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13. The transport properties of liquid penetrants into the thermoplastic resin, poly aryl ether ether ketone were investigated. The primary objective of this work was to study the effect of external applied stress on the diffusion and solubility/swelling of fluids with PEEK. The solubility and rate of penetration, i.e., diffusion, into the resin system are greatly increased by the application of stress: we cal this phenomenon SEDS (stress enhanced diffusion and solubility/swelling). All eight fluids studied, benzene, toluene, methylene chloride, chloroform, carbon disulfide, methanol, acetone, and even water exhibit SEDS. The effect is particularly striking for crystalline PEEK where the solubility is markedly increased and the time to reach saturation, i.e., the induction period is reduced when the applied stress exceeds a critical value. For example, at 22'C the solubility of toluene into 29% crystalline PEEK increases from 9 wt% to almost 40 wt% upon the application of a tensile stress of 35 MPa. Furthermore, the time for 0.25 mm thick crystalline PEEK film to reach its saturation value was reduced from 1000's of hours to less than 10 hours.

SEDS is associated with a critical stress (or strain) value which depends upon the crystallinity of the material, the particular penetrant, and the temperature. Although samples yield at high stress levels, they do not craze or crack.

The sorption of aromatic hydrocarbons and chlorinated solvents follows non-Fickian transport with three primary regions: an induction period, a limiting solubility, and a diffusion or penetration rate region. Both the induction period and the limiting solubility are strongly affected by external stress. The diffusion rate is a weak function of stress.

Both water and methanol exhibit Fickian (or pseudo-Fickian) transport. Water in amorphous PEEK exhibits a critical stress of 26 MPa. Neither water nor methanol exhibit an induction period.

FINAL REPORT

Effect of External Stress on the Transport of Fluids in Thermoplastic Resin Systems

Air Force Office of Scientific Research
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ABSTRACT

The transport properties of liquid penetrants into the thermoplastic resin, poly aryl ether ether ketone were investigated. The primary objective of this work was to study the effect of external applied stress on the diffusion and solubility/swelling of fluids with PEEK. The solubility and rate of penetration, i.e., diffusion, into the resin system are greatly increased by the application of stress: we call this phenomenon SEDS (stress enhanced diffusion and solubility/swelling). All eight fluids studied, benzene, toluene, methylene chloride, chloroform, carbon disulfide, methanol, acetone, and even water exhibit SEDS. The effect is particularly striking for crystalline PEEK where the solubility is markedly increased and the time to reach saturation, i.e., the induction period is reduced when the applied stress exceeds a critical value. For example, at 22°C the solubility of toluene into 29% crystalline PEEK increases from 9 wt% to almost 40 wt% upon the application of a tensile stress of 35 MPa. Furthermore, the time for 0.25 mm thick crystalline PEEK film to reach its saturation value was reduced from 1000's of hours to less than 10 hours.

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INTRODUCTION

High performance lightweight modern aerospace systems use organic based polymeric materials in a variety of applications ranging from resin matrix based carbon fiber composites to windshield canopies. New materials for these numerous applications are constantly being developed. Many of these materials will be subjected to a harsh aerospace environment which is a complex mixture of high and low temperature, mechanical (and thermal) stress and strain, aggressive organic fluids, water and active aqueous solutions, and other potentially active environmental sources. Because of the chemical and mechanical complexity of polymeric materials in general and their projected long-life in most aerospace systems, it is extremely important to determine the overall properties of potential new materials, as well as existing materials, to the aerospace environment. Many investigators describe these type of experiments as "aging," however, in reality this is a relatively poor term derived from biological aging and a better more realistic term is durability or lifetime. Two important factors must be considered before one can discuss or define lifetime or durability of a material:

1) a well defined definition of the environment in which the material is expected to function is required:

2) a definition of "lifetime" is required in order to determine if and when a material (or system) has reached the end of its useful life.
An explicit statement or definition for either of these two requirements is rare.

Either the true failure process must be known or the environment accurately known in order to predict life-time. If the environment is known, the material (system) can be aged in either the actual environment or a carefully simulated environment. On the other hand, establishing the failure mechanism is the best way to utilize simulation methods. This can be a large task if all the 'possible' failure processes are considered!

In the past few years, great interest has arisen in the use of thermoplastic resin systems for aerospace applications. One of the many advantages of thermoplastic resins

is their toughness, that is, high impact strength and fracture resistance. Other advantages of thermoplastic polymers include long shelf life at room temperature; postformability, that is, thermal reforming; ease of repair by thermal welding or solvents; and ease of handling, that is, they are not tacky. (1) One particular class of semi-crystalline thermoplastic resins of major importance is the aromatic poly ether ketone series typified by poly aryl ether ketone (PEK), poly aryl ether ketone ketone (PEKK), and poly aryl ether ether ketone (PEEK). PEEK, manufactured and distributed by ICI, is a widely used engineering thermoplastic. A commercial thermoplastic based composite, containing approximately 40% PEEK, is sold and distributed by ICI as APC-2. APC-2 is used extensively in the aerospace industry for a variety of applications. For example, it is used for:

- landing gear door and access panels of the F-5 fighter
- aircraft belly skin of the C-130 military transport
- landing gear door of the V-22 tilt rotor helicopter
- access doors on the F-17 stealth fighter.

Furthermore, either PEEK or PEKK (a close relative supplied by the E. I. DuPont Company) is under consideration for use on the new F-22 fighter.

In addition to its extreme toughness and high temperature capability ($T_g \simeq 145°C$ and $T_m \simeq 345°C$), PEEK has been classified as a stable inert material that is "insoluble in all common solvents" (2). As part of a program to determine the durability of PEEK and PEEK composites, several investigators have examined the effects of organic fluids on this materials. However, recent work has shown that several fluids including methylene chloride, chloroform, carbon disulfide, benzene, and toluene are readily absorbed by and swell PEEK (3-11). The equilibrium concentration of these fluids in amorphous PEEK ranges from 50 wt% for chloroform to 20 wt% for toluene. Two specific types of fluids are of particular interest, methylene chloride because it is the active ingredient in many paint strippers, and aromatic hydrocarbons, such as toluene, because they are a major

ingredient of jet fuel. Nominally, PEEK is approximately 30% crystalline and material of this crystalline has been reported to be essentially impervious to fluids such as toluene. In fact after immersion in toluene at 35°C (95°F) for 1800 h, 30% crystalline PEEK sorbed approximately 1 wt%; thus, PEEK was considered essentially impervious to many fluids. However, we have observed that external stress, either uniaxial tensile stress or fabrication residual stress, produces an enhanced equilibrium solubility and an accelerated rate of penetration. In fact, we have observed that 30% crystalline PEEK stressed to approximately 30% of its ultimate tensile strength sorbed 25 wt% toluene in just 16 hours at 22°C.

This raises two very important questions which form the basis of this study:

1. What other fluids exhibit stress enhanced diffusion solubility/swelling, SEDS, in PEEK? and

2. How general is this phenomenon, what other thermoplastics resins which are considered inert exhibit SEDS?

BACKGROUND

This particular research project is confined to one particular aspect of the lifetime or durability of thermoplastic composites, i.e., the effect of environmental fluids, particularly when subjected to a stress field.

The process in which liquids penetrate polymers and resins is extremely complex and has been studied for many years. In many cases the sorption leads to pronounced swelling, loss in mechanical properties, and ultimate failure of the polymeric material. A general discussion of the Faraday Society on Swelling and Shrinking was held in 1946 (12) at which time it was noted that in some penetrant-polymer systems sharp boundaries, which moved linearly with time, existed between the swollen and unswollen regions. Twenty years later Alfrey characterized the process as "Case II" diffusion or sorption (13), also known as anomalous diffusion.

The transport of a penetrant into a polymeric material can be divided into a thermodynamic and a kinetic component. The former is usually discussed as solubility or swelling and the latter as diffusion.

Solubility/Swelling: The general question of solubility is usually formulated in terms of a solubility parameter, in a manner similar to that originally proposed by Hildebrand, which is based on thermodynamic considerations (for example, see Ref. 14). The solubility parameter, δ, is described in terms of the internal pressure or energy density of the liquid. For non-polar solvents the solubility parameter is equal to the square root of the energy of vaporization (ΔE) per unit volume (V)

$$\delta = \left(\frac{\Delta E}{V}\right)^{\frac{1}{2}}. \tag{1}$$

In order for solution to occur, the free energy of mixing, ΔG, must decrease, i.e.

$$\Delta G = \Delta H - T\Delta S < 0 \tag{2}$$

Since the entropy term, $T\Delta S$, is positive, the enthalpy of mixing should be small: the free energy is negative when the magnitude of $T\Delta S$ is greater than ΔH. According to

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Hildebrand, the heat of mixing of a solvent-solute pair is proportional to the square of the difference in their solubility parameters, i.e.

$$\Delta H_m \propto \left(\delta_1 - \delta_2\right)^2. \tag{3}$$

When $\delta_1 = \delta_2$, the enthalpy is zero and the free energy is negative. This is the thermodynamic equivalent to the well known concept that "like dissolves like." For non-polar materials, the energy of vaporization is equal to the heat of vaporization (ΔH_v) less the energy required to push back the atmosphere (RT). Making use of equation 1, we have

$$\delta = \left(\frac{\Delta E}{V}\right)^{\frac{1}{2}} = \left(\frac{\Delta H_v - RT}{V}\right)^{\frac{1}{2}}. \tag{4}$$

Other terms, such as hydrogen bonding or polar forces, can be added to the energy term, but the primary factor controlling the solubility parameter is the heat of vaporization.

The phenomenon of swelling is closely related to solubility except that the final solution is a solid or gel rather than a liquid. However, identical or nearly identical solubility parameters are not sufficient for swelling, the molecular dimensions of the penetrant molecule must be small enough to enter into the lattice network of the polymer. As the network is swollen by the sorption of the penetrant, the network chains assume an elongated configuration and an elastic retractive force develops in opposition to the swelling process. A state of equilibrium is reached when the elastic restoring force of the network chains exactly balances the osmotic pressure driving the penetrant into the polymer. The basic theory was developed by Flory (15) to account for the swelling of lightly crosslinked rubber and, although useful for qualitative predictions, cannot completely account for the swelling of semi-crystalline thermoplastic resins below Tg. In particular, it cannot explain the anisotropic stress induced swelling observed in PEEK.

Diffusion: The rate of penetration, usually called diffusion, of the liquid (or vapor) into the solid matrix is normally described in terms of Fick's Laws. Fick's first law (in one

dimension) is usually written in terms of the flux (F) through a surface. The flux is proportional to the concentration gradient ($\partial c/\partial x$);

$$F = -D\frac{\partial c}{\partial x} \qquad (5)$$

where D, the constant of proportionality, is the diffusion coefficient. His second law relates the concentration change as a function of time to the change in flux with respect to position; thus, for unidirectional diffusion:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \qquad (6)$$

In the simplest case, when the diffusion coefficient D is only a function of temperature and independent of concentration, we have classical Fickian diffusion

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) \qquad (7)$$

For a large flat surface at constant surface concentration with sorption only occurring in one dimension, solution of equation (7) leads to

$$D = \frac{\pi \ell^2}{16}\left(\frac{S}{C_\infty}\right)^2 \qquad (8)$$

where the thickness of the sample is ℓ, C_∞ is the surface concentration (solubility) at the temperature of interest and S is the slope of the weight gain versus square-root time curve, i.e., $dw/dt^{1/2}$, during the initial portion of the sorption process. [For an excellent discussion of the diffusion process, see Ref. 16.] Thus, Fickian diffusion predicts that the penetrant is sorbed at a rate proportional to the square root of time. Furthermore, Fickian diffusion predicts that the diffusion coefficient is independent of sample thickness; and, at a given concentration gradient, the rates of sorption and desorption are the same. A fundamental criterion for Fickian sorption is that surface concentration immediately attains its equilibrium value upon a change in conditions and remains constant throughout the sorption process, i.e., in a resin matrix system the polymer chain segments in the surface layers must "instantaneously" equilibrate. Fickian diffusion is rarely observed for the transport of a liquid through a glassy polymer, i.e., below T_g.

In most polymers, deviations from 'Fickian' diffusion arise as a consequence of the finite rates by which changes in polymer structure occur in response to stresses imposed upon the material before and during the sorption-desorption process.

Non-Fickian behavior is so broad and general that no simple model or theoretical description can account for all the diverse time-dependent phenomena which have been reported. In general, the fractional weight gain, M_t/M_∞, (where M_t is the mass sorbed after time t and M_∞ is the equilibrium value) can be expressed as:

$$\frac{M_t}{M_\infty} = kt^n \tag{9}$$

For planar geometry, if n = 1/2, the diffusion is classified as Fickian or pseudo-Fickian if the other criteria for Fickian diffusion are not met; Case II if $1/2 < n < 1$; and Super Case II if $n > 1$. One of the characteristics usually observed in non-Fickian diffusion is that the penetrant advances through the resin as a sharp front rather than exhibiting a classical exponential type profile. If the polymer is partially crystalline, the transport process is markedly dependent upon the degree of crystallinity as well as the temperature. In addition, the polymer may exhibit solvent (or more appropriately penetrant) induced crystallization (SIC) and show orthotropic swelling which further compounds the complexity of the process.

Numerous investigators have attempted to model non-Fickian diffusion and its associated swelling (17-22).

Crank proposed a history dependent diffusion coefficient which contained a term which instantaneously changed with concentration to an equilibrium value (18). He was able to predict many of the features of Case II diffusion, although not the sharp front directly. He introduced the concept of differential swelling stresses at the boundary due to the expansive and compressive forces in the swollen and non-swollen regions.

Long and Richmond (19) assumed that the penetrant did not instantaneously attain its equilibrium value at the surface of the polymer, a subtlety implicitly implied in Fickian diffusion. They assumed that the concentration in the surface layers of the polymer

increased with time from its initial instantaneous value to a final equilibrium value. This concept is important as it introduces the idea of the relaxation of a physical process rather than a discontinuous jump or change in the diffusion coefficient.

Petropoulos and Roussis (20) extended the work of both Crank and Long and Richmond by using an activity gradient term rather than a concentration term and then applied the relaxation term to the bulk of the material rather than just to the surface term.

Thomas and Windle (21,22) made a major advance in understanding Case II diffusion; their model is able to account, at least qualitatively, for many of the features observed. The model assumes that as the penetrant diffuses into the polymer, it creates an osmotic pressure. The initial swelling at the surface creates space for additional penetrant. The plasticizing action of penetrant causes a viscous creep to occur. The creation of the "surface sites" is not an instantaneous process and an induction period is predicted. The model represents a coupling between the osmotic pressure driven viscous response, i.e., polymer chain reaction, and Fickian diffusion. They assume that the relaxation process, i.e., mechanical response, varies with the viscosity of the polymer which is an exponential function of the penetrant concentration. However, external stress (or strain) was not considered in their model.

Only a limited number of reports have appeared concerning the effect of either external or residual stress on the transport of fluids in polymers. Treloar has discussed some of the earlier work on the effect of tensile stress on swelling of rubber (23). He discussed the work of Flory (24), Gee (25), and Treloar (26) who noted that stained rubbers sorbed more fluid than the unstrained material. The rubbers were swollen, stretched, and swollen again.

Broutman and Kim (27) measured the diffusion of water in graphite-epoxy tensile bars and noted that stress levels up to 25% of ultimate produced a factor of 2 increase in the diffusion constant but had little effect upon the solubility. Gellat and Broutman (28) reported on similar studies to those of Kim and Broutman but used 65% of ultimate stress

on the same system. The uptake was Fickian at all levels of stress and D increased slightly.

Maron and Broutman (29) measured water diffusion at 95°C into fiber glass and graphite epoxy composites in stressed and unstressed states. They varied ply angle to affect stress, i.e., residual stress. Stress enhances both the diffusion rate and the solubility. However, the differences in diffusion coefficient are about a factor of 2 for stressed and unstressed composites, while the solubilities show only a slight increase of 10-20%.

Williams discussed the effect of drawing on the transport of gases and vapors in polymers (30). Normally, in cold drawing, plastic deformation reduces the number of sorption sites and increases the activation energy for diffusion. The changes in sorption and transport properties are a direct consequence of the denser packing and ordering of the tie molecules in the amorphous region as a result of the drawing process. For example the solubility of methylene chloride in polyethylene decreases an order of magnitude for a sample cold drawn 9-fold; the diffusion constant decreases two-orders of magnitude for the same draw ratio. However, when polyethylene is drawn in the plasticized (with benzene) state, both the solubility and diffusion coefficient of methylene chloride are greatly increased. Furthermore, the measured permeability was 75 times greater than expected on the basis of the product of the solubility and diffusion coefficient, suggesting the presence of "holes" or micro channels in the drawn polymer. Additional permeability data confirm the presence of micro channels with diameters less than 2000 Å.

Gent and Liu (31) studied sorption of linear liquids of cis-polyisoprene in fine threads of cis-polyisoprene and investigated the effect of tensile strain and penetrant molecular weight on the transport. They noted that the diffusion coefficient was essentially independent of the strain for extensions up to 300% but the degree of swelling increased

by more than 100% for the same strain. The solubility data is in agreement with the theory described by Treloar (23); however, the theory is not applicable to diffusion.

As previously noted several fluids, including benzene, toluene, methylene chloride, chloroform and carbon disulfide were reported to be sorbed by and swell PEEK (3-11). The rates of sorption of these fluids in crystalline PEEK are quite low at room temperature, in fact both benzene and toluene exhibit essentially zero solubility (less than 0.2 wt%) even after immersion at 35°C for 1400 h.

This is an extremely important point: it appears as if crystalline PEEK does not sorb toluene at low temperatures. However, upon closer examination in which we made a systematic study of the effects of the initial PEEK crystallinity and temperature on the sorption process, we noted that toluene has a marked effect upon PEEK (9).

The effect of both crystallinity and temperature can be explained, at least quantitatively, by the theory proposed by Thomas and Windle (21,22), i.e., a slow viscosity dependent relaxation of the surface sites of the resin accompanied by conventional sorption and subsequent transport.

The transport of toluene into PEEK is a complex process, strongly dependent upon temperature, crystallinity, and, if in solution, upon the toluene concentration. In general the sorption of fluids into PEEK all exhibit three major regions whose value and importance depend upon the initial crystallinity and temperature: (1) an initial period which can exhibit either a classical induction period or an accelerated absorption, (2) a steady weight gain which is approximately linear with root-time, and (3) a limiting constant equilibrium value. Furthermore, the limiting solubility, or swelling, decreases with temperature, for toluene this decrease corresponds to a heat of solution of -0.93 kcal/mol (9).

In an earlier study (32) on the effects of environmental fluids in composites, we observed that residual stress had a pronounced effect on the sorption of jet fuel by PEEK composite.

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In a series of experiments in which APC-2 (ICI composite containing approximately 60% AS-4 carbon fiber and 40% PEEK) fabricated with different ply orientations to yield different values of residual stress was immersed in jet fuel (jet reference 2 containing approximately 20% toluene), we observed marked differences in the sorption processes. The composites containing only unidirectional plies (little or no residual stress) did not exhibit a weight gain even after 1400 hours immersed in the fuel. However, the composites fabricated with cross-plies (± 45 or 45/90/-45) did show a pronounced weight gain. The primary component sorbed was toluene. This lead to an investigation of the effect of stress, either applied tensile or residual stress, on the sorption of fluids in PEEK.

An example of the effect of external stress on the sorption of toluene into crystalline PEEK is illustrated in Figure 1. The temperature was 22°C and the immersion time was 16 hours! Note that the induction period for any sorption in crystalline PEEK exceeds 1500 h at 35°C in the absence of stress (9,11). The induction period is so long at room temperature that we have been unable to measure it; yet, in 16 hours with a tensile stress greater than 25 MPa (corresponding to strain less than 1%), the weight gain is 20 wt%. The yield stress is approximately 120 MPa; the stress used in the stress/diffusion-solubility experiment is less than 25% of the UTS! Furthermore, the same general phenomenon is observed for PEEK of lower crystallinity except that less stress is required. The values shown in Figure 1 represent the amount sorbed in 16 hours and are not necessarily the equilibrium values. Highly crystalline samples (29%) prepared by different methods, give similar results even though we have previously shown that their crystalline dimensions are slightly different. We used samples crystallized directly from the melt (high temperature crystallized, HT), and samples crystallized at low temperatures (approximately 160°C) from amorphous PEEK (LT). The dimensions of the unit cell of the two samples are similar except that the a-axis in the HT sample is slightly smaller. Furthermore, we have also shown that the unit cell of solvent-crystallized samples, whether formed from toluene, benzene, chloroform, methylene

chloride, or carbon disulfide, tend to be tighter and less disorganized than those from thermally crystallized samples. SIC samples form smaller but more perfectly organized crystals than those formed thermally (10).

Although the induction period for toluene sorption was too long to be measured at 22°C, it can be estimated from the data reported in reference 9. The induction period varies with the fourth power of the crystallinity and has an activation energy of 50 kcal/mol. An 11.5% crystalline sample has an induction period of 145 h at 50°C while an 18.8% crystalline has an induction period of 50.6 h, at 65°C. These can be used to estimate induction periods of 150 h (at 50°C) and 286 h (at 65°C) for the 12% and 29% crystalline samples, respectively. Based on this data, the expected induction periods at 22°C are 230,000 h for the 12% crystalline sample and 14×10^6 hours for the 29% crystalline sample! Therefore, we have gone from a system which is essentially benign towards toluene to one which readily absorbs it.

The primary objective of this study was to determine what fluids exhibit the SEDS effect in PEEK and to characterize the basic mechanism responsible for SEDS.

EXPERIMENTAL

1. Materials

Polymer: PEEK is a thermoplastic semi-crystalline resin; its melting point is 345°C and its T_g is 145°C. The molecular weight of the monomer is 288 and its structure is given below:
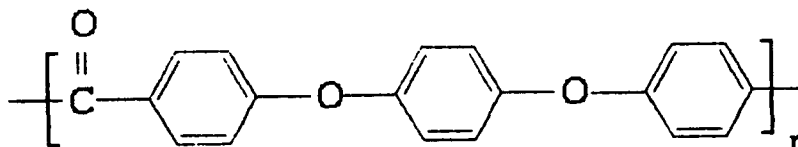
It is a partially ordered material whose nominal degree of crystallinity is approximately 30%, although it is readily available in either crystalline or amorphous form. PEEK was obtained in the form of 0.25 mm thick films under the trade names Stabar®K200 (amorphous PEEK), and Stabar®K300 (29% crystalline PEEK), from ICI Americas Inc. (Wilmington, DE, USA).

Liquid Penetrants: Toluene, benzene, methylene chloride, chloroform, acetone, methanol and carbon disulfide were reagent or HPLC grade and obtained from Fisher Scientific Company. They were used without further purification.

2. Sample Preparation

Amorphous PEEK films were annealed in a forced air oven for selected time intervals at approximately 160°C to obtain samples whose crystallinity could be varied from less than 1% to approximately 20%. Higher crystallinity was obtained by heating the film at 270-290°C in a forced air oven.

The crystallinity (%C) of the sample was determined from the measured density by using the relationship reported by Dawson and Blundell (33):

$$\%C = 1015.4 - 1282.05/\rho$$

The density $\rho(g/cm^3)$ was measured using Density Determination Kit (Mettler 33360) with an electronic analytical balance.

Films approximately 25x10x0.25 mm were cut from 8.5x11 in master sheets using a sharp razor blade.

3. Methods and Procedures

Unstressed Sorption and Desorption: Sorption of the unstressed films was accomplished by immersing the samples in liquids contained in 2.5x15 cm culture tubes which were placed in a thermostatted aluminum block. At appropriate intervals, samples were removed from the culture tubes, blotted dry, and weighed on an analytical balance. The results are reported in terms of percent weight gain.

The dimensional changes accompanying the sorption of liquids by PEEK films were measured. Samples were removed from the sorption chamber, blotted dry, and measured. Thickness was measured in three places with a precision caliper and averaged; width and length were measured with the same caliper while the film was maintained in a flattened position. All dimensional changes are reported as relative values rather than as absolute values.

The penetrants were desorbed from the films by placing the saturated specimen in a sealed culture tube (volume 50 cm^3) containing dry activated charcoal (10g, 14 mesh) in a thermostatted block; samples were removed at selected time intervals and weighed.

Stressed Sorption: PEEK film approximately 50x5x0.25 mm was mounted between parallel grips as shown in Figure 2 using a jig specially designed for aligning the specimen. The lower grip was retained by a loose-fitting pin at the bottom of an immersion chamber (Figure 3), the loose fit ensured that no flexural stresses were imposed upon the specimen when loaded in tension. The upper grip was also self aligning, it was suspended by a steel wire which passed over two low-friction pulleys, via a tensioning device, to a balance pan. The force on the specimen was carefully controlled by an appropriate mass (metal blocks and lead shots) on the pan. Eight immersion

chambers (cylinders) filled with fluids of interest were placed in a bath. The bath was filled with coolant (as heating media) in between the immersion chambers. An electrical heater was placed at the bottom of the bath. The heater, containing a thermocouple and a temperature controller, heats the bath medium and is capable of controlling the temperature to approximately $\pm 1°C$.

The weight change of a stressed sample was obtained by removing the sample from the clamps, blotting dry, sealing it in a culture tube and weighing on an analytical balance. The results are reported in terms of percent weight change.

Another stressed sorption unit, shown in Figure 4, was used to investigate sorption. In this unit, the sample was stressed along the horizontal direction. The initiation of surface cracks and their development can be observed and recorded. Length changes were obtained by measuring the changes in the height of the balance pan. Changes in length are reported relative to the initial length of the sample.

Environmental Stress Yielding: The time for stress (or strain) yielding to begin while the sample was immersed in the fluid of interest at either constant load or strain was monitored by several methods. The general procedure is similar to the environmental stress crazing/cracking test, and we refer to it as environmental stress yielding, ESY.

The ESY tests were conducted in three different experiments:

a) Constant strain experiment was used and the time for the initiation of surface cracks which were the precursor to polymer yielding was recorded. The fluid, toluene, was applied to the top surface of the strained PEEK. Constant strain was applied by a Polymer Laboratories Minimat miniature materials tester (Figure 5) and the time for yielding to begin was measured as a function of strain and temperature.

b) Constant stress (constant load) experiment was used; the time for the initiation of surface cracks was recorded. Fluids, toluene, benzene, methylene chloride, chloroform and carbon disulfide were applied to the top surface of stressed PEEK. The constant

stress was applied by the device shown in Figure 4. The time for yielding to begin was measured as a function of stress at room temperature for the different fluids.

c) An improved variable strain bending form was used to determine the environmental craze/crack resistance of PEEK. The strain-bending apparatus, shown in Figure 5, is based on the design of Stolki and Haslett (34). The shape of the surface curve was calculated using a commercial mathematical computer program. A test specimen was flexed over the surface of the apparatus and conformed to the metal form by fixing the clamps at both edges as shown. The strain ε in the test specimen at any point is defined as

$$\varepsilon = d/2R \qquad (10)$$

where d is the thickness of the specimen and R is the radius of curvature at the neutral axis of the flexed sample. A scale was etched on one edge of the apparatus perpendicular to the mounting surface, and the strain was measured as a function of position along the surface. The strain-bending apparatus, with test specimen mounted, was placed in an open glass vessel containing the fluid at the temperature of interest.

The strain in this apparatus increases linearly with specimen length which provides a rapid and accurate measurement of the "critical strain." The critical strain is the minimum strain that produces a noticeable physical change in the polymer specimen in the presence of a given environment during a given time interval. Critical strains and the time to reach this value were measured for several fluids.

Sample Surface Treatment-Etching: The etching solution used here is based on the solution used by Olley (35) and Blundell (36). The preferred etch is 2 wt% potassium permanganate in a 5:3:2 mixture of sulfuric acid, orthophosphoric acid and distilled water. The acids are first mixed with the water, then the potassium permanganate is added, and the mixture stirred for 15 min. Amorphous and 29% crystalline PEEK were placed in the solution for various time intervals. After removal from the etching solution, the samples were washed with 30% hydrogen peroxide solution and finally rinsed with distilled water and blotted dry.

RESULTS AND DISCUSSION

In the first phase of this program, the primary areas of interest are three fold:

1) determine what fluids exhibit the SEDS effect in PEEK,

2) for those fluids which exhibit SEDS, what are the transport parameters, and

3) is the SEDS effect associated with a critical stress (or strain), σ_C (ε_0).

In addition, the basic mechanism and phenomena responsible for SEDS were investigated. Some of the critical factors for each of the fluids studied are summarized below:

TOLUENE: We have investigated toluene in depth because of its importance as a major constituent of jet fuel; a great deal is known about the sorption of toluene in unstressed PEEK; and it forms an excellent system to compare SEDS transport to that in an unstressed system.

We have extended the measurement reported previously (10) to include 30% crystalline PEEK. A typical gravimetric sorption curves at 80°C for samples whose crystallinity ranged from 0 (amorphous) to 30.6% are shown in Figure 7. Note that the induction period for the 30.6% crystalline material is approximately 1600 h and approximately 5000 h are required before equilibrium is attained. The limiting solubilities, and induction periods, as a function of temperature and crystallinity are summarized in Table 1.

The effect of external applied stress is illustrated in Figure 8 where the weight gain in 29% crystalline PEEK is shown as a function of time for samples stressed to 25 and 30 MPa at 22° and 35°C. Note that the time scale is linear compared to Figure 7 where the time scale is square-root time. In addition to the obvious effect of stress (compared to Figure 7) on the induction period, the rate of penetration, and the solubility, both temperature and the magnitude of the applied stress are important. At 22°C an applied stress of 25 MPa has little effect on the sorption process, however an increase of only 5 MPa to 30 MPa decreases the induction period to approximately 10h and increases the

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solubility to almost 40 wt%. At 35°C the solubility increases from 28 to 36 wt%, a 30% increase, when the applied stress is increased from 25 to 30 MPa. At a given stress level, the solubility decreases with increasing temperature; a similar observation was noted for the sorption of toluene in unstressed PEEK where the heat of solution was reported to be -0.93 kcal/mol (9).

The sorption of toluene into amorphous, 15% crystalline and 29% crystalline PEEK at different temperatures as a function of applied stress is shown in Figures 9, 10 and 11 respectively. The weight gain of toluene in stressed and unstressed PEEK polymer at these temperatures is given in Table 2. The weight gain, i.e., swelling, is markedly increased by the application of external stress and becomes even more pronounced if we assume, as is usually done, that the penetrant only enters into the amorphous regions of the polymer. The weight gain in the polymer and solubility based on the amorphous fraction in the polymer [(%wt gain)/(1-ϕ_c)] as a function of temperature and applied stress are also listed in Table 2 [ϕ_c is the crystalline fraction]. The stress enhancement factor (SEF) which is the ratio of the solubility in the stressed state relative to that in the unstressed material is also given in Table 2. In the 15% crystalline material with stress levels less than 20 MPa the rate of sorption, even at 50°C, is so slow that it is difficult to measure. Similarly, in 29% crystalline PEEK for stress levels less than 25 MPa the sorption rate is extremely slow (see Figure 8). Thus, there exist a critical stress (σ_c) level, below which the material appears impervious to toluene and above which it rapidly sorbs a large quantity of toluene. The magnitude of the critical stress is dependent upon both the initial crystallinity and the temperature. For stress levels greater than σ_c additional stress has little effect: for example for stresses greater than 20 MPa in 15% crystalline or 25 MPa in 29% crystalline PEEK, the rate of toluene uptake with additional stress is only 0.2 to 0.3 wt% per MPa. This value is quite small, particularly in view of the sharp increase shown in Figure 8 for 29% crystalline PEEK at 22°C. Interestingly, the solubility of toluene in amorphous PEEK appears to increase with stress; the rates of

increase, dwt%/dσ, determined from the slope of the amorphous portions in Figures 9 are summarized in Table 3. The slopes decrease with temperature and based on a simple Arrhenius plot yield a temperature coefficient of -6.8 kcal/mol. The increase in solubility with stress is particularly pronounced in the 29% crystalline material where stresses greater than 30 MPa produce a four-fold increase in the amount of toluene sorbed. Although stress has a similar effect in the amorphous material, at 22°C the enhanced solubility is only 60% for an applied stress of 10 MPa. It is important to note that in all cases the applied stress is significantly below the yield stress of either crystalline or amorphous PEEK. According to the manufacturer of PEEK film, the yield stress and strain for 29% crystalline PEEK is 120 MPa and 3.75%, respectively (37). Our experiments at 30 MPa correspond to an engineering strain of approximately 1%.

The sharp front separating the swollen from the unswollen region moves through the film at a rate which is proportional to the diffusion of the penetrant into the boundary region. During the initial stages of the sorption process the penetrant must diffuse into an immobile matrix with a high T_g and/or crystalline regions. The penetrant produces three primary effects: 1) it plasticizes the resin thereby increasing the molecular motion of the polymer chains, 2) the polymer swells, primarily in the z-direction (i.e., perpendicular to the surface), thereby producing a small amount of molecular alignment in the z-direction, and 3) it produces a large stress gradient at the boundary between the swollen and unswollen regions. The induction period corresponds to the time required for either 1) the "surface" to undergo sufficient relaxation to reach the "equilibrium solubility," or 2) to sorb sufficient penetrant to lower the T_g to the point where the "surface region" rapidly swells and generates a large stress gradient at the boundary between the two regions. The movement of the front is controlled by the diffusion of penetrant from the surface or swollen region into the bulk of the polymer. The diffusion into the bulk follows root-time kinetics and by analogy with equation (8) we can determine a pseudo-

Fickian diffusion constant (D_b) which represents the flow of penetrant from the swollen (or surface) region into the unswollen region:

$$D_b = \frac{\pi \ell^2}{16} \left(\frac{S}{C_b} \right)^2 \tag{11}$$

where S is the slope in the linear region of the weight gain versus root-time curve and C_b is the concentration gradient across the moving boundary region which we assume to be equal to the equilibrium weight gain. The pseudo-diffusion coefficients as a function of initial crystallinity, applied stress, and temperature are summarized in Table 4. The effect of stress and temperature on the diffusion process are quite evident. For example in the 15% crystalline material at 50°C, D_b increases a factor of 100 when the stress is increased from 15 to 25 MPa. Similarly at 22°C with the 29% crystalline material D_b increases a factor of 60 when the stress is increased 5 MPa. The pseudo-diffusion coefficient increases a factor of 20 for the 15% crystalline material held at 25 MPa when the temperature is increased 28°C. When the 29% crystalline material is stressed to 30 MPa a 28°C temperature increase produces a 30-fold increase in D_b. Based on a simple Arrhenius plot, these increases in D_b correspond to temperature coefficients of 20 and 23 kcal/mol in the 15% and 29% crystalline material, respectively.

The induction periods as a function of applied stress and temperature for the penetration of toluene into amorphous, 15% and 29% crystalline PEEK are summarized in Table 5. The induction period is a strong function of stress, for example, in 15% crystalline material at 50°C, the time for rapid penetration to begin is reduced from 16 hours at an applied stress of 15 MPa to approximately 2.5 minutes at 25 MPa, a decrease in the induction period by a factor of 400. A similar decrease is to be noted for the 29% crystalline material at 22°C where the induction period is greater than 1000 hours with an applied stress of 25 MPa but only 1.8 hours when the stress is increased to 35 MPa. The induction period is also strongly dependent upon temperature; based on a simple Arrhenius plot, a temperature coefficient is 25 kcal/mol was observed for both the

15% and the 29% crystalline material when stressed to 25 and 30 MPa, respectively. For the penetration of toluene into unstressed 11.5% crystalline PEEK the activation energy is 50 kcal/mol (9).

In unstressed PEEK swelling occurs primarily in the thickness direction, however during SEDS the primarily dimensional change is in the direction of the applied stress, i.e., the length. A typical curve comparing the relative changes in length and weight gain as a function of root-time for the sorption of toluene in 29% crystalline PEEK at 22°C is shown in Figure 12.

In a series of constant strain experiments we measured the time for yielding to begin. The time-to-yield is a strong function of the applied strain and can be approximated by an exponential equation of the type

$$t = A \cdot \exp(B \cdot \varepsilon) \tag{12}$$

where B is a constant which is a function of temperature and penetrant and A is function of the initial crystallinity. Typical time-to-yield curves for toluene in crystalline PEEK at 22°C, 35°C, and 50°C are shown in Figure 13. The form of this curve suggests that a critical strain (ε_c) exists; when the strain is less than this value the time-to-yield is quite long and when greater the yield time is short. We arbitrarily choose a time-to-yield of 4 minutes and use equation (12) to estimate the critical strain. For strains less than the critical strain (or stress, since strain and stress are directly related), the applied strain has little effect on toluene sorption. Above the critical value the rate of sorption is markedly increased. Critical strains for the sorption of toluene into PEEK at different temperatures are listed in Table 6. The critical strain increases with increasing crystallinity and decreases with temperature. The apparent activation energy based on an Arrhenius plot [ln(ε_c) versus 1/T] is -1.7 kcal/mol for both 15% and 29% crystalline PEEK and -3.8 kcal/mol for amorphous PEEK. Critical stresses can be estimated from the measured strain values reported in Table 6 by making use of the simple definition of Young's modulus (E):

$$E = \frac{\sigma}{\varepsilon} \qquad (13a)$$

hence

$$\sigma_c = E \cdot \varepsilon_c. \qquad (13b)$$

The reported value for Young's modulus (secant) is 3200 and 2600 MPa for crystalline and amorphous PEEK, respectively (37). [We assume an average value of 2900 MPa for 15% crystalline PEEK.] The critical stresses, shown in parentheses in Table 6, are in reasonable agreement with the critical stress values estimated from the weight gain curves (Figure 9-11) and the induction period data shown in Table 5 The induction period data suggest σ_c of 20-25 and 25-30 MPa for the 15% and 29% crystalline material, respectively. The slightly higher values shown in Table 6 arise because of the arbitrary value of 4 minutes assigned to the time-to-yield in the constant strain experiments.

When immersed in penetrant and stressed above the critical value, all the samples exhibit the same general phenomenon: surface cracks emanate from the film edge and move across the entire width of the sample. The film does not crack, but yields into a stable neck. The sample necks uniformly with a 10 to 20% decrease in both width and thickness. In the unstressed swelling experiments reported in Reference 9, amorphous PEEK swells anisotropically with the predominant swelling in the thickness direction (approximately 20-30%) accompanied by a small 2-3% decrease in length and no change in width; but for 29% crystalline PEEK, the thickness and length swell 2-3% with little change in width. The swelling phenomenon observed in stressed PEEK is quite different in both the amorphous and 29% crystalline PEEK. The relative changes in length as a function of root time for the sorption of toluene in amorphous PEEK subjected to an external stress of 10 MPa and subjected to an external stress of 40 MPa in 29% crystalline PEEK are shown in Figure 14. Again, note that three regions are evident: an apparent induction period in which the sample does not elongate, a region in which the length changes rapidly, i.e., yields, and a third region in which the samples creeps after

fully saturated. These three regions correspond to the three regions observed in the stressed sorption kinetics curves.

The long and unusual nature of the induction period suggest a strong surface dependence. Therefore, a series of experiments was conducted in which the film was etched in a solution used to etch PEEK (35,36). The effect of etching on the sorption of toluene in amorphous PEEK is shown in Figure 15. The time of etch varied from 10 to 60 minutes and three important observations are to be noted: 1) etching increases the induction time, 2) the rate of penetration, i.e., $dw/dt^{1/2}$ in the linear region, is essentially unaffected by the etching process, and 3) the limiting solubility is not affected by the etching process. These observations are consistent with the hypothesis that the attainment of surface equilibrium between toluene and the polymer surface of the film is the rate controlling step. The effect of etching on toluene sorption in 29% crystalline PEEK is illustrated in Figure 16. Again the equilibrium solubility and rate of penetration in the linear region are independent of the time the film is etched although the initial portion of the sorption curve is affected. However, etching, i.e., surface removal, has no effect upon the SEDS phenomenon in crystalline PEEK; see Figure 17 where the sorption curves for the stressed (35 MPa) etched and unetched films show identical sorption curves.

BENZENE: The SEDS sorption of benzene is, as expected, quite similar to that exhibited by toluene. Only a few studies were conducted with benzene because of its potential carcinogenic nature and its chemical similarity to toluene. The effect of stress is summarized in Table 7 where the stress enhanced solubility in amorphous PEEK is shown. The amorphous material gains 30.7% benezene when stressed with 5 MPa compared to 19.9 wt% in an unstressed sample; the 29% crystalline materials exhibits a major reduction in the induction period.

The environmental stress yielding curves for amorphous, 13.4% , and 29% crystalline PEEK at 22°C are shown in Figure 18: the critical stresses, determined according to

equation 7, are given in the insert in Figure 18. The σ_c values are considerably greater than those reported for toluene (see Table 6).

METHYLENE CHLORIDE: The SEDS sorption of methylene chloride in amorphous and 29% crystalline PEEK at 22°C are summarized in Figures 19 and 20, respectively. The sorption in amorphous PEEK is quite rapid even in the absence of external stress: the most notable effect produced by stress is the increased solubility. For example, the solubility increases from 37 wt% in unstressed amorphous PEEK to greater than 50 wt% when stressed to 10 MPa. The effect of external stress is much more pronounced on the crystalline material; but, again, the major effect is increased solubility.

The environmental stress yielding curves for amorphous, 13.4%, and 29% crystalline PEEK are shown in Figure 21. The critical stresses were calculated according to equation 12 and are shown as an inset in Figure 21. Again, it must be noted that these values correspond to stresses which cause yielding to begin after 4 min immersion. These values are considerably smaller than the corresponding va. les observed for benzene.

CHLOROFORM: The SEDS sorption of chloroform into amorphous and 29% crystalline PEEK at different stress levels are summarized in Figures 22 and 23, respectively. The effect is quite similar to that observed for the sorption of methylene chloride. However, of particular interest is the strong effect of stress on the crystalline material: the sorption in unstressed PEEK is quite slow, only 3 wt% was sorbed in 816 hours at 22°C, but when stressed to only 15 MPa 40 wt% was sorbed in less than 400 hours.

The environmental stress yielding for amorphous, 13.4% and 29% crystalline PEEK is given in Figure 24. The critical stress (4 min value) is shown in the insert of Figure 24. These values are similar to those reported for methylene chloride sorption.

CARBON DISULFIDE: A large study of the CS_2 sorption process was undertaken because of the unique nature of CS_2 sorption in PEEK; it is the only fluid which is readily

desorbed from PEEK; and the only solvent which leads to a more open structure following solvent induced crystallizatin (10,11). X-ray analysis and gravimeric analysis of the resin following complete desorptin of CS_2 from PEEK suggest that an open structure, a "super amorphous" region, surrounds the crystals following SIC.

The sorption of CS_2 as a function of time at 25°, 30°, 35°, and 40°C into amorphous, 9.1, 13.4, 19.1, and 30.6% crystalline PEEK were measured. The sorption curves are summarized in Figures 25-28. The limiting solubilities are summarized in Table 8.

The effect of solvent induced crystals on the sorption process was investigated by preparing a series of samples which had been saturated with CS_2 and then the CS_2 was resorbed into the SIC crystallized samples.

Typical desorption curves in which the CS_2 had been sorbed at 40°C and desorbed at 50°C is shown in Figure 29. Similar curves in which the initial sorption was at 40°C followed by desorption at either 70° or 95°C were observed. Desorption is essentially independent of the initial crystallinity, an observation identical for that reported earlier for the desorption of toluene (6). The rate of desorption does depend upon temperature, the process is faster at the higher temperatures.

The resorption of CS_2 compared to the initial sorption curves for the amorphous, 9.1, 13.4, 19.1, and 30.6% crystalline material are shown in Figures 30-34, respectively. The difference between the initial and resorption curves decreases as the degree of crystallinity increases. The limiting solubilities and diffusion coefficients based on the initial rate of sorption (Fickian diffusion coefficients) are given in Table 9. The solubility in the resorbed system is 18 to 6% lower than in the original sample. The diffusion coefficient which is extremely similar to morphology is only reduced a factor of 54 following SIC. We have previously shown that the final crystalline is approximately 34% (based on wide angle X-ray analysis) following SIC in amorphous PEEK (10). A change in crystallinity of this magnitude would be expected to produce at least a 30% decrease in solubility and several orders of magnitude decrease in diffusion coefficient if

thermal and SIC produced crystals lead to the same internal structure. These data also suggest a large difference in the morphology of SIC and thermal crystals.

The solubility of CS_2 in unstressed 30% crystalline PEEK at 35°C is approximately 10 wt%, the solubility increases to more than 30 wt% when the same material is subjected to an applied stress of 35 MPa (see Figure 35).

METHANOL: Methanol is a highly polar low molecular weight alcohol which exhibits a low solubility/swelling in PEEK. The weight gain for the sorption of methanol into amorphous, 15%, and 31% crystalline PEEK at 22°C is shown in Figure 36. The weight gain is linear with root-time, suggesting Fickian transport. The solubility and diffusion coefficients are summarized in Table 10. Although the slopes for the three curves vary by more than a factor of two, the diffusion coefficients, which are based on the fractional weight gain, are similar. There is no induction period, i.e., the transport appears Fickian, and crystallinity has little effect other than reducing the solubility.

The SEDS sorption of methanol into amorphous, 15% crystalline and 30% crystalline PEEK is shown in Figure 37. The weight gain shown in Figure 37 represents the amount sorbed in 24 hours; note that 400-500 hours are required to reach equilibrium in the unstressed state (see Figure 36). The critical stress in amorphous and crystalline PEEK is approximately 30 and 45 MPa, respectively.

ACETONE: Although acetone is considered a non-swelling solvent for PEEK, it too exhibits SEDS. The solubility as a function of applied stress in amorphous and 29% crystalline PEEK are summarized in Table 11. The rate of sorption for the stressed amorphous sample is significantly greater than that of the unstressed material and indicates that the critical stress is less than 7 MPa. The critical stress for the crystalline material is between 15 and 30 MPa.

WATER: The solubility of water into PEEK is low, of the order of 0.5 wt%. The transport of water in PEEK seems to follow Fickian diffusion, i.e., the weight gain is a linear function of the square root time and the measured rates of sorption and desorption

are essentially the same (38,39). The transport is well behaved, but its most important and notable feature is the fact that the total amount sorbed is small. A typical weight gain curve for the sorption of water in amorphous PEEK at 22°C is shown in Figure 38. The transport appears Fickian and the linearity of the initial stages in the sorption plot can be used to determine true diffusion coefficients. The measured diffusion coefficient for the sorption of water at 22°C is 0.8×10^{-12} m^2/s, in agreement with the results reported previously (38). The solubility, or equilibrium weight gain, is 0.52 wt%. Equilibrium is obtained in approximately 4 hours and does not change even after immersion for an additional 46 h.

The effect of external tensile stress on the sorption of water in amorphous PEEK is illustrated in Figure 39 where the equilibrium weight gain after immersion in distilled water at 22°C for 24 hours is shown as a function applied load. The solubility is constant, at 0.52 wt% for an applied stress less than 26 MPa. The solid straight line shown in Figure 39 is a linear regression fit to the data for stresses greater than 30 MPa. The slope of the line 8×10^{-3} wt%/MPa, and at an applied stress of 55 MPa the solubility has increased 44% from its zero stress value. The data suggest a critical stress, σ_c, of 26 MPa. Below σ_c, stress has no effect upon the sorption of water by PEEK but for values greater than σ_c, the equilibrium solubility increases rapidly.

According to the supplier of PEEK, the modulus (secant) and ultimate tensile strength of amorphous PEEK (Stabar K-200) are 2600 and 120 MPa, respectively (37). The yield strength is approximately 100 MPa. Thus, the applied stresses reported in this work are in the elastic region and are considerably below values which induce permanent damage to the films. The critical yield of 26 MPa corresponds to a critical strain of approximately 1%.

It is important to note that the transport of water in PEEK appears Fickian: one of the basic assumptions of Fickian transport is the assumption that the liquid penetrant and the solid surface rapidly reach equilibrium, i.e., in a time period small compared to the mean

diffusion time. SEDS sorption of the organic liquids reported in this work follow a different path. the transport is definitely non-Fickian and the data suggest that equilibration between the liquid penetrant and the polymer surface is slow

SUMMARY

- All the materials investigated, ranging from aromatic hydrocarbons, to chloromated solvent, to oxygenated solvents, and even water exhibit SEDS.

- The SEDS enrichment factor, the ratio of the amount sorbed in the stressed state to that in the unstressed state, is much larger for crystalline than amorphous PEEK.

- The sorption of the aromatic hydrocarbons and chlorinated solvents follows non-Fickian transport with three primary regions: an induction period, a limiting solubility, and a diffusion or penetration rate region. Both the induction period and the limiting solubility are strongly affected by external stress. The diffusion rate is a weak function of stress.

- Both water and methanol exhibit Fickian (or pseudo-Fickian) transport. Water in amorphous PEEK exhibit a critical stress of 26 MPa. Neither water nor methanol exhibit an induction period.

- The critical stress (or strain) for the various fluids was determined. Two separate measurements were made: 1) the stress required for rapid sorption, and 2) the stress (or strain) for the sample to begin yielding.

- The stress enhanced solubilities of the various penetrants into amorphous and crystalline PEEK are summarized in Table 12.

ACCOMPLISHMENTS

- The equipment and personnel were moved from Michigan Molecular Institute (Midland, MI) to the Materials Research Laboratory, Washington University, St. Louis, MO.

  - Three manuscripts were submitted for publications

    - Stress Enhanced Transport of Organic Liquids in Poly Aryl Ether Ether Ketone to J. Polym. Sci. Phys. Ed.

    - Stress Enhanced Sorption of Water in Poly Aryl Ether Ether Ketone to J. Polym. Sci. Phys. Ed.

    - Stress Enhanced Solubility/Swelling of Thermoplastic Resins to Chemtech.

  - Two papers were presented at technical meetings

    - Stress Enhanced Solubility/Swelling of Thermoplastic Resins to 205th National Amer. Chem. (PMSE) 29 Aug. 1993. [Polym. Matl. Sci. Eng. 69, 370 (1993)].

    - Stress Enhanced Solubility/Swelling of Thermoplastic Resins to Gordon Research Conf.: Composites, 12 Jan 1994.

  - External Publicity

    - Chemical and Engineering News selected paper on Stress Enhanced Solubility/Swelling of Thermoplastic Resins as one of the noteworthy papers at the 205th National American Chemical Society meeting.

    - Chemtech requested article on Stress Enhanced Solubility/Swelling for general readership.

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Table 1
Solubility and Induction Period of Toluene in Unstressed PEEK
as a Function of Temperature and Crystallinity

Crystallinity (%)	Temp. (°C)	Solubility (wt%)	Induction (hours)
Amorphous	50	17.5	0
	65	15.9	0
	80	14.4	0
	95	12.8	0
9.1	50	---	712
	65	13.3	76
	80	13.4	1.6
	95	11.6	0
13.4	65	12.7	843
	80	12.6	5
	95	11.6	0
19.1	80	11.7	228
	95	10.9	0.3
30.6	80	8.1	1330
	95	7.5	14

Table 2

Weight Gain, Solubility (in the Amorphous Region), and Stress Enhancement Factor (SEF) for the Sorption of Toluene into PEEK.

Temperature

Material	Stress (MPa)	22°C			35°C			50°C		
		%wt gain	Sol*	SEF**	%wt gain	Sol*	SEF**	%wt gain	Sol*	SEF**
Amorphous	0	21.2	21.2	1.00	19.8	19.8	1.00	1.72	17.2	1.00
	4	25.0	25.0	1.18	21.2	21.2	1.07	18.2	18.2	1.06
	7	31.4	31.4	1.48	27.1	27.1	1.37	20.6	20.6	1.20
		34.1	34.1	1.61	29.7	29.7	1.50	22.0	22.0	1.28
15% Cryst.	0	13.2	15.5	1.00	13.2	15.4	1.00	1.30	15.3	1.00
	25	37.0	43.5	2.81	32.7	38.5	2.50	28.0	32.9	2.15
	28	38.3	45.1	2.91	33.8	39.8	2.58	28.8	33.9	2.22
	32	38.9	45.8	2.95	35.2	41.4	2.69	29.6	34.8	2.27
29% Cryst.	0	9.1	12.8	1.00	9.0	12.7	1.00	8.9	12.5	1.00
	30	36.5	51.4	4.02	32.3	45.5	3.58	31.4	44.2	3.54
	35	39.2	55.2	4.31	35.8	50.4	3.97	34.6	48.7	3.90
	40	39.5	55.4	4.33	36.7	51.7	4.07	30.6	43.1	3.45

* Based on amorphous fraction

** Stress Enhancement Factor $\left[\dfrac{\text{wt. gain (stressed)}}{\text{wt. gain (unstressed)}} \right]$

Table 3

Effect of Applied Stress on the Solubility of Toluene in Amorphous PEEK

Temperature	Change in Solubility with Stress
22°C	1.36 wt%/MPa
35	1.06
50	0.50

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Table 4

**Pseudo-Diffusion Coefficients for the Penetration of Toluene into PEEK
as a Function of Crystallinity, Applied Stress, and Temperature**

</div>

Material	Stress		Diffusion Coefficients (D_b)	
	(MPa)	22°C	35°C ($\times 10^{-12}$ m²/s)	50°C
Amorphous	0		0.35	
	7	8.9		
15% Cryst.	15			0.4
	20		4.0	6.3
	25	2.2	5.0	40
29% Cryst.	25		0.2	0.9
	30	0.8	4.7	24
	35	50		

Table 5

Induction period for the Sorption of Toluene into PEEK as a Function of Applied Stress and Temperature

Material	Applied Stress (MPa)	Induction Period (h) 22°C	35°C	50°C	ΔE (kcal/mol)
Amorphous	0		0.3		
	7	1			
15% Cryst.	15			16	
	20	> 40	1.4	0.5	
	25	1.7	1	0.04	25
29% Cryst.	25	>1000	13	1	
	30	10	3	0.25	25
	35	1.8			

Table 6

Critical Strain and Stress for the Sorption of Toluene into PEEK

Material	Critical Value					
	22°C		35°C		50°C	
	Strain (%)	Stress (MPa)	Strain (%)	Stress (MPa)	Strain (%)	Stress (MPa)
Amorphous	0.32	(8)	0.26	(7)	0.18	(5)
15% Cryst.	1.05	(30)	0.87	(25)	0.82	(24)
29% Cryst.	1.33	(43)	1.19	(38)	1.04	(33)

Table 7

Stress Enhanced Solubility of Benzene in PEEK

Sample	Temperature	Time	Stress (%wt gain)		
			0	5 MPa	30 MPa
Amorphous	22°C	65 h	19.9	30.7	---
28% cryst.	22°	720	0.9	---	19.1

Table 8

Solubility and Diffusion of CS_2 into Unstressed PEEK

Sample Crystallinity (%)	Temperature							
	25°C		30°C		35°C		40°C	
	C_∞ (%)	D ($\times 10^{-12}$ m²/s)	C_∞ (%)	D ($\times 10^{-12}$ m²/s)	C_∞ (%)	D ($\times 10^{-12}$ m²/s)	C_∞ (%)	D ($\times 10^{-12}$ m²/s)
Amorphous	23.0	2.16×10^{-12}	22.7	3.32×10^{-12}	22.0	3.39×10^{-12}	21.5	5.82×10^{-12}
9.1% cryst.	18.6	1.75×10^{-14}	19.0	1.08×10^{-13}	19.3	3.74×10^{-13}	18.1	6.31×10^{-13}
13.4% cryst.	17.5	6.92×10^{-15}	17.9	1.19×10^{-14}	17.7	1.54×10^{-14}	17.4	6.25×10^{-14}
19.1% cryst.	13.4	4.49×10^{-15}	14.4	6.00×10^{-15}	14.9	5.78×10^{-15}	14.7	7.90×10^{-15}
30.6% cryst.	10.2	3.32×10^{-15}	10.1	5.01×10^{-15}	10.5	5.83×10^{-15}	10.4	6.84×10^{-15}

Table 9

Sorption and Resorption of CS$_2$ in PEEK at 40°C

Crystallinity	Sorption	C_∞ (%) Resorption	C_S/C_R*	Sorption	$D_b (m^2/s)$ Resorption	D_S/D_R*
Amorphous	21.5	18.2	1.18	5.82×10^{-12}	1.08×10^{-13}	54
9.1% cryst.	18.1	16.2	1.12	6.31×10^{-13}	2.77×10^{-14}	23
13.4% cryst.	17.4	15.1	1.15	6.25×10^{-14}	2.47×10^{-14}	2.5
19.1% cryst.	14.7	13.9	1.06	7.90×10^{-15}	1.64×10^{-15}	0.5
30.6% cryst.	10.4	9.7	1.07	6.84×10^{-15}	6.88×10^{-15}	1

Initial sorption at 40°C

Desorb 95°C (to complete desorption)

Resorb 40°C

*Ratio of value during sorption to that in resorption

Table 10
Sorption of Methanol into PEEK at 22°C

Material	Solubility (wt%)	Diffusion Coefficient (m^2/s)
Amorphous	4.2	9.6×10^{-15}
15% cryst.	2.9	9.2×10^{-15}
30% cryst.	2.4	6.5×10^{-15}

Table 11

Stress Enhanced Solubility of Acetone in PEEK at 22°C

Sample	Stress (MPa)	%wt Gain	Time* (h)
Amorphous	0	1.5	48
	7	30.0	24
	10	30.5	48
29% Crystalline	15	1.5	912
	30	22.5	408
	35	26.2	6

*Time of immersion

Table 12

Stress Enhanced Solubility (wt%) of Liquids into PEEK at Room Temperature

Penetrant		Stress (MPa)	0	5	10	20	32	38
			% Weight Gain					
Methylene Chloride	Amorphous		40	47	50			
	29% Cryst		22			52		
Chloroform	Amorphous		59	70	81			
	29% Cryst					62		
Benzene	Amorphous		20	31				
Toluene	Amorphous		23	28	34			
	29% Cryst		9				37	
Carbon Disulfide	Amorphous		24					
	29% Cryst.		12				34	
Acetone	Amorphous		7		31			
	29% Cryst		---				23	
Methanol	Amorphous		4					25

LIST OF FIGURES

20. Sorption of methylene chloride in 29% crystalline PEEK at 22°C as a function of applied stress.

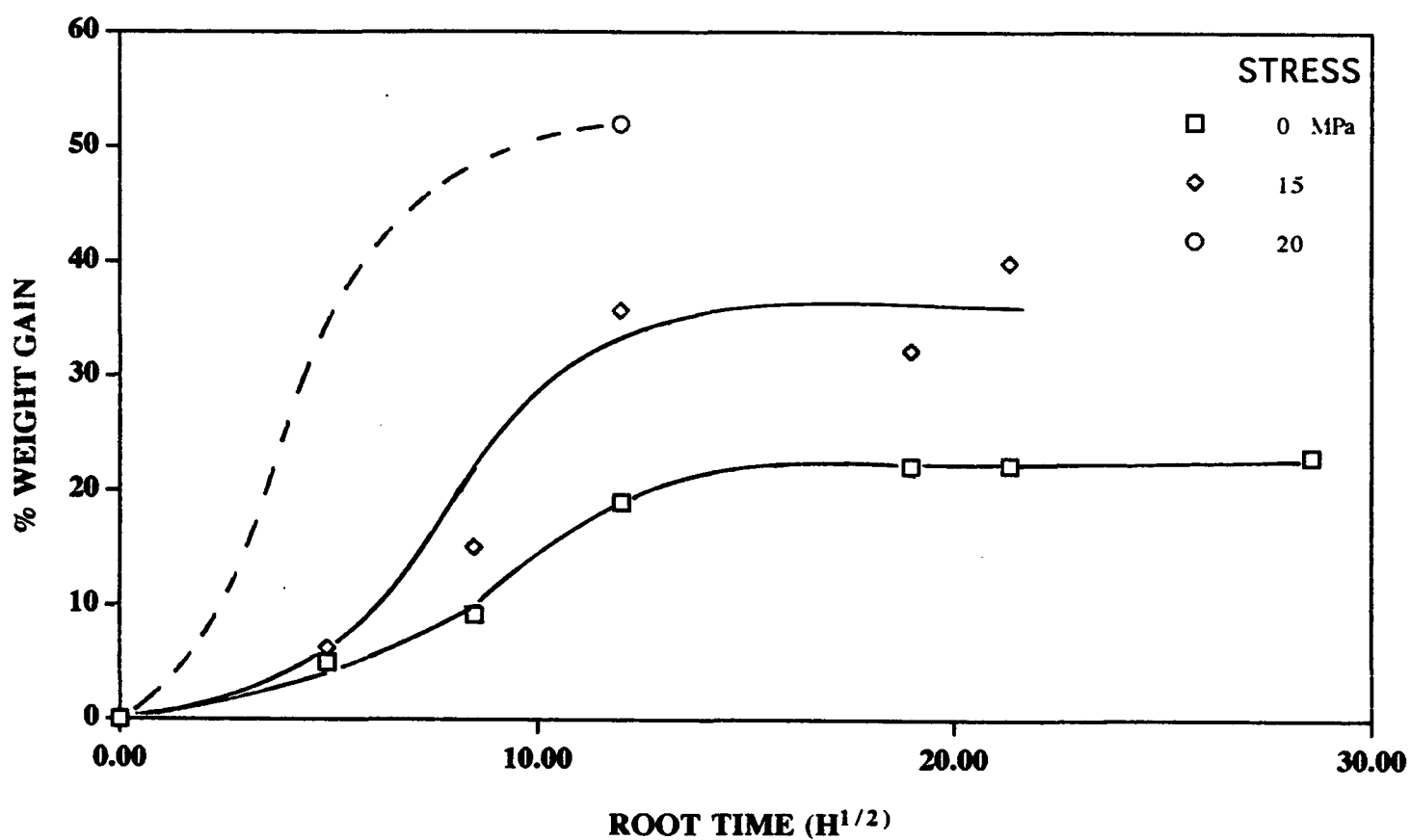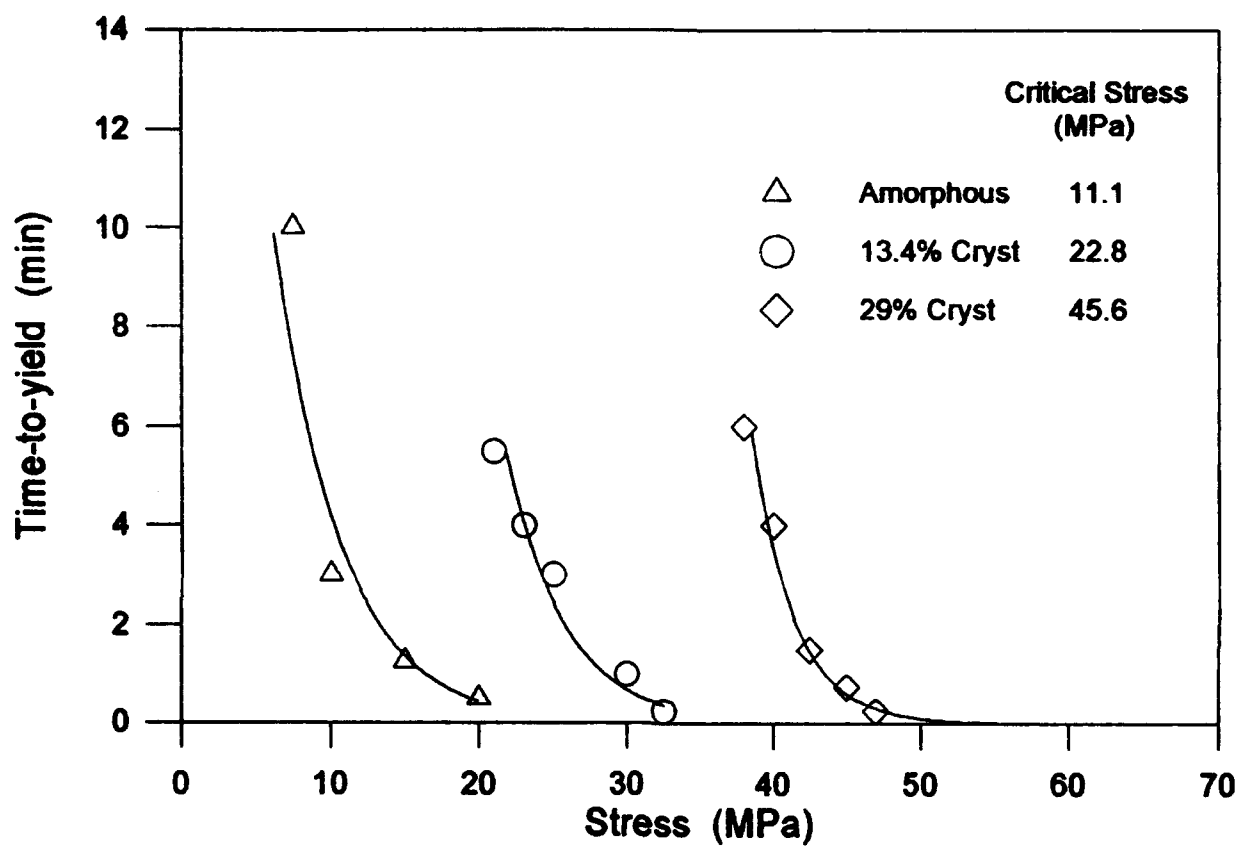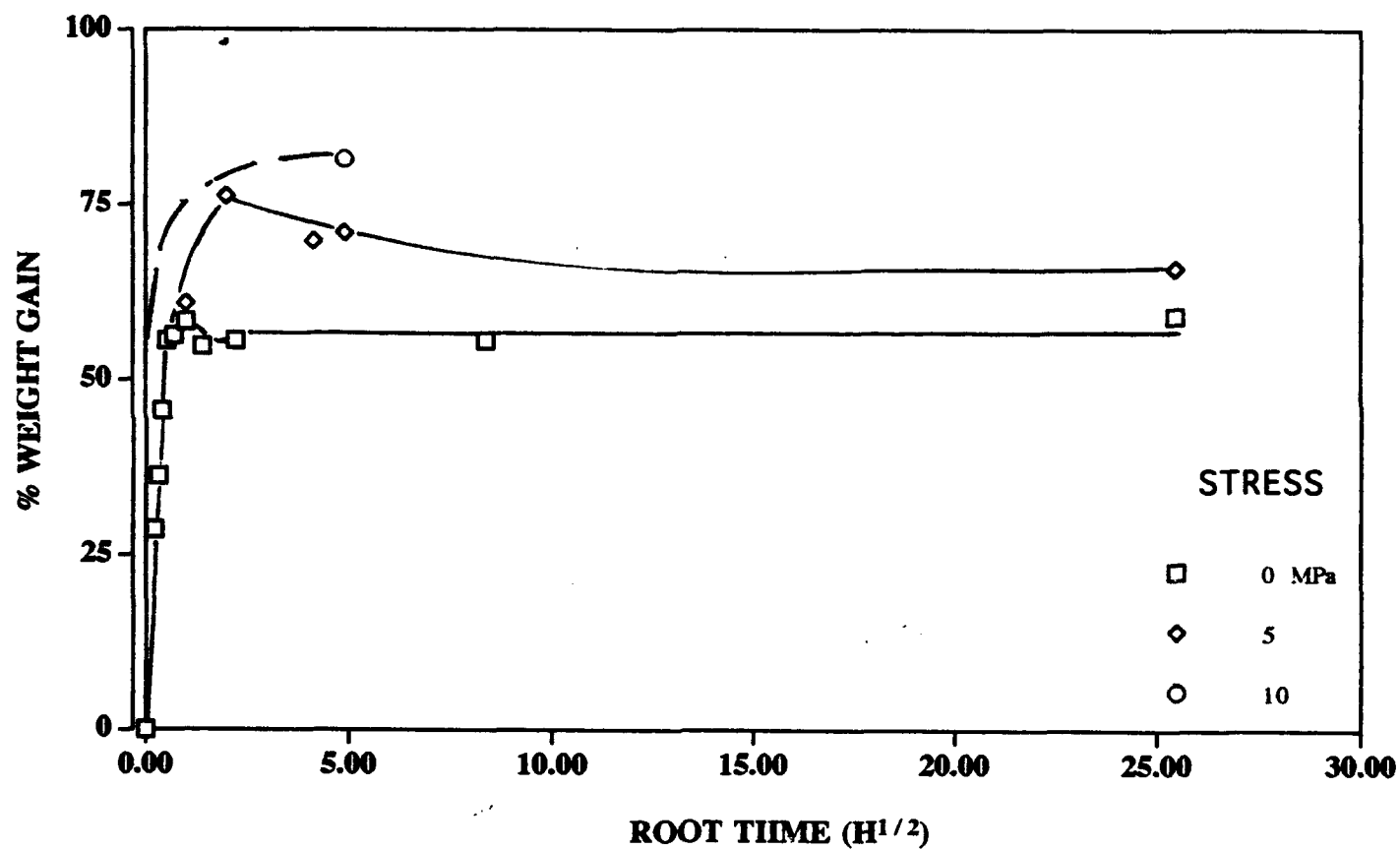21. Environmental stress yielding for sorption of methylene chloride in PEEK at 22°C.

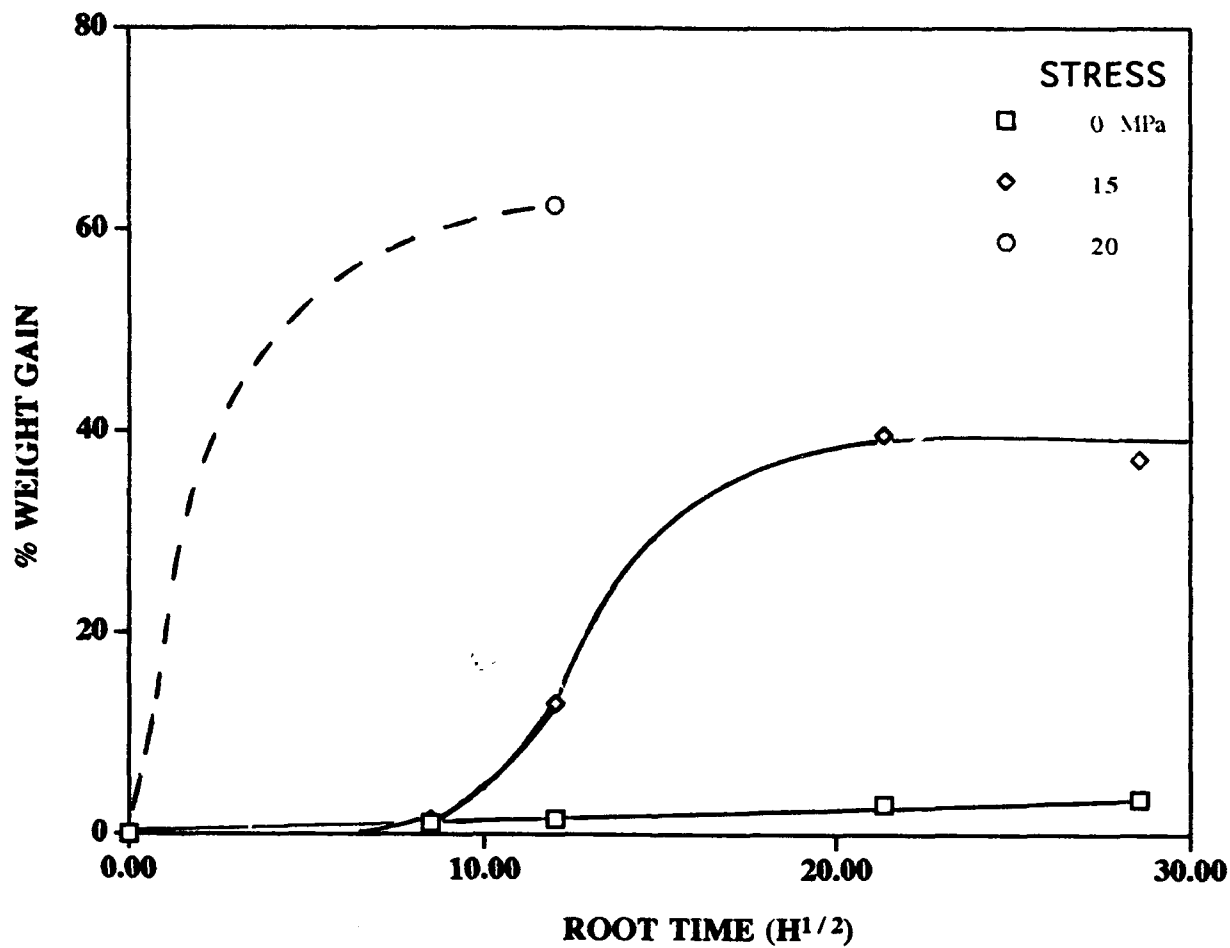22. Sorption of chloroform in amorphous PEEK at 22°C as a function of applied stress.

23. Sorption of chloroform in 29% crystalline PEEK at 22°C as a function of applied stress.

24. Environmental stress yielding for sorption of chloroform in PEEK at 22°C.

25. Sorption of carbon disulfide into PEEK at 25°C.

26. Sorption of carbon disulfide into PEEK at 30°C.

27. Sorption of carbon disulfide into PEEK at 35°C.

28. Sorption of carbon disulfide into PEEK at 40°C.

29. Desorption of carbon disulfide from PEEK. Initial sorption: 40°C; Desorption: 50°C.

30. Sorption and resorption of carbon disulfide into initially amorphous PEEK Sorption: 40°C; Desorption: 95°C, Resorption: 40°C.

31. Sorption and resorption of carbon disulfide into initially 9.1% crystalline PEEK: Sorption: 40°C; Desorption: 95°C; Resorption, 40°C.

32. Sorption and resorption of carbon disulfide into initially 13.4% crystalline PEEK: Sorption: 40°C; Resorption: 95°C; Desorption: 40°C.

33. Sorption and resorption of carbon disulfide into initially 19.1% crystalline PEEK: Sorption: 40°C; Desorption: 95°C; Resorption: 40°C.

34. Sorption and resorption of carbon disulfide into initially 30.6% crystalline PEEK: Sorption: 40°C; Desorption: 95°C; Resorption: 40°C.

35. SEDS sorption of carbon disulfide in 29% crystalline PEEK at 35°C: Applied stress: 30 MPa.

36. Sorption of methanol into PEEK at 22°C.

37. SEDS sorption of methanol into PEEK at 22°C (sorption time: 24 hours).

38. Sorption of water by amorphous PEEK at 22°C.

39. Sorption of water in amorphous PEEK at 22°C as a function of applied stress.
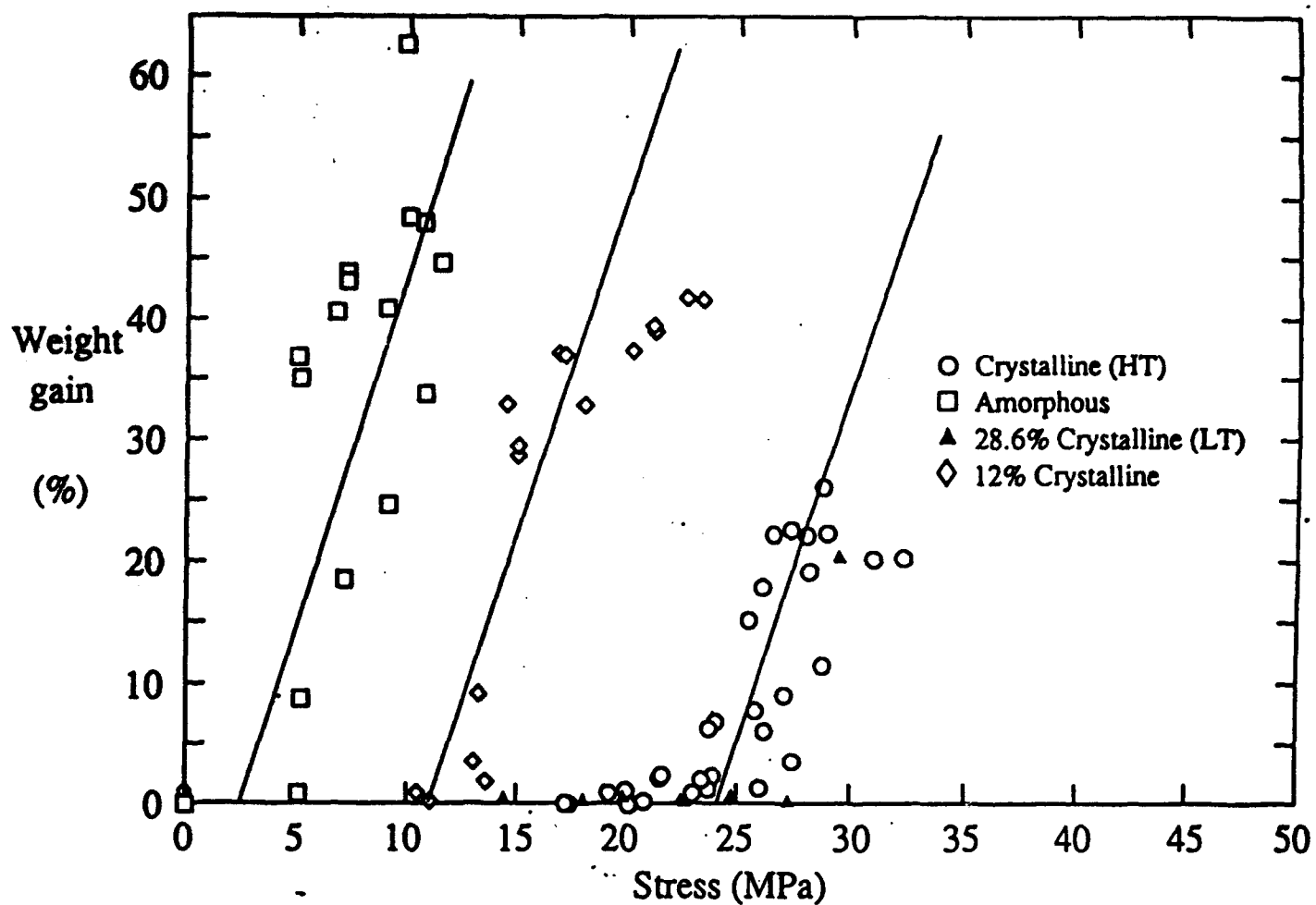
Figure 1   Effect of tensile stress on the sorption of toluene in
30% crystalline PEEK at 22°C.
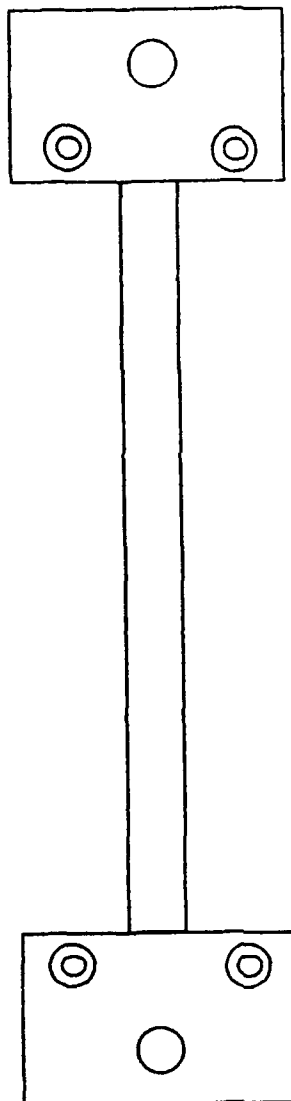
Figure 2.   PEEK film clamped with grips
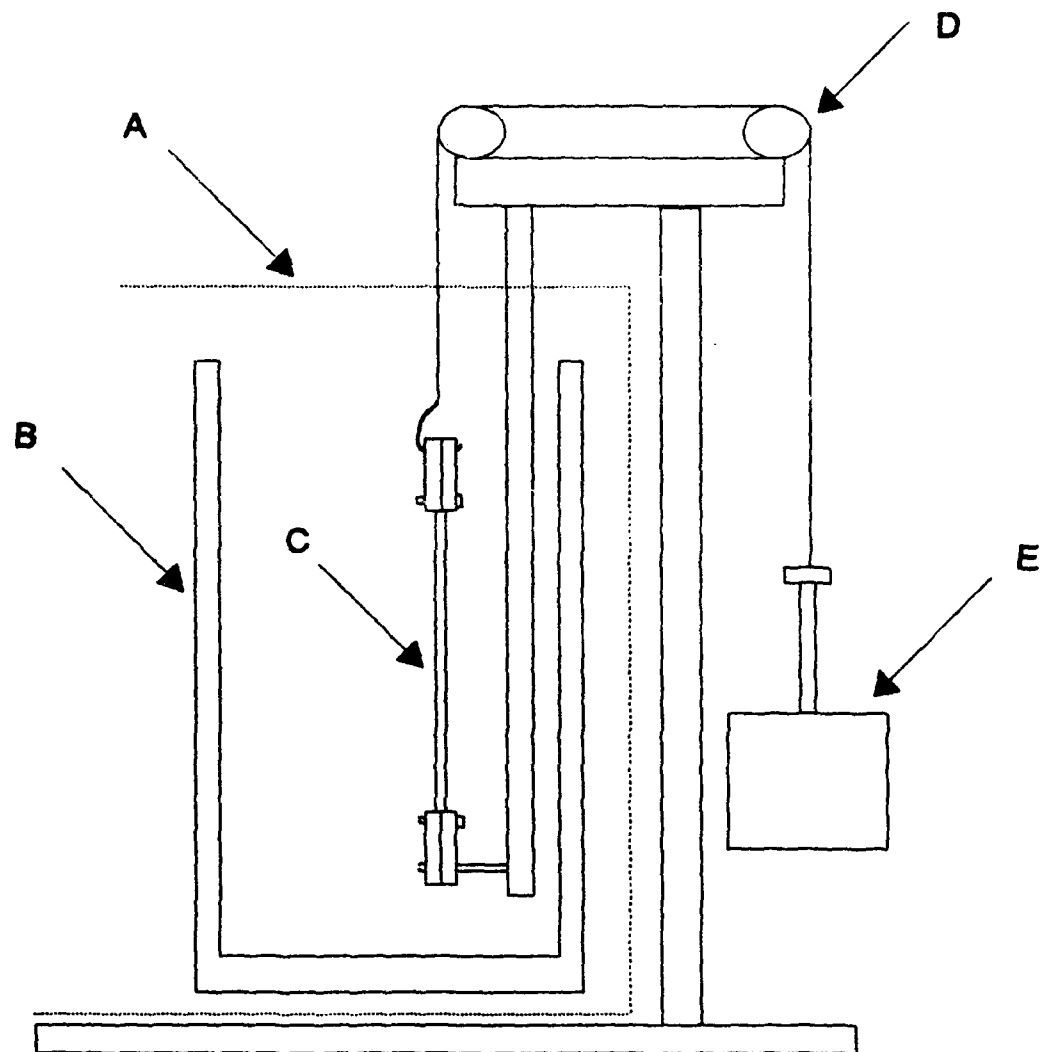
Figure 3. Edge-on view of specimen immersion chamber showing
self-aligning grips and balance pan: A, bath;
B, immersion chamber (cylinder); C, specimen;
D, pulley; E, balance pan.
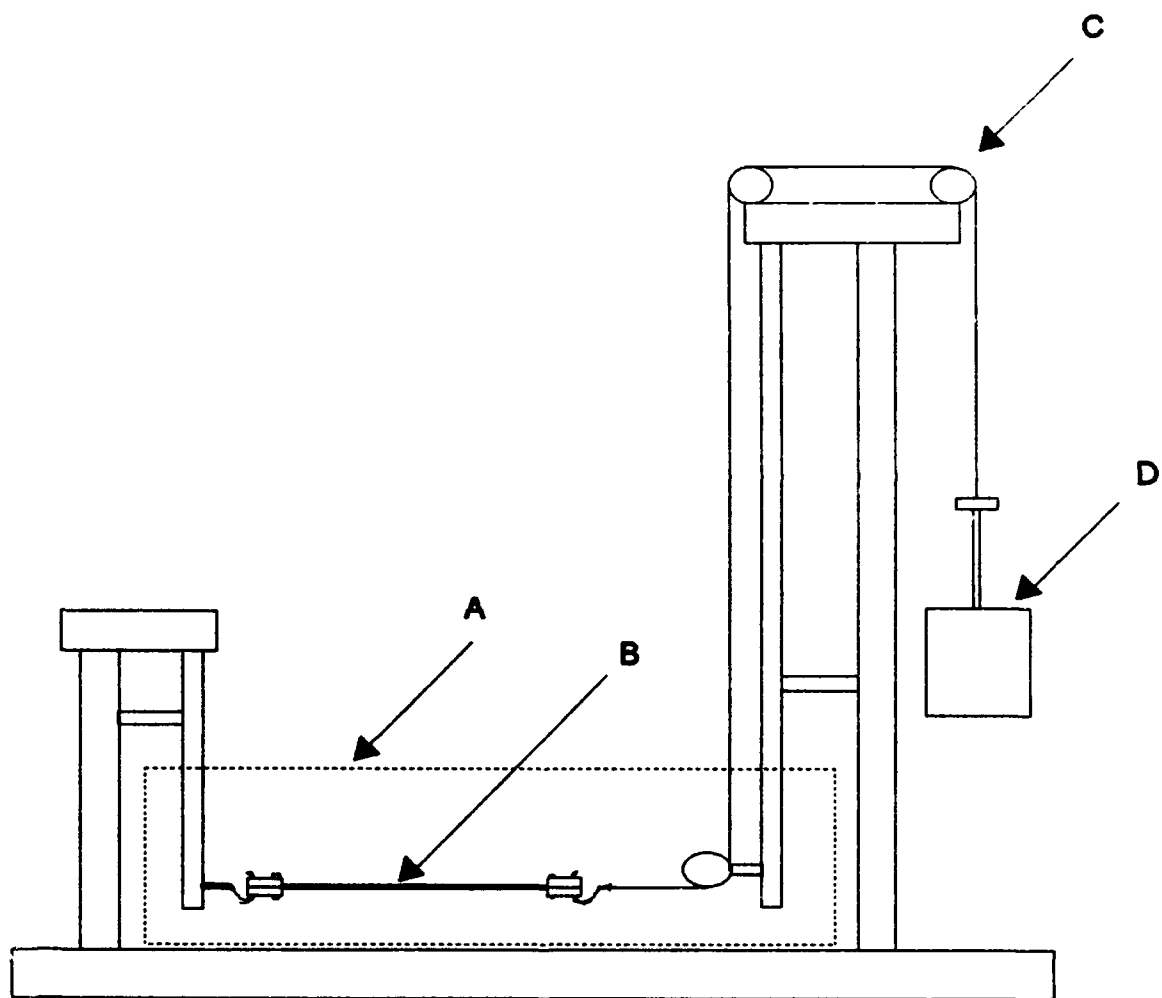
Figure 4. Edge-on view of horizontal stressed specimen immersion
chamber showing self-aligning grips and balance pan:
A, immersion chamber; B, specimen; C, pulley;
D, balance pan.
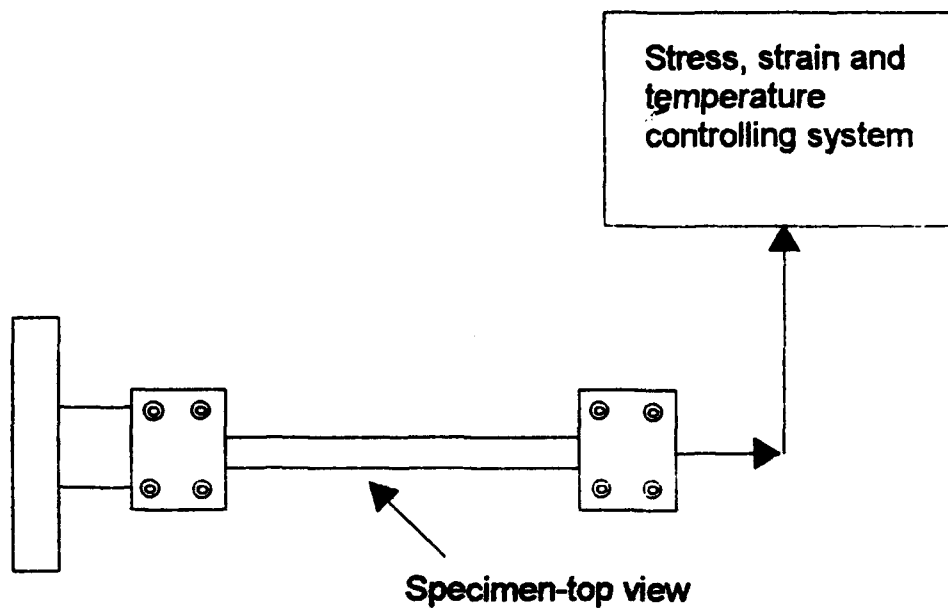
Figure 5. Schematic drawing of Minimat miniature materials tester

Edge-on view
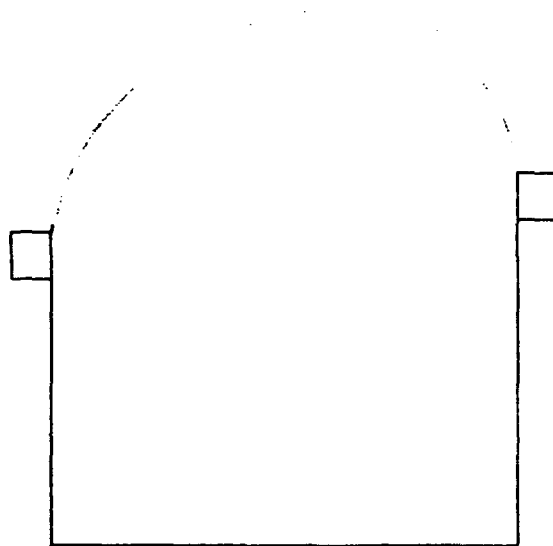
Top view

Specimen

Figure 6. Schematic drawing of strain-bending apparatus
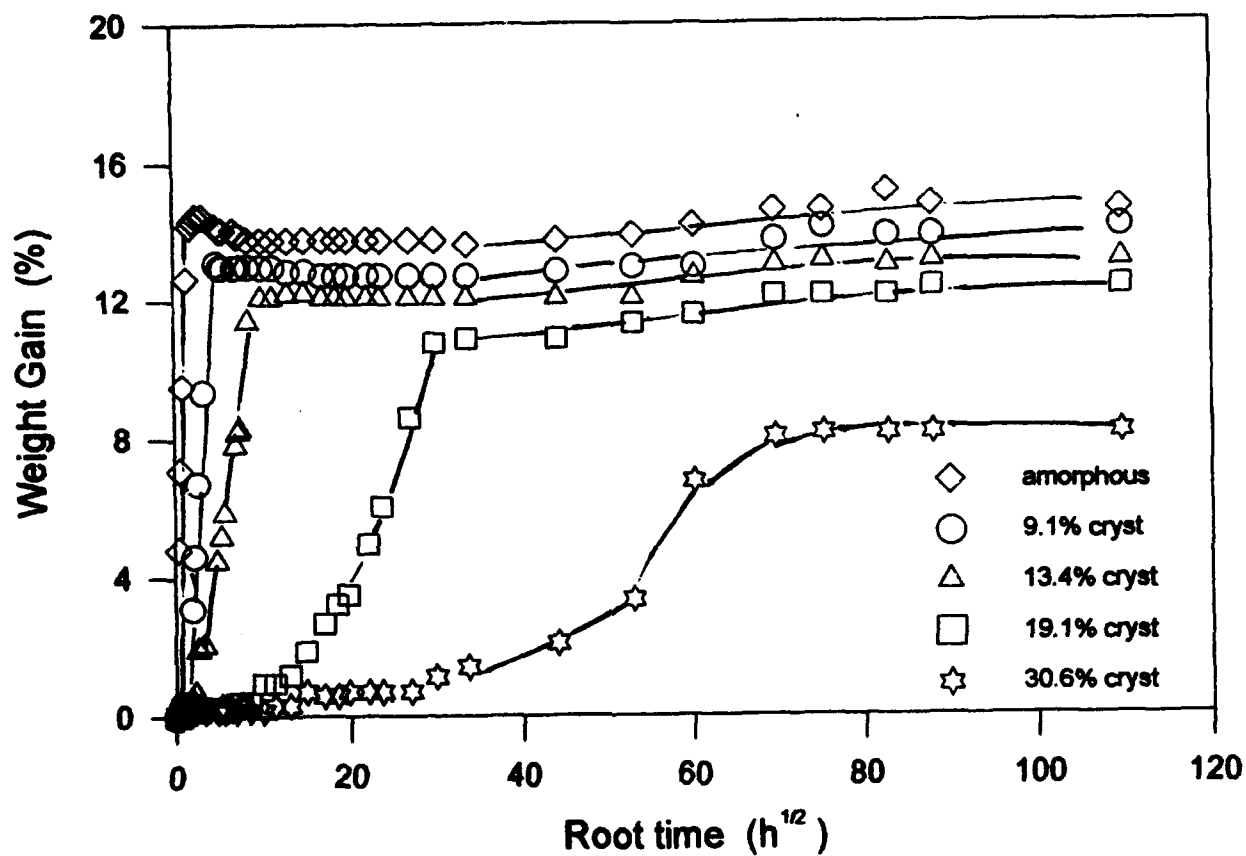
Figure 7　Sorption of toluene into PEEK at 80°C
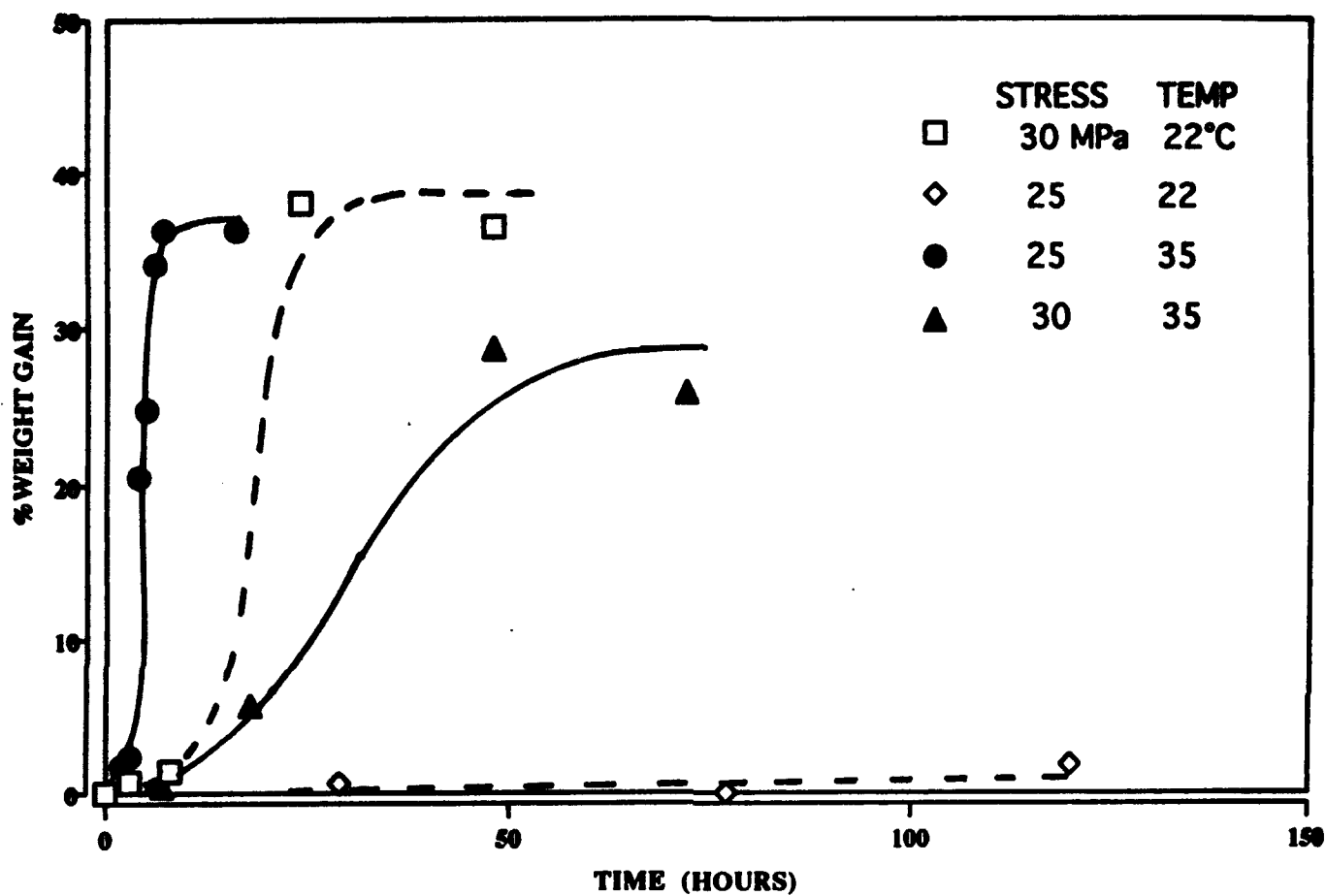
Figure 8 Sorption of toluene in 29% crystalline PEEK as a function of
applied stress, temperature and time.
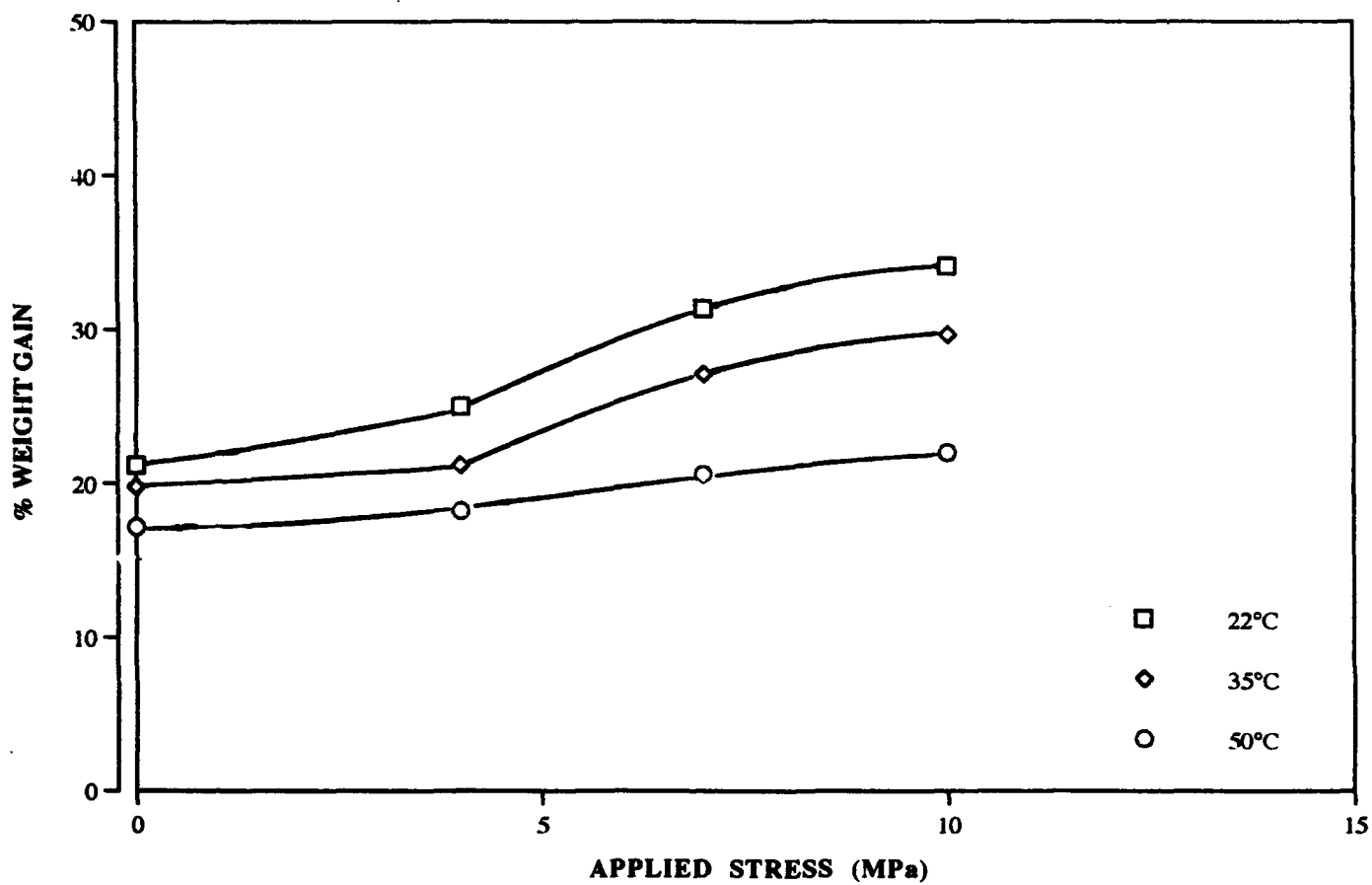
Figure 9   Sorption of toluene in amorphous PEEK as a function
of applied stress and temperature.
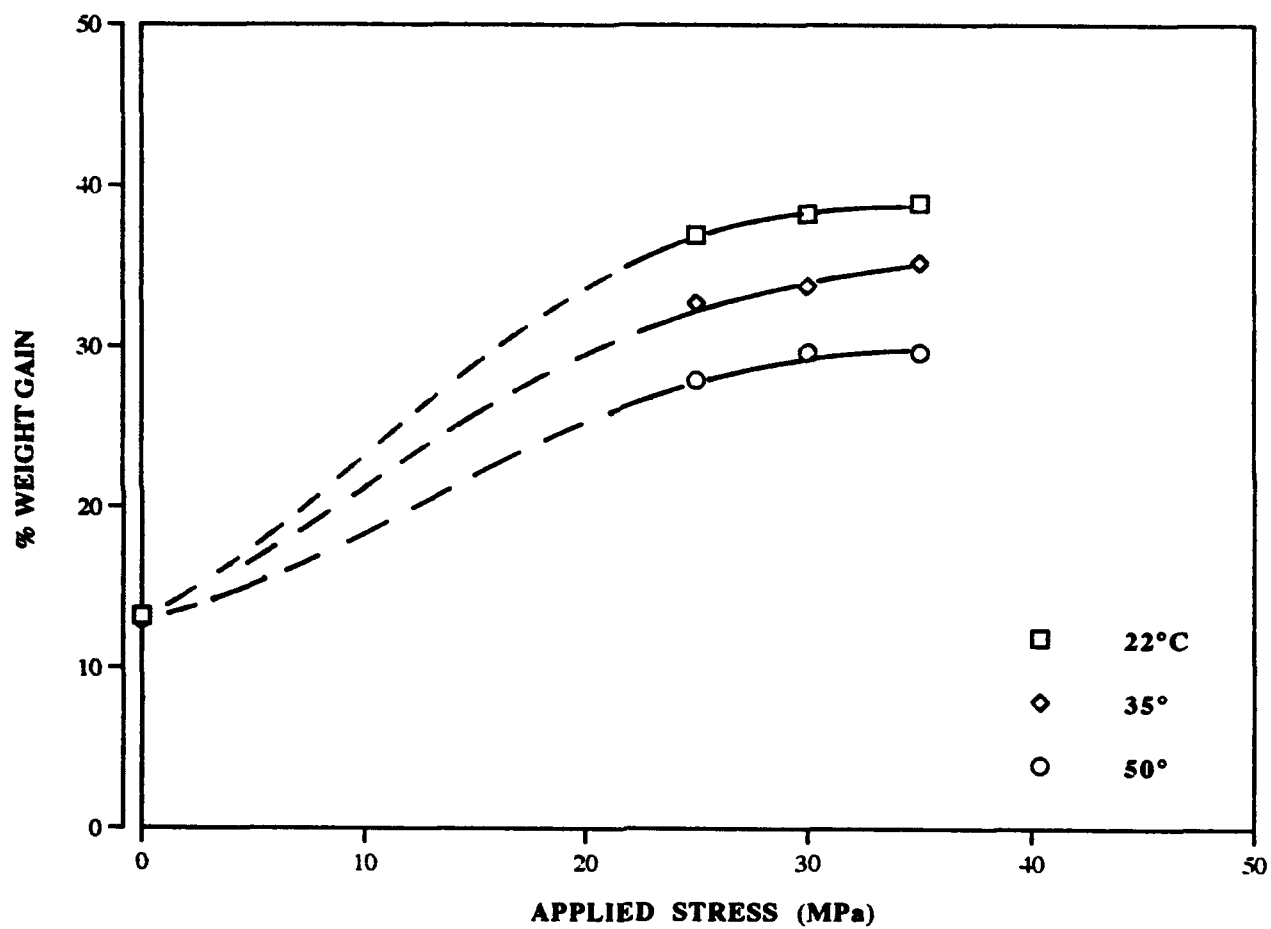
Figure 10 Sorption of toluene in 15% crystalline Peek as function of applied stress and temperature.
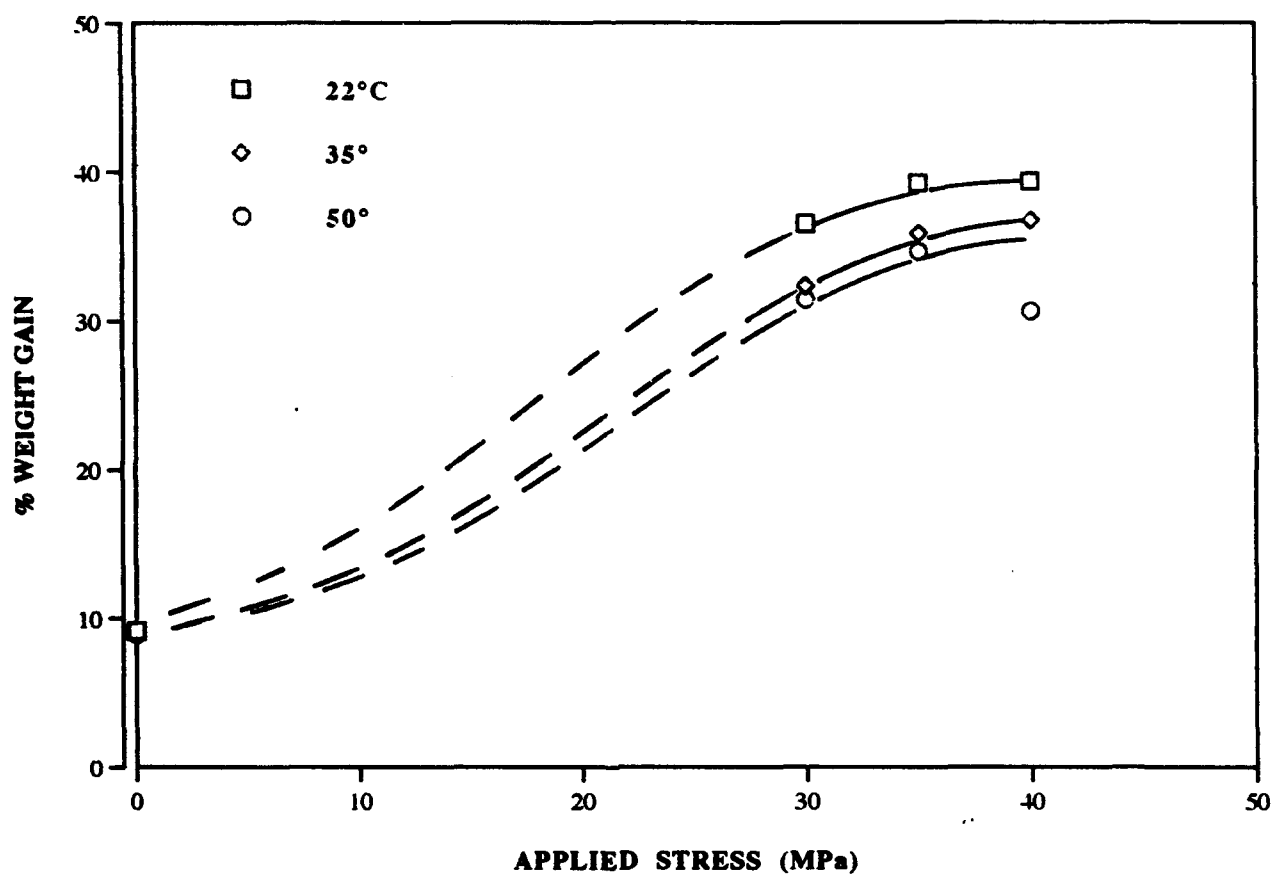
Figure 11   Sorption of toluene in 29% crystalline PEEK as a function
of applied stress and temperature.
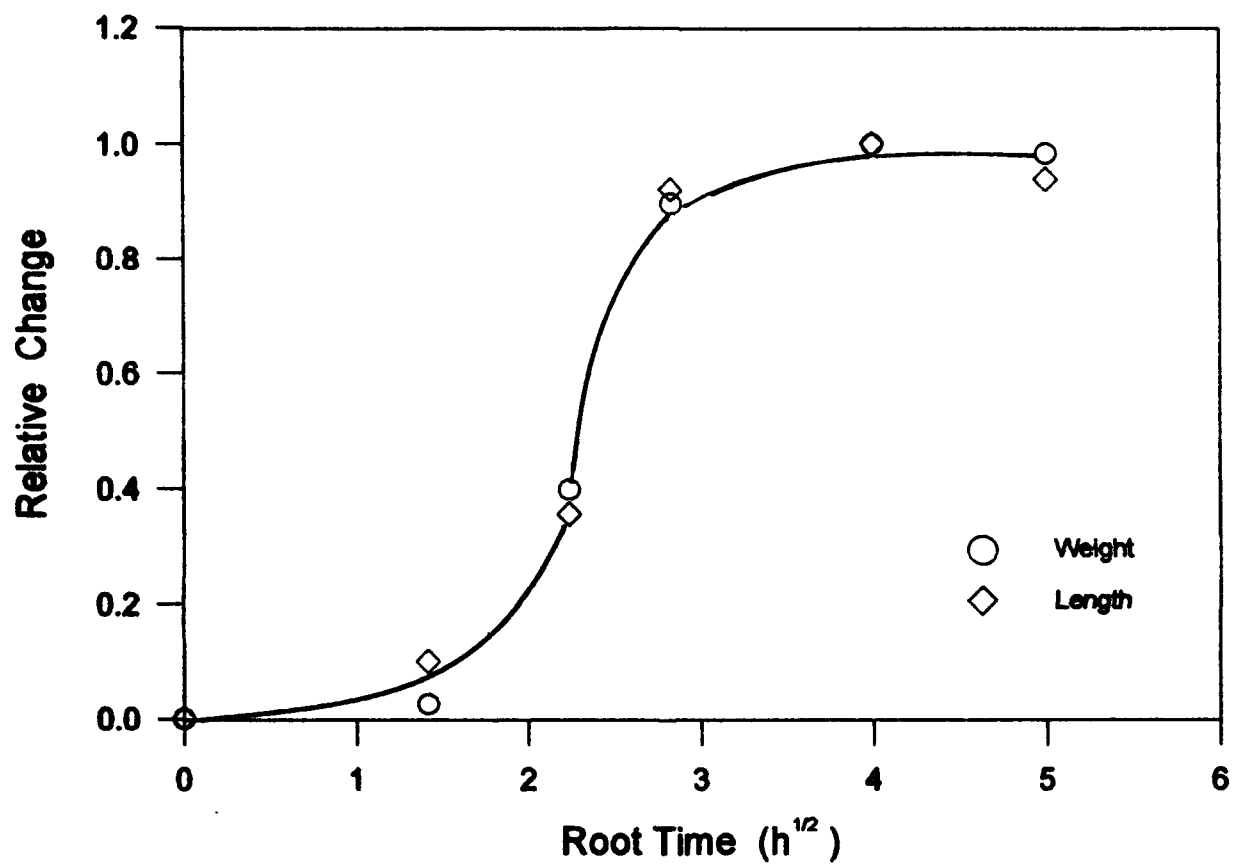
Figure 12   Relative change in length and weight gain as a function of time in stressed (40MPa) 29% crystalline PEEK at 22°C.
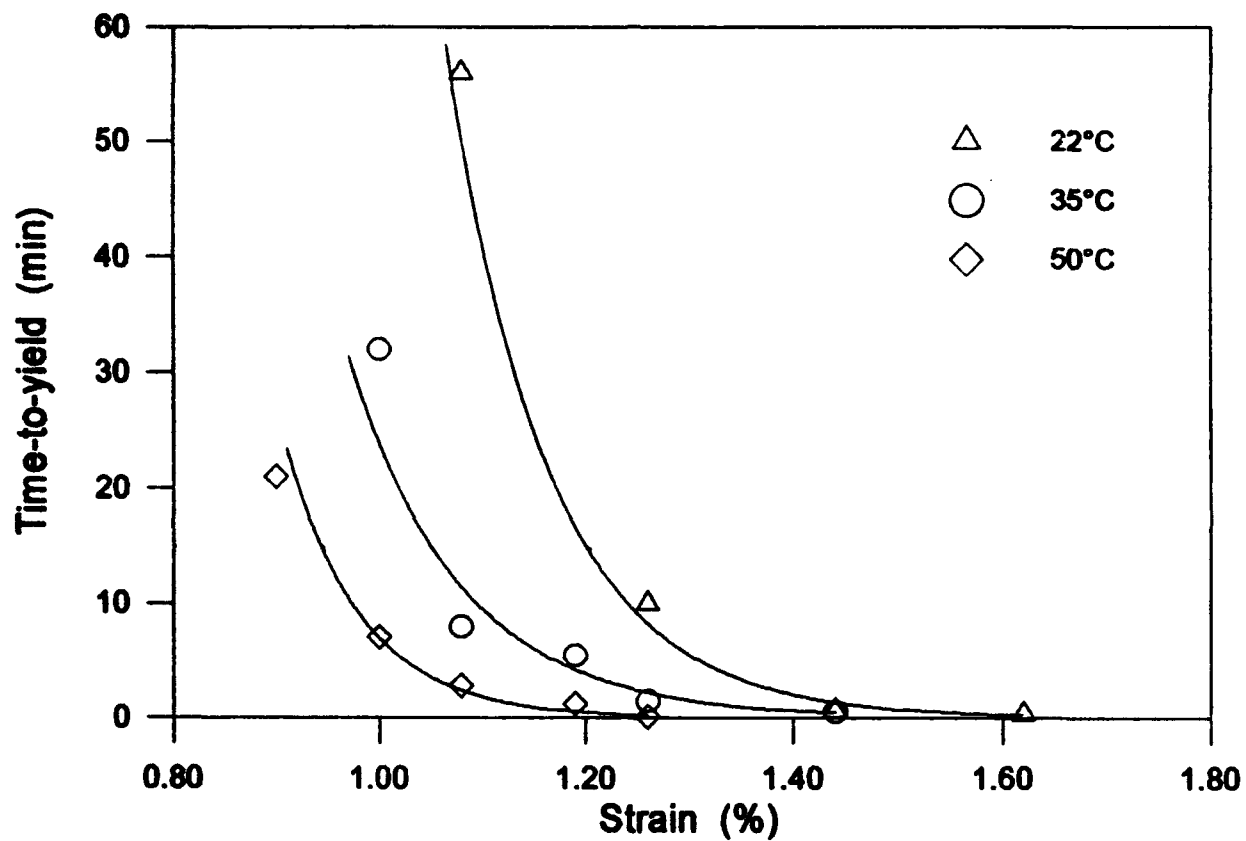
Figure 13 Time-to-yield for 29% crystalline PEEK immersed in toluene as a function of applied stress and temperature.
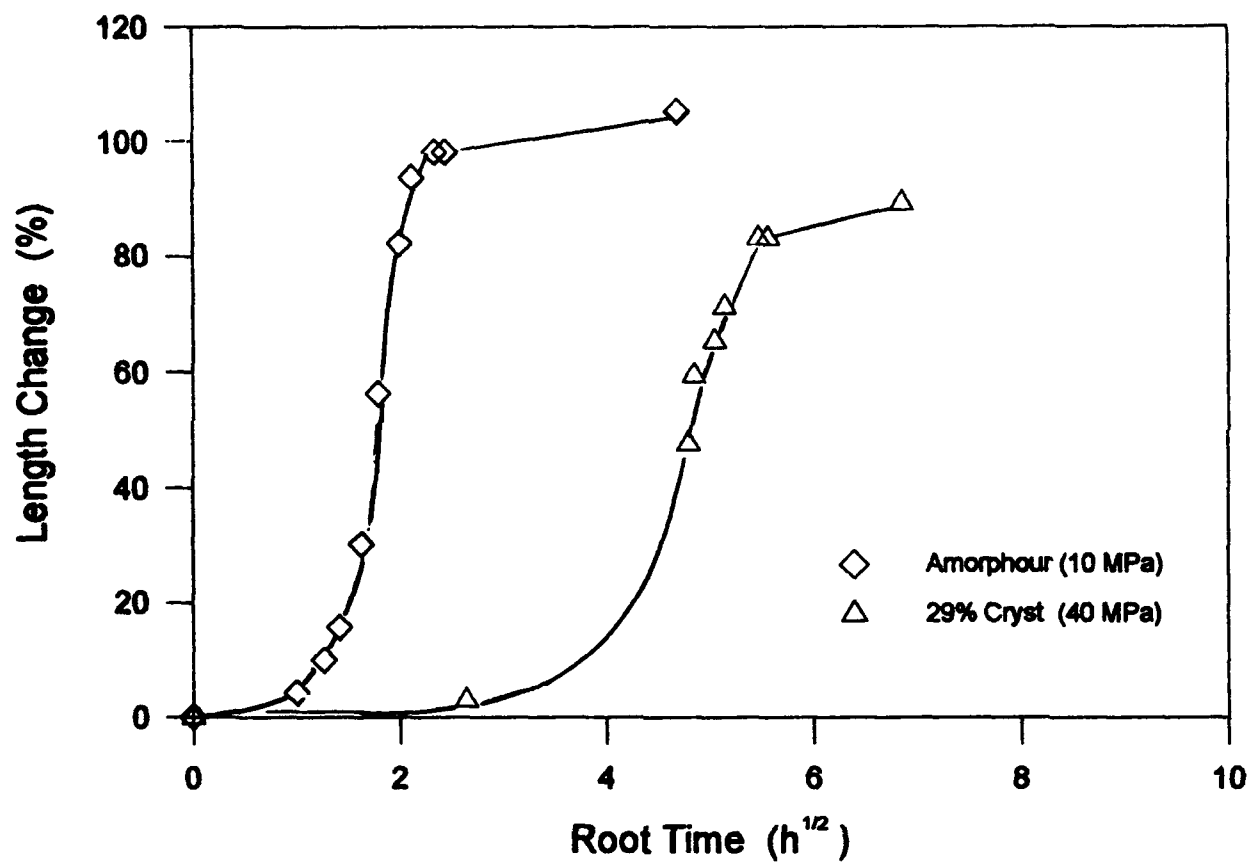
Figure 14   Relative change in length for PEEK immersed in toluene
at 22°C as a function of root time.
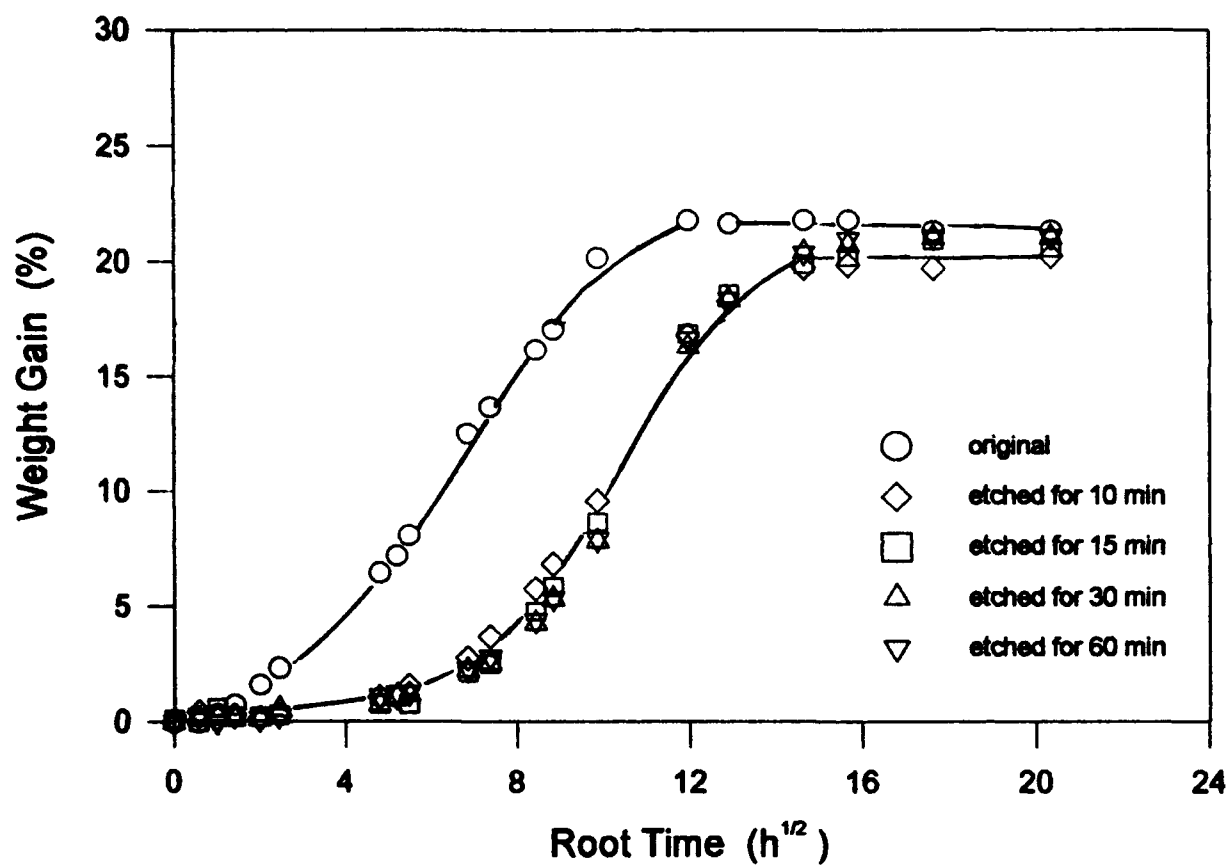
Figure 15   Sorption of toluene into etched amorphous PEEK at 22°C.
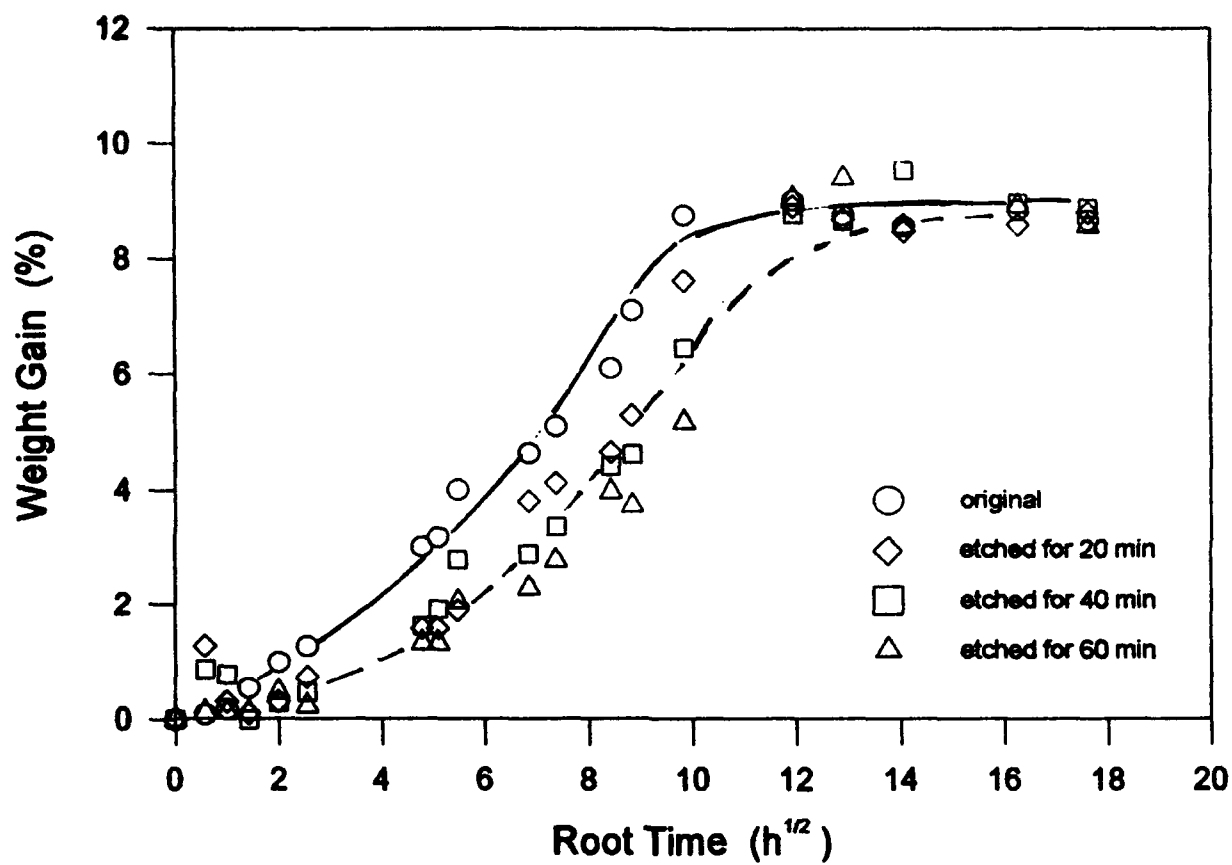
Figure 16 Sorption of toluene into etched 29% crystalline PEEK at 90°C .
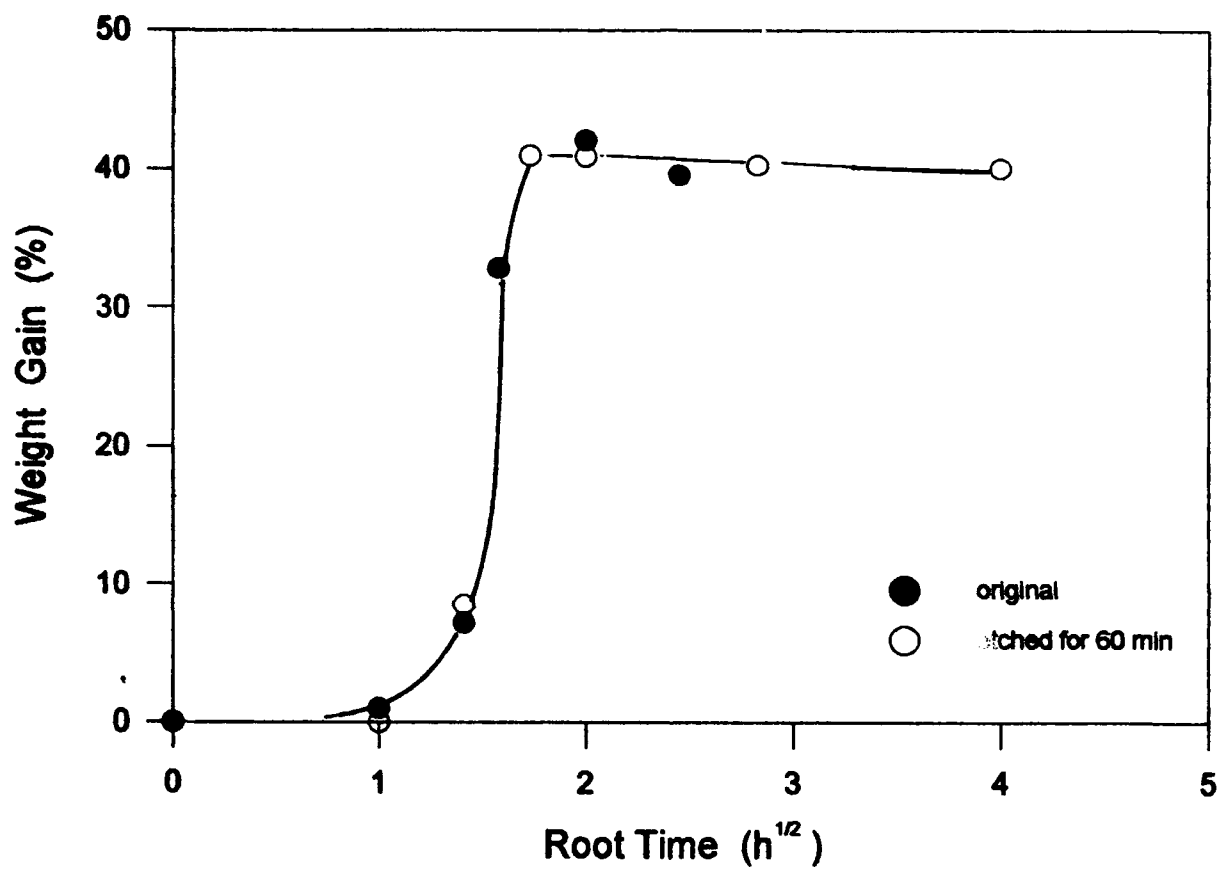
Figure 17   SEDS sorption of toluene into etched 29% crystalline PEEK at 22°C
(Etched for 60 min; Stress 35 MPa).
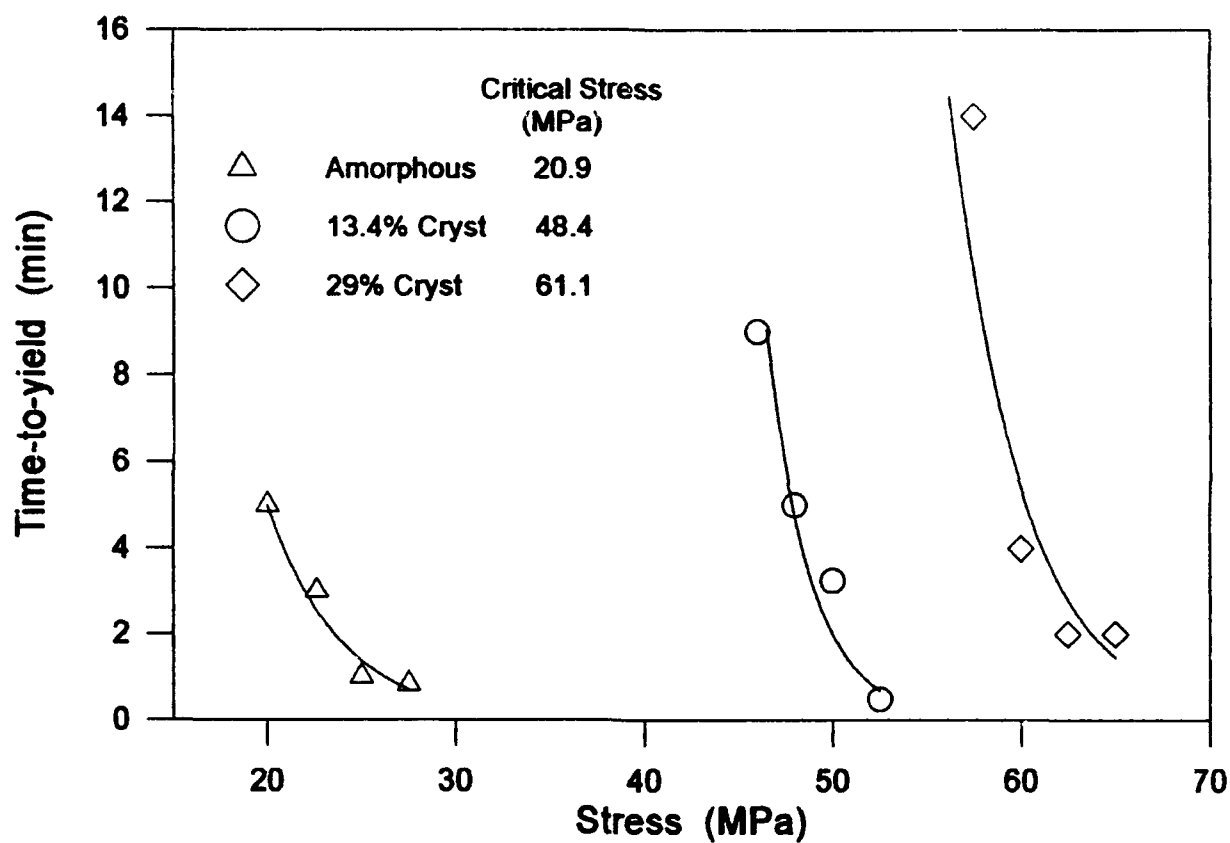
Figure 18   Environmental stress yielding for sorption of benzene in PEEK at 22°C
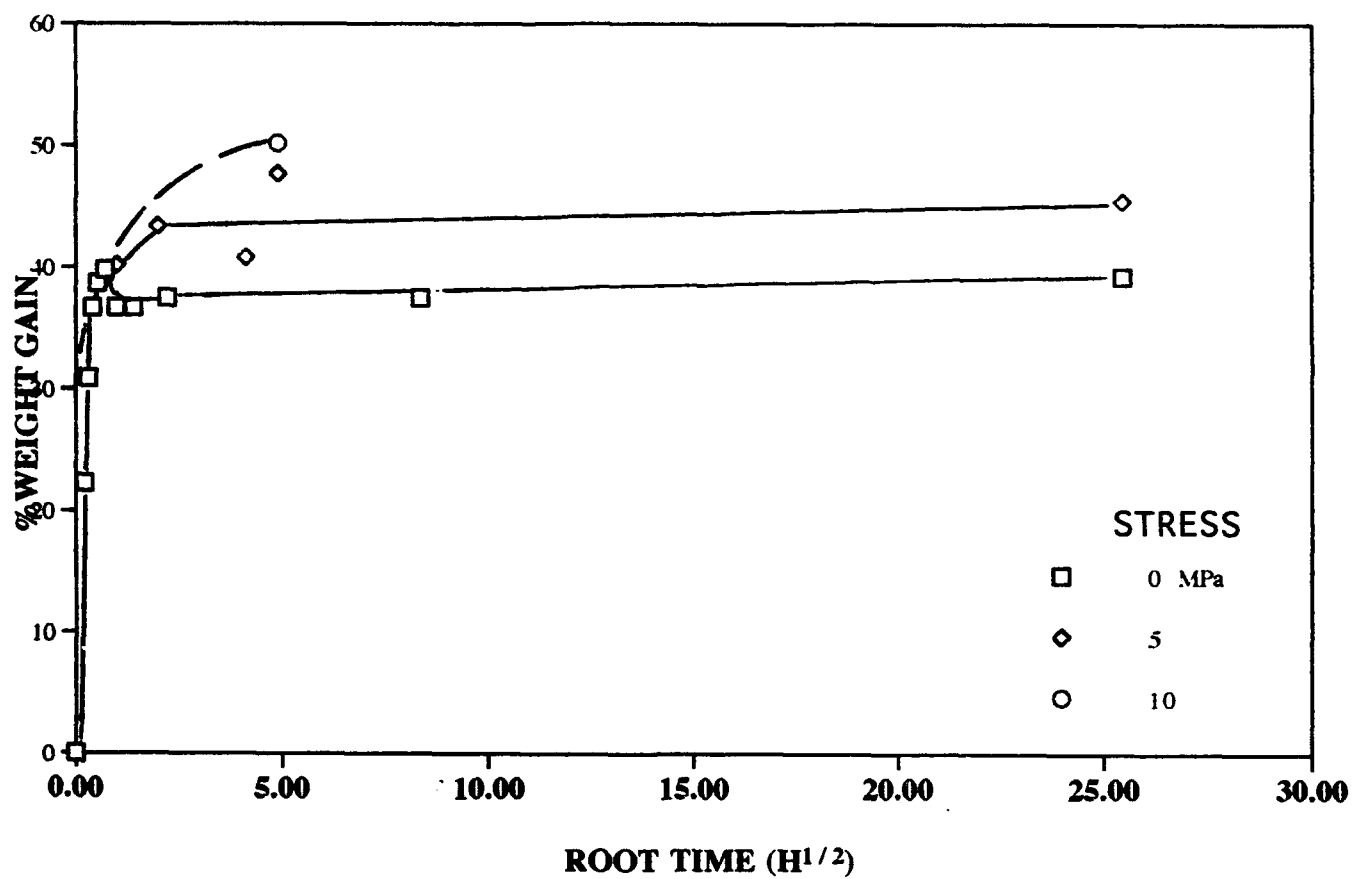
Figure 19 Sorption of methylene chloride in amorphous PEEK at 22°C as a function of applied stress.

Figure 20 Sorption of methylene chloride in 29% crystalline PEEK at 22°C as a function of applied stress.

Figure 21   Environmental stress yielding for sorption of methylene chloride
in PEEK at 22°C

Figure 22   Sorption of chloroform in amorphous PEEK at 22°C as a function of applied stress

Figure 23   Sorption of chloroform in 29% crystalline PEEK at 22°C as a function of applied stress.
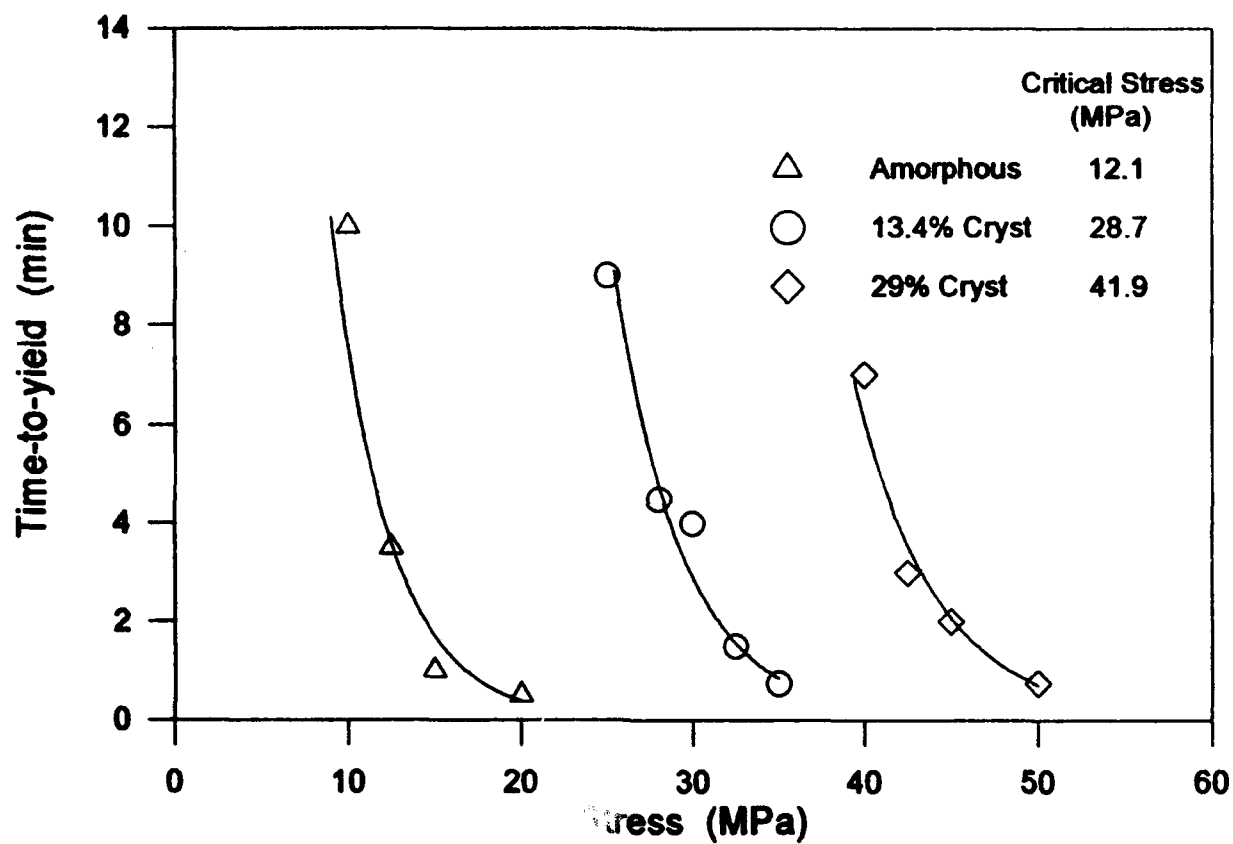
Figure 24   Environmental stress yielding for sorption of chloroform in PEEK at 22°C
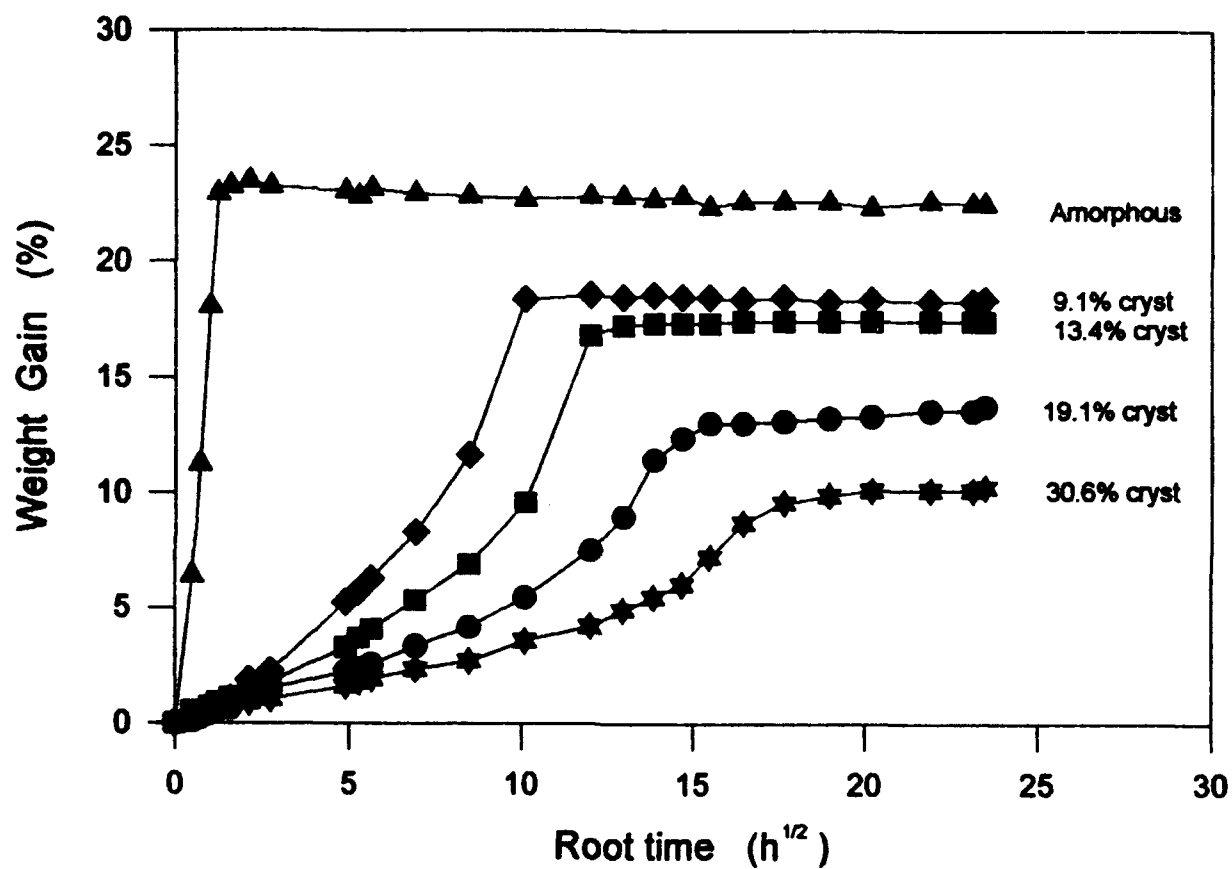
Figure 25   Sorption of carbon disulfide into PEEK at 25°C
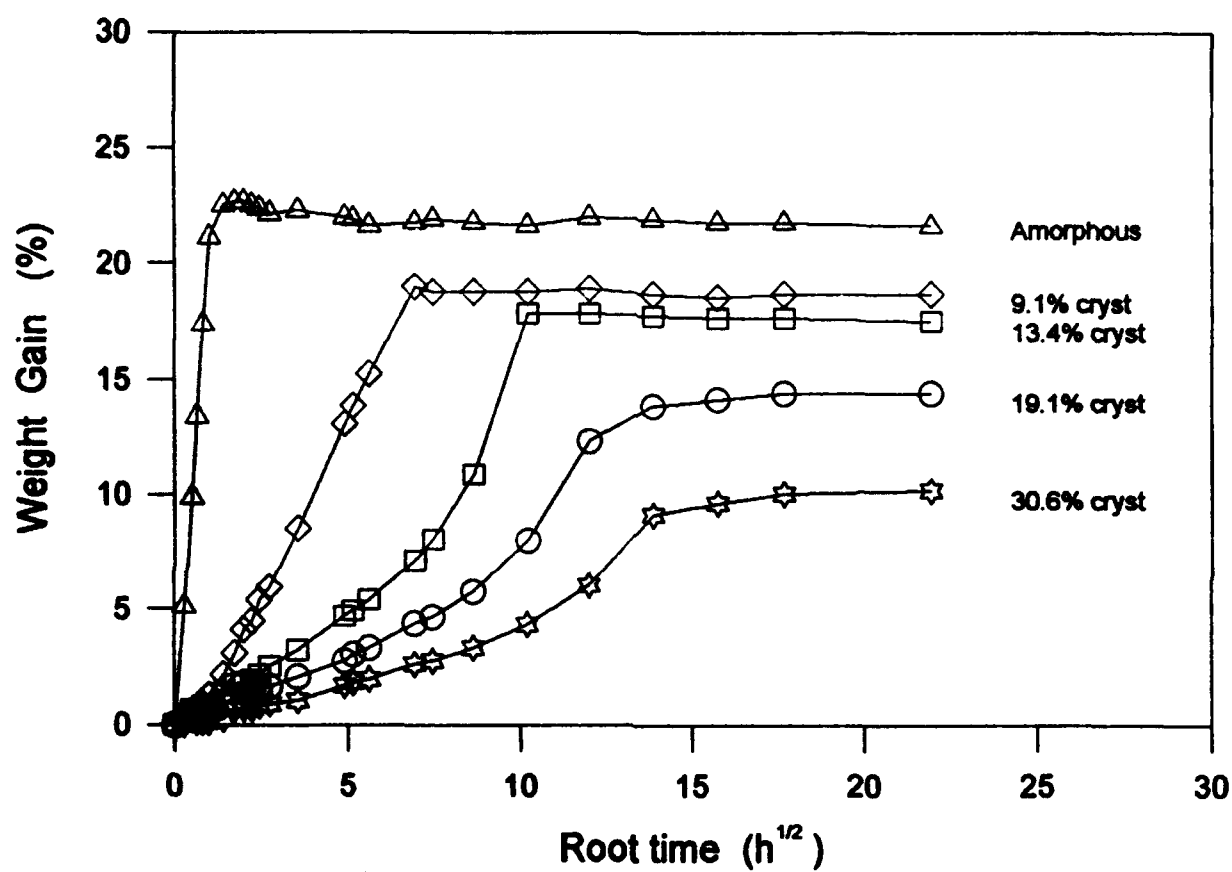
Figure 26   Sorption of carbon disulfide into PEEK at 30°C
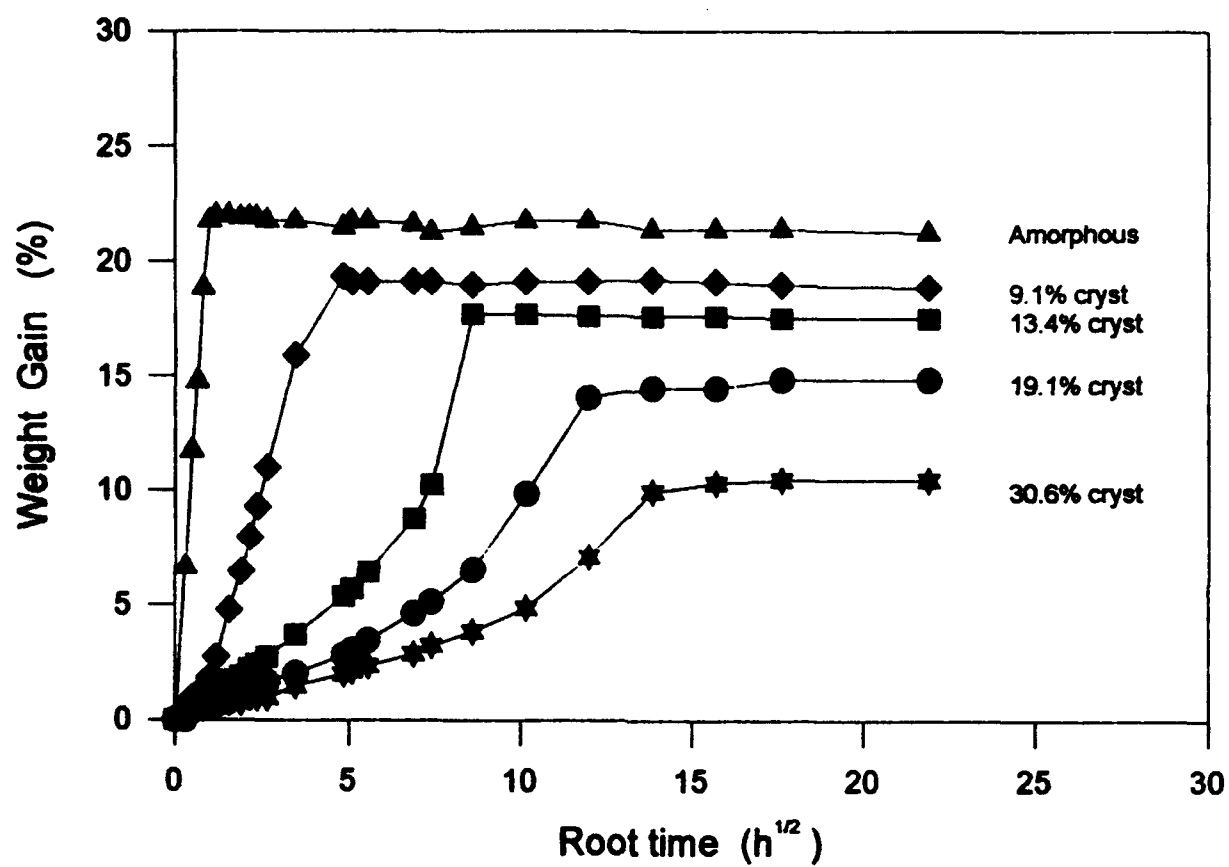
Figure 27 Sorption of carbon disulfide into PEEK at 35°C
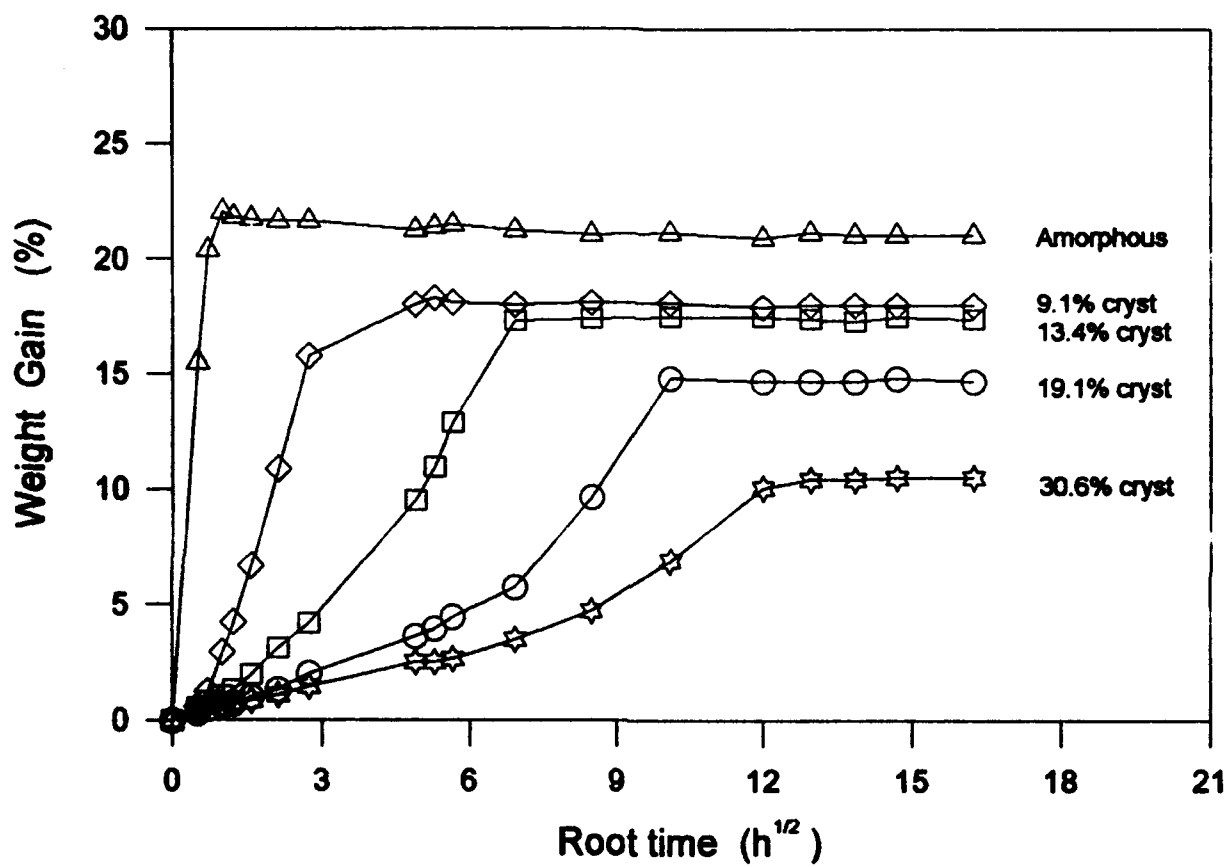
Figure 28   Sorption of carbon disulfide into PEEK at 40°C
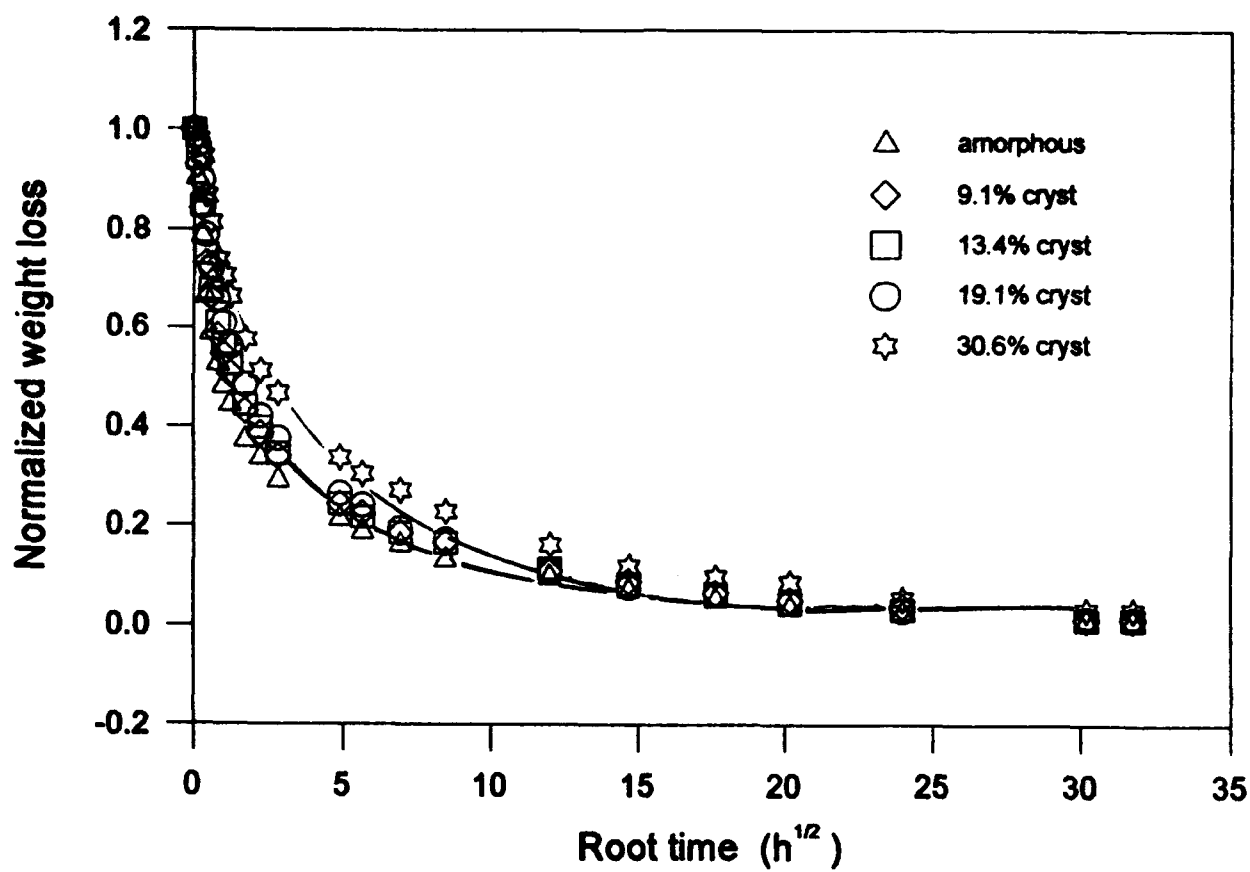
Figure 29 Desorption of carbon disulfide from PEEK.
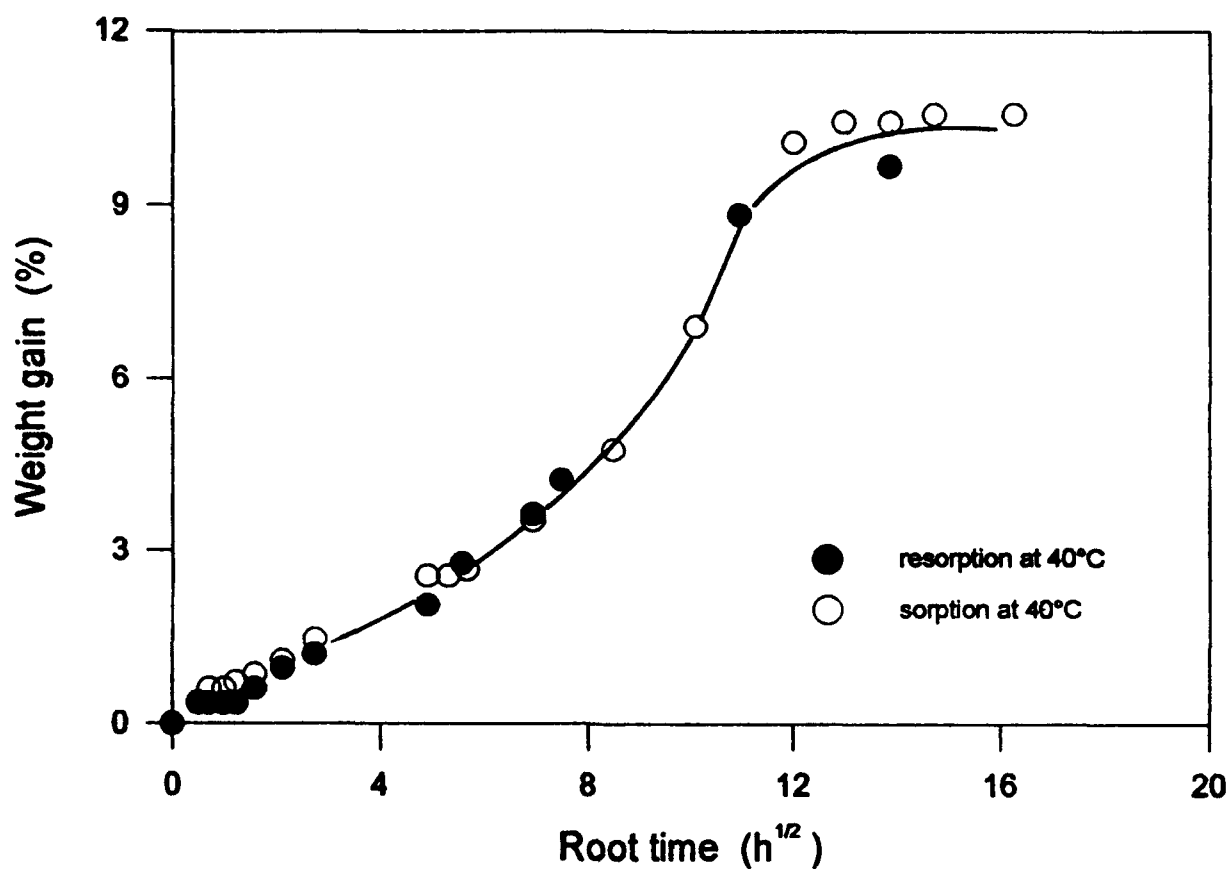Initial sorption: 40°C
Desorption: 50°C
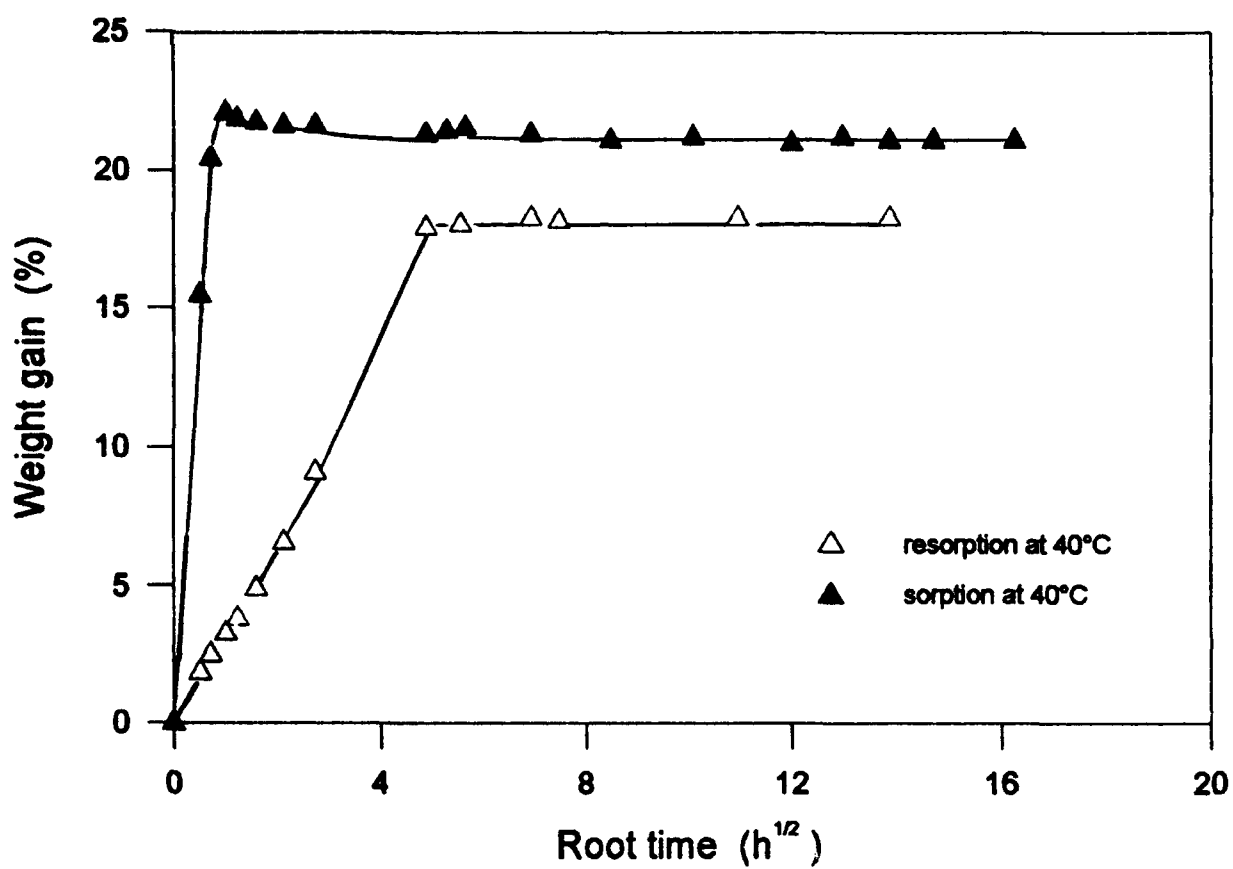
Figure 30 Sorption and resorption of carbon disulfide into initially amorphous PEEK
Sorption: 40°C; Desorption: 95°C; Resorption: 40°C.
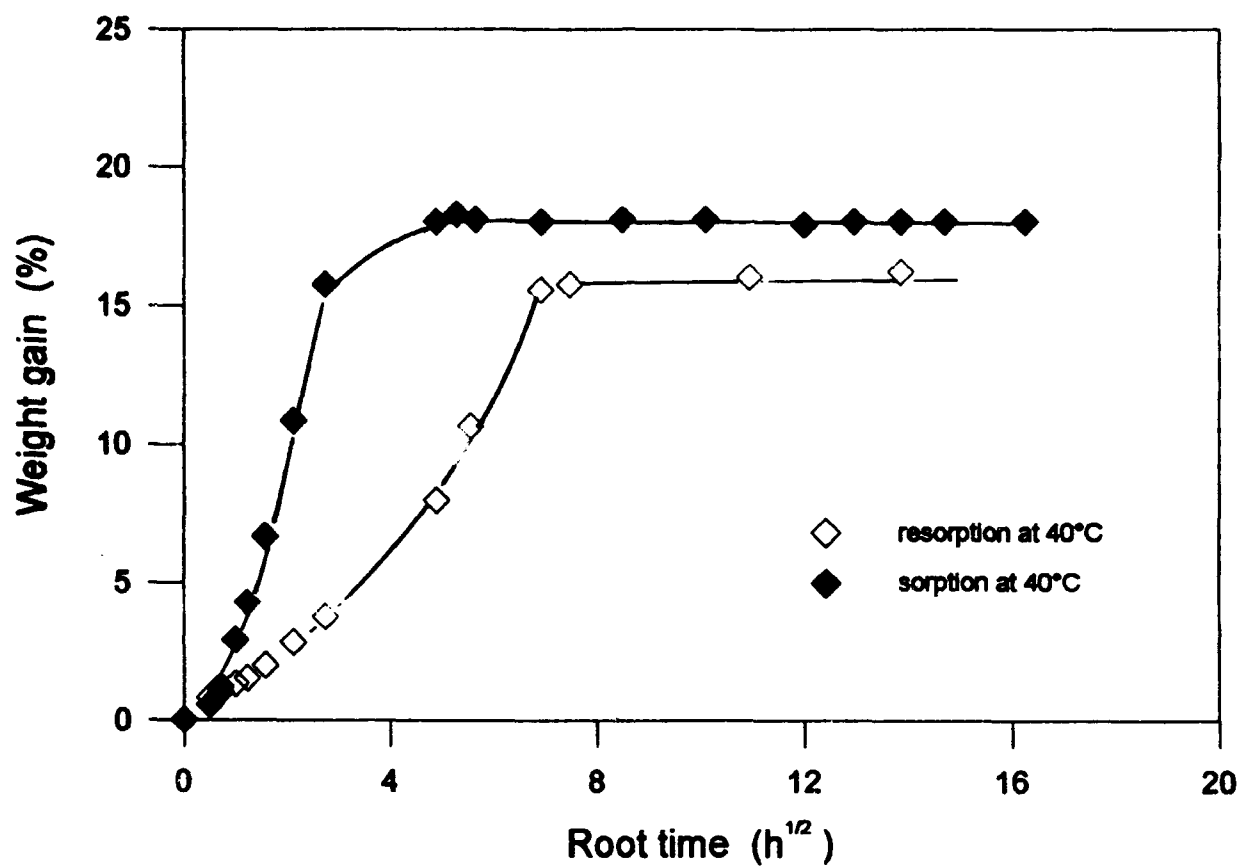
Figure 31 Sorption and resorption of carbon disulfide into initially 9.1% crystalline PEEK
Sorption: 40°C; Desorption: 95°C; Resorption: 40°C.
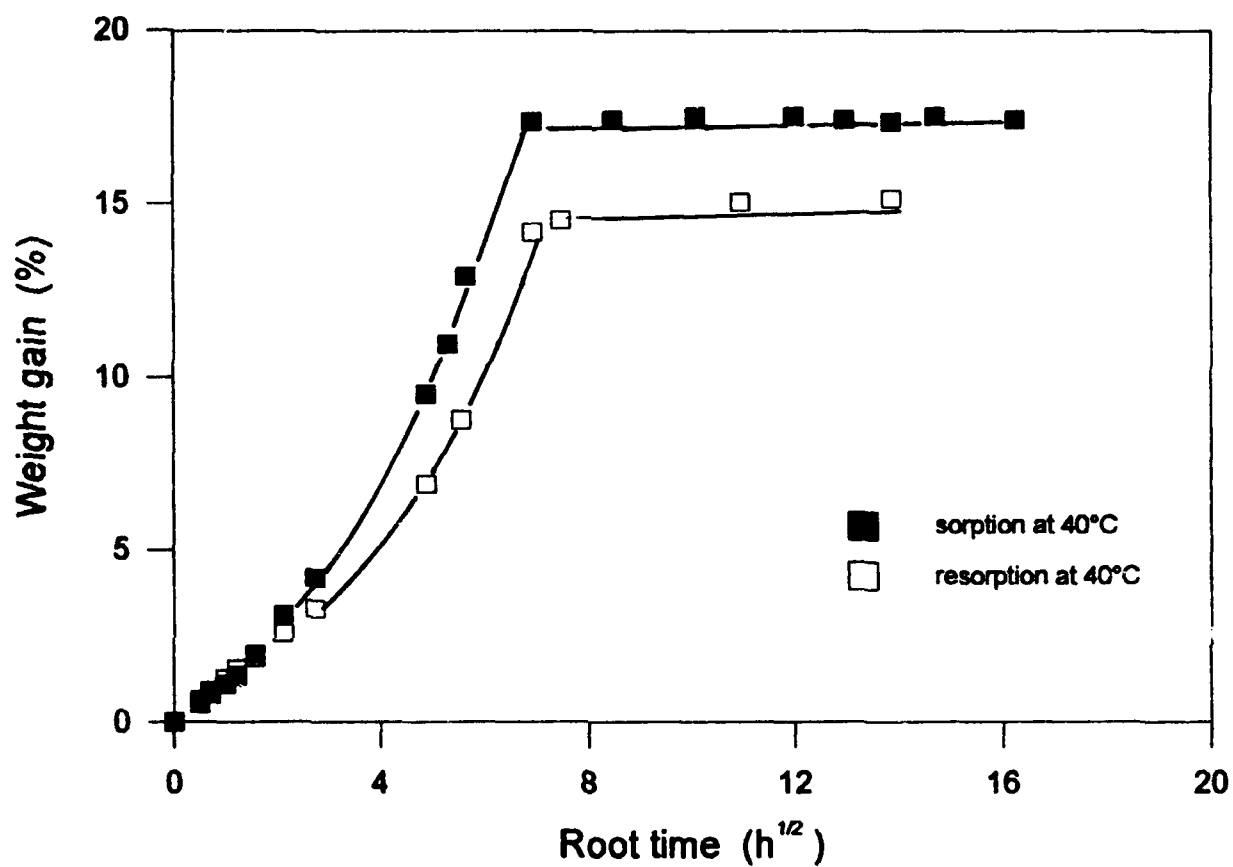
Figure 32   Sorption and resorption of carbon disulfide into initially 13.4% crystalline PEEK
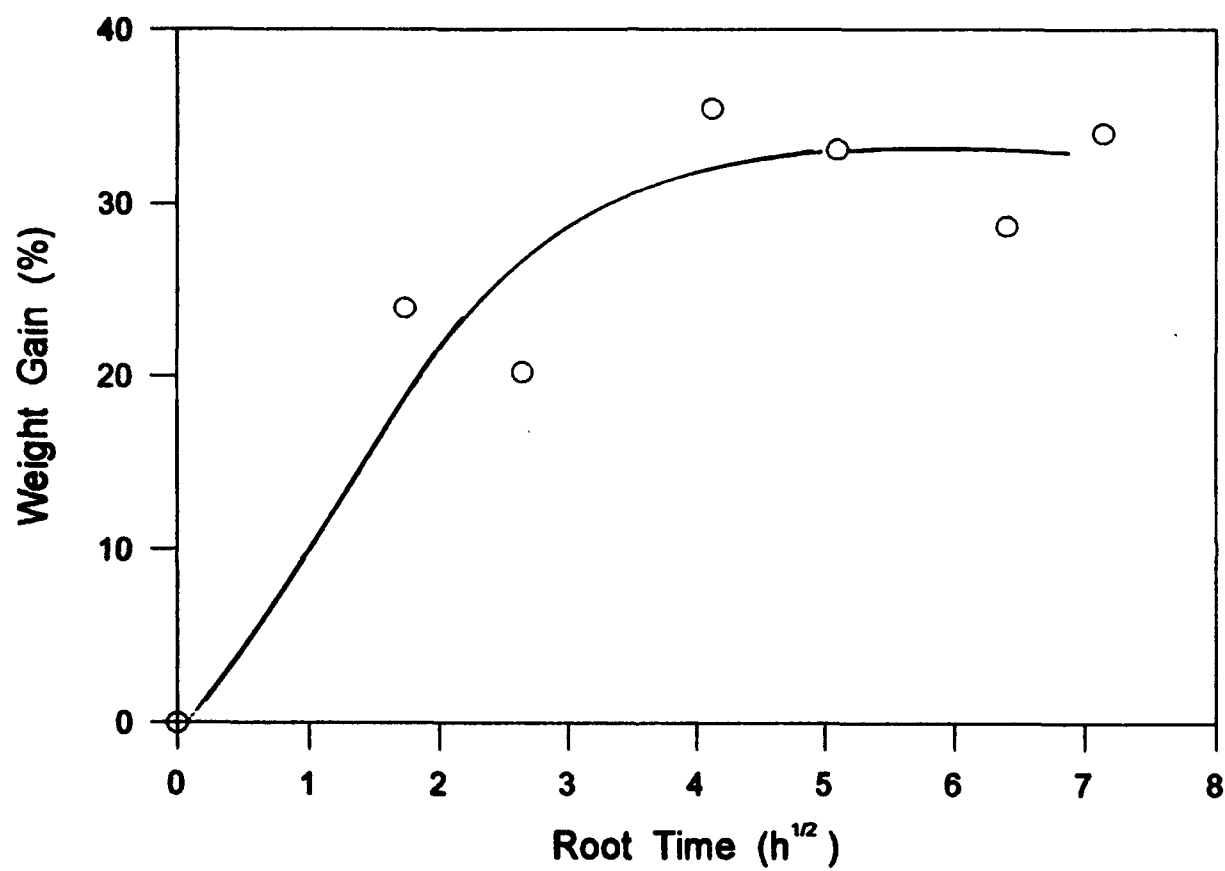Sorption: 40°C;   Desorption: 95°C;   Resorption: 40°C.
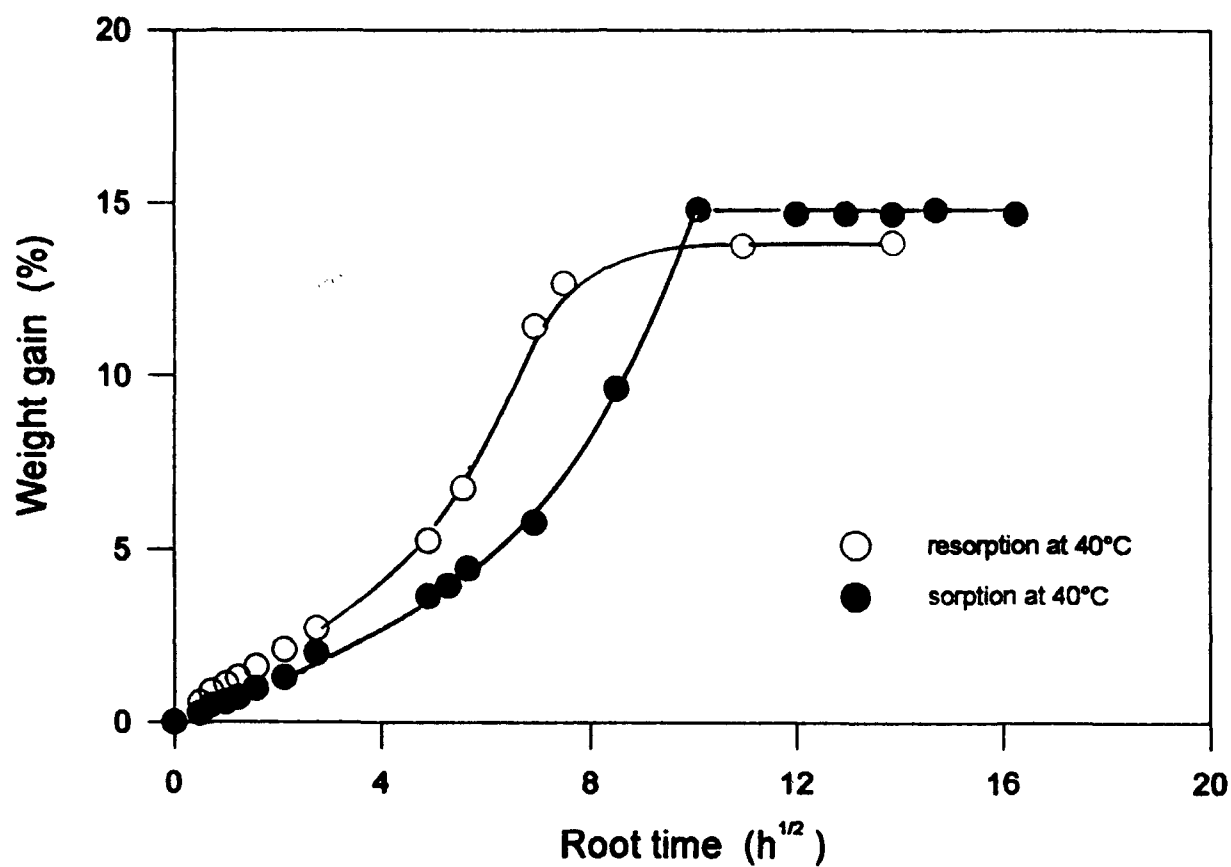
Figure 33 Sorption and resorption of carbon disulfide into initially 19.1% crystalline PEEK
Sorption: 40°C; Desorption: 95°C; Resorption: 40°C.

Figure 34 Sorption and resorption of carbon disulfide into initially 30.6% crystalline PEEK
Sorption: 40°C;   Desorption: 95°C;   Resorption: 40°C.

Figure 35   SEDS sorption of carbon disulfide in 29% crystalline PEEK
at 35°C: Applied stress: 30 MPa.
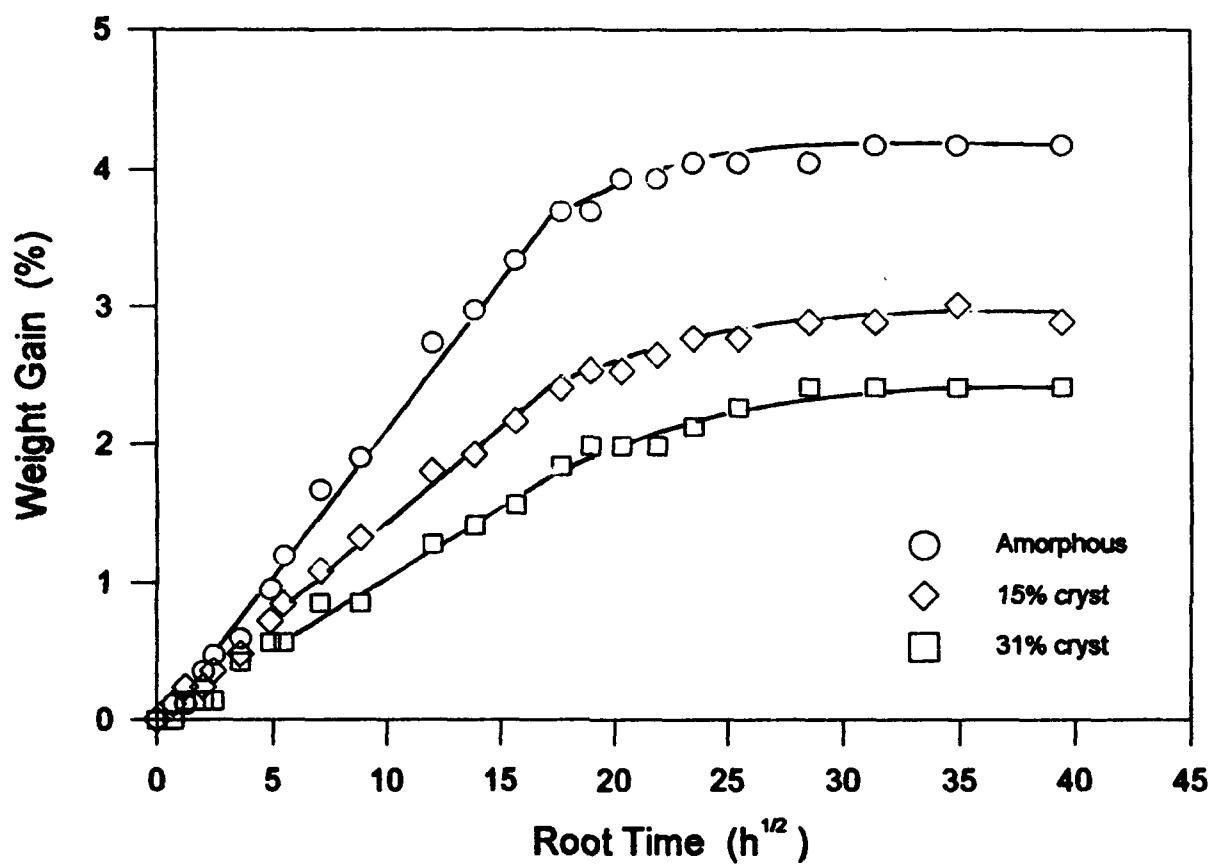
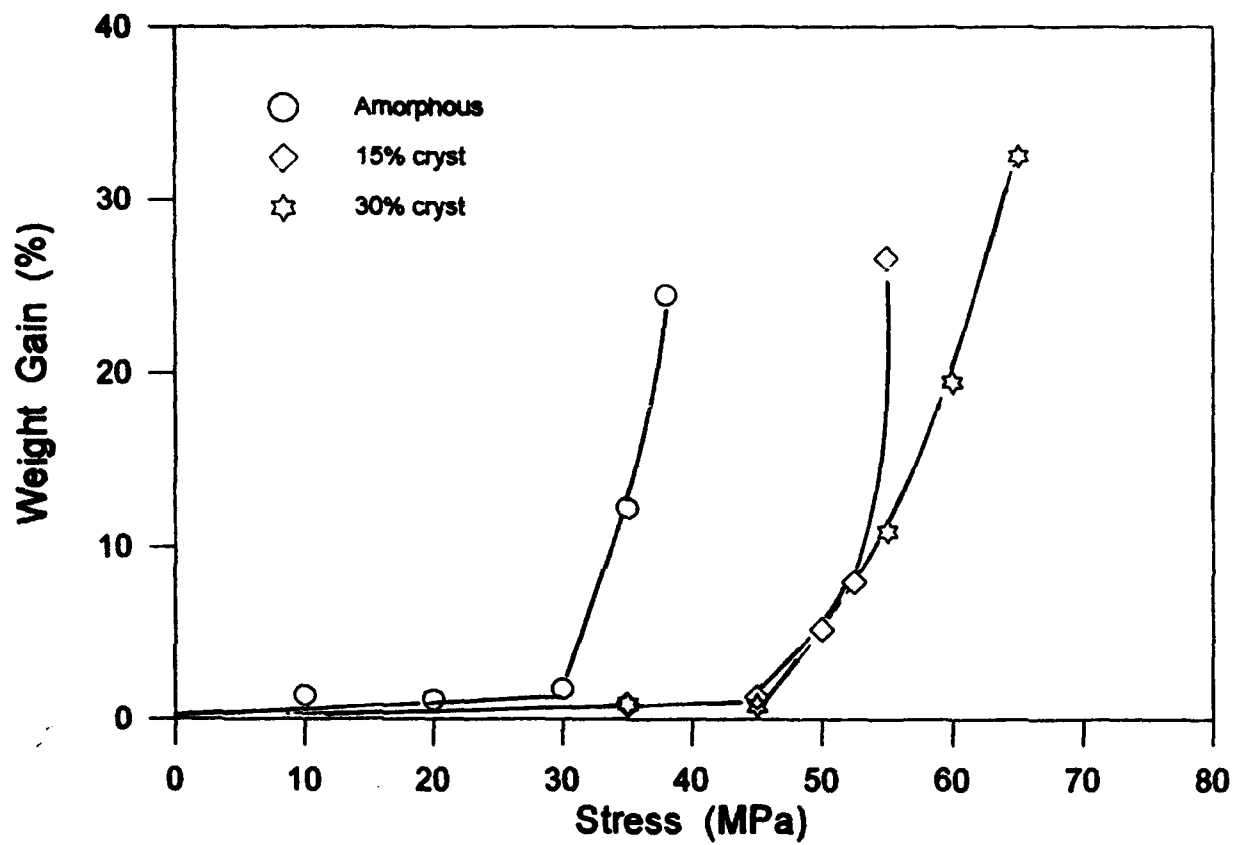Figure 36   Sorption of methanol into PEEK at 22°C.

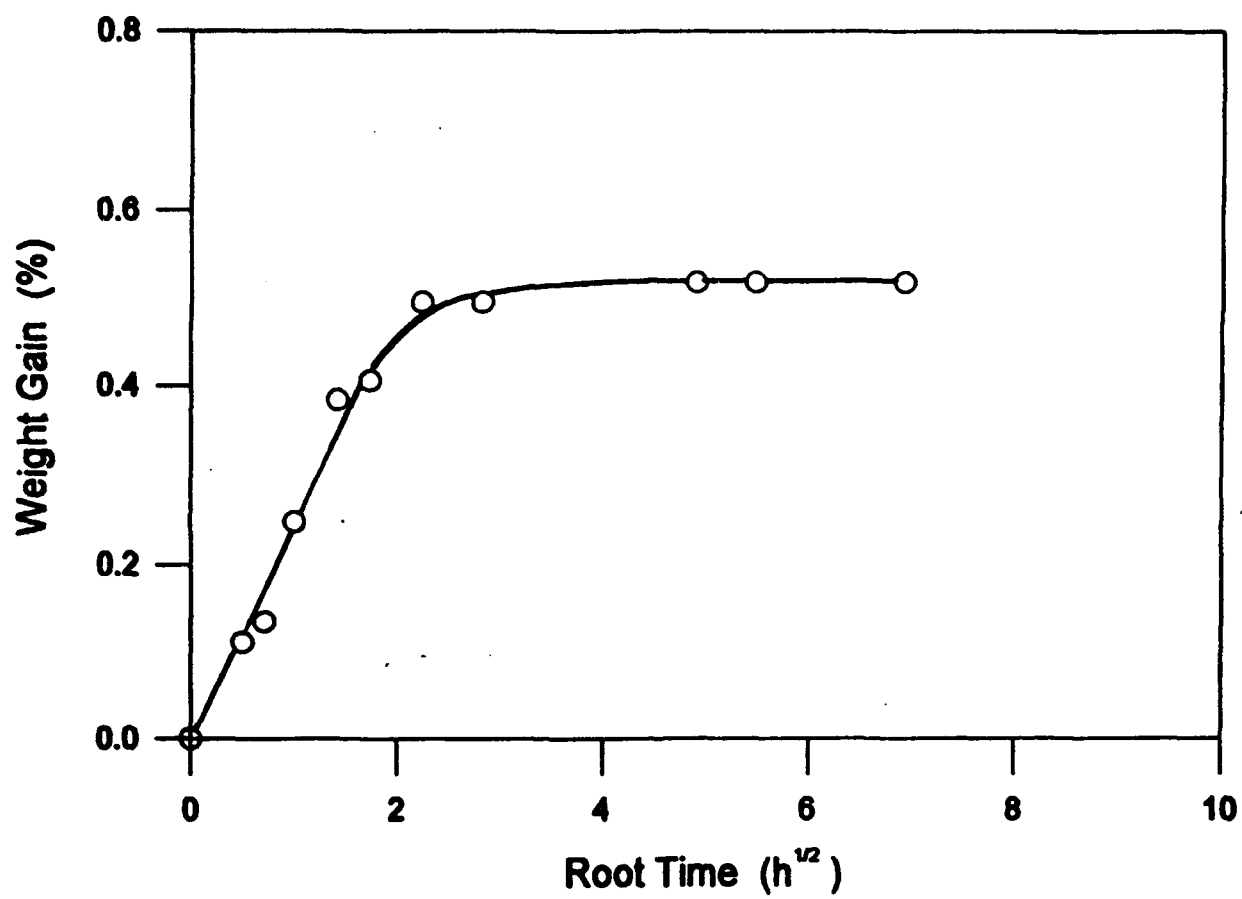**Figure 37   SEDS sorption of methanol into PEEK at 22°C (sorption time: 24 hours).**

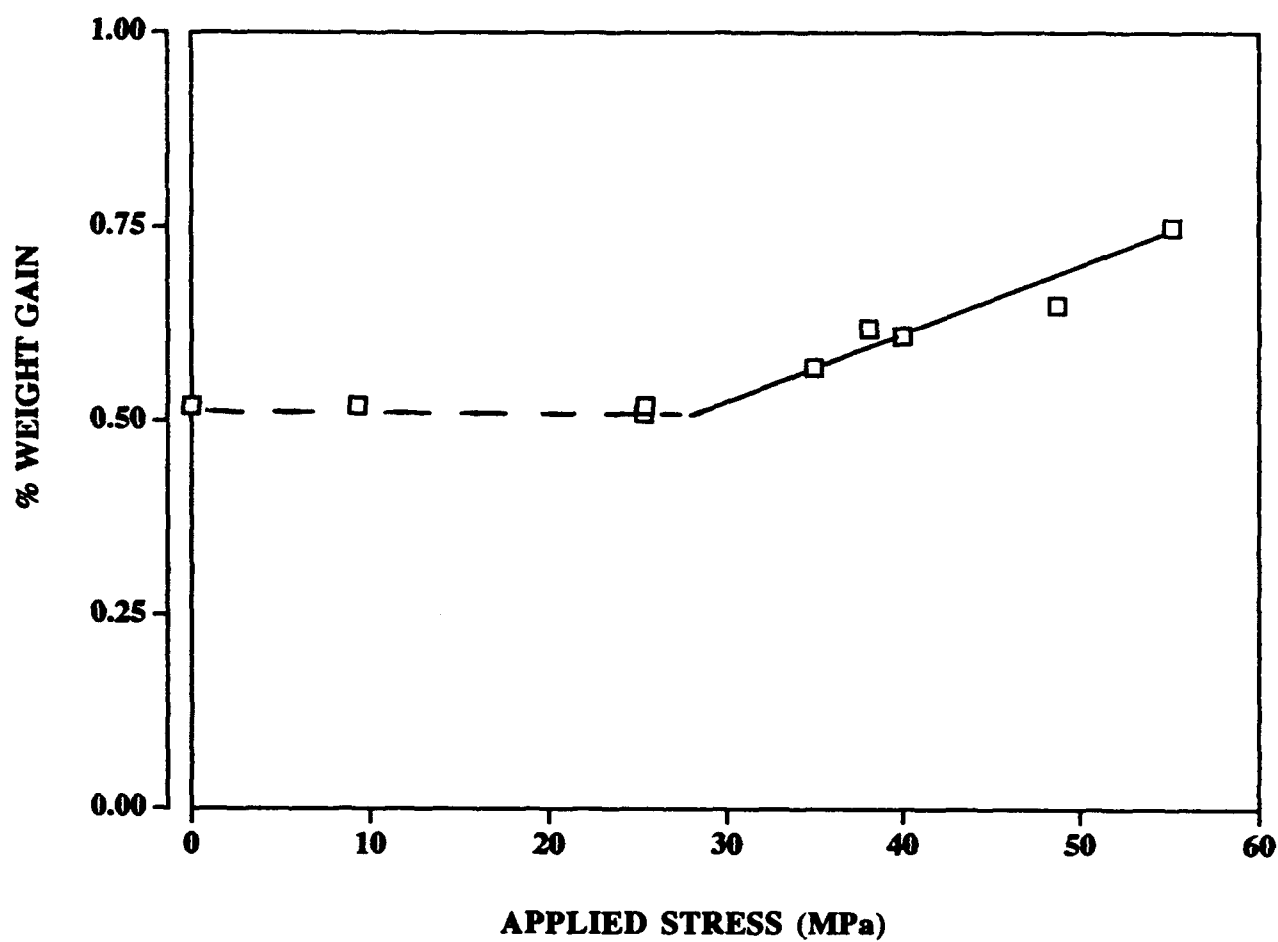Figure 38 Sorption of water by amorphous PEEK at 22°C.

Figure 39 Sorption of water in amorphous PEEK at 22°C as a function of applied stress.