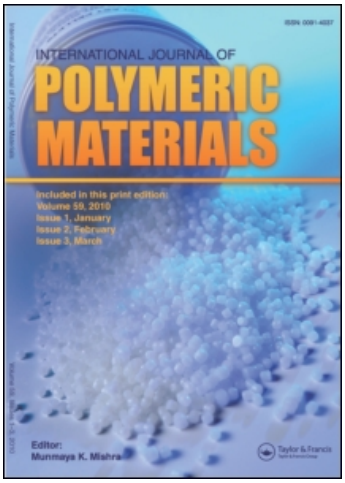


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# SEM Analysis of Polymeric Mechanical Failures in Polyetherimide

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# SEM Analysis of Polymeric Mechanical Failures in Polyetherimide

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Different modes of fracture, which consisted of tension, bending, impact, biaxial flexure, torsion, fatigue, and cutting, were selected to determine fracture surface characteristics of polyetherimide under controlled conditions. Fractography, examination of fracture surfaces, was performed using a stereomicroscope and scanning electron microscope (SEM) to characterize and compare modes of failure. The stressed samples exhibited ductility, deformation, and finally brittle fracture shown by a primary fracture surface: mirror, transition region with mists and hackles, and a rough region with Wallner lines. The impacted samples exhibited stress cracking from the point of impact. The cut sample exhibited tear characteristics. Stress corrosion cracking was exhibited by dissolving polyetherimide in a partially halogenated hydrocarbon, trichloroethane.

KEY WORDS Fractography, SEM, engineering plastics, fracture analysis



## INTRODUCTION

If external forces are made to act upon polymers, the polymer will first deform elastically or visco-elastically. If the load is removed, the deformation disappears. If the force exceeds a certain threshold, permanent, plastic, irreversible deformation occurs which is called yielding. Polymer chains tend to wander in many directions and become raveled and matted. When a stress is applied, these chains have the mobility to rearrange; thus, most polymers continue to deform for a long time after stress application while the chains untangle themselves. The mechanical properties of polymers are dependent on the flexibility of the bonds in the chains and the ease with which the chains can slide over one another during deformation.[1,2]

Polymers can have ductile or brittle fracture. Ductile fracture usually requires more energy than brittle fracture. Before rupture in a ductile fracture, there is considerable plastic deformation that is not recovered. In ductile fracture, the pieces usually are impossible to refit. Macroscopically, ductile fractures show a fibrous surface; while under the SEM, these fractures show uniform fiber pullout. Peaks and fibrils are characteristic SEM features of ductile failure.[1]

Brittle fracture requires less energy than ductile fracture. In brittle fracture the broken parts can usually be refitted together to the original dimensions; there has

been elastic behavior, not permanent deformation. Macroscopically, brittle fractures appear smooth; while under the SEM, these fractures display shorter isolated fiber structure characteristics. Microscopically, brittle failures have sometimes two fracture surfaces after separation, forming oval lids or torn-open blisters, steps and striped patterns. The rims of the microstructures are edged with fine beads and sometimes short fibrils. Brittle fractures have level brittle failure bands and sometimes splintering chips so that the direction of propagation can be determined. Very flat peaks and dimple structures are also observed. The main characteristic of embrittlement is smooth fracture surfaces divided into bands by steps.[1]

Cyclic stresses result in fatigue fracture and sample heating. This heat increases the mobility or stretching of the molecular chains and may cause many of the molecules to melt or soften. This softening or melting causes the surface characteristics of fracture to be rounded thus resembling continuous creep fracture. This change in state would also camouflage striations, crazing, and crack propagations. The softening of the surface's features shown as dimples and small indentations or voids are characteristic of creep fracture. When the crack propagation is not camouflaged, the surface appears crease-like and rounded with flap-like features, striations, between the propagating cracks. The roundness of features is again caused by the inherent heating due to fatigue testing of the sample.[1]

Tear fractures are characterized microscopically by V- or U-shaped ramps parallel to the crack propagation direction. The tips of the ramps point in the direction opposite to that of crack propagation.[1]

Polyetherimide is an amorphous high performance thermoplastic introduced in 1982 by GE Plastics under the trademark of Ultem. Ultem 1000, a low viscosity, unmodified, and unreinforced polyetherimide, was the material studied. This amorphous thermoplastic is characterized by its high strength and rigidity at elevated temperatures, long-term heat resistance, and highly stable dimensional and electrical properties combined with broad chemical resistance (most hydrocarbons, alcohols, and fully halogenated solvents and mineral acids), UV and gamma radiation resistance, and processability. Partially halogenated solvents can be good solvents for polyetherimides. It exhibits inherent flame resistance and low smoke generation without the use of additives, and is used in automotive and electronics parts, composites, and wire and cable insulation.[3-5]

Polyetherimide has a chemical structure based on repeating aromatic imide and ether units as shown in Figure 1. This commercial engineering plastics is prepared by nucleophilic aromatic substitution with the leaving group being activated by an

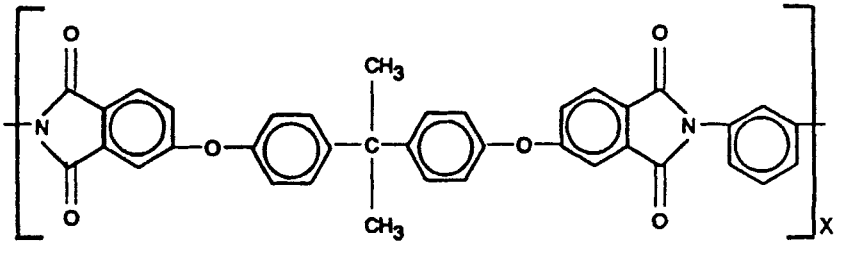


FIGURE 1 Structure of polyetherimide.

electron-withdrawing substituent. This polymer uses the two functionalities of the ether and the imide. The rigid imide groups provide the high-performance strength characteristics at elevated temperatures. The ether linkages give the chain flexibility that is necessary for good melt processability and flow.[3]

Some physical and mechanical properties are a specific gravity of 1.27, continuous-use temperature rating of 170°C to 180°C, and a glass transition temperature of 215°C. At 180°C, the tensile strength and flexural modulus remain in excess of 6000 and 300,000 psi, respectively. It can be readily processed on most conventional thermoplastic equipment. The resin must be dried thoroughly prior to melt processing. Injection molding uses a melt temperature of 327°C to 427°C and a mold temperature of 150° to 350°C. Extrusion, thermoforming, and compression molding are also used for producing components.[4,5]

## EXPERIMENTAL



The fracture surface was examined using a Hitachi S-450 scanning electron microscope at an accelerating voltage of 20 KV. Prior to examination, the fracture surface was coated with a thin evaporated layer of gold in order to improve conductivity of the examined fracture surface and prevent electron charging on the surface.

The tensile sample had dimensions of 100.59 mm length, 3.17 mm thickness, and 12.66 mm width. The length from the start to the end of the neck was 31.50 mm. A tensile bar was tested under tension by a standard Instron test. The specimen was extended at a constant speed of 0.254 cm/min for one trial and a constant speed of 25.4 cm/min for another trial.

The sample used for bending or flexure had dimensions of 126.73 mm length, 3.18 mm thickness, and 12.68 mm width. The specimen was placed in a vise and bent by holding the sample with a crescent wrench close to the clamped section and bending until fracture. This was three point loading. The Charpy Impact Test stresses a specimen in flexure by means of a swinging pendulum. Samples are notched to have stress concentrations for fracture. The test piece, a rectangular bar similar to the one used for bending fracture, was mounted on a span support and struck in the center on the opposite side of the notch by a swinging pendulum.

For testing biaxial flexure, a sheet of Ultem 1000 was supported on a hollow steel cylinder with an internal diameter of 50.8 mm and impacted by a striker with a hemispherical striking surface of 12.7 mm in diameter. The striker assembly slides freely in vertical guides and is released from a predetermined height to strike centrally on a specimen which is supported on the base of the equipment.

For torsion testing, a test piece, a rectangular bar, similar to the one used for bending fracture, was placed in a vise and twisted by rotation with a crescent wrench.

Fatigue testing involves the application of cyclic stresses. The sample used for the fatigue test was a tensile bar. The cyclic stresses applied were tensive (tending to pull the molecules apart) and compressive (tending to push the molecules close together).

A sample of the material was cut.

For solubility and possible stress corrosion cracking, a sample was placed in a beaker of trichloroethane for a few hours and then remained in the solution for an additional twenty-four hours.

## RESULTS AND DISCUSSION

### Tension

There are five principal types of behavior in the simple tensile test as follows: 1) uniform extension, 2) cold drawing, 3) necking rupture, 4) brittle fracture, 5) necking rupture of the second kind. The uniform extension is a consequence of the high extension of the molecules which occurs as the chains approach their maximum extension, and the molecules become oriented toward the direction of the applied force. This molecular orientation makes the specimen harder to extend. In polymers this is referred to as "orientation hardening" as opposed to "strain hardening" or "work hardening" in metals, since the polymers only become harder in the direction of the applied tension.[2,6,7]

"Necking rupture" is defined when the specimen necks and then breaks without restabilization of the neck. It has been noted that specimens which fail by necking rupture, occasionally whiten in the neck. This white coloration is usually attributed to the occurrence of very small voids, presumably as a consequence of the triaxial tensile component of the applied tension. This occurrence of voids is understood by considering the stresses on the surface. The material tries to maintain a constant volume under extension, but because neighboring material which has not extended prevents contraction, tensile stresses appear in all directions. These triaxial tensile stresses naturally cause cavitation or microvoiding.[6]

Similarities exist between necking rupture and brittle fracture by four important features: 1) The yield strain has been exceeded in part of the specimen in both cases, 2) The fracture surface in both cases consists partly of oriented polymer materials, 3) The material on both fracture surfaces is partially void, 4) Because of the restraining influence of the neighboring material, the stress system in both modes of fracture have a high triaxial tensile component. The main difference between these two forms of fracture is the depth of material in which the strain exceeds the yield strain. It is much smaller in brittle fracture than in necking rupture. Therefore, brittle fracture can be considered to be an extremely localized form of necking rupture and involve deformation instabilities. Both instability of deformation and fracture toughness are dependent on the rate of orientation hardening beyond the yield point.[6]

As the primary crack advances, secondary cracks may originate. The interactions of these primary and secondary cracks create hyperbolic or parabolic fracture traces, known as Wallner lines. As the crack progresses further, its velocity increases and the surface becomes rougher. The mirror region indicates the primary fracture source.[2,7] In necking rupture of the second kind, the sample becomes very thin at higher temperatures and lower stresses.

The fracture surface is normal to the applied tensile stress. When a tensile specimen fractures in a brittle manner, four characteristic different regions exist

as follows: a) primary fracture surface, b) mirror, c) transition region with mists and hackles, and d) rough region with Wallner lines.[2,7] The sample displayed uniform extension until a load of 189.5 psi was applied. At this loading of 189.5 psi cold drawing was observed. The deformation of the polymer was localized near the narrowest section and a neck formed. The neck length was 85 mm at a constant speed of 0.254 cm/min. When the constant speed was increased to 25.4 cm/min, the neck was 40 mm. At a loading of 199.7 psi the polyetherimide fractured. An increase in speed demonstrated a decrease in the length of the neck, which is to be expected since the molecules do not have as much time to untangle.

The characteristic behaviors of a polymer in tensile test were observed in the sample: The polyetherimide first uniformly extended, then experienced cold drawing with the formation of a neck, and then fractured. A small whitened area indicating voids of necking rupture was observed. The mirror area covered 3/16 of the fracture surface, while the mists and hackles found in the transition region along with the hyperbolic or parabolic fracture traces known as Wallner lines covered 4/16 of the fracture surface. The rough region covered 9/16 of the fracture surface. The experimental conditions did not permit the observation of necking rupture of the second kind. Using a SEM, the mirror region (Figure 2), the transition region (Figure 3), and the rough region (Figure 4) were distinguishable.

White spheres were observed throughout the samples under SEM investigations as shown in Figure 2. These white spheres had their highest concentration near the fracture origination. A possible explanation for these minute particles can be related to entropy. It is possible that the polymer chains under stress break away from one another and form what may be referred to as "strings" or long microfibrils. These microfibrils want to have the lowest possible energy under stress so they form spheres. This process would be the most obvious nearest the fracture origination since the stresses are concentrated at this point and more microfibrils would be formed; thus, the formation of many spheres.[8]



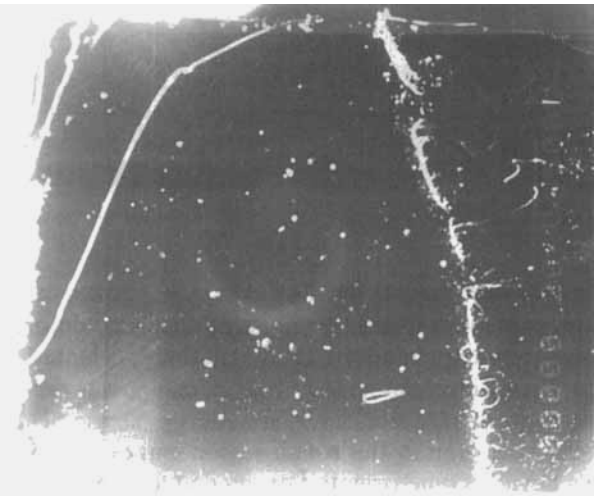

FIGURE 2 SEM photograph of mirror region of tensile fracture.

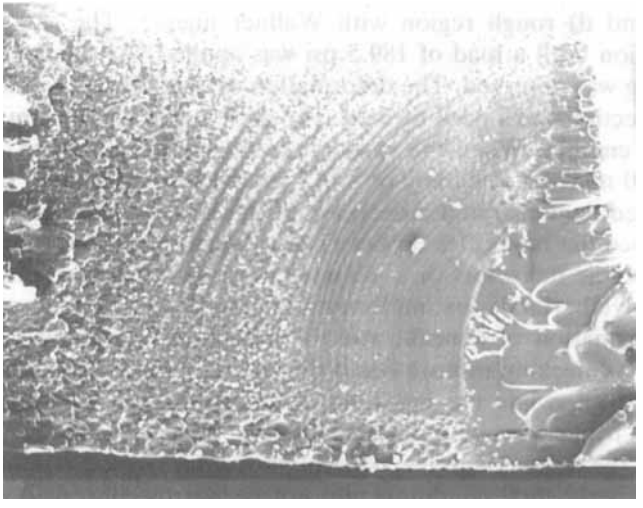

FIGURE 3 SEM photograph of the transition region of tensile fracture.

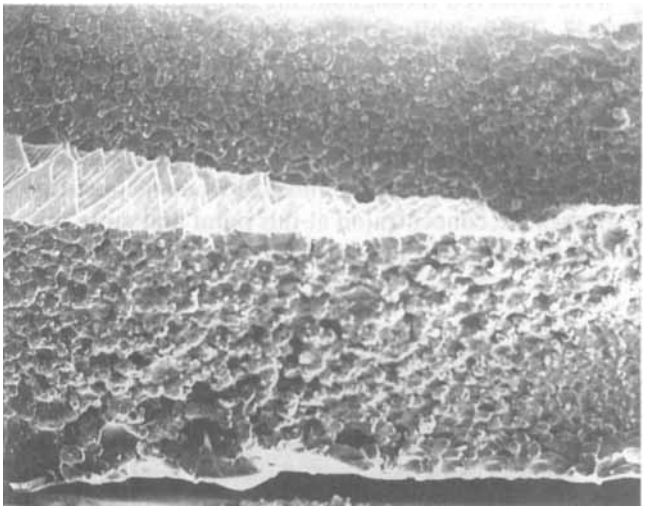

FIGURE 4 SEM photograph of the rough region of the tensile fracture.

The white threads that appear on the surface are crazes as shown in Figure 2. Crazes are minute surface cracks with enhanced localized deformation or yielding. These crazes constitute expanded material containing oriented fibrils interspersed with small (1 to 2 μm) interconnected voids. Crazing is a precursor of crack formation and represents a large sink for strain energy release. The differences in the appearance of the specimen in the rough region can be attributed to this crazing where the fibrils have become oriented or aligned as shown in Figure 4. Since the craze is weaker, it is an ideal path for crack propagation which is displayed in the fracture on this surface. In the photograph, the raised area and the matching valley

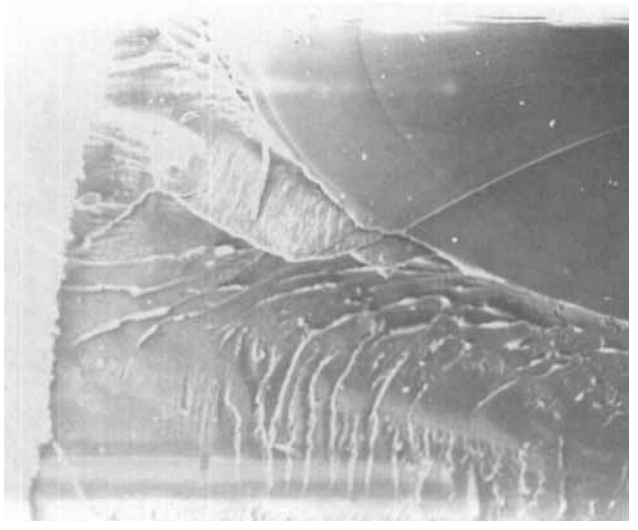

FIGURE 5 SEM photograph of mirror and rough region of bending fracture.

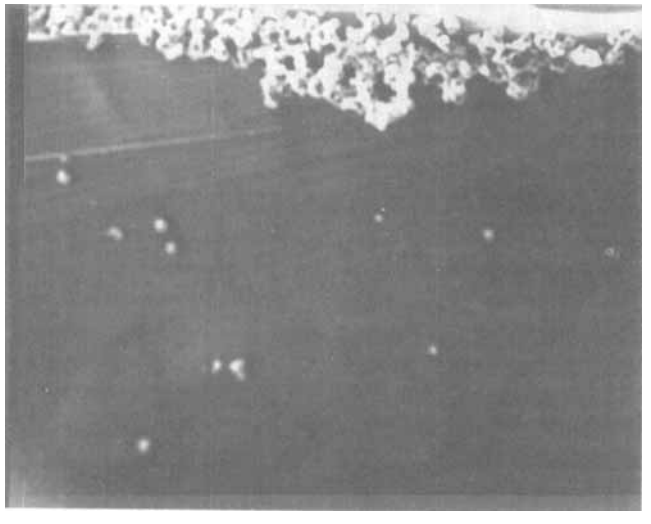

FIGURE 6 SEM photograph of white spheres concentrated at fracture origin in the mirror region of the bending fracture.

where the fracture occurred can be observed. The darker areas on either side of the lighter craze area represent dimples, voids, and unoriented chains.[8]

### Bending and Torsion

The sample showed uniform extension and deformation until fracture. The deformation was permanent since the fractured parts still had curvature after rupture. The fracture surface was very simple, mostly a mirror with a small rough region. The specimen twisted through 360° before fracture. The material remained per-

FIGURE 7 SEM photograph of the bending fracture surface.

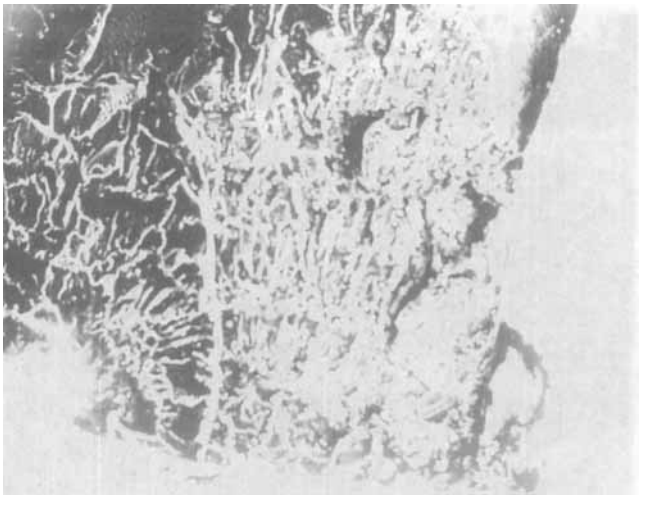

FIGURE 8 SEM photograph of notched edge of Charpy impact fracture surface.

manently deformed and experienced brittle fracture. When another test specimen was used under the same experimental conditions with both torsion and bending, the sample fracture was at 135°. The fracture from torsion with bending was also brittle, and the material was permanently deformed. With two modes of fracture, failure occurred sooner.

The characteristics of brittle fracture are also observed for rupture by bending. There is a large mirror region surrounding the origin. Figure 5 is a SEM photograph of a part of the sample near an edge which shows the mirror, mist, hackles, and rough region. A craze can be noted running from upper right to

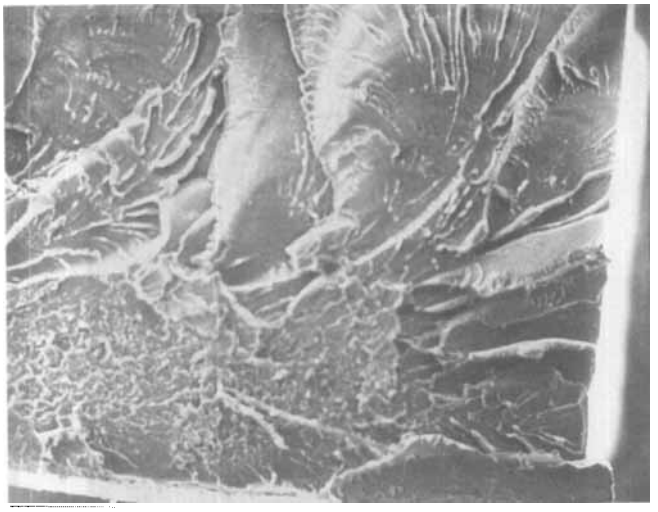

FIGURE 9 SEM photograph of notched edge at higher magnification.

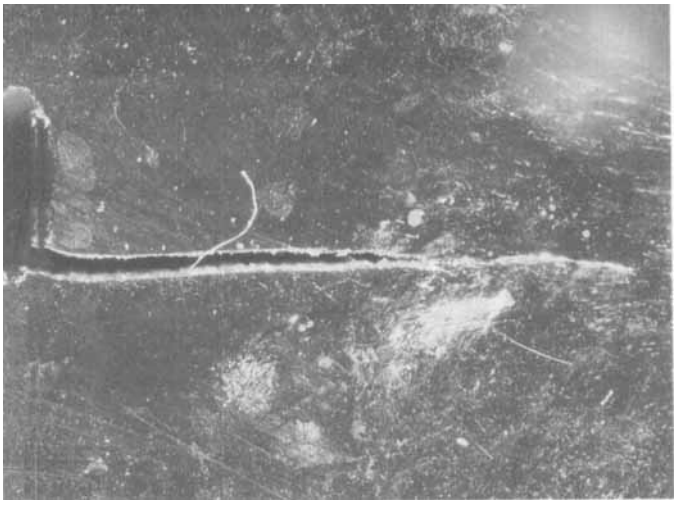

FIGURE 10 Stereomicroscope photograph of impacted surface in biaxial flexure.

lower middle. Level brittle failure bands can be observed in the rough region. The parallel fracture paths combine in the direction of crack propagation. Concentric beach marks can also be observed in the rough region. These marks lie at right angles to the fracture bands.[1,7] White spheres are again present throughout the sample, and they are concentrated at the fracture origin in the mirror region as shown in Figure 6.

A pronounced void was revealed in the sample at the upper left side of the slightly mirrored fracture surface in Figure 7. Crazing and fracture bands can be observed at the edge of the mirror. A wavy formation of a tear fracture can also be noted in the SEM photograph shown in Figure 7.


FIGURE 11 SEM photograph of fatigue fracture surface ($X$ = 39).

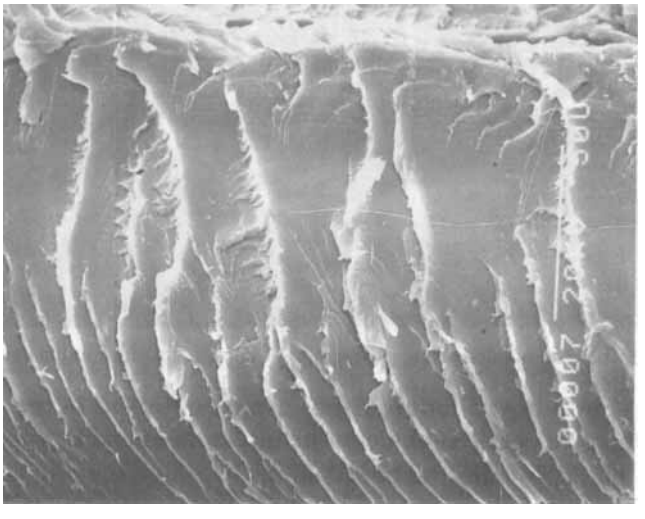

FIGURE 12 SEM photograph of fatigue fracture surface ($X$ = 670).

The characteristics of failure are similar for samples fractured by bending and torsion to those of tension. These samples exhibited ductility, deformation, and finally brittle fracture shown by a primary fracture surface, mirror, transition region with mists and hackles, and a rough region with Wallner lines.

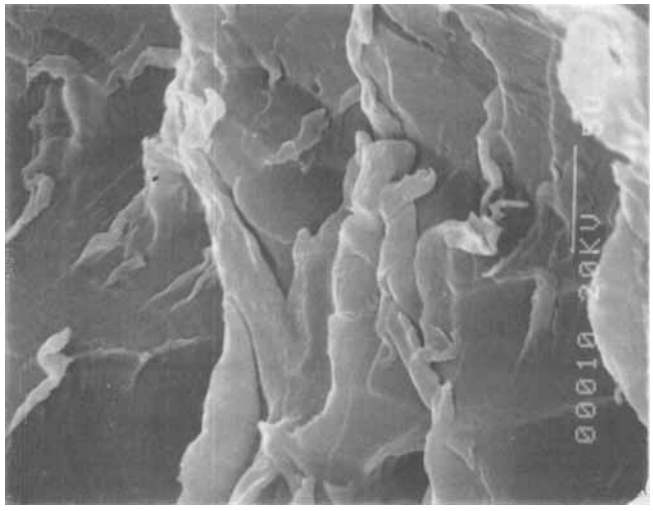

FIGURE 13 SEM photograph of fatigue striations ($X$ = 4100).

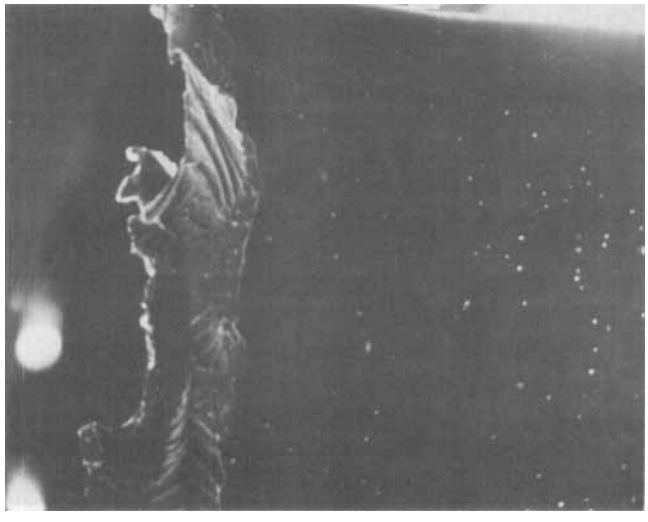

FIGURE 14 SEM photograph of tear fracture caused by cutting.

### Impact and Biaxial Flexure

The notched samples used in impact testing should show the natural crack (notch) increasing in length. The energy needed to create this new surface comes from the strain energy of the sample. The notch represents a point of stress concentration. These samples should exhibit crazing and cracking and brittle fracture. In this mode of fracture, the natural crack (the notch) increases in length. Characteristic fine, knot-like structures and short peaks of brittle fracture can be observed in the SEM photographs. These structures and peaks radiate out from the crack origin at the notched edge as shown in Figure 8.[1,9] Under the SEM, brittle impact failures display

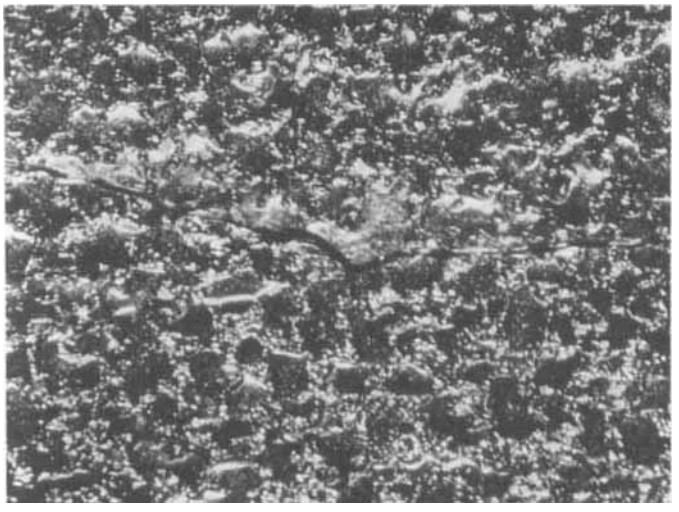

FIGURE 15 Stereomicroscope photograph showing stress corrosion cracking.

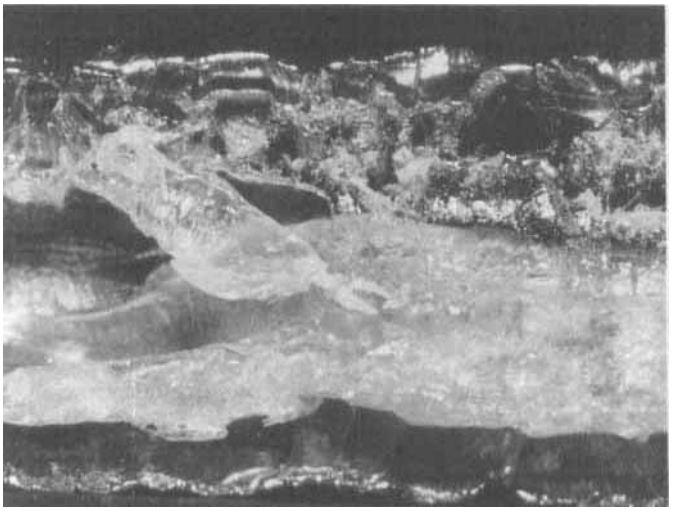

FIGURE 16 Stereomicroscope photograph upon dissolution in trichloroethane.

a "flaky" fracture surface morphology over the entire surface and a feathery texture of the concave areas within the fracture paths as shown in Figure 9.[1]

In biaxial flexure, the striker showed impact on the surface with some crazing, but no cracking, with the presence of white spheres and a similar surface to the Charpy Impact specimen. Upon notching this same sample, crack propagation was noted because of stress concentration at the notch as shown in Figure 10.

### Fatigue

Fatigue fracture results from a large number of cyclic stresses. The sample was subjected to cyclic stresses at 6 cycles/second for approximately 6 hours before

failure. This amounted to $1.3 \times 10^5$ cycles, which is considered to be a low value for fatigue failure. The stress is far below that needed for yielding. The repetitive nature of fatigue causes fracture since a number of the macromolecules are ruptured during each cycle. As with other modes of fracture, the fatigue sample will show diffusion of the molecules, disentanglement, fibrillation, and chain scission, which appear under microscopic observation as crazes, shear bands, and voids respectively.

Fatigue fracture is dependent on time. The first phenomenon observed is crazing or localized yielding which appears as white lines. The second phenomenon is whitening or microvoiding, and the third is necking, followed by fracture. The three principal mechanisms that contribute to fatigue failure are as follows: 1) thermal softening, 2) excessive creep or flow, and 3) initiation and propagation of cracks. Thermal softening is caused by the dissipation of mechanical energy as heat. The temperature of the sample rises because of high internal friction and the characteristic low thermal conductivity of polymers. Creep or plastic deformation is caused by the disentanglement and rearrangement of the macromolecules. The crack growth is parallel to the load direction and proceeds across crazes. Characteristics of brittle fracture should be observed in fatigue failure as mirror, mists, stress whitening, striations, and crazing.[6,9-12]

Disentanglement and chain scission appear under microscopic observation as crazes, shear bands, and voids. The fatigue fracture surface displayed the crack propagation by white lines, crazes, parallel to the direction of the growth of the crack, with smaller parallel lines perpendicular to the crack propagation. These smaller parallel lines are referred to as fatigue striations. Within these striations, secondary cracks can also be observed. Each striation represented the incremental advance of the crack front as a result of one loading cycle.[8] Crazes and fatigue striations are shown in Figure 11. Thermal softening which gives rise to very rounded surfaces is usually observed in fatigue failure. This polymer is heat resistant; therefore, the features were not very rounded. The fatigue striations appeared crease-like and rounded with flap-like features as shown in Figure 12 with further magnification in Figure 13. Dimples and small indentations or voids are also noted under microscopic investigation as polymer chains were pulled apart.



### Cutting

A cut sample should exhibit characteristics of a tear fracture. These characteristics are ramps showing direction opposite to the crack propagation with walls that have been pulled and strained. SEM investigation of the cut surface showed characteristics of a tear fracture: the U- or V-shaped ramps, whose tips point in the direction opposite to crack propagation and walls which have been pulled up forming beads with wavy crests[1] as shown in Figure 14. The presence of white spheres can also be observed.

### Stress Corrosion Cracking

Stress Corrosion Cracking from dissolving the sample in a solvent should exhibit a crack on a highly dimpled surface,[1] as was observed in Figure 15. If the sample

was allowed to remain in the solution of trichloroethane for a long period of time, dissolving of the sample occurred as shown in Figure 16.

## CONCLUSION

As an engineering plastics, polyetherimide exhibited characteristic fracture surfaces under all the modes of fracture tested: tension, bending, impact, biaxial flexure, torsion, fatigue, and cutting. Ultem 1000 is an amorphous thermoplastic and as such processes no crystalline areas and much entanglement and flexibility of its molecules. These polymeric characteristics lead to a conclusion of a great deal of inherent deformation and lack of crack propagation due to imperfections or changes in structure. The smooth fracture surface divided into bands by steps with short fiber structures could be refitted, thus indicating brittle fracture.

In non-impact modes of fracture, the same characteristic behavior of brittle fracture was observed. Ultem deformed elastically or visco-elastically at the beginning of stress application due to disentanglement and diffusion. This appeared as necking or a decrease in dimension perpendicular to the applied stress. Whitening was noted at the point of fracture because of the occurrence of very small voids created by triaxial tensile stresses. Four characteristic regions were observed under SEM investigation: primary fracture surface, mirror transition with mists and/or hackles, and rough with Wallner lines (the interaction of primary and secondary cracks). Crazes, minute surface cracks, and white spheres, the lowest entropy form of individual molecular chains, were also observed. Cracks formed along crazes because of the inherent weakness of these minute cracks or oriented or aligned molecular chains.

The impacted samples had the same characteristics of brittle fracture. Since failure was sudden, the surface characteristics were smaller than in the non-impacted samples. The surface is called "flaky and feathery" with short peaks. The concentration of stresses at the notch led to extension of the notch with crazing and cracking. Again white spheres were noted.

The fatigue samples exhibited crazes, fatigue striations, and a rough region with white spheres. The fatigue striations showed microscopic features that were crease-like, rounded, and flap-like. Dimples and voids were also noted due to separation of the polymer chains. Heating of the sample during fatigue testing was not noted.

Under SEM investigation U- or V-shaped ramps were observed in the cut sample. Stress corrosion cracking was observed upon solution in trichloroethane, a partially halogenated hydrocarbon. Polyetherimide was an excellent amorphous polymeric material for fractography. It was difficult to fracture, but gave characteristic macromolecular surfaces for identification of brittle fracture.

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