and the amount of damage induced in different damage regimes might not exist and hence quantitative determinations of λ from the number of hits vs stroke plot have not been made. However, it can be seen from Figures 5.12 through 5.15 that the hits vs stroke plot shows a general straight line behavior with kinks corresponding to the points of initiation of new damage regimes listed in Tables 5.2 and 4.5.

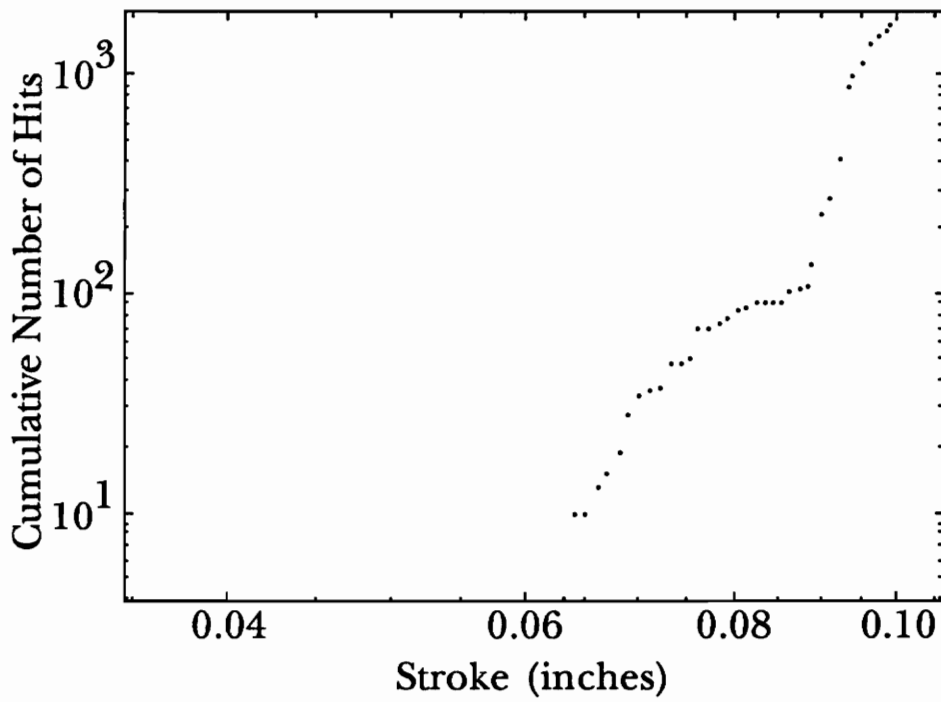


Figure 5.12 The cumulative number of hits obtained from acoustic monitoring of damage in static three point bend using an amplitude gain of 60 dB plotted on a log-log scale against the applied stroke for the quenched AS4 carbon fiber reinforced 60-40 PEKK sample.

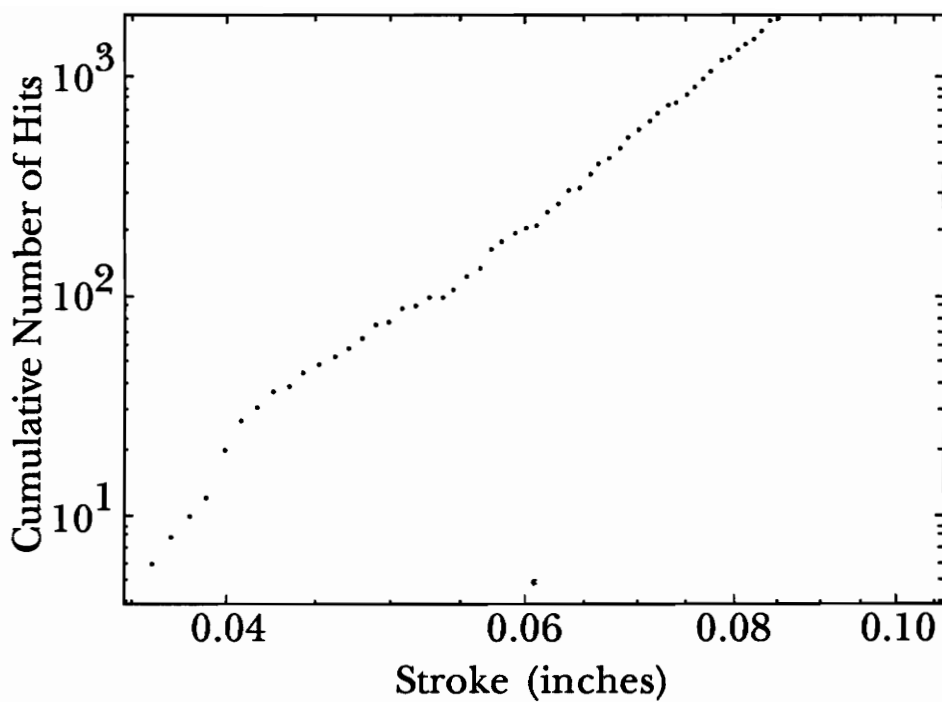


Figure 5.13 The cumulative number of hits obtained from acoustic monitoring of damage in static three point bend using an amplitude gain of 60 dB plotted on a log-log scale against the applied stroke for the AS4 carbon fiber reinforced 60-40 PEKK sample crystallized at 280° C.

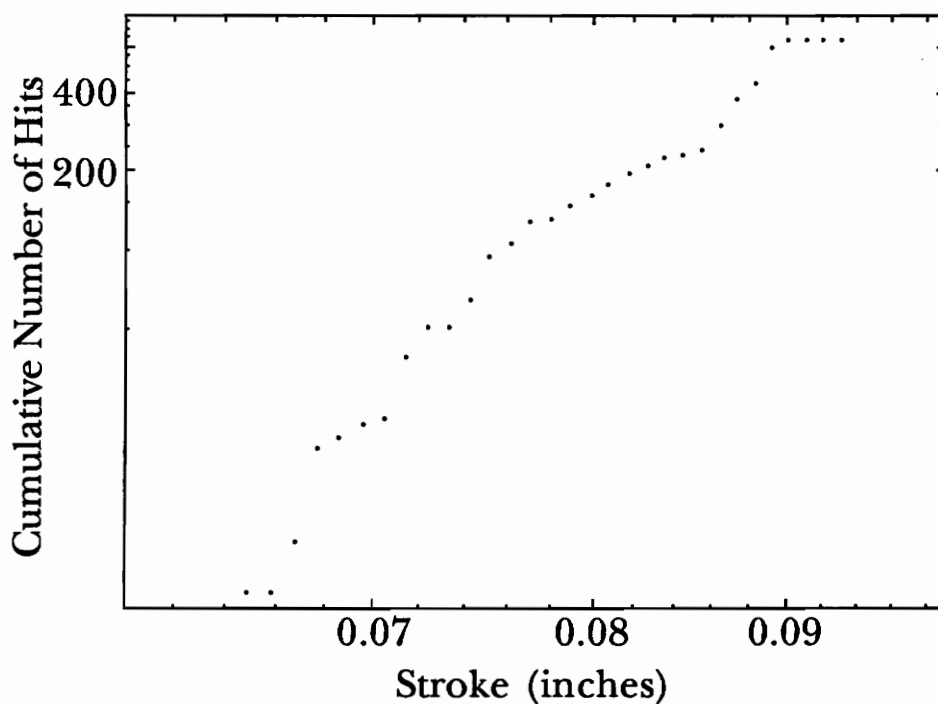


Figure 5.14 The cumulative number of hits obtained from acoustic monitoring of damage in static three point bend using an amplitude gain of 60 dB plotted on a log-log scale against the applied stroke for the AS4 carbon fiber reinforced 60-40 PEKK sample crystallized at 260° C.

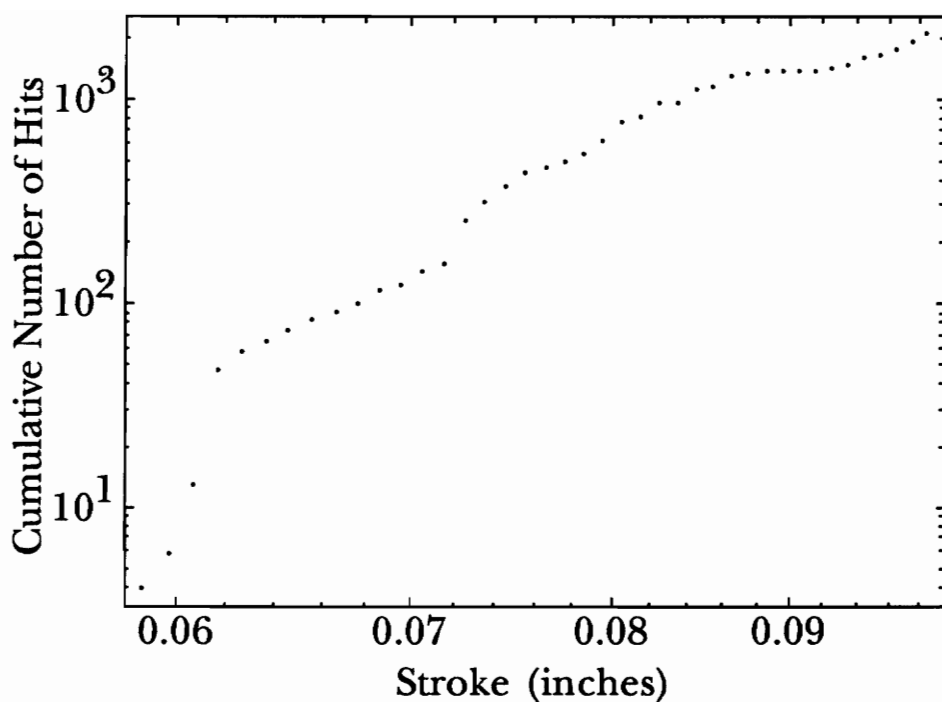


Figure 5.15 The cumulative number of hits obtained from acoustic monitoring of damage in static three point bend using an amplitude gain of 60 dB plotted on a log-log scale against the applied stroke for the AS4 carbon fiber reinforced 60-40 PEKK sample crystallized at 230° C.

In order to better characterize the damage accumulation process, the deviation in the loads from the linear beam theory loads at low strokes are plotted on a log log scale versus the applied stroke for the four composite systems in Figures 5.16 through 5.19. At low strokes, the deviations are small and hence, any errors are magnified on the log scale. However, the plots indicate a kink in the straight line behavior at low strokes suggesting a change in the damage mechanism. The points of initiation of these low stroke kinks for the four composite systems are listed in Table 5.3. Since these kinks take place before initiation of interfacial failure, it can be concluded that there is a change in the damage mechanism involving the PEKK matrix. This fact reinforces the conclusion made in section 4.2 that the acoustic hits recorded at low strokes using high amplitude gains are generated by some kind of damage to the matrix material. These hits were assigned to type 1 events, and the above analysis indicates that there is a change in the damage mechanism corresponding to the stroke level at which type 1 events are generated.

The conclusions made in the above paragraph should be qualified with the remark that the experimental errors are very high in the regime investigated in Figures 5.16 through 5.19. Any error in computing the load deviations are magnified on the log-log scale. In addition, the kinks can also possibly be assigned to other experimental factors such as errors in zeroing the loads and strokes etc. Therefore, Figures 5.16 through 5.19 cannot be used to make any conclusions as a *standalone* technique. However, when combined with Figures 4.5 through 5.8 (which depict the type 1 events), Figures 5.16 through 5.19 suggest a change in the damage mechanism at low strokes.

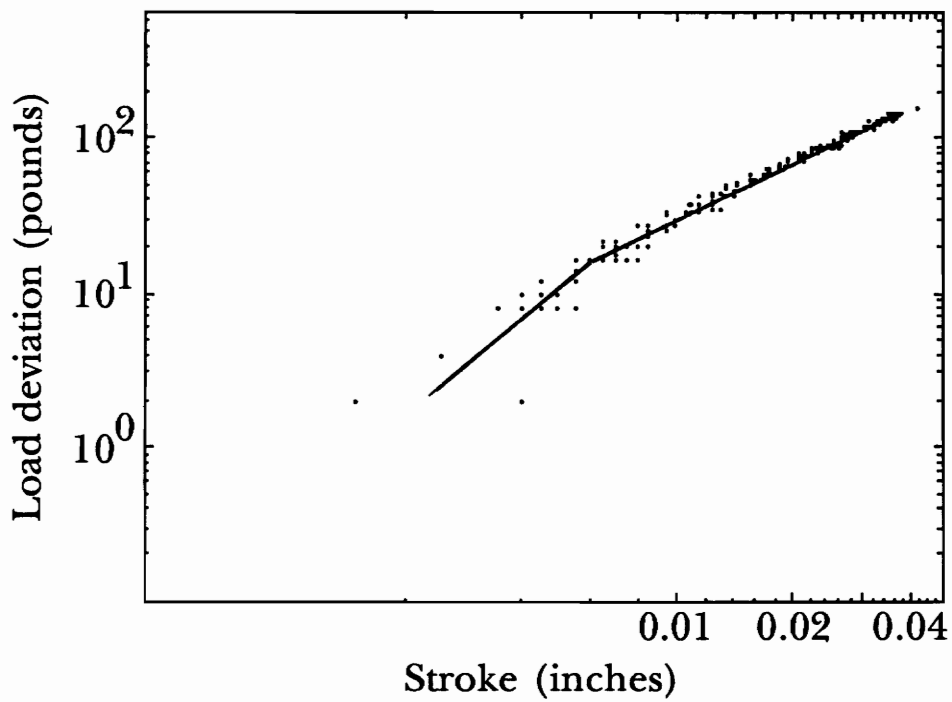


Figure 5.16 The deviation of the loads from the linear beam theory load at low strokes plotted on a log log scale against the applied stroke for the quenched AS4 carbon fiber reinforced 60-40 PEKK.

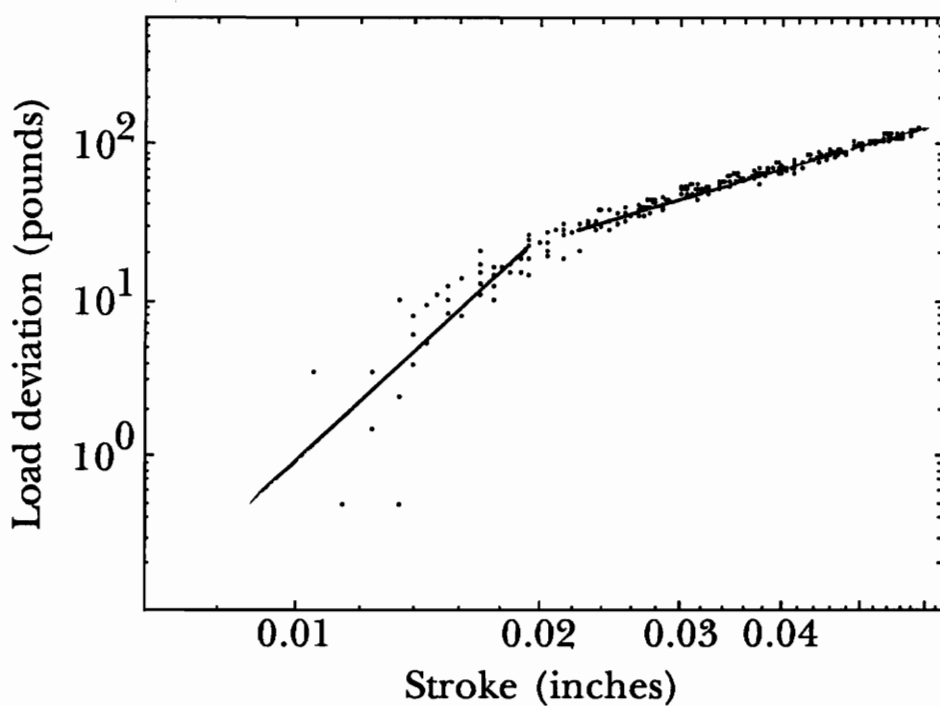


Figure 5.17 The deviation of the loads from the linear beam theory load at low strokes plotted on a log log scale against the applied stroke for the AS4 carbon fiber reinforced 60-40 PEKK crystalized at 280° C.

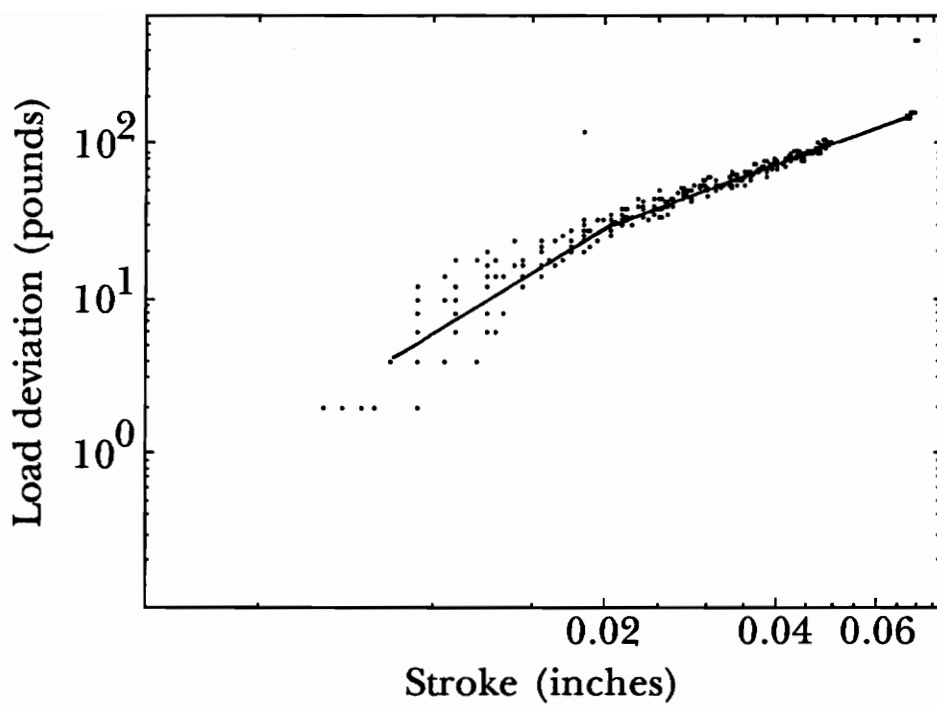


Figure 5.18 The deviation of the loads from the linear beam theory load at low strokes plotted on a log log scale against the applied stroke for the AS4 carbon fiber reinforced 60-40 PEKK crystalized at 260° C.

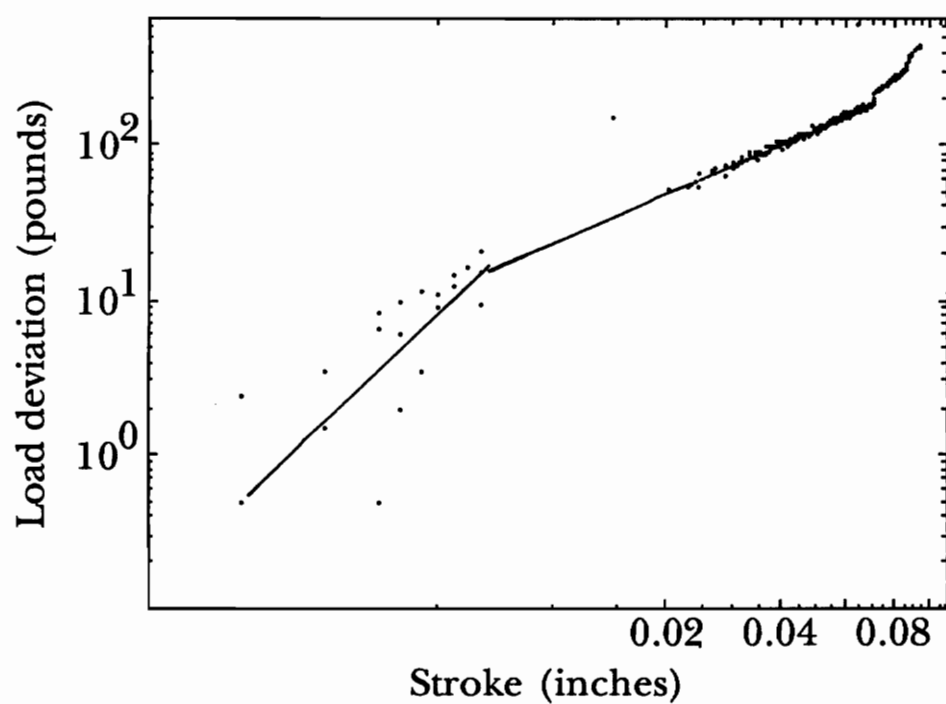


Figure 5.19 The deviation of the loads from the linear beam theory load at low strokes plotted on a log log scale against the applied stroke for the AS4 carbon fiber reinforced 60-40 PEKK crystalized at 230° C.

Table 5.3 : Points at which a kink occurs at low strokes in the log-log plot of the load deviation from the linear beam theory load vs the stroke for AS4 Carbon fiber reinforced 60-40 PEKK composite systems.

Treatment	Kink at low stroke
Quenched	0.006 inches
280° C	0.014 inches
260° C	0.016 inches
230° C	0.014 inches

It has been demonstrated that the proposed model accurately predicts the points of initiation of new damage mechanisms in the composite materials (as confirmed by acoustic emission monitoring). It can be therefore be concluded that the proposed damage model successfully simulates the damage accumulation process in the unreinforced and the carbon fiber reinforced 60-40 PEKK composite systems. However, it is also obvious that the different damage mechanisms (damage of the amorphous and crystalline parts of the matrix, damage of the interface, and damage of the fiber) are manifested in different values of the constants used in the model (α , β , and ϵ_c). Hence for the four damage mechanisms discussed, there will be at least 12 different material constants which need to be determined in order to fully characterize the damage accumulation process. Also, the constants for the matrix will potentially be a function of the carbon fiber loading. For example, the values of the constants for the unreinforced resin are different from the values of the constants for the matrix cracking mode in the reinforced composite systems. The practical value of modelling the damage accumulation process is negated if a damage equation which incorporates 12 constants is developed, even if the 12 constants can be determined experimentally. Hence for the purpose of this thesis, the damage accumulation process in the composite material was homogenized in order to develop an equation which related the overall damage accumulation process to the applied stroke (or the number of cycles in a fatigue test) using only three constants. This approach assumes that the overall damage accumulation process can be simulated by a model incorporating only three constants without introducing significant errors in the final results.

The cumulative number of hits vs stroke and the number of acoustic events vs location recorded during acoustic monitoring of the 4 AS4 carbon fiber reinforced PEKK 60/40 composite systems investigated is depicted in Figures 5.20 through 5.23. The figures also include a best fit of the number of hits vs stroke plot using a power function with the exponent λ (see equations 5.7 and 5.8). A prediction of the number of events vs location relation using the proposed model (equations 5.7 and 5.8) and same value of λ is also included in these figures. On comparing the predicted number of events vs location plot with the experimental data for the 4 different composite systems, it can be concluded that homogenizing the damage accumulation process works well in the quenched system and the system crystallized at 280° C but not as well for the other two composite systems. The values of the constant λ used in constructing the best fit in Figures 5.20 through 5.23 are listed in Table 5.4.

It should be pointed out that the difference between the predicted number of events vs location relation and the experimental data can be attributed to experimental errors in determining the event locations, in addition to shortcomings in the model development and the assumptions made. In high stiffness materials (like the samples being tested), the velocity of the acoustic waves is high. This implies that the time difference between the hits at the two sensors is small, and thus difficult to resolve. Hence the location of the acoustic events obtained from the time difference between these acoustic hits are inaccurate (see section 3.2 for an outline of the location calculation method).

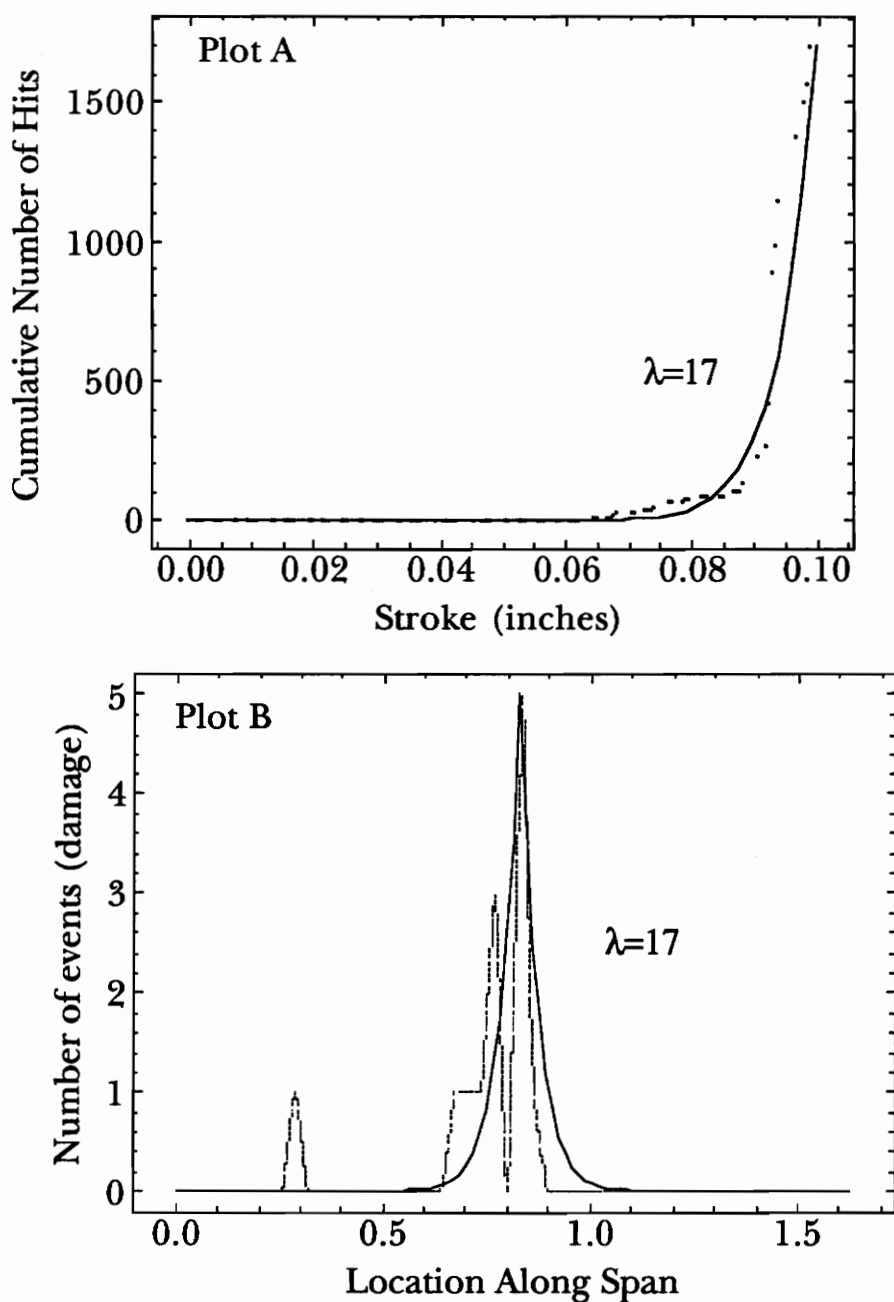


Figure 5.20 The hits vs stroke plot (plot A) and the location vs number of events plot (plot B) for the quenched AS4 carbon fiber reinforced 60-40 PEKK obtained from acoustic monitoring of damage using an amplitude gain of 60 dB.

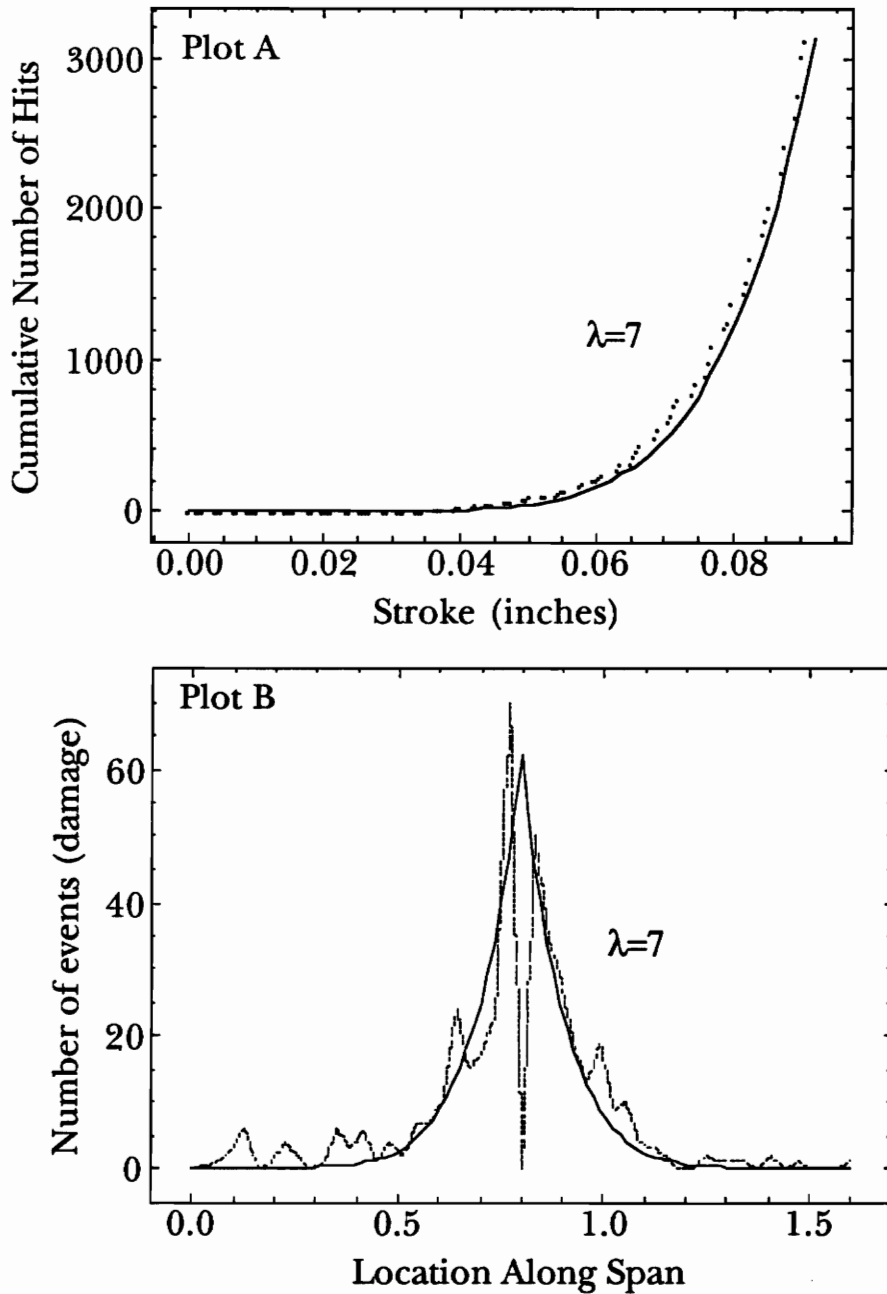


Figure 5.21 The hits vs stroke plot (plot A) and the location vs number of events plot (plot B) for the AS4 carbon fiber reinforced 60-40 PEKK crystallized at 280° C obtained from acoustic monitoring of damage using an amplitude gain of 60 dB.

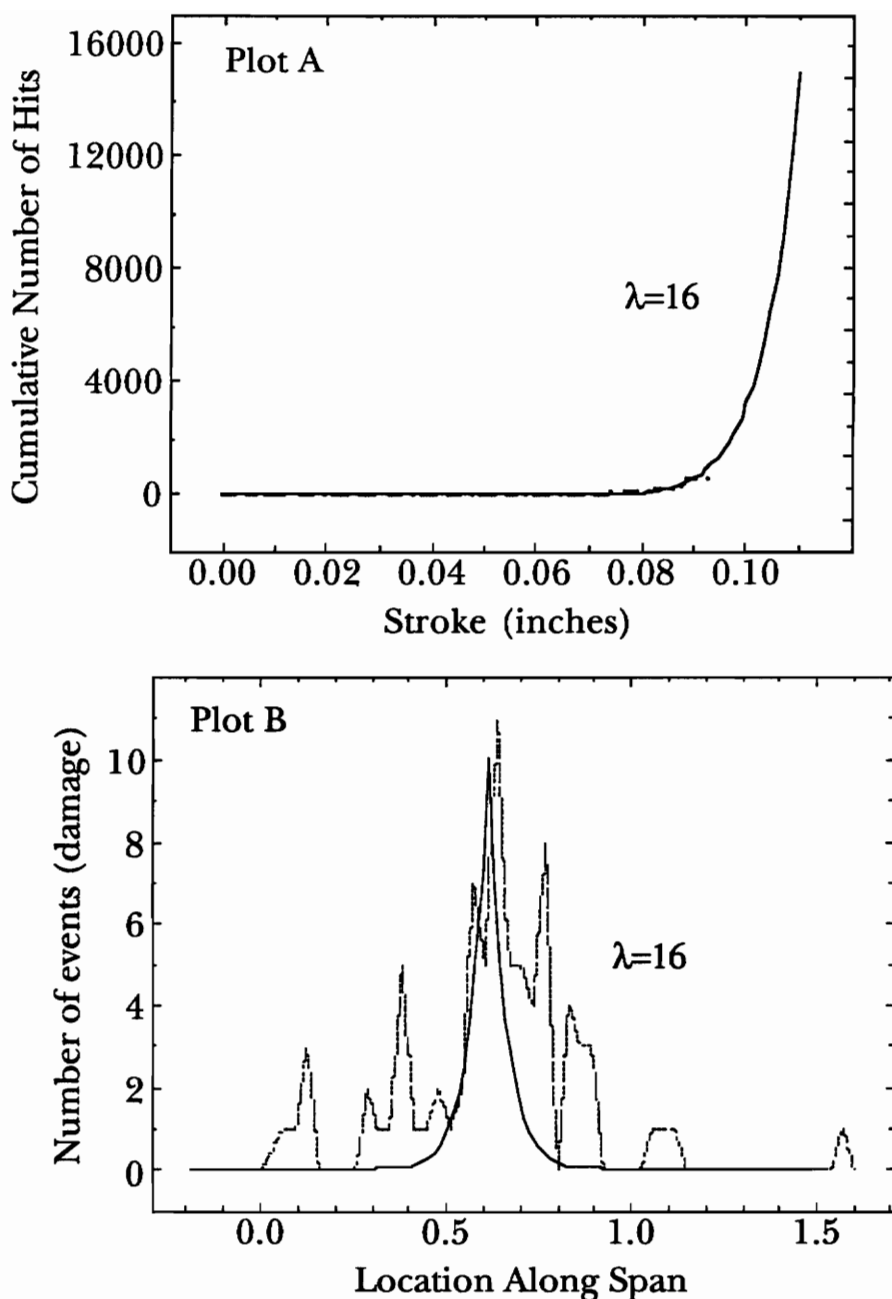


Figure 5.22 The hits vs stroke plot (plot A) and the location vs number of events plot (plot B) for the AS4 carbon fiber reinforced 60-40 PEKK crystallized at 260° C obtained from acoustic monitoring of damage using an amplitude gain of 60 dB.

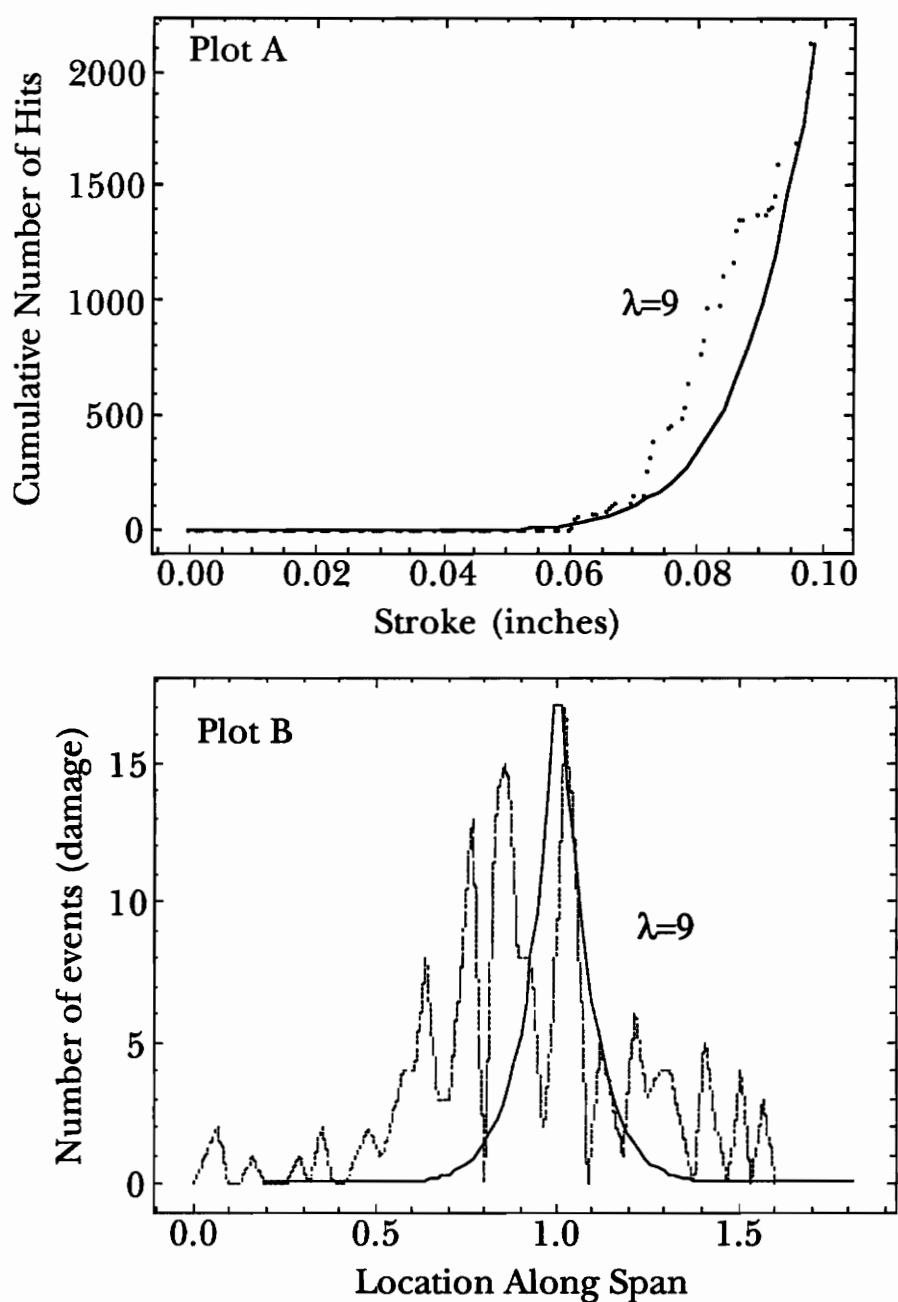


Figure 5.23 The hits vs stroke plot (plot A) and the location vs number of events plot (plot B) for the AS4 carbon fiber reinforced 60-40 PEKK crystallized at 230° C obtained from acoustic monitoring of damage using an amplitude gain of 60 dB.

Table 5.4 : Values of λ obtained by homogenizing the damage accumulation process in AS 4 Carbon fiber reinforced 60-40 PEKK undergoing quasi-static stroke controlled loading.

Treatment	λ
Quenched	17
280° C	7
260° C	16
230° C	9

Also, the simplistic assumption made regarding the damage accumulation process, where the entire damage accumulation process was homogenized in order to enable modelling using only three constants, might give rise to a difference between the predicted and the experimental location vs number of events plots. In addition to the experimental errors and the simplistic assumptions, the difference can also be attributed to shortcomings in the model which are not readily apparent at this point. However, it should be noted that in spite of the simplistic assumptions and/or model shortcomings, the model simulates the entire damage accumulation process in the composite systems using three constants with a reasonable degree of accuracy.

5.4.3 Fatigue tests of AS-4 Carbon fiber reinforced 60-40 PEKK

The cumulative number of hits recorded during the fatigue test is plotted versus time for the four AS4 carbon fiber reinforced PEKK 60/40 composite systems in Figures 5.24 through 5.27. According to the proposed model (see equation 5.10), cumulative number of hits should be some power law function of the number of cycles (and therefore the time). The exponent of this power law function should equal γ . Figures 5.24 through 5.27 also include plots of the best fit of the experimental data using this power law function.

Figures 5.28 through 5.31 depict the logs of the drop in loads from the load at maximum stroke in the first cycle versus log time for the four carbon fiber reinforced PEKK 60/40 systems. According to the proposed model (equation 5.14), logs of the load at maximum stroke in the first cycle minus the load at maximum stroke during the test should yield a straight line with a slope of γ when plotted against log number of cycles. The values of γ have been calculated from these plots and are listed in Table 5.5 (γ from load drops) together with the values of γ calculated from Figures 5.24 through 5.27 (γ from hits).

The values of α and β can be calculated from the values of λ and γ using equations 5.8 and 5.11. Table 5.6 lists the values of α and β calculated based the two values of γ in Table 5.5 and the value of λ from Table 5.4 (obtained by homogenizing the damage accumulation process during static three point bend tests of the carbon fiber reinforced PEKK 60/40 composite systems).

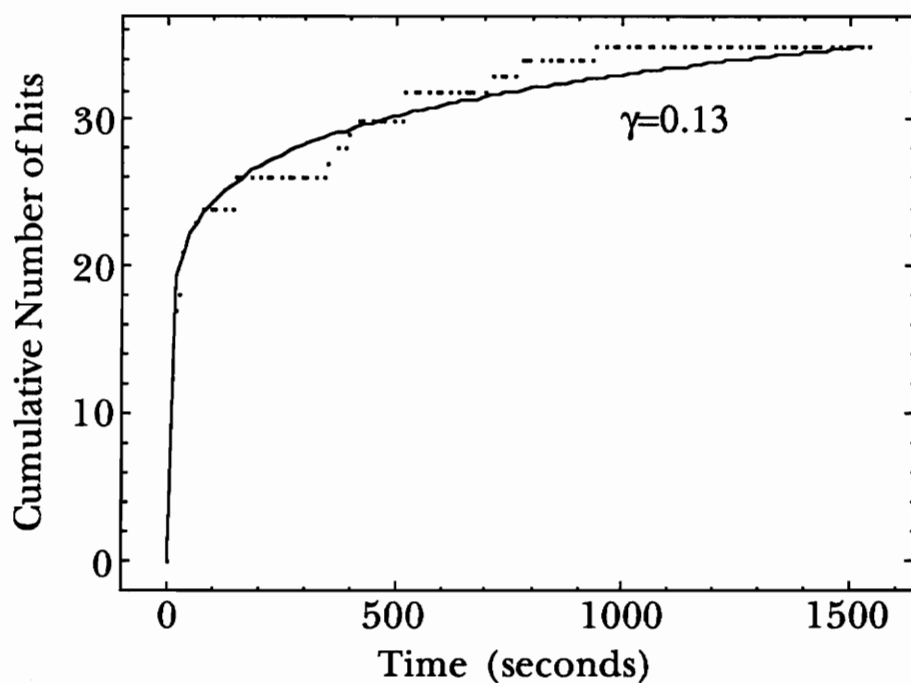


Figure 5.24 The number of hits vs time plot obtained by ignoring the hits which take place at lower stroke during a stroke controlled fatigue test of a quenched AS4 carbon fiber reinforced 60-40 PEKK. The acoustic monitoring was performed using an amplitude gain of 65 dB.

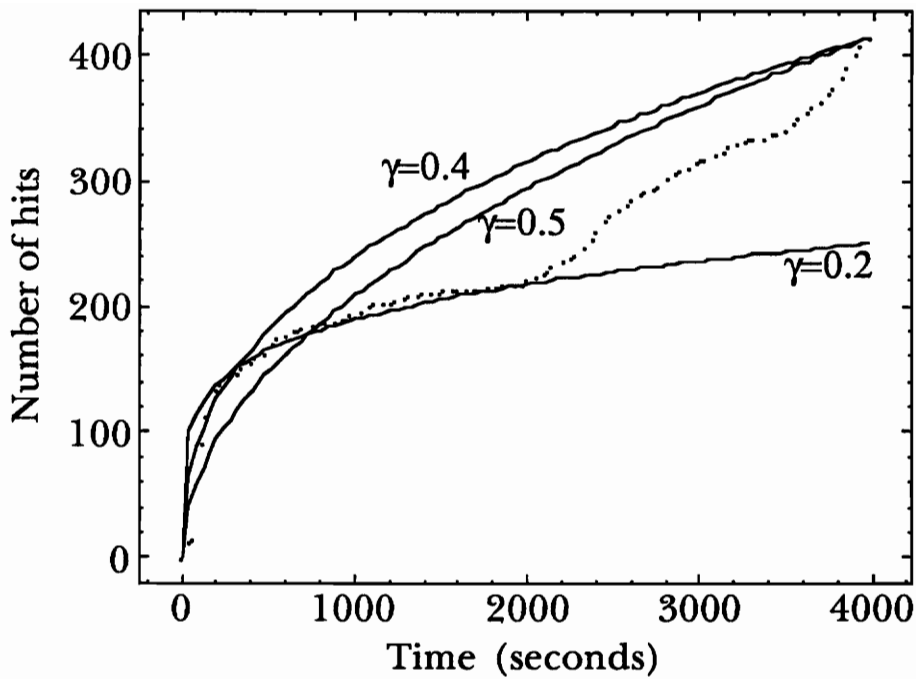


Figure 5.25 The number of hits vs time plot obtained by ignoring the hits which take place at lower stroke during a stroke controlled fatigue test of an AS4 carbon fiber reinforced 60-40 PEKK crystallized at 280° C. The acoustic monitoring was performed using an amplitude gain of 65 dB.

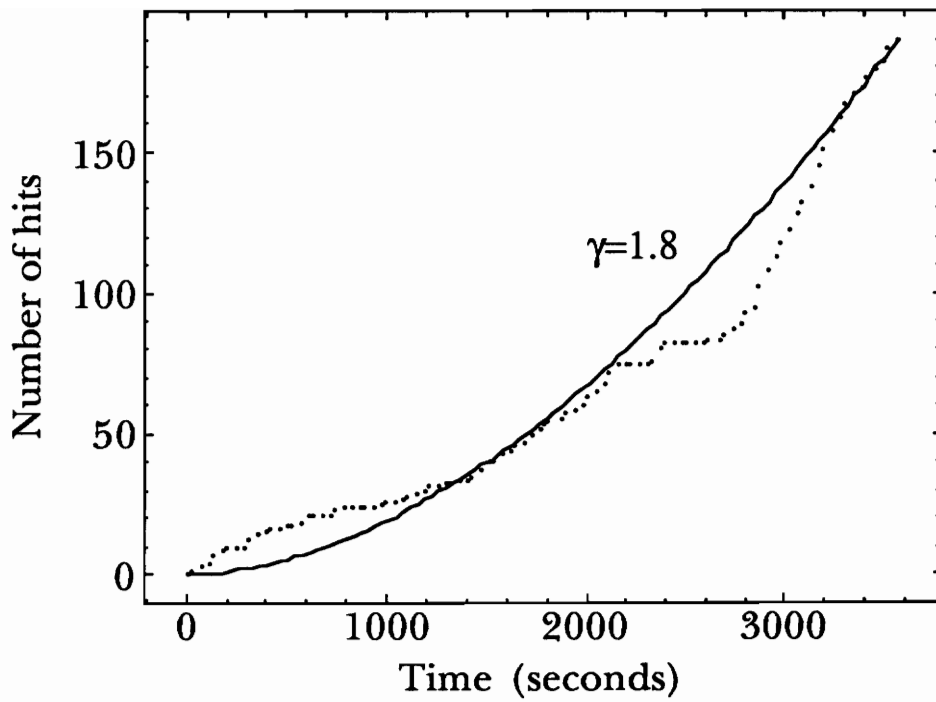


Figure 5.26 The number of hits vs time plot obtained by ignoring the hits which take place at lower stroke during a stroke controlled fatigue test of an AS4 carbon fiber reinforced 60-40 PEKK crystallized at 260° C. The acoustic monitoring was performed using an amplitude gain of 65 dB.

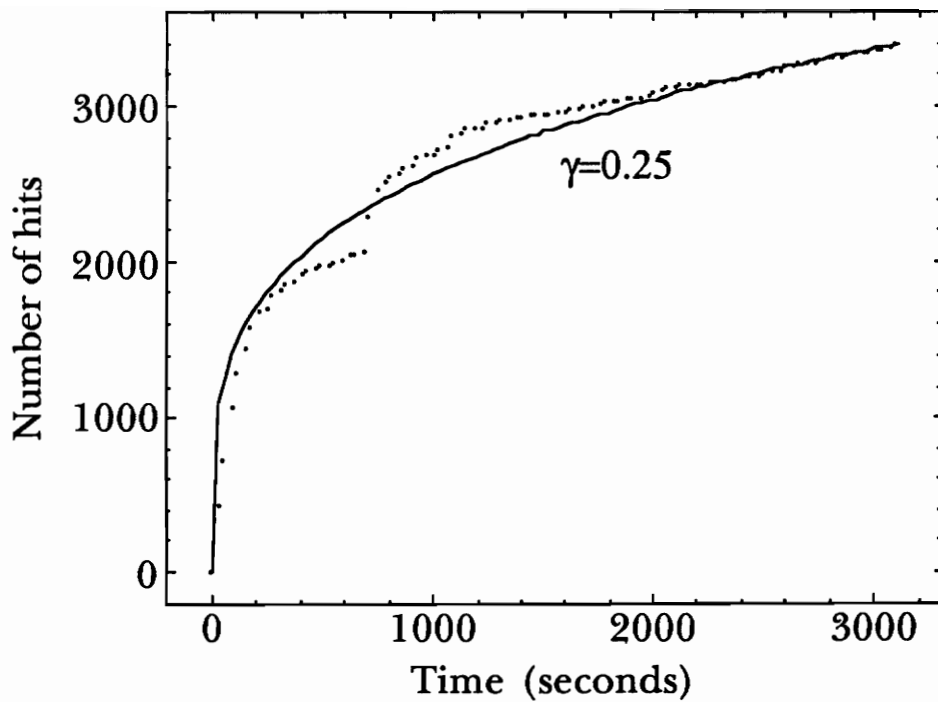


Figure 5.27 The number of hits vs time plot obtained by ignoring the hits which take place at lower stroke during a stroke controlled fatigue test of an AS4 carbon fiber reinforced 60-40 PEKK crystallized at 230° C. The acoustic monitoring was performed using an amplitude gain of 65 dB.

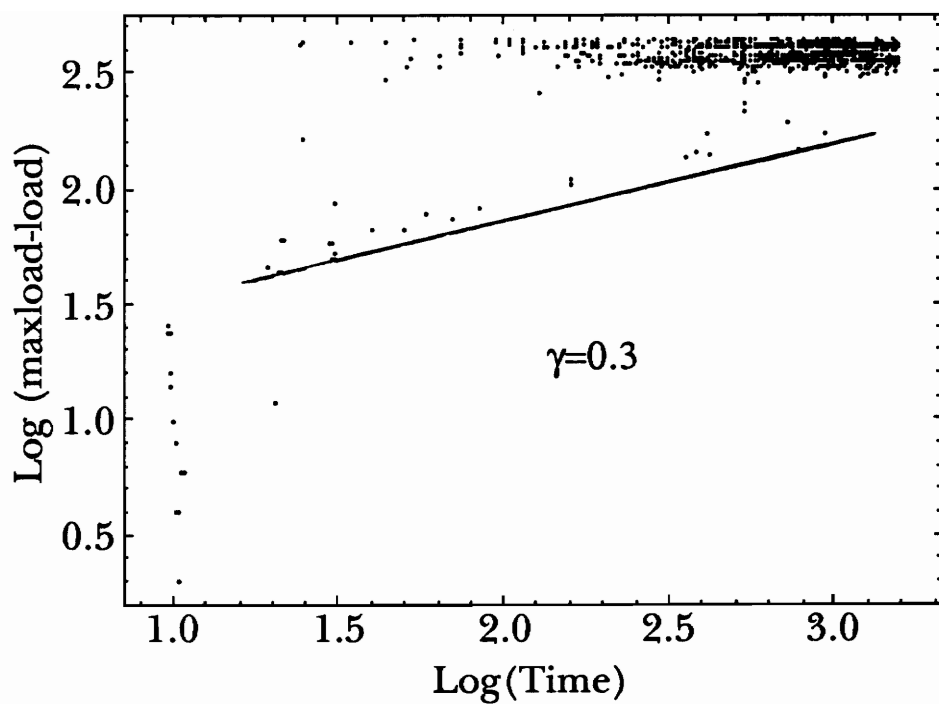


Figure 5.28 The drop in loads at maximum stroke plotted on a log-log scale against time for a stroke controlled fatigue test of a quenched AS4 carbon fiber reinforced 60-40 PEKK.

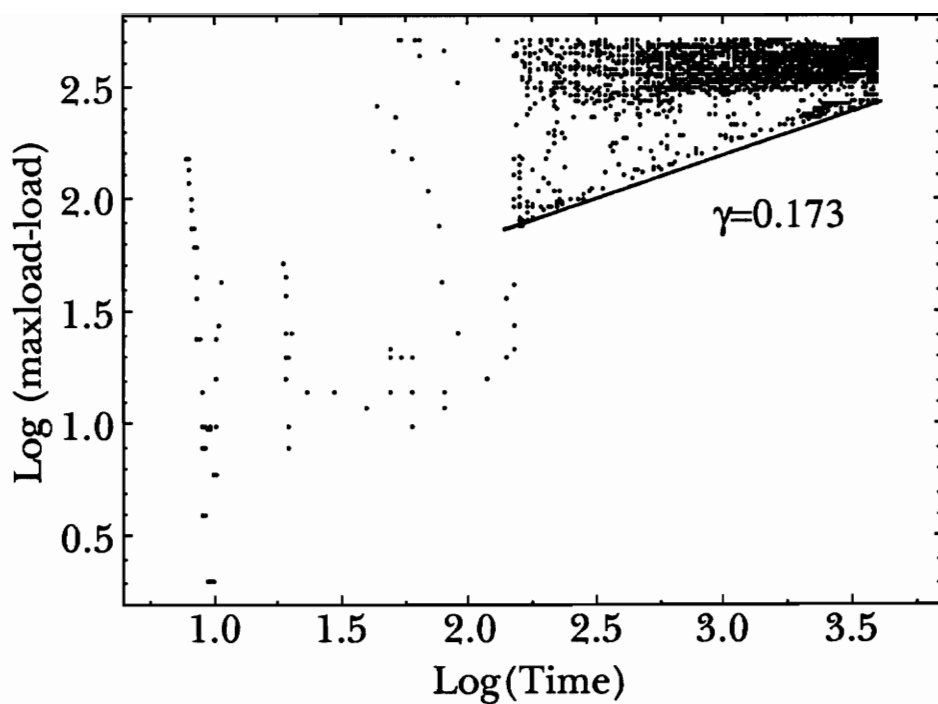


Figure 5.29 The drop in loads at maximum stroke plotted on a log-log scale against time for a stroke controlled fatigue test of an AS4 carbon fiber reinforced 60-40 PEKK crystallized at 280° C.

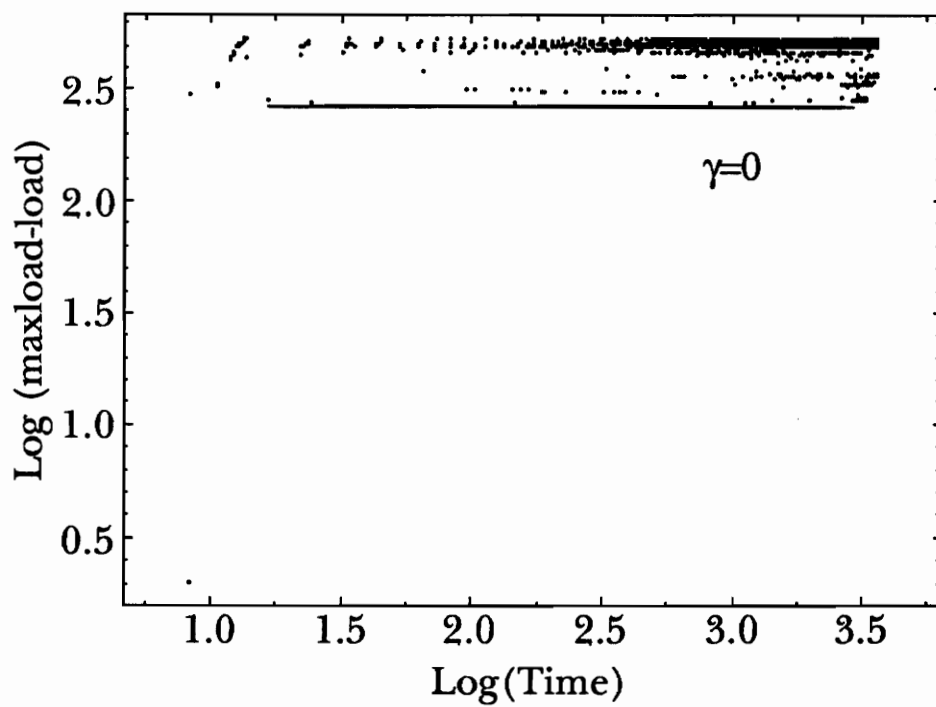


Figure 5.30 The drop in loads at maximum stroke plotted on a log-log scale against time for a stroke controlled fatigue test of an AS4 carbon fiber reinforced 60-40 PEKK crystallized at 260° C.

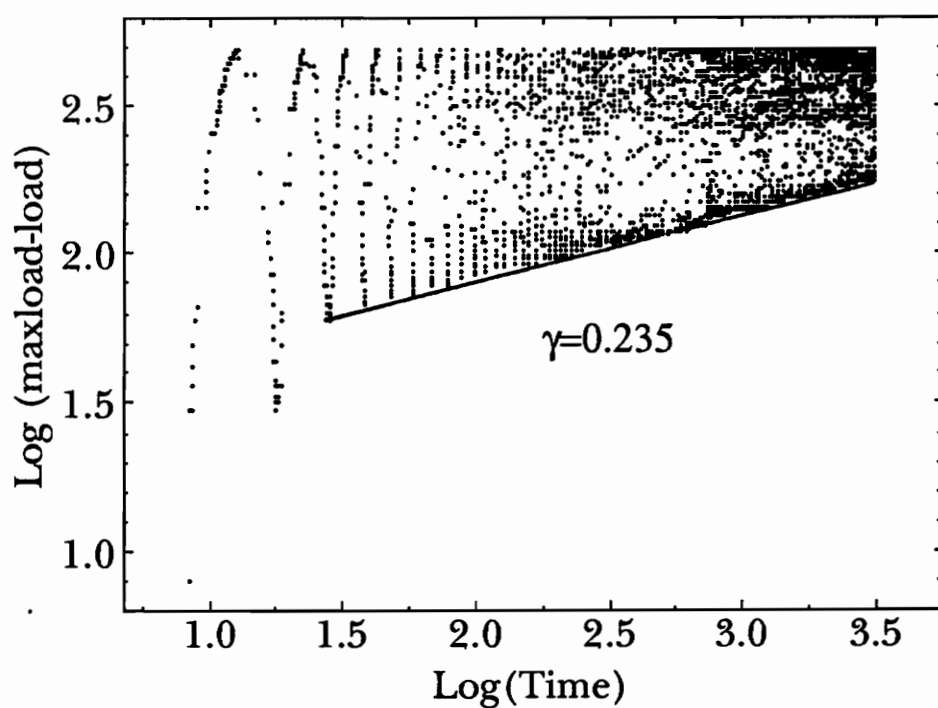


Figure 5.31 The drop in loads at maximum stroke plotted on a log-log scale against time for a stroke controlled fatigue test of an AS4 carbon fiber reinforced 60-40 PEKK crystallized at 230° C.

Table 5.5 : Values of γ calculated from the number of hits and the drop in loads.

Treatment	γ from load drops	γ from hits
Quenched	0.3	0.13
280° C	0.173	0.2
260° C	0	2
230° C	0.235	0.22

Table 5.6: The values of α and β obtained from the values of λ in Table 5.4 (obtained by homogenizing the damage accumulation process during static three point bend tests of the carbon fiber reinforced PEKK 60/40 composite systems) and the values of obtained from the cumulative hits vs time relation in Figures 5.24 through 5.27 (α and β from hits) and the load drops vs time relation in Figures 5.28 through 5.31 (α and β from load drops)

Treatment	α from load drops	β from load drops	α from hits	β from hits
Quenched	55	-2.3	130.76	-6.69
280° C	39	-5.78	35	-1.5
260° C	high	—	8	-0.45
230° C	37	-3.25	39	-3

At this point, the only remaining unknown constant is ϵ_c , which can be determined from the absolute values of the load drops as discussed in section 5.3. Since the damage accumulation process in the composite systems has been homogenized in order to obtain single values of the other two constants (α and β), the three constants will not accurately model the load-stroke relation (in fatigue or in static three point bend). However, in order to complete the analysis, ϵ_c can be calculated by ignoring the effect of homogenizing the damage accumulation process. ϵ_c has been calculated based on the assumption that the load in the three point bend test will go to zero at the point of catastrophic failure (in actual practice, the loads do not go to zero). Using this assumption (and equation 5.13), and the values of α and β listed in Table 5.6 (α and β from load-drops) the values of ϵ_c have been calculated and reported in Table 5.7 for three of the composite systems.

The three constants can now be used to predict the load-stroke relationship in a quasi-static three point bend test using equation 5.13. The predicted load-stroke relationship for three AS4 carbon fiber reinforced composite systems are given in Figure 5.32 through 5.34. The figures also include the experimental load stroke relation. The constants used in these figures are listed in Tables 5.6 (α and β from load-stroke relation) and 5.7 (ϵ_c). It is obvious from the three figures that the model only gives approximate solutions for the composite systems when used with three constants. This is expected from the simplistic treatment applied in this analysis where the damage accumulation process in the composite systems was homogenized in order to characterize the entire process using only three constants.

Table 5.7: ϵ_c calculated from the values of α and β calculated from the value of γ calculated from load drops during the fatigue test and the value of λ calculated from the static test.

Treatment	ϵ_c from load drops in fatigue
Quenched	1.752%
280° C	2.4%
230° C	1.46%

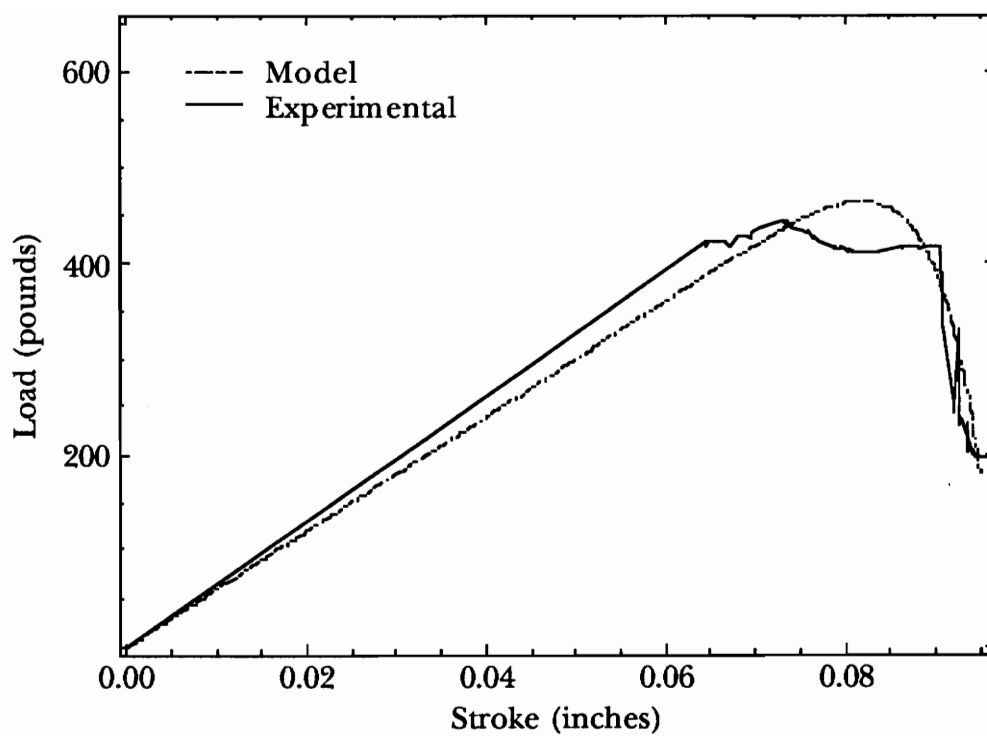


Figure 5.32 Predicted and Experimental Load-Stroke response of a quenched AS4 carbon fiber reinforced PEKK 60/40 sample.

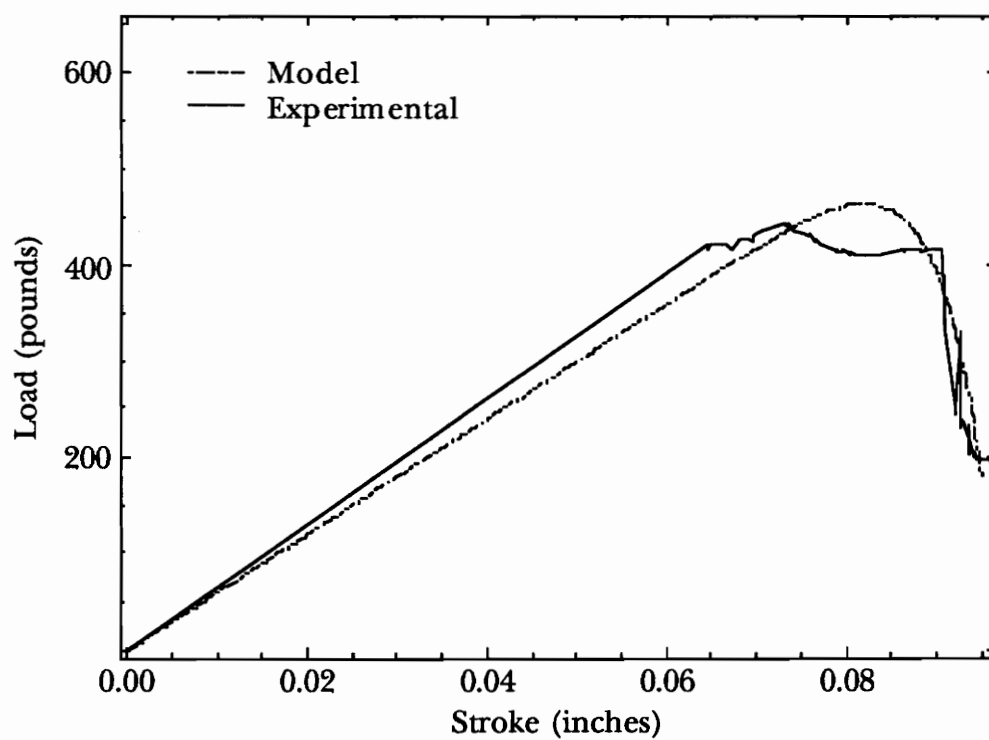


Figure 5.32 Predicted and Experimental Load-Stroke response of a quenched AS4 carbon fiber reinforced PEKK 60/40 sample.

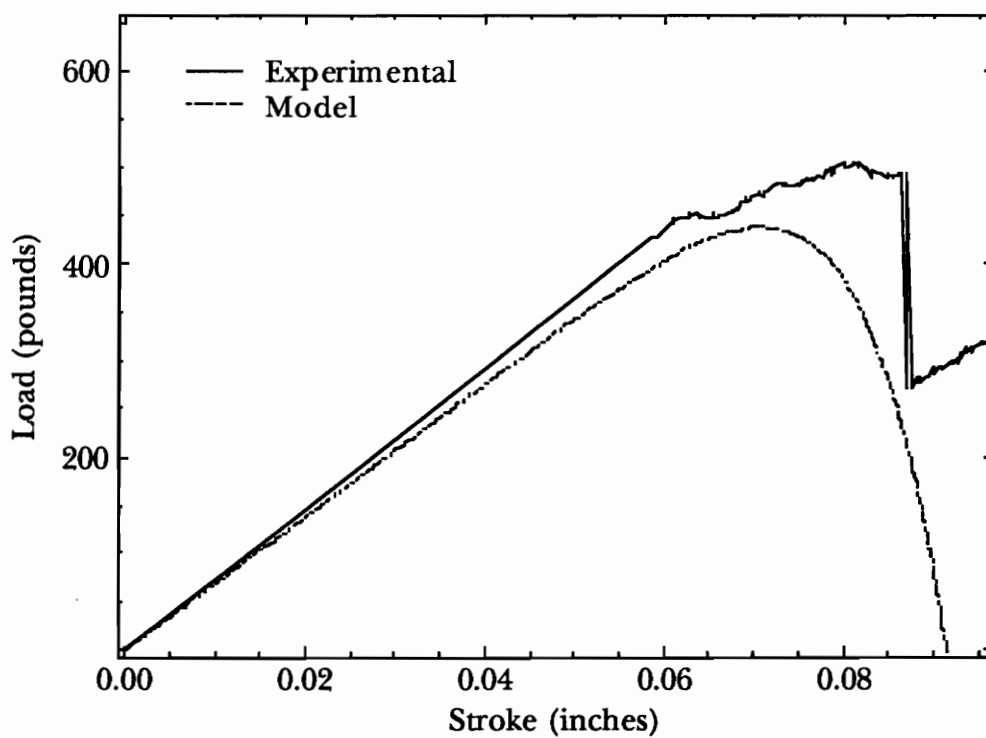


Figure 5.33 Predicted and Experimental Load-Stroke response of an AS4 carbon fiber reinforced PEKK 60/40 sample crystallized at 280° C.

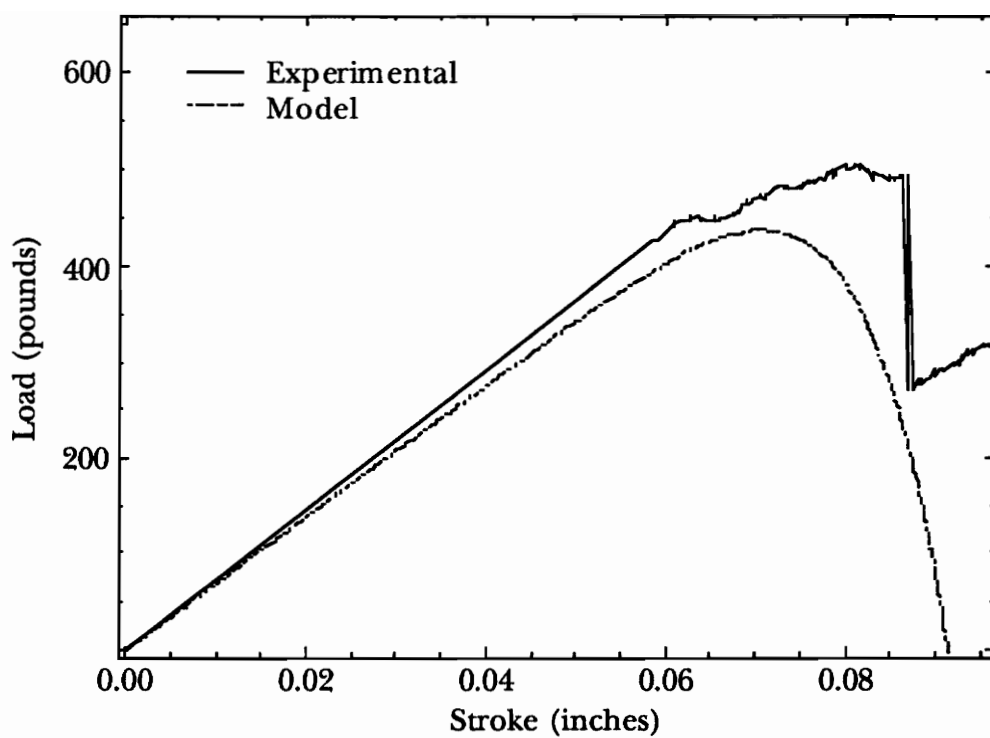


Figure 5.34 Predicted and Experimental Load-Stroke response of an AS4 carbon fiber reinforced PEKK 60/40 sample crystallized at 230° C.

5.4.4 Predicted Fatigue S-N Curves

The fatigue S-N curves for the four composite systems predicted using equation 5.12 and the constants listed in Table 5.6 are shown in Figures 5.35 and 5.36. Figure 5.35 depicts the predicted fatigue S-N curve using the constants obtained from the cumulative number of hits vs cycles relation in fatigue and Figure 5.36 depicts the predicted fatigue S-N curve obtained from the load drop vs cycles relation in fatigue. As already pointed out previously, the three constants associated with the model (α , β , and ϵ_c) can be determined with greater accuracy using the load drops, hence Figure 5.36 represents a better prediction than Figure 5.35. Figure 5.35 and 5.36 indicate that the fatigue lives should follow the order “Quench > 230 °C > 280 °C > 260 °C”. Note that in Figure 5.36, the prediction for the system crystallized at 260° C is not included. This is because the value of α could not be quantitatively determined for this system using the load drops in fatigue. However, the value of α is high, indicating that this system should have a very high fatigue life in stroke control. Also note that Figures 5.35 and 5.36 show the same general trend except for the lower predicted life for the sample crystallized at 260° C in Figure 5.35 (in Figure 5.36, the S-N curve corresponding to samples crystallized at 260 °C will lie to the right of the the S-N curve corresponding to the quenched sample. This is because the value of α measured using the load drops in Table 5.6 is high.)

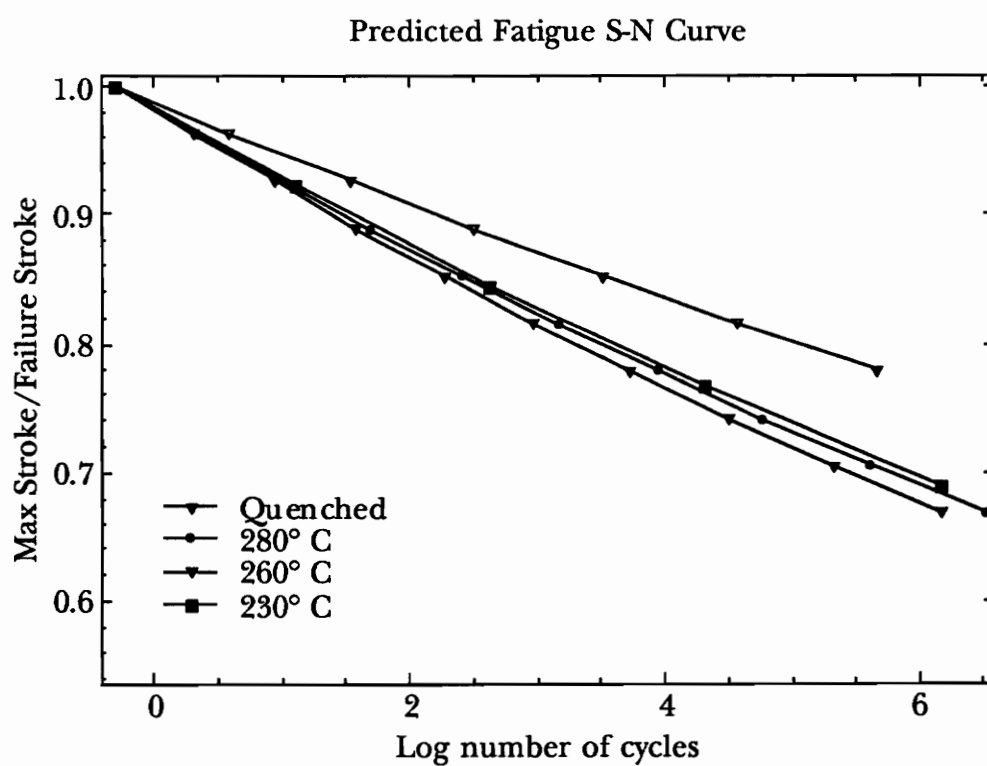


Figure 5.35 The predicted fatigue S-N curve obtained from the model and the constants obtained from the hits vs time relation in fatigue.

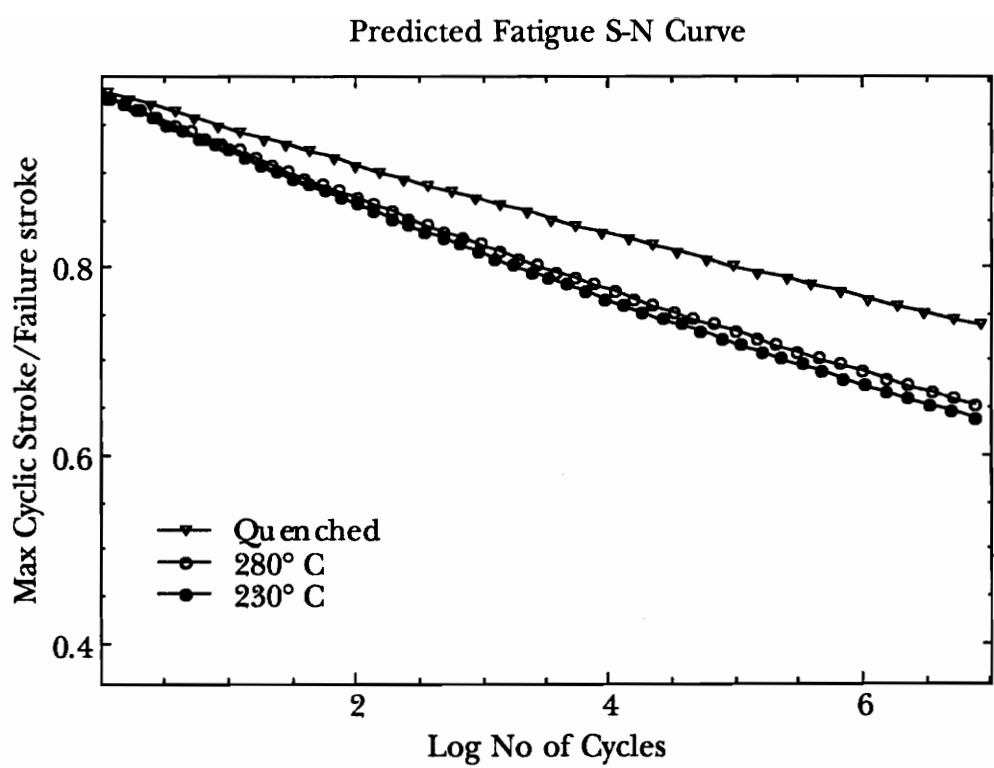


Figure 5.36 The predicted fatigue S-N curve obtained from the model and the constants obtained from the load vs time relation in fatigue.

5.5 Discussion

The proposed model was used to simulate the damage accumulation process in the unreinforced PEKK 60/40 samples. From the results of this modelling, it was concluded that in samples crystallized at 210° C, the crystalline region damages before the amorphous region, and that in samples crystallized at 300° C, the amorphous region damages before the crystalline region. This reversal in the initial damage mode might be due to the fact that crystallizing at 210° C (diffusion controlled crystallization) results in larger inter-lamellar spacing as compared to crystallization at 300° C (nucleation controlled crystallization). Since the degree of crystallinity is constant, the amorphous chains have to be more oriented in samples crystallized at 210° C. Hence, when a load is applied, damage is probably initiated by chain unfolding in the crystalline region for the samples crystallized at 210° C. In the sample crystallized at 300° C, the interlamellar spacing is smaller. Hence the amorphous chains are probably less oriented as compared to the sample crystallized at 210° C. Therefore damage probably initiates in the amorphous region in samples crystallized at 210° C resulting in an increased orientation of the amorphous chains. Once the amorphous chains have oriented to a certain degree, failure in the crystalline region initiates.

It has been demonstrated that the damage accumulation process in both the unreinforced and the carbon fiber reinforced composite systems can be modelled using the proposed equations in this chapter. However, the damage accumulation process in the composite systems is too complex to be modelled by three constants. Hence the damage accumulation process in the composite

systems was homogenized in order to develop a simple relationship. It has been demonstrated that this simplistic assumption works fairly well for most of the composite systems.

The values of λ for the AS4 carbon fiber reinforced PEKK 60/40 composite systems are listed in Table 5.4. The values of λ were obtained by homogenizing the damage accumulation process during static three point bend testing. Table 5.5 lists the values of γ obtained from fatigue testing. The values of the three fundamental model constants (α , β and ϵ_c) are listed in Tables 5.6 and 5.7.

The values of ϵ_c calculated based on this assumption are given in Table 5.7. The predicted and experimental load stroke relations for three carbon fiber reinforced PEKK 60/40 composite systems are shown in Figures 5.32 through 5.34. The predicted load-stroke relation was obtained from the model using the constants obtained from the homogenizing treatment applied to the damage accumulation process in the composite systems. It can be seen from Figures 5.32 through 5.34 that the simplistic treatment applied to the damage accumulation process results in a model which qualitatively follows the load-stroke relation, however, it is not quantitatively accurate.

Cromans data (Figure 2.10) has been used to generate an S-N curve (depicted in Figure 5.37) based on the failure strength values listed in Table 4.2. Figure 5.37 indicates that actual fatigue lives in stress control follow the order “Quenched < 280° C < 230° C < 260° C”. By comparing the predicted fatigue S-N curves with actual data points obtained by Croman⁴⁴ (see Figure 5.37), one can conclude that there is a definite qualitative but no quantitative

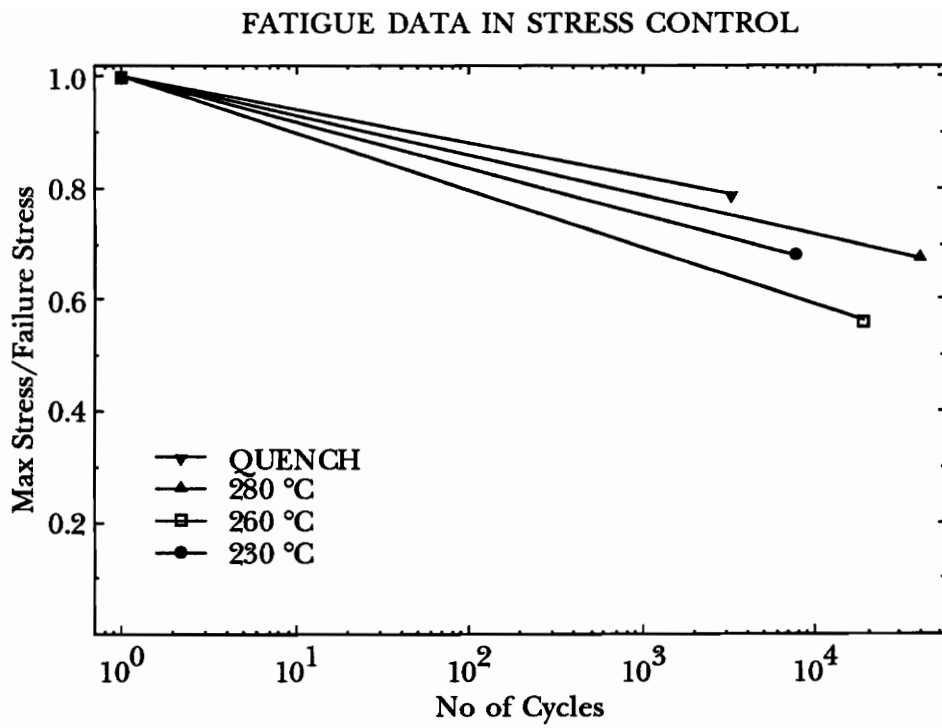


Figure 5.37 Experimental fatigue data points constructed using Table 4.2 and the experimental fatigue lives in stress control as measured by Croman⁴⁵.

agreement between the predicted fatigue S-N curve in stroke control and the actual S-N curve in stress control. Both the predicted fatigue performance and the experimental fatigue performance follow the same order, with the predicted fatigue performance in stroke control being higher than the experimentally observed values in stress control. This is expected because in a stress controlled fatigue test, higher strains are applied as the material damages and the modulus drops, resulting in lower fatigue lives. One can therefore conclude that there is some correlation between the model and the available experimental data. However, this conclusion should be qualified with the remark that data scatter in fatigue tests is high, and therefore construction of fatigue S-N curve from the two data points shown in Figure 5.37 might result in erroneous conclusions.

6. Conclusions

From the available data on the spherulitic center to center distances, and the spherulitic diameter, it can be seen that the size and the distance of the spherulites decrease as the crystallization temperature is decreased. This is expected because decreasing the crystallization temperature will increase the number of nuclei. The degree of crystallinity in the crystalline samples used in this study has been maintained nearly constant. This is ensured by holding the samples at the crystallization temperatures long enough to ensure complete crystallization. Therefore, this study is focused on the effect of changing morphologies on the mechanical properties and the damage accumulation process.

From the results of the mechanical tests presented in section 4.1, it can be concluded that there is very little difference in the mechanical properties (strength, modulus and elongation etc.) of the carbon fiber reinforced PEKK 60/40 composite systems as the heat treatment is changed. In general, the quenched samples tend to have a higher toughness and lower modulus and strength when compared to the crystallized samples. This is expected because quenched polymeric samples generally tend to have higher toughness than semicrystalline ones. The quenched samples show a weaker fiber-matrix adhesion which results in lower energy absorption in impact. Also, the fatigue performance of the quenched composite systems is better than that for the crystallized systems. Therefore, for engineering applications, the quenched composite systems have the best potential for use. However, the damage accumulation process during static three point bend testing in PEKK 60/40 and carbon fiber reinforced PEKK 60/40 changes dramatically as a function of heat treatment, even though the ultimate mechanical properties remain essentially unchanged.

The type 1 acoustic events observed during the static tests of the Carbon fiber reinforced 60/40 PEKK are generated by some damage mechanism in the matrix material. This damage mechanism caused insignificant drops in the loads from the linear load-stroke behavior and, for all practical purposes, can be ignored.

Although the overall mechanical properties remain substantially unchanged, the damage accumulation process changes dramatically as a

function of processing. A fundamental approach towards studying the factors contributing to this change is not part of this study.

In section 2.3, several models dealing with the damage accumulation process and fatigue life predictions were discussed. All these models were empirical in nature. In this thesis, a relatively simple model was proposed to simulate the damage accumulation process. One underlying assumption was made regarding the damage accumulation process. It was assumed that the damage accumulation process in any material system can be described by an equation which is independent of the testing configuration (equation 5.3). This approach has not been taken by any of the authors discussed in section 2.3. It was found that the proposed model accurately simulates the damage accumulation process in static three point bend. The accuracy of the model was demonstrated using a number of different correlations in quasi-static testing for both the unreinforced and the carbon fiber reinforced PEKK 60/40 composite systems. However, use of the simple model in the composite systems becomes difficult because of the multiplicity of the damage mechanisms involved. In order to apply the proposed model on composite systems, the multiplicity of the damage mechanisms was ignored. It was found that this approach works fairly well for most of the composite systems investigated. The damage model (equation 5.3) was then extended to simulate the damage accumulation process in fatigue and predict the fatigue S-N curve in stroke control.

It was stated that in section 4.4 that the dramatic change observed in the damage accumulation process probably manifests itself in the dramatic change in the reported fatigue properties of carbon fiber reinforced PEKK 60/40. The

available experimental data points in stress controlled fatigue were explained qualitatively in terms of the rates of damage accumulation as manifested in the calculated values of α . Therefore, it was concluded that the proposed fatigue model accurately simulates the damage accumulation process in fatigue, and qualitatively explains the trends in the measured fatigue S-N curves, although the inevitable scatter in the available experimental fatigue data points makes quantitative comparison impossible.

7. Future Work

From the conclusions made in this thesis, a number of recommendations can be made for possible future work. These are discussed below.

The exact nature of the type 1 acoustic events, which had been identified as being generated by some damage mechanism in the PEKK matrix, should be examined in more detail. A number of possible approaches are listed below:

- Simultaneous SEM and three point bend flexure tests. This approach involves damaging polished samples (both unreinforced and composite) in an SEM and correlating the morphology of the damaged areas with type 1 acoustic events.
- Low stroke flexure tests followed by SEM and X-ray scattering. This approach involves damaging the samples in flexure, and stopping the flexure test at low strokes (after the occurrence of type 1 events) followed by an

examination of the damaged areas in an SEM (both after and before polishing) and X-ray studies. X-ray studies (both small angle X-ray scattering SAXS and wide angle X-ray scattering WAXS) will determine whether the crystal structure etc change during the damage accumulation process. SAXS will give information on the interlamellar spacing and WAXS will give information on the crystal structure.

- Simultaneous Birefringence and flexure. This involves stretching thin PEKK films in a microtensile stage and studying the birefringence under polarized light. This approach will determine whether the polymer chain configuration is changing at low strokes.

In section 5 of this thesis, a new model to simulate the damage accumulation process was outlined. This model can potentially be used with great accuracy in systems showing a single dominant failure mode (e.g. unreinforced PEKK). This model can be used to simulate the damage accumulation process and to predict the fatigue S-N curve in unreinforced PEKK.

In section 5, it was also stated that use of the proposed model to predict the fatigue S-N curve in composite systems is difficult because of the multiplicity of the damage mechanisms. In order to predict the fatigue S-N curve, the multiple damage mechanisms were “homogenized”. A new approach can be used in order to develop a fatigue equation which incorporates all the observed damage mechanisms. This can be done by integrating equation 5.9 between appropriate limits (points of initiation of new damage mechanisms) and developing an equation similar in form to equation 5.10, but with a series of terms representing

the multiplicity of the damage mechanisms. The three constants (α , β , and ϵ_c) in the original damage model (equation 5.3) will be different for each damage mechanism. These constants can be determined by a battery of tests involving different testing configurations. For example, the three constants associated with matrix cracking can be obtained from flexure tests (static and fatigue) restricted to a point below the initiation of interfacial failure. The three constants associated with interfacial failure can potentially be obtained by single filament pull-out tests (using a combination of quasi-static pullout and fatigue pullout). Fiber fracture can be ignored for the purpose of fatigue life predictions because fatigue tests are rarely done at high enough stress levels to cause fiber fracture. (The only exception to the above generalization is a stress controlled fatigue test near catastrophic failure. However, since the damage accumulation rates are high in this region, failure can be defined as the point of initiation of fiber fracture, thus totally obviating the need for modelling the fiber fracture regime.)

Once the constants associated with the different damage mechanisms are determined, the proposed model can be used to predict the load-stroke relation in a quasi-static three point bend test. These predictions should be more accurate than the ones shown in Figures 5.32 through 5.35.

In this thesis, the experimentation, analysis and modelling has concentrated on stroke controlled testing. A similar model can be developed for damage induced in tests involving stress control. Since stresses cannot be easily calculated in a flexure test, this new model would have to use data from quasi-static and fatigue tests performed in tension. However, this new model

should give rise to a damage relation in stress controlled fatigue , which would allow one to predict the fatigue S-N curve in stress control. The new model can potentially be developed in a manner analogous to the development of the model in this study starting with an equation similar to equation 5.3, but with the strains replaced by stresses.

In this thesis, the predicted fatigue S-N curves (as a function of heat treatment in the PEKK 60/40 composite systems) in stroke control were qualitatively correlated with the experimental data points in stress control. Fatigue testing needs to be performed in stroke control in order to make a more direct correlation between theory and experiment.

Also, once the new model in stress control is developed, possible attempts can be made to quantitatively correlate fatigue lives in stress and strain (stroke) control.

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9. Appendix

Summary of Linear Beam Theory Flex Equations

The linear Beam theory flexure equations used in some calculations in this study are summarized below:

$$\sigma = \frac{3}{2} \left(\frac{S}{WD^2} \right) P$$

$$E = \frac{1}{4} \left(\frac{S^3}{WD^3} \right) \frac{P}{V}$$

$$\epsilon = 6 \left(\frac{D}{S^2} \right) V$$

where σ is the stress, S is the Span, D is the depth, W is the width, P is the load, E is the modulus, V is the stroke and ϵ is the strain.

10. Vita

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