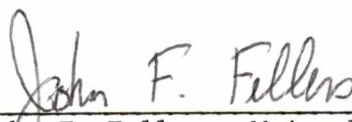


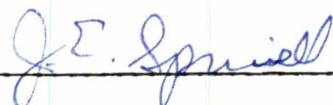
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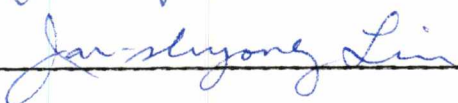
I am submitting herewith a thesis written by Jeong S. Lee entitled "SAXS Study of Failure Mechanisms in Kevlar^R Fiber Reinforced Epoxy Composites." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.



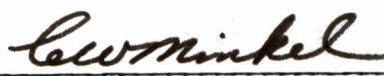
John F. Fellers, Major Professor

We have read this thesis and
recommend its acceptance:





Accepted for the Council:



The Graduate School

SAXS STUDY OF FAILURE MECHANISMS IN
KEVLAR^R FIBER REINFORCED
EPOXY COMPOSITES

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Jeong S. Lee

March 1984

DEDICATED TO MY PARENTS

AND TO SUE

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ABSTRACT

The failure mechanisms of the Kevlar^R 49 fibers, the epoxies and the uniaxial Kevlar^R 49 fiber reinforced epoxy composites under tensile loads have been studied using the 10 meter Small Angle X-ray Scattering (SAXS) facility at the National Center for Small Angle Scattering Research and the scanning electron microscope (SEM) at The University of Tennessee, Knoxville. The behavior of specimens of uniaxial Kevlar^R 49 fiber reinforced epoxy with various fiber orientations has also been studied under tensile load using an Instron Mechanical Tester.

The results show that the Kevlar^R 49 fibers fail due to increases in the volume fractions of microvoids and enlargements of larger microvoids along the fiber axis direction. Degradation of Kevlar^R 49 fibers was accompanied by roughening of the surfaces and by decreases in the mass densities. The epoxies and the composites failed in a catastrophic dynamic process, the crack originating from the surface flaws or the air bubbles entrapped in the epoxies during the curing process. The SEM investigations on the failed composites revealed fiber-splits and fiber-pullouts. The results of mechanical tests showed that the composite moduli, the composite ultimate strengths and the elongations at break decrease as the angle between the fibers and loading axis increase. The maximum work theory fitted well with the experimental ultimate strength results of the composites.

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CHAPTER I

INTRODUCTION

Although composites have been in use for considerable time and their usage is expected to grow due to their weight savings in the aerospace and auto industries, the properties of these materials are not as well characterized as the conventional materials. The unique properties of Kevlar^{R1} [poly(p-phenylene terephthalamide), E. I. duPont de Nemours and Co.]/epoxy composites make them attractive for use in many applications. However, these materials have received very little attention in the literature.

It is well known that the strength of a material is sensitive to its structure, as opposed to quantities such as Young's modulus and density which are relatively structure-insensitive. Despite these facts there has been relatively little work done which relates macroscopic material strength to material structure. The study of strength has generally proceeded on two levels: the continuum, in which the material is considered to be homogeneous, and the microscopic and submicroscopic, in which one attempts to recognize the fine details of the material structures. There has been relatively little work done in relating these two approaches.

Also understanding of the fracture behavior of composites is important to improve design efficiency and reliability. This demands a fundamental understanding of how the fracture process initiates and progresses to final failure.

¹Superscripted R indicates registered trademark.

It is the purpose of this thesis to report on a research program to elucidate the mechanisms of failure of unidirectional Kevlar^R fiber reinforced epoxy composites using the high resolution Small Angle X-ray Scattering (SAXS) facilities at the National Center for Small Angle Scattering Research (NCSASR). With the recently installed deformation device, it is possible to conduct on-line studies of the failure mechanisms of composites. Attention is focused on the dependence of the strength of loading angles, and the question of damage accumulation before complete failure of the components of composites and in the composites.

CHAPTER II

BACKGROUND REVIEW AND LITERATURE SURVEY

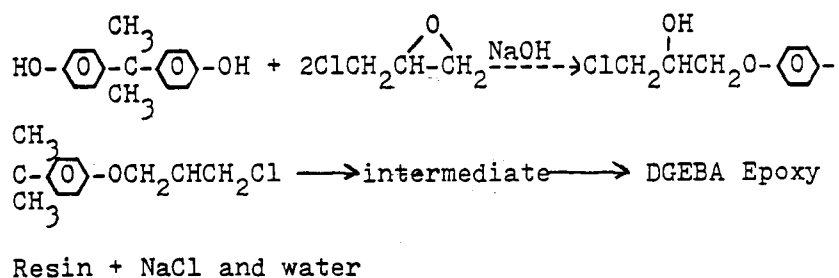
II.1 COMPONENTS OF COMPOSITES

II.1.A Epoxy Resins

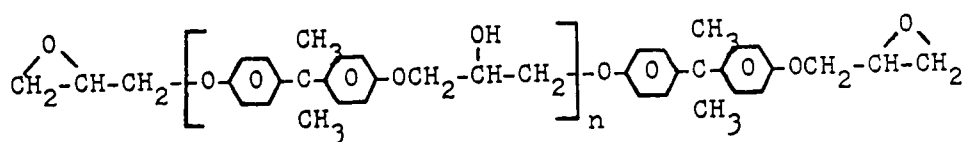
Epoxy, unsaturated polyester, polyimide, and phenolic resins are the principal thermosetting matrix resins used in composites. Among the thermoplastic materials which have been reinforced with glass fibers are nylon, polyethylene, polycarbonate, polypropylene, and polystyrene. Of these, the epoxies exhibit good handling characteristic, good mechanical properties, low shrinkage, good adhesion and good toughness and are presently used for the majority of high performance composite applications (164). The epoxy resins were first introduced commercially in 1947 (107).

Synthesis of epoxy resins. There are many kinds of commercially available epoxy resins. They are synthesized by various procedures. The details of their synthesis have been reviewed by Lee and Neville (98), Potter (133) and May and Tanaka (107).

Bisphenol A/Epichlorohydrin (DGEBA) resins are the most widely used epoxies and are prepared by the condensation of bisphenol A and epichlorohydrin in the presence of aqueous caustic soda (27). The synthesis is to occur in two steps: the formation of a chlorohydrin intermediate and the dehydrochlorination of the intermediate to the glycidyl ethers as shown:



The resulting resins can be represented by the general formula:



The number of repeat units, n , varying from zero to nine, depends essentially on the molar ratio of epichlorohydrin and bisphenol A used during the polymerization. Therefore, a series of resins may be obtained, each grade consisting of a mixture of molecules differing in chain length and molecular weight (M.W.). Resins of short chain length and low molecular weight (i.e., M.W. = 370 $\approx$ 400) are syrupy viscous liquids whereas resins of longer chain length and higher molecular weight (i.e., M.W. = 1,000) are hard, brittle and amber colored solids at room temperature.

Discussion of synthesis of other epoxies is reviewed by Potter (133) and by May and Tanaka (107).

Curing agents. The curing agents are categorized into two general classes; active hydrogen compounds, which cure by polyaddition and ionic catalysts. Among the curing agents currently used with epoxy

resins based on polyaddition reactions, the most widely used are aliphatic and aromatic polyamines and aliphatic and aromatic polyamides. Another group of curing agents that undergo polyaddition reactions with epoxy groups include dibasic and polybasic acids and acid anhydrides (107). In general, linear and branched primary and secondary aliphatic amines give the glycidyl ether resins good fast room temperature cures (133), resulting in heat deflection temperatures in the range of 70° - 110°C.

Diethylenetriamine (DETA) is a pungent low-viscosity liquid widely used with DGEBA resins for fast cures or where room temperature curing is required (133). Possessing a molecular weight of 103 and five active hydrogen atoms per molecule, DETA should be used at a concentration of about 10 - 11 per 100 parts of resin (phr) with a liquid resin of WPE (weight per epoxide), being defined as the weight of resin in grams which contains one gram equivalent of epoxide (175 - 210), for the full stoichiometric value to be obtained (98).

m-Phenylenediamine (MPDA) provides a cured resin with excellent chemical resistance and retention of physical and electrical properties at elevated temperatures (4). Possessing an M.W. of 108 and four active hydrogen atoms, MPDA is used at a concentration of 14.5 phr with a liquid resin. MPDA is in solid form at room temperature.

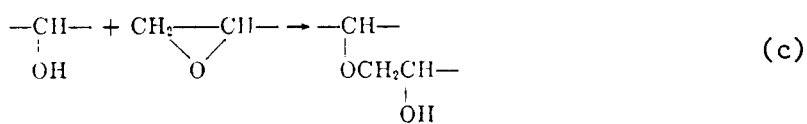
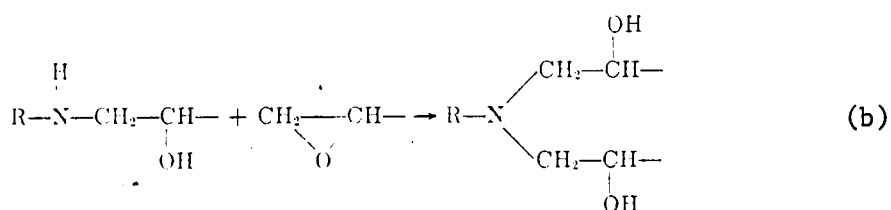
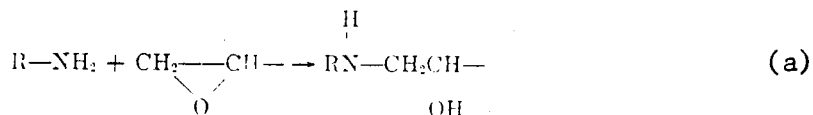
Anhydrides provide cured systems that are light in color and have good mechanical and electrical properties and better high temperature stability than the amine-cured systems (133). The limitation to the use of anhydrides is the long and high temperature cure schedules

needed to obtain optimum properties, although the use of catalysts overcomes this drawback (133). Nadic methyl anhydride (NMA) is the most versatile of all the anhydrides, since the balance of properties of the final casting can be varied over a wide range by altering the resin to curing agent ratio, changing the type and concentration of the accelerator, and modifying the cure schedule. NMA is a liquid at room temperature and is readily soluble in resins (133).

Epoxy resin curing mechanisms. The term "Curing" describes the process by which one or more kinds of reactants are irreversibly transformed from low molecular weight material to a highly crosslinked three-dimensional network. Curing normally proceeds through transformations from the liquid state to gelation, rubbery state, and finally to a vitrified glassy state (56).

In epoxy curing systems, the curing agents generally fall into two categories, catalytic and polyfunctional (133). The catalytic curing agents serve as initiators for homopolymerization, whereas the polyfunctional curing agents are used as comonomers. Aliphatic polyamines and polyamides, aromatic polyamines and polyamides, polymercaptans, polyphenols, and polybasic acids, acid anhydrides and their derivatives belong to the class of the polyfunctional curing agents. For each epoxy-curing agent system, the curing mechanism is very complex, and hence never been conclusively described. Tanaka and Mika (155) reviewed the mechanism of the curing reaction of various epoxy-curing agent systems.

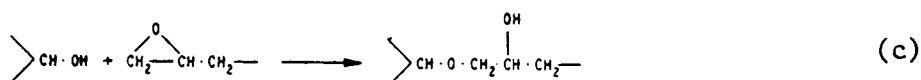
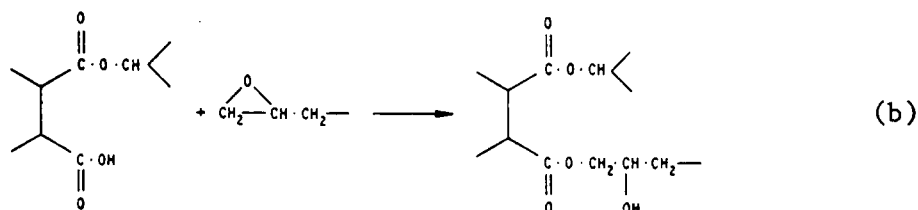
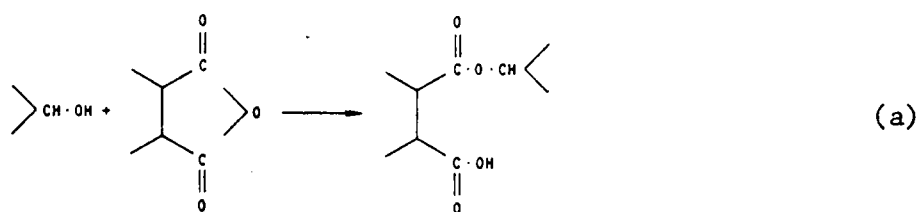
Schechter et al. (141) have investigated glycidyl ether reactions with amines. They suggested three possible reactions (a) - (c).



Schechter et al. found that the amine reactions (a) and (b) predominate. It was thus concluded that although epoxide groups can couple by ring-opening mechanisms in appropriate reagents, this apparently does not occur to any appreciable extent during the reaction of near stoichiometric amounts of diamines with diepoxy molecules (141, 44). The homopolymerization reaction (c) is favored when the epoxy is in excess or in the presence of Lewis bases or acids (133) or when the reaction temperatures are high (142). Even in stoichiometric systems, nonhomogeneous mixing of the reactants, which results in local regions of high epoxy concentrations, could favor homopolymerization in such regions (110). Morgan and Mones (110) found evidence that tetraglycidyl-diaminodiphenylmethane (TGDDM) epoxies do not form exclusively from epoxy-amine addition reactions. Anderson (5) found that aliphatic

amines such as diethylaminopropylamine, 1,6-hexanediamine, and diethylenetriamine were basic enough to cause a substantial amount of reaction (c), whereas m-phenylenediamine did not promote reaction (c).

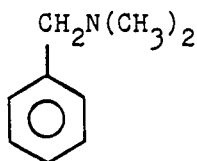
For anhydride-epoxy system cured without a catalyst, epoxide and anhydride react sluggishly at 200°C. Fisch and Hofmann (53) proposed the following reaction mechanism:



The anhydride ring is opened by a hydroxyl group found in the high molecular weight epoxy resins, forming a half-ester as in reaction (a). This half-ester then reacts through its acid group with the epoxide ring forming a hydroxy diester as in reaction (b). The hydroxy group of the diester can react with anhydride to form another carboxyl group, and so on to give an exclusively diester group. However, in studying the epoxy-phthalic anhydride system, Fisch and Hofmann noticed that the epoxide groups were consumed at a greater rate than could be accounted for by reactions (a) and (b) alone, and hence they postulated

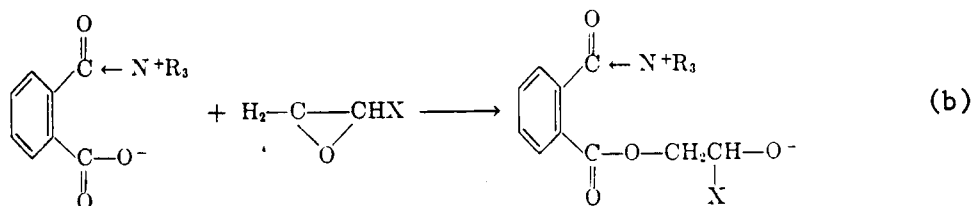
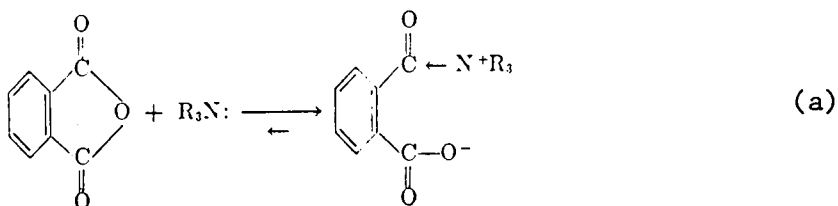
as a possible cause reaction (c) under the catalytic influence of carboxyl or anhydride groups.

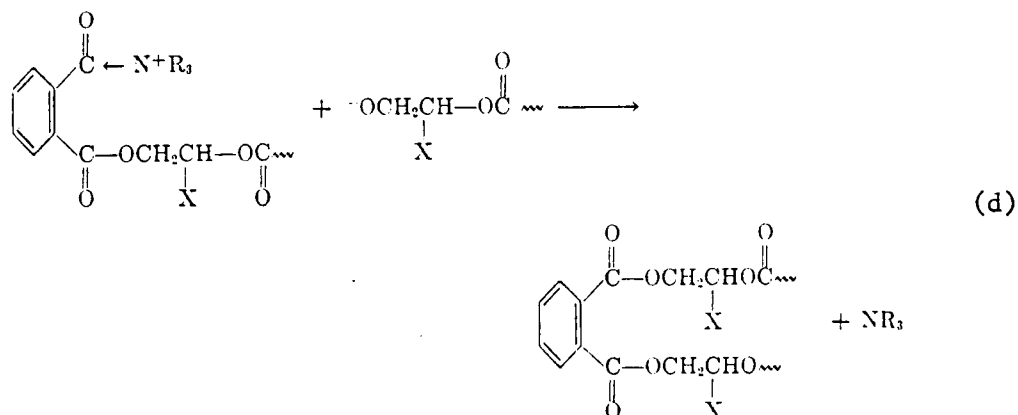
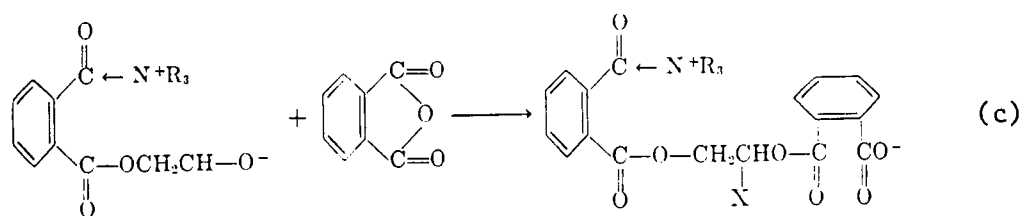
With the incorporation of Lewis base such as benzyldimethyl amine (BDMA) the curing time is reduced since tertiary amines are able to open anhydride rings and hence act as catalysts. Tertiary amines are catalysts which not only affect the rate of the anhydride-epoxy reaction, but its course as well (38).



Benzyldimethyl Amine (BDMA)

For tertiary amine catalyzed systems, Fisch and Hofmann (53) and later Fischer (54) proposed the following reaction mechanism:





In this system, Fischer proposed that the amine activates the anhydride reaction generating a carboxyl anion as in reaction (a). This anion reacts with the epoxide yielding the alkoxide anion as in reaction (b). This alkoxide anion reacts with the anhydride as in reaction (c). Continuation of these alternating reactions would give rise to the polyester. A displacement of the amine by alkoxide as in reaction (d) would also continue polyester formation. Dearborn et al. (38) report that the highest crosslinking in amine-catalyzed anhydride-epoxy resin cures was obtained at a 1:1 anhydride-epoxide ratio.

Morphology of cured resin. Optimally cured epoxy resins are three-dimensional network structures with a regular network. Carothers (25) proposed that molecular units of high functionality could polymerize into infinitely large, three-dimensional molecules--the size

of which was limited only by the volume of the reaction vessel. In agreement with Carothers, Flory (50, 51) proposed that an insoluble gel consists of a giant three-dimensional network that extends throughout the material and that the formation of this molecule is responsible for the abrupt change of physical properties at gelation and finally that low molecular weight material that does not take part in the formation of the network yields comparatively small molecules that are interspersed throughout the larger matrix. The development of the network is schematically represented in Figure 1 (56). However, gross discrepancies between calculations of the physical properties based on this model and actual measurements (15) led some (73) to believe that these discrepancies were due to the rupture of weak regions (Lockerstellen) created during network formation.

More recently, results from diverse investigations (37, 47, 85, 90, 76) using techniques such as electron and optical microscopy, thermomechanical measurements, differential swelling, differential scanning calorimetry, and mechanical testing led some to believe a view of the network essentially as a high crosslink density region (essentially spherical) embedded in a less crosslinked matrix. In contrast, the use of small angle X-ray scattering (143, 106) failed to prove two-phase structures. In general, two levels of sizes have been reported in the literature: one ranging from $60\text{\AA}$ to $900\text{\AA}$, and the other ranging from $20\text{ }\mu\text{m}$ to $200\text{ }\mu\text{m}$. Erath and Spurr (48) reported the occurrence of globular formations of $400 - 900\text{\AA}$ diameter as a frequent problem in epoxy resins. Misra et al. (108) concluded from their

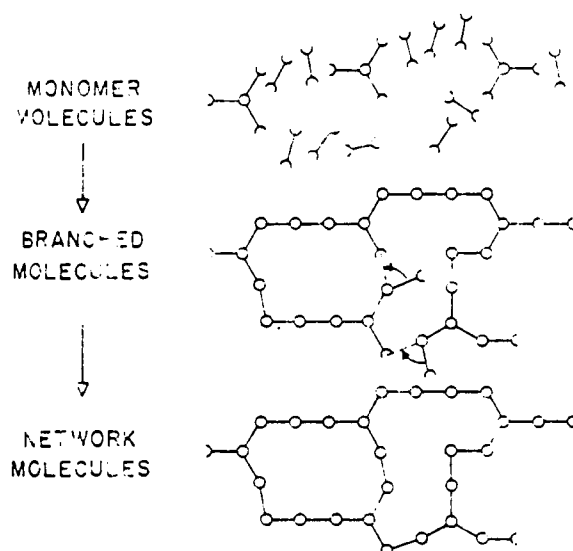


Figure 1. Development of the network (56).

electron microscopic studies that globular particles form prior to gelation and they observed two levels of inhomogeneity sizes: 100Å to 500Å and 2 μm to 50 μm. These smaller high crosslink density regions have also been observed by Racich and Koutsky (135) and larger high crosslink density regions of sizes ranging 6 to 10 μm have been observed by Morgan and O'Neal (116).

The effects of different variables on morphology are discussed by some investigators. The results of Misra et al. (108) show that the size of the high crosslink density phase increases with deviation from stoichiometry. Rapid curing schedule (i.e., high temperature cure) produces small high crosslink density phases in large numbers (36).

Consequences of the existence of nonhomogeneities on the mechanical properties of the bulk sample have been studied by Labana et al. (96), and it was shown that the ultimate properties were sensitive to slight variations in chemical composition and network topology. Misra et al. (108) also studied the effect of network morphology on the mechanical behavior and concluded that the tensile properties were governed by the strength of the connections between the inhomogeneities. Others (85, 100, 123, 121) studied the effect of stoichiometry on the creep and dynamic mechanical behavior and found glass transition temperatures, creep and dynamic mechanical behavior vary depending on stoichiometry.

The mechanisms of network formation have been proposed by several investigators (96, 108, 13) and are reviewed by Shen (145).

Factors which affect the properties of cured epoxies are (145): molecular weight and molecular weight distribution of epoxy resins (49), curing agents, modifying agents, stoichiometry of reactants (145), and cure history (36, 145). At a given reactant composition, it was found that a long post cure yields constant properties (145).

Modes of deformation and failure. Cured epoxy resins, like polystyrene (PS) and polymethylmethacrylate (PMMA) are glasses. They are relatively rigid materials with low elongations to break. For small strains they are roughly elastic.

Although the modes of fracture in PS and PMMA have received much attention, the modes of fractures in epoxies have received little attention. It is well known that in PMMA and PS cracks grow with a small plastic zone at the crack tip (17, 43, 97, 11, 79, 77) containing voids. These are known as crazes. Crazes are different from cracks in that crazes have a continuity of material across the craze plane, whereas cracks do not possess any continuity. Consequently crazes are capable of bearing loads. Comprehensive reviews on crazing have been made by Kambour (78) and Kausch (80).

Crazes have also been observed in epoxy. van den Boogaart (17) has reported seeing crazes around crack tips in incompletely cross-linked Epikote 828, and Lilley and Holloway (101) have reported that crazes were seen not only in incompletely crosslinked epoxies but also in completely crosslinked epoxies. Localized plastic flow has also been reported to occur by a number of investigators (18, 30, 57, 122,

128) during the failure of thermosets. Morgan et al. (116, 101, 114, 115, 117, 118) have investigated the fracture topographies of amine-cured epoxies fractured in tension as a function of temperature, strain-rate, chemical composition and environmental exposure and the topographical features have shown that microscopic flow can occur in epoxies and that such flow can involve either crazing or shear banding. Based on these observations they proposed the mechanisms of craze initiation and growth in epoxies similar to the mechanisms of craze initiation and growth in thin PS films described by Lauterwasser and Kramer (97). They are illustrated schematically in Figure 2. The fracture topographies of epoxies failed in tension were then related to this mechanism (111). Morgan et al. (111) observed three regions on the surfaces of fractured epoxies: i) a coarse initiation region, ii) a slow crack-growth, smooth region and iii) a fast crack growth, rough region. The initiation region was believed to have been caused by a crazing process. The fibrillar structures that lie parallel to the fracture surface and the nodular topographies were believed to be associated with fractured craze fibrils. The smooth region was believed to have been caused by a small plastic zone produced ahead of the crack tip. The fast crack, rough region was believed to have been caused by complex, unstable, brittle fracture. The surface roughness was believed to be primarily caused by the generation of secondary crack fronts ahead of primary crack front and the interconnection of these fronts from different fracture planes. The ability of epoxies

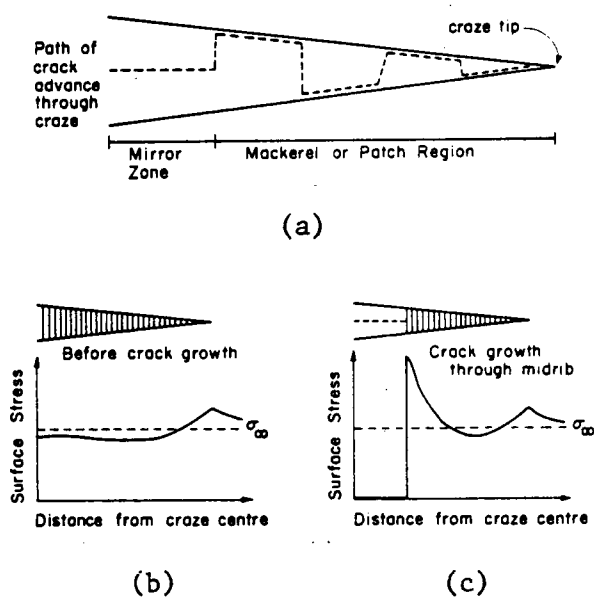


Figure 2. The mechanisms of craze initiation and growth in polystyrene (97).

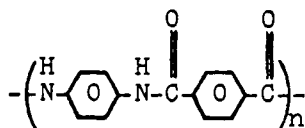
- a) Schematic diagram of a crack advancement
- b), c) Craze surface stress profile
- c) Results in rough morphologies

to undergo microscopic flow has been explained by Morgan et al. (111) as caused by either i) incomplete cure reaction and/or epoxide homopolymerization which result in a lower crosslink density network, ii) regions of low crosslink density controlling the flow process or iii) bond breakage under stress, which result in a lower overall crosslink density. Gent (55) suggested yet another mechanism of plastic flow caused by the concurrence of high dilatational and shear forces near the tip of crack causing the transformation of the material from a glassy to a softer rubbery state.

II.1.B Kevlar^R Fibers

Kevlar^R 49 is an organic aramid fiber with a high modulus and high tensile strength which is being used to reinforce various matrix resins, primarily epoxies in a variety of applications.

Production methods. Kevlar^R is made by polymerizing the acid chloride of terephthalic acid with p-phenylenediamine in a suitable solvent (12, 93, 94, 95). Chemically it is poly (p-phenylene terephthalamide) (130, 24).



The Kevlar^R fibers are dry-jet wet spun from liquid crystalline poly (p-phenylene terephthalamide) (PPD-T) concentrated H_2SO_4 dopes (18 to 23 wt% PPD-T) (12). The yarn from the spinneret is washed with H_2O and neutralized with either NaOH or Na_2CO_3 . It is then dried at 150°C for two to six seconds and finally drawn 0.5% further at 550°C for one to six seconds (113). Kevlar^R 49 is hot stretched following spinning of the polymer solution into a coagulant. Kevlar^R 29 is apparently not hot stretched (75).

Kevlar^R fiber is characterized by a high intrinsic rigidity of the individual molecular rod-like chains due to (-CONH-) links in the para position between aromatic rings and considerable orientation along the fiber axis. In the case of rod-like polymers, at some critical value of polymer concentration the isotropic solutions of rods undergo phase separation resulting in the formation of a partly ordered solution (92). Kevlar^R fibers are spun from this anisotropic solution.

Morphology of Kevlar^R fibers. The crystal structures of Kevlar^R have been previously studied by few investigators (125, 129) and is reproduced in Figure 3 (42). X-ray diffraction studies by Northolt (125) indicate there are two molecular chains in each monoclinic unit cell where $a = 0.79 \text{ nm}$, $b = 0.51 \text{ nm}$, $c = 1.29 \text{ nm}$, $\gamma = 90^\circ$. Interchain hydrogen bonding occurs only along the (100) planes whereas weak van der Waal forces operate in other lateral directions.

The apparent crystallite size was determined by Ballou (9) and Northolt and Van Aartsen (126). Ballou determined the crystallite

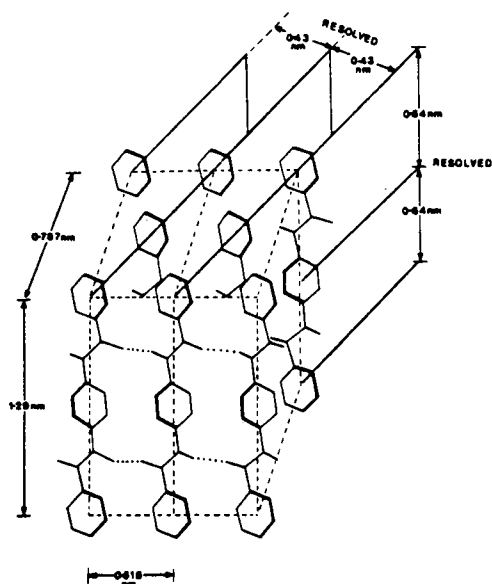


Figure 3. The crystal structure of Kevlar^R (42).

dimensions along the c axis to be $100\text{\AA}$ with lateral dimensions in the range of $20 - 140\text{\AA}$. Northolt and Van Aartsen on the other hand measured the crystallite dimension along the c axis to be $700\text{\AA}$ and the lateral to be about $50\text{\AA}$. The data of Dobb et al. (39) agree with those of Northolt and Van Aartsen, and they are presented in Table 1. The percent crystallinity of Kevlar^R 49 fiber has not been determined but is presumed to be exceedingly high (129).

SAXS studies on Kevlar^R fibers show an elliptical equatorial streak without any discrete interference and this scattering has been attributed to microvoids parallel to the fiber axis (126, 39, 40, 69, 42). The void dimensions determined by Dobb et al. (39) using SAXS and TEM (transmission electron microscope) are presented in Table 2. Dobb et al. (39) also noted much larger cracks of approximately $0.08\text{ }\mu\text{m}$ across and of length up to $16\text{ }\mu\text{m}$ near the center of Kevlar^R 49 fibers.

The origin of the voids have been discussed by Dobb et al. (39) and Morgan et al. (113). As considerable volume contraction occurs during removal of the H_2SO_4 to form well-ordered fibers, some voiding would be expected to arise during the solidification of the extruded polymer in the coagulating bath. Thus regions corresponding to the inclusion of coagulating solvent or residual solvent may be permanently incorporated within the fiber structure. Further evidences of this phenomenon were found by Penn and Larson (129) from the elemental analysis of ashed fibers showing the ash is largely Na_2SO_4 . This Na_2SO_4 is believed to be introduced during the manufacturing process

Table 1. Apparent Crystallite Size (39)

Reflection hkl	Spacing nm	Crystallite Size nm		
		PRD 49	Kevlar ^R 49	Kevlar ^R
110	0.433	8.53	6.54	4.81
200	0.388	3.63	5.28	3.95
004	0.322	18.38	17.68	10.98
006	0.215	13.42	10.87	6.28

Table 2. Void Dimensions (39)

Specimen		Void width (nm)	Void width (nm)	Void length (nm)
		X-ray data	EM data	
Kevlar 29	Dry untreated	7.6	-	-
	Dry stained	5.8	6.1 $\sigma = 1.1$	24.7 $\sigma = 7.8$
Kevlar 49	Dry untreated	10.6	-	-
	Dry stained	5.0	5.6 $\sigma = 0.8$	25.1 $\sigma = 8.0$

σ is the standard deviation.

when the filaments are washed with a solution of sodium carbonate to neutralize and remove sulfuric acid. Subsequent heat treatment may also be responsible for void formation since some localized shrinkage would be expected from the improvement in molecular packing (39).

Slutsker et al. (148) obtained long periods of $190\text{\AA}$ for poly-p-phenyleneterephthalamide (PPD-T) fibers from SAXS studies and concluded these periods may consist of crystalline and intercrystalline amorphous regions alternating along the fiber axis.

Dobb et al. (39, 41) studied the molecular organization of Kevlar^R using a combination of electron microscope dark-field image techniques and X-ray and electron diffraction analysis and suggested that Kevlar^R 49 fibers consisted of a system of H-bonded sheets regularly pleated along their long axes and arranged regularly. This structure is thought to lead to a periodic banding along the fiber axis, with band spacings of 250 nm. These periodic bands were also observed by Morgan et al. (113) on the fracture surfaces of longitudinally split fibers and also by Simmens and Hearle (147) using high magnification polarizing microscope.

Morgan and coworkers (113, 135) suggest yet another physical model for Kevlar^R 49 in which there is an amorphous skin and crystalline core. The non-crystalline skin consists of randomly arranged chain ends and the core consists of periodic transverse defect planes spaced ~ 200 nm along the fiber. The skin is believed to be devoid of such transverse weak planes. Differences between the core and the skin are also pointed out by Penn and Larson (129) who report that at

the fiber surface there is about one and half times as much carbon and three times as much oxygen than that for bulk of the fiber. Oxidation of the Kevlar^R fiber in air as the initial degradation process is suggested by Brown and Hodgeman (20).

Physical and mechanical properties. Kevlar^R 49 has a strong absorption in the ultraviolet region around 250 nm and a low broad absorption centered around 330 nm (129). This requires that the fiber must be shielded not only from ultraviolet light but also from sunlight. However, Watt (164) report that the fiber is self-screening in that only the fiber surface is degraded.

The chemical resistance of yarns and rovings of Kevlar^R is reported to be excellent except in a few strong acids such as sulfuric acid and bases (164).

Fibers of Kevlar^R 49 have good thermal stability and retain a high percentage of room temperature properties when tested at temperatures up to 180°C. The fiber is flame resistant and does not melt but will decompose at about 500°C (164). At temperatures as low as -196°C, the tensile strength and modulus are not affected substantially. Fibers of Kevlar^R 49 have a moisture absorption of three and half to four percent when tested at 55 percent relative humidity (164). Kevlar^R 49 fiber has density of 1.43 g/cm³ (125), elastic modulus of 131.0 GPa (19,000,000 psi), tensile strength of 3620 MPa (525,000 psi), and elongation to break of ~5% (164).

Failure mechanisms. The surfaces of filaments examined under the optical microscope and in the SEM show a generally smooth structure, but there are longitudinal splits in places, with many separated fibrils and ribbon-like fibrillar strands wound around the filament (88,135). From this Konopasek and Hearle (88) inferred a weak cohesion between fibrils in the outer layer of the filaments. They also noticed slightly bulging lines around the surface at various places along the filament. In Kevlar^R 49 and Kevlar^R 29 dark lines of two different intensities were seen when viewed in polarized light under the optical microscope, and they were located at various angles between +45° and -45° to the filament cross-sectional plane (88) (Figure 4).

The fracture morphology of Kevlar^R 49 in tensile loading has been studied by Konopasek and Hearle (88) and evidence of severe splitting in the longitudinal direction was seen. The two broken ends were usually different in appearance: one end showed extensive splitting while the other was a single solid piece (Figure 5). The solid end has split off from the other end and tapers in an elliptical cross section from the place where the split starts to a small tip. A possible mechanism of fracture development has been presented by Konopasek and Hearle and is presented in Figure 6. They argue that an imperfection of the surface of the filament may act as the initiation point in the break up of the fibrillar unit under the increasing tensile load. The longitudinal shear stresses induced at the root of the initial flaw cause longitudinal splitting of the first bundle of fibrils. There are also tensile stresses acting around the flaw and

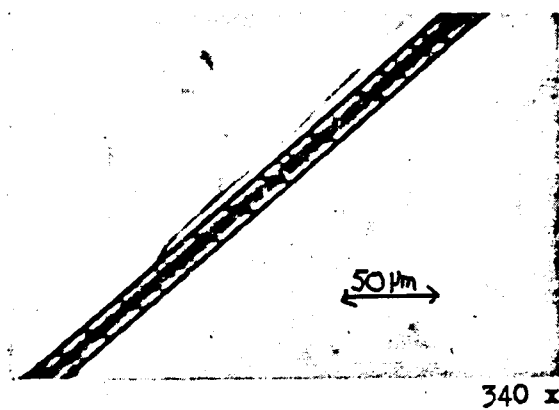


Figure 4. Kevlar[®] 29 fiber examined under a polarized microscope (88).

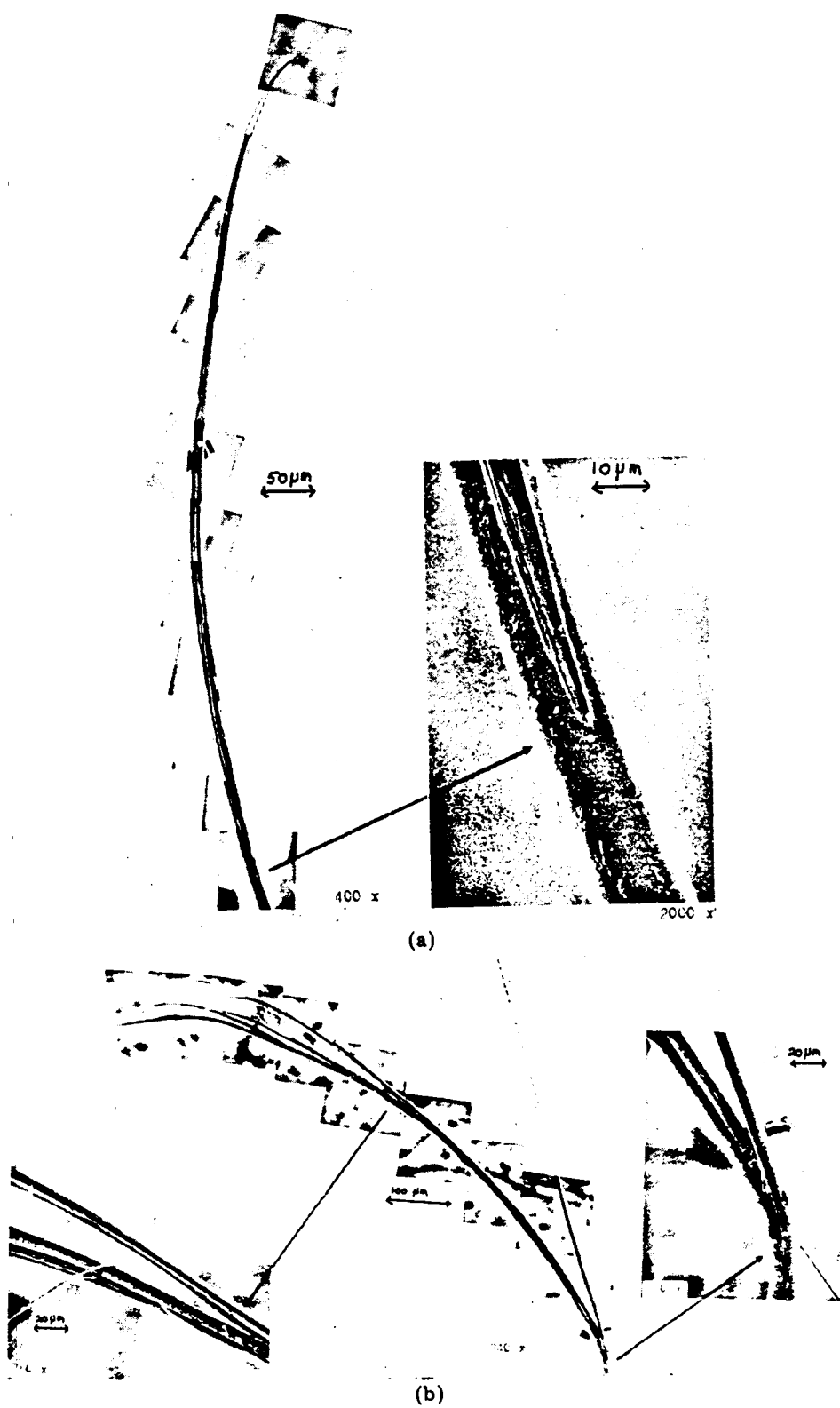


Figure 5. The fracture morphology of Kevlar^R 49 in tensile loading (88).

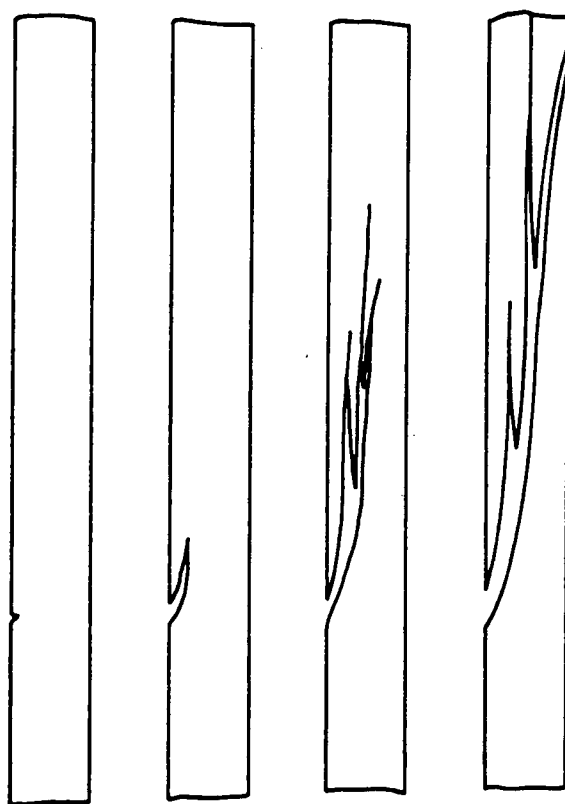


Figure 6. Schematic representation of simple tensile fracture development in Kevlar^R fibers (88).

since the tensile modulus and strength are much higher than the shear modulus and strength, the crack develops at a steep angle. After the next layer of fibrils has broken, a new crack is opened up, and there is again a concentration of shear stresses which results in splitting the next layer of fibrils. Therefore the break is transmitted from one fibrillar unit to the next until the filament is broken completely. When the whole length of the broken fibers was examined, bulging lines located some distance from the fractured end were found, and they were thought to occur as a result of compression forces during the snapback after fracture.

Morgan and his coworkers (113, 135) also studied the deformation and failure processes of Kevlar^R 49. They observed a continuous ribbon tearing away from the fiber when Kevlar^R 49 failed under tension. This observation confirms the fracture morphology of Kevlar^R 49 reported by Konopasek and Hearle (88). Morgan and his coworkers, however, report that in the case of a fiber in which the skin has completely unravelled, the fiber core fails by transverse crack propagation without splitting.

The fiber split lengths were carefully studied by Morgan and his coworkers (113, 135), and they were 20 - 70 times their diameter or ~ 200 to $700\text{ }\mu\text{m}$. From these observations Morgan and his coworkers concluded that the crack transverses a path that follows the original macromolecular chain ends inherent in the fiber, and these periodic weak planes clustered with the chain ends occur every $\sim 200\text{ nm}$ along the fiber axis.

II.2 FAILURE OF COMPOSITES

Many workers have studied the longitudinal tensile deformation behavior of composites. The longitudinal tensile modulus and the strength are fiber controlled when the volume fraction of fibers is sufficiently high.

When a fiber composite is loaded continuously parallel to the fiber axis, fracture may involve fiber breakage, matrix cracking, fiber-matrix debonding and lamina delamination (65, 91, 140, 146, 156). The various fracture models in a composite depend on the relative strength and ductilities of the filament, the matrix and the interface between them. These parameters in turn depend on the chemical composition of the constituents, processing history, and external conditions such as temperature, strain rate, and environment under which the composite is loaded (65, 156). The volume fraction of fibers also influence the failure modes (83, 84). It has been reported that at high volume fractions catastrophic failure occurs when the fibers fail and at low volume fractions failure is not catastrophic after the first fiber break. At high volume fractions failure of composites is immediate since the volume of matrix worked in tensile loading is insufficient to absorb the stored elastic energy of the specimen and the testing machine. At low volume fractions the matrix can absorb the energy and hence fibers will fracture on another cross section. A classification based on this distinction led Cooper et al. (7, 32, 33) to a definition of "single" and "multiple" fracture.

The fracture strength of reinforcing filaments is influenced by many factors. It is reported that the length and diameter of filaments have a large effect on fiber strength (139). It is also reported that small microcracks that are present on the surface or in the interior of the fibers lower the fracture strength of fibers (139, 156). The statistical nature of the strengths of filaments attributed to an inherent variation of strength and of stress throughout microscopic regions of their volume (134) led to the development of statistical failure theory of composites (87, 127, 138).

The strengths of the matrix and interface are influenced by several factors. The strength of the matrix decreases with increasing temperature and decreasing strain rate. The strength of the matrix also depends on the degree of crosslinking between polymer chains as already discussed as well as on the density of voids formed during processing (64, 87, 162). The results of an investigation on the origin of microvoids in glass fiber reinforced epoxy composites are reported by Bascom and Romans (10). By microscopic examination of sections of filament-wound glass fiber epoxy composites they observed interfilament air bubbles in a density of 10^7 to 10^9 voids per cubic inches. These voids had diameters of 10 μm and lengths of 10 μm to over 500 μm . The origin of these microvoids was believed to be in part due to the capillary phenomena involved in the impregnation process. Interfacial strength was also reported to be affected by the amount of voids (34, 87).

When all filaments have the same strength such as in the metal matrix-metal fiber composites, then the failure of all the filaments at the same stress level immediately leads to composite failure. This type of behavior was observed in tungsten fibers-copper matrix by Kelly and Tyson (83, 84).

However, many of the fibers currently used, such as boron, graphite, glass, alumina have a distribution of strength and if the matrix is brittle, the sudden fracture of a weak filament imbedded in the matrix will cause the matrix adjacent to the filament break to be loaded rapidly and hence the crack propagates into the matrix (119, 120). The crack propagation can continue until either the specimen fails or the crack reaches the next adjacent filament, causing it to fracture until the specimen breaks completely. In a brittle solid under tension, it is well known once a crack is on the move complete fracture will occur suddenly (31).

On the other hand, if the matrix is tough, filament failure is followed either by debonding between broken fiber ends and matrix or by large localized plastic strains in the matrix (157), which in turn load the adjacent fibers above the average strain of the composite. These fibers or their interface may crack. Alternatively the next fracture could occur elsewhere in the composite.

When the fiber-matrix interface or the matrix is weak, the transverse tensile stresses and shear stresses at the advancing crack tip may be able to cause longitudinal splitting. For completely elastic solids, it has been shown that the transverse tensile stresses are

about one fifth the longitudinal tensile stresses at the crack tip, so that if the fiber is less than five times stronger in tension than the matrix or interface, splitting should occur (31). Thus for fibers with cleavage planes, this splitting mechanism could contribute in increasing their effective strength (31). These failure mechanisms of composites are summarized schematically in Figure 7.

Physical observations of composite failure were carried out by both optical and Scanning Electron Microscope (SEM) (86, 119, 120, 157). When graphite fiber-epoxy composites were studied by Kline and Chang (86), two characteristics of failure surfaces were revealed. One is the presence of platelets of epoxy which are raised from the surface and lay on top of one another. The other is the presence of a cleavage-like branched structure in the matrix between fibers. The former structures have been observed in unreinforced epoxy resins. It was noted by Kline and Chang that relative orientation of these structures with respect to one another is a valuable aid in determining the direction of damage propagation (86). Kline and Chang also monitored the sequence of events leading to failure using an X-ray technique, and it was found that damage growth was generally found to proceed relatively slowly until a critical stress value. After reaching this level, growth was found to be more rapid.

Marom and White (104) studied the transverse fracture process in glass fiber reinforced epoxy composites and found in low volume fraction fiber composites, the wide matrix zones between the fiber layers show brittle fracture without any plastic deformation. They also found in

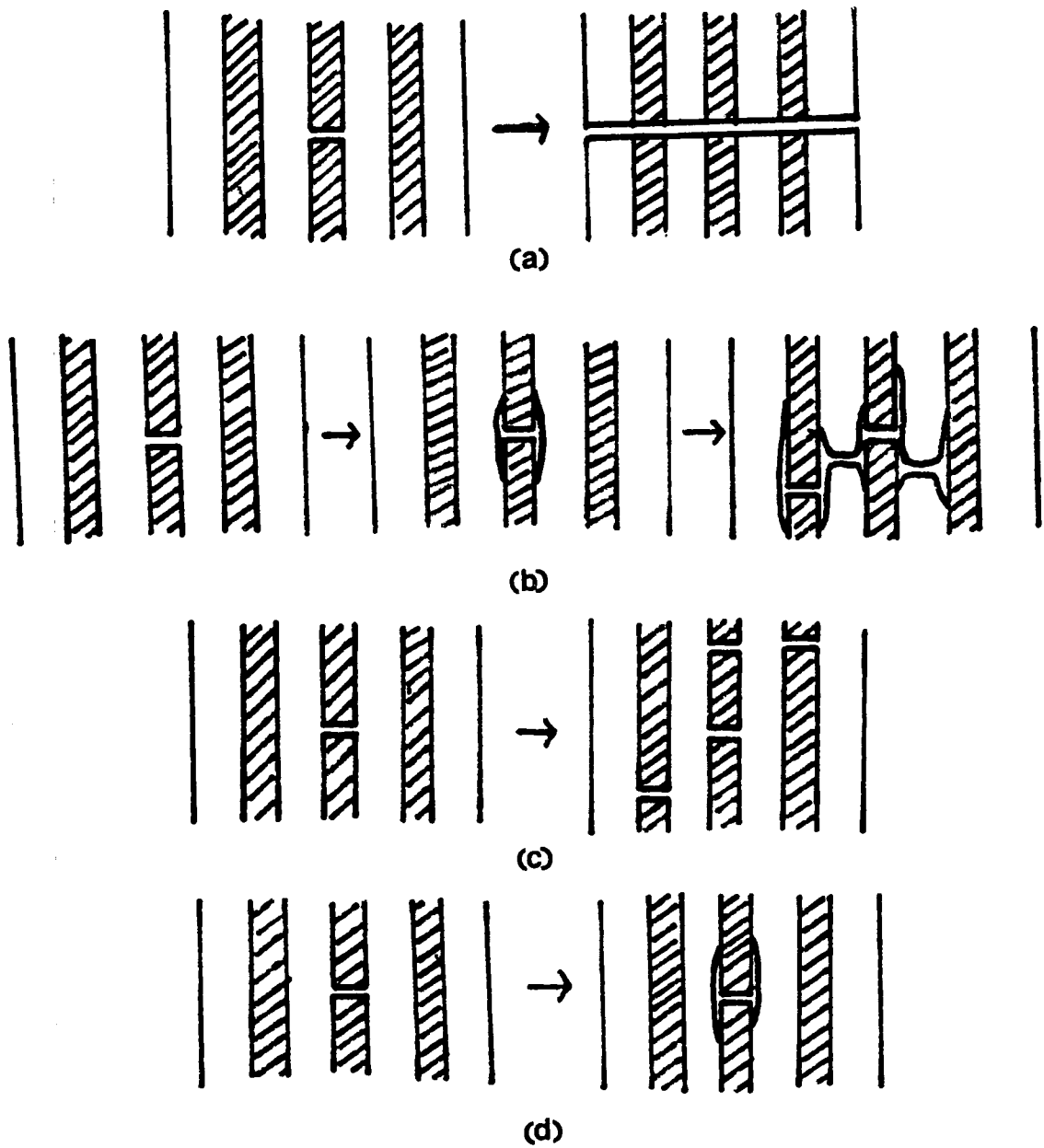


Figure 7. Schematic representation of the failure mechanisms in composites.

- a) Brittle fiber- brittle matrix (good adhesion)
- b) Brittle fiber- brittle matrix (weak adhesion)
- c) Brittle fiber- ductile matrix (good adhesion)
- d) Brittle fiber- ductile matrix (weak adhesion)

spite of the fact that the fracture developed parallel to the direction of fibers, broken fibers were found in both fracture surfaces. From these observations they concluded that the transverse fracture process is composed of two simultaneous processes: one which is concerned with the matrix only which is catastrophic, and the other which concerns the fibers and the fiber-matrix interface which is a controlled fracture process and the nature of the overall process is to be determined by volume fraction of fibers.

Using an optical microscope, Mullin and Mazzio (119, 120) examined the fracture mechanisms occurring in an epoxy-novolac matrix and the interfacial region surrounding carbon fibers as the fibers fail. They presented a sequence of photographs showing progressive damage with increasing load. They concluded that single fibers and tows fail catastrophically when the resin is unmodified. When the resin is modified to give ~20 percent elongation, single fibers and tows exhibited cumulative damage with numerous fractures visible along the fibers (Figure 8a and Figure 8b).

II.3 FAILURE OF KEVLAR^R FIBER COMPOSITES

Although the use of Kevlar^R 49 fibers in high performance epoxy composites is increasing, the deformation behavior and failure modes of Kevlar^R/epoxy composites have received very little attention (46, 112). Because of the relatively larger ultimate elongations of 3 to 4 percent compared to boron or graphite fibers whose ultimate elongations are less than 1 percent, the incorporation of Kevlar^R fibers into composites can increase the energy to fracture.



(a)



(b)

Figure 8. Failure mechanisms of carbon fibers in epoxy-novolac matrix (119, 120).

(a) In unmodified resin

(b) In modified epoxy-novolac resin at 70 percent ultimate load

Morgan et al. (112) studied the failure modes of Kevlar^R 49/epoxy composite strands and multilayer composites in the form of pressure vessels. The Kevlar^R 49 fibers in the composite strands failed by a fiber splitting mechanism (Figure 9). The Kevlar^R 49 fibers in the multilayer composite pressure vessels also failed by a splitting mechanism. The failed tip of each yarn in the fractured region of the composite exhibited split fibers similar to those shown in Figure 9.

For a composite vessel that was initially dropped full of water prior to the application of pressure, the burst strength of the vessel decreased by about 30 percent, and the composite failed in the region of the impact. The impact region showed some of the fibers deformed by a kinking mechanism. Furthermore, interyarn failures within the multilayer composites readily occurred along the fiber-matrix interface. This was believed by the authors to be due to poor adhesion between epoxy and the Kevlar^R 49 fibers.

However, Eagles et al. (46) studied interfacial properties of Kevlar^R 49 reinforced thermoplastics using a single-filament pull-out test and reported that the bond strengths of the Kevlar^R 49 are of the same order as the bond strengths of the glass fibers.

II.4 SMALL ANGLE X-RAY STUDIES OF VOIDS

SAXS gives information about colloidal, supermolecular structures, microstructures, microdomains, etc., of $10 - 1000\text{\AA}$ size. It is well known that when solid polymers produce strong diffuse scattering, microvoids within the solid are involved. Statton (149) reviewed

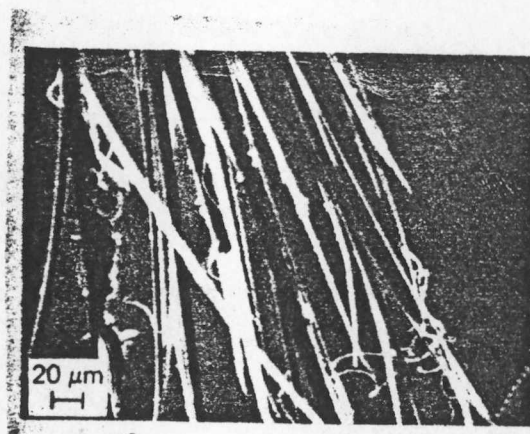


Figure 9. Scanning electron micrograph of split fibers in a Kevlar^R 49/epoxy composite strand (112).

the evidence accumulated to 1956 and concluded that the diffuse small-angle scattering of cellulose must be produced largely by microvoids and that these voids are elongated parallel to the fiber axis. A later review of diffuse small-angle scattering by Statton (150) has extended the interpretation that the most probable cause of diffuse scattering in all polymers is due to voids. It was also shown by Statton (151) that the amount of diffuse X-ray scattering given by a fiber depends upon the method used to form the fiber. Dry-spun fibers have many voids when spun, but these are susceptible to collapse by thermal treatments.

Void elongation has been studied by Statton (151), and it was shown that the amount of void elongation increases as windup tension is increased. The result is an increase of the scattering along the equator and a decrease of the meridional scattering. A simple parameter to measure this void elongation can be obtained from the ratio of the extent of film blackening in the equatorial and meridional directions (16).

Some drawn fibers yield a scattering pattern that has both equatorial and meridian streaks, and it is believed to be an indication of elongated voids running across the fiber in addition to along the fiber axis (151). When drawn films are studied, it is found that the voids are lamellar in shape (152).

Statton and Hoffman (153) studied the relation of SAXS to the preparation conditions of glass fibers from molten silicate and found that both diffuse scattering and discrete scattering were present in

the silicate fibers. They attributed diffuse scattering to voids whereas discrete scattering could be due to either a regularity of voids or of dense lumps. On the other hand, Cartz (26) carried out SAXS experiments on glass plate, and he concluded no small-angle diffraction effects of any sorts have been observed.

Dusek et al. (45), Uhlmann et al. (161) and Matyi et al. (106) have used SAXS to study glassy amorphous polymers such as polycarbonate, polymethylmethacrylate, polyethyleneterephthalate and epoxy, and their results show SAXS of amorphous polymers are caused by foreign particles or air bubbles entrapped in the matrix. The findings of Wendorff and Fischer (165) support this. Recently SAXS has also been used to identify the microporous nature of non-polymeric materials such as coal (102).

Although crazes in solid polymers are not real voids, SAXS studies on crazes are included here since they are related in that both could be categorized as incipient fractures. Legrand et al. (99) have studied SAXS from crazes and fractures in polystyrene and determined the craze being approximated as a collection of spheroidal or irregular shaped voids surrounded by material with anisotropic density distribution arising from its orientation in the stress direction. More recently, Brown and Kramer (19) used SAXS to study crazes in bulk samples of polystyrene. Westbrook (166) studied the polystyrene crazes using SAXS with a pinhole geometry and a two-dimensional position-sensitive detector.

II.5 THEORETICAL BACKGROUND

II.5.A Mechanics of Composites

Several investigators have used constituent material properties to predict the overall elastic properties of composites. Composites are treated as an anisotropic continuum, thus permitting the composite behavior to be described by a mechanical constitutive equation. The simplest and one of the earliest was a "rule of mixture" (81), and this was used by many investigators to predict the axial properties, modulus of elasticity, and major Poisson's ratio. The transverse and shear stiffness have been treated in a variety of ways. A strength-of-materials approach was taken by Shaffer (144). He used a series-parallel arrangement of equivalent bars of matrix and fiber to predict the transverse stiffness. Hashin and Rosen (66) used variational principles of the theory of elasticity to establish the upper and lower bounds on the elastic properties. Work by Adams and Doner (1) has been directed on the elasticity solution of the multiple inclusion problem. In general, methods for predicting elastic constants are well under control.

Elastic properties. If the state of stress at a point in a body is described by the stress tensor, σ_{ij} , corresponding to this there is a strain tensor, ϵ_{ij} . The stress tensor σ_{ij} is related to the strain tensor ϵ_{ij} by Hooke's law (6):

$$\sigma_{ij} = E_{ijkl} \epsilon_{kl} \quad (\text{II.5.A.1})$$

and

$$\epsilon_{ij} = S_{ijkl} \sigma_{kl} \quad (\text{II.5.A.2})$$

where E_{ijkl} represents the stiffness tensor and S_{ijkl} the compliance tensor.

The fourth-rank stiffness and compliance tensors have, for most general case, 81 components. However, by symmetry, these reduce to 36 independent elastic constants. These may be reduced to 21 by thermodynamic consideration. From material symmetry considerations for the fiber reinforced systems where three axes of symmetry exist, these reduce to nine. This material is known as an orthotropic material. For isotropic material they reduce to two.

In this study, two-dimensional states of stress are of primary interest and in such case, either the stress or strain in the third dimension is dependent upon the properties of the other two dimensions. In such a case, the number of elastic constants reduces to four. Thus the constitutive equation for a uniaxial composite subjected to plane stress is expressed as:

$$\begin{vmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \end{vmatrix} = \begin{vmatrix} E_{11}/(1-\nu_{12}\nu_{21}) & \nu_{12}E_{11}/(1-\nu_{12}\nu_{21}) \\ \nu_{21}E_{11}/(1-\nu_{12}\nu_{21}) & E_{22}/(1-\nu_{12}\nu_{21}) \\ 0 & 0 \end{vmatrix} \begin{vmatrix} \epsilon_{11} \\ \epsilon_{22} \\ 2\epsilon_{12} \end{vmatrix} \quad (\text{II.5.A.3})$$

and

$$\begin{vmatrix} \epsilon_{11} \\ \epsilon_{22} \\ 2\epsilon_{12} \end{vmatrix} = \begin{vmatrix} 1/E_{11} & -\nu_{12}/E_{22} & 0 \\ -\nu_{21}/E_{11} & 1/E_{22} & 0 \\ 0 & 0 & 1/G_{12} \end{vmatrix} \begin{vmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{12} \end{vmatrix} \quad (\text{II.5.A.4})$$

where G_{12} represents the shear modulus,
 E_{11} the axial stiffness parallel to fibers,
 E_{22} the transverse stiffness perpendicular to fibers,
 ν_{12} the major Poisson's ratio (transverse contraction due to axial extension), and
 ν_{21} the minor Poisson's ratio (axial contraction due to transverse extension).

and where

$$\nu_{12}E_{22} = \nu_{21}E_{11}.$$

The constitutive equation for a unidirectional composite with arbitrary fiber orientation, θ , with the reference coordinate axes is given by,

$$\begin{vmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{12} \end{vmatrix} = \begin{vmatrix} \bar{Q}_{11} & \bar{Q}_{12} & \bar{Q}_{16} \\ \bar{Q}_{12} & \bar{Q}_{22} & \bar{Q}_{26} \\ \bar{Q}_{16} & \bar{Q}_{26} & \bar{Q}_{66} \end{vmatrix} \begin{vmatrix} \epsilon_{11} \\ \epsilon_{22} \\ 2\epsilon_{12} \end{vmatrix} \quad (\text{II.5.A.5})$$

where $\bar{Q}_{ij}$ are reduced stiffness for plane stress. The formulas necessary for the calculation of these values are given in Table 3.

Alternatively, the resultant stresses in the axes of symmetry (axes 1, 2) may be expressed in terms of the applied stresses (in axes x, y) as (71) (Figure 10):

$$\begin{aligned}\sigma_{11} &= \sigma_x \cos^2 \theta + \sigma_y \sin^2 \theta + 2\tau_{xy} \sin \theta \cos \theta \\ \sigma_{22} &= \sigma_x \sin^2 \theta + \sigma_y \cos^2 \theta - 2\tau_{xy} \sin \theta \cos \theta \quad (\text{II.5.A.6}) \\ \sigma_{12} &= -(\sigma_x - \sigma_y) \sin \theta \cos \theta + \tau_{xy} (\cos^2 \theta - \sin^2 \theta)\end{aligned}$$

G_{12} , E_{11} , E_{22} and ν_{12} are in turn correlated to the properties of the components of the composite by the utilization of micromechanics. A simple approximate formula derived by Halpin and Tsai (61) is given as:

$$\begin{aligned}E_{11} &\approx E_f V_f + E_m V_m \\ \nu_{12} &\approx \nu_f V_f + \nu_m V_m \quad (\text{II.5.A.7})\end{aligned}$$

$$\bar{P}/P_m = \frac{1 + \xi \eta V_f}{1 - \eta V_f}$$

where $\eta = (P_f / P_m - 1) / (P_f / P_m + \xi)$
 $\bar{P}$ = composite moduli, E_{22} , G_{12} or G_{23}
 P_f = corresponding fiber modulus, E_f , G_f

Table 3. Transformed Lamina Stiffness Matrices

$$\bar{Q}_{11} = U_1 + U_2 \cos (2\theta) + U_3 \cos (4\theta)$$

$$\bar{Q}_{22} = U_1 - U_2 \cos (2\theta) + U_3 \cos (4\theta)$$

$$\bar{Q}_{12} = U_4 - U_3 \cos (4\theta)$$

$$\bar{Q}_{66} = U_5 - U_3 \cos (4\theta)$$

$$\bar{Q}_{16} = -\frac{1}{2}U_2 \sin (2\theta) - U_3 \sin (4\theta)$$

$$\bar{Q}_{26} = -\frac{1}{2}U_2 \sin (2\theta) + U_3 \sin (4\theta)$$

where

$$U_1 = \frac{1}{8} (3 Q_{11} + 3 Q_{22} + 2 Q_{12} + 4 Q_{66})$$

$$U_2 = \frac{1}{2} (Q_{11} - Q_{22})$$

$$U_3 = \frac{1}{8} (Q_{11} + Q_{22} - 2 Q_{12} - 4 Q_{66})$$

$$U_4 = \frac{1}{8} (Q_{11} + Q_{22} + 6 Q_{12} - 4 Q_{66})$$

$$U_5 = \frac{1}{8} (Q_{11} + Q_{22} - 2 Q_{12} + 4 Q_{66})$$

where

$$Q_{11} = E_{11} / (1 - \nu_{12} \nu_{21})$$

$$Q_{22} = E_{22} / (1 - \nu_{12} \nu_{21})$$

$$Q_{12} = \nu_{21} E_{11} / (1 - \nu_{12} \nu_{21}) = \nu_{12} E_{22} / (1 - \nu_{12} \nu_{21})$$

$$Q_{66} = G_{12}$$

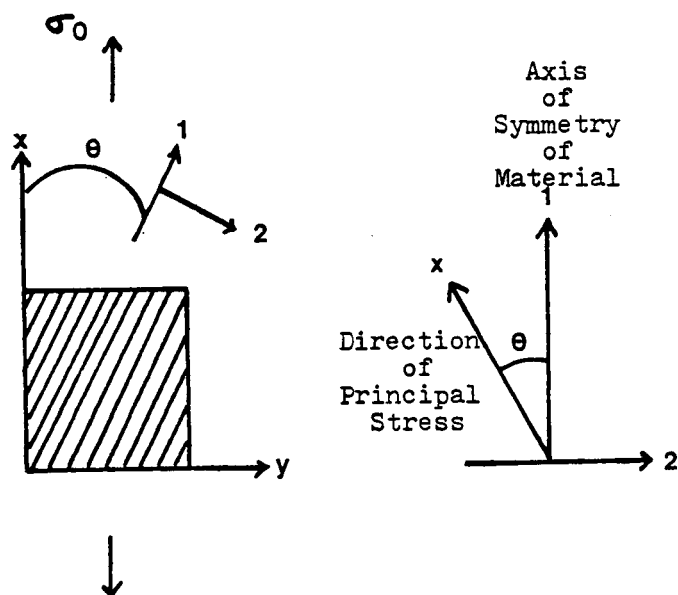


Figure 10. Coordinates in the analysis of orthotropic materials with fiber axis, θ .

P_m = corresponding matrix modulus, E_m , G_m

ξ = a measure of reinforcement which depends on the boundary conditions (Halpin and Tsai have suggested that a value of $\xi = 2$ may be used for fibers with circular cross section for transverse composite modulus E_{22} and $\xi = 1$ for shear composite modulus G_{12})

V_f = volume fraction of fibers

V_m = volume fraction of matrix

The Halpin-Tsai equation is a reasonably accurate representation of the transverse Young's modulus and the longitudinal shear modulus of the composite, provided that V_f is not large. A rigorous generalization of the Halpin-Tsai formula has been derived by Nielson (124). He has extended the Halpin-Tsai formula to take into account the packing of the reinforcing phase.

II.5.B Strength Theories

Structural applications of composites are often concerned with strength. This section presents the theories of anisotropic strength by which the strength of composites can be predicted once their basic strength properties are known. It may be mentioned here that strength is an elusive and ambiguous term. It covers many aspects associated with the failures of materials such as fracture, fatigue and creep. Failures of composites are further complicated by a multitude of independent and interacting mechanisms which include fiber breakage and buckling, delamination, matrix cavitation, dewetting and crack propagation.

There are basically four different approaches to the theoretical study of the strength of the composites. They are the phenomenological theory of strength, the rate process theories, the fracture mechanics approach and finally the statistical approach. Only the first two are relevant to the present study, and they will be discussed here.

Phenomenological theory of strength. The phenomenological theory of strength does not explain the actual mechanisms of failure. Rather it is intended only as a useful tool for material characterization.

Imagine an elementary volume $dx\ dy\ dz$, loaded on its surface by stresses σ_{ij} . It receives the stresses σ_{ij} and delivers the strains ϵ_{ij} . If the parameters describing the system include the temperature T , the system is considered close. Then the strains ϵ_{ij} are completely determined by the quantities σ_{ij} , T and their history. In such case, infinitesimal increments in the output quantities are described by means of the corresponding increments in $d\sigma_{mn}$, dt and dT as (28)

$$d\epsilon_{ij} = A_{ijmn} d\sigma_{mn} + B_{ij} dt + C_{ij} dT \quad (\text{II.5.B.1})$$

where t is time. A_{ijmn} , B_{ij} and C_{ij} are functionals of the parameters $\epsilon_{ij}(x, y, z, t)$, $\sigma_{ij}(x, y, z, t)$ and $T(x, y, z, t)$.

In strength theory it is usually assumed that the fracture of a body occurs as soon as the combination of parameters σ_{ij} , ϵ_{ij} , T and t reaches a critical value at some point in the body. The criterion usually selected is the maximum principal stress, the maximum principal

strain, the maximum shear stress, the specific distortion energy, or the total specific energy of strain (28).

The maximum stress and strain theories are very similar. If the maximum stress (or strain) value exceeds the critical level along any material principal direction, the composite is assumed to have failed. In application of the maximum stress (or strain) criterion, the stresses (or strains) in the body under consideration must be transformed to stresses (or strains) in the material principal directions. Consequently, for off-axis testing, the applied stress (σ_o) is transformed as follows:

$$\begin{aligned}\sigma_{11} &= \sigma_o \cos^2 \theta \\ \sigma_{22} &= \sigma_o \sin^2 \theta \\ \tau_{12} &= \frac{1}{2} \sigma_o \sin 2\theta\end{aligned}\tag{II.5.B.2}$$

where θ = off-axis fiber orientation

1,2 = material principal direction.

The transformed stresses are then compared to the corresponding strengths. Explicitly, the maximum stress failure theory for the off-axis composite becomes (154)

$$\begin{aligned}\sigma_o &< \frac{X}{\cos^2 \theta} \\ \sigma_o &< \frac{Y}{\sin^2 \theta} \\ \sigma_o &< \frac{T}{\sin^2 \theta}\end{aligned}\tag{II.5.B.3}$$

where X = ultimate longitudinal tensile strength

Y = ultimate transverse tensile strength

T = ultimate shear strength.

Similarly, the maximum strain theory (58) is

$$\epsilon_{11} = \frac{1}{E_{11}} (\cos^2 \theta - \nu_{12} \sin^2 \theta) \sigma_o < X'$$

$$\epsilon_{22} = \frac{1}{E_{22}} (\sin^2 \theta - \nu_{21} \cos^2 \theta) \sigma_o < Y' \quad (\text{II.5.B.4})$$

$$\epsilon_{12} = \frac{1}{G_{12}} (\sin \theta \cos \theta) \sigma_o < T'$$

where X' = ultimate longitudinal tensile strain

Y' = ultimate transverse tensile strain

T' = ultimate shear strain.

It is noted that in both theories, there is no interaction between the modes of failures. There are actually three criteria in each theory.

On the other hand, the maximum work theory has one single criterion. The theory of total elastic energy of deformation was first proposed by Beltrami (80). Since under high hydrostatic pressure, large amounts of elastic energy may be stored without causing either fracture or permanent deformation, the elastic energy as such seems to have no significance as a limiting condition. This led to the idea of subtracting the "hydrostatic" part of the energy from the total amount of elastically stored energy. Thus, it was assumed that only the energy of distortion determines the criticality of a state of stress. Accordingly, von Mises in 1913 (163) proposed a yield criterion for isotropic materials.

Generalizing the von Mises isotropic yield criterion to include orthotropic materials, Hill (70) assumed the yield criterion to be quadratic in stress components as given by

$$F\sigma_{11}^2 + G\sigma_{22}^2 + H(\sigma_{22} - \sigma_{11})^2 + 2N\tau_{12}^2 = 1. \quad (\text{II.5.B.5})$$

F, G, H, N are material orthotropic coefficients and 1, 2 are coordinates corresponding to the principal materials directions. For an orthotropic material under plane stress, the above equation is modified as

$$\frac{\sigma_{11}^2}{X^2} + \frac{\sigma_{22}^2}{Y^2} - \left| \frac{1}{X^2} + \frac{1}{Y^2} - \frac{1}{T^2} \right| \sigma_{11}\sigma_{22} + \frac{\sigma_{12}^2}{T^2} = 1. \quad (\text{II.5.B.6})$$

X, Y, T are yield stresses along the 1, 2, 3 axes respectively, and σ_{11} , σ_{22} and σ_{12} are applied stresses in the 1-2 plane. If a material is linearly elastic up to its ultimate strength, then yielding and strength become synonymous, and hence the above equations describe not only the yielding but also the failure of the material.

Azzi and Tsai (8) found the above equation is a valid strength criterion for orthotropic unidirectional fiber-reinforced composites loaded in tension. If there is a rotational symmetry about the 1 axis, the above equation can again be modified as follows:

$$\frac{\sigma_{11}^2}{X^2} + \frac{\sigma_{22}^2}{Y^2} - \frac{\sigma_{11}\sigma_{22}}{X^2} + \frac{\sigma_{12}^2}{T^2} = 1. \quad (\text{II.5.B.7})$$

For off-axis composites loaded under tension, substitution of the stress transformation equations (II.5.B.2) yields the Tsai-Hill equation as (8, 159)

$$\frac{\cos^4 \theta}{X^2} + \frac{\sin^4 \theta}{Y^2} + \left| \frac{1}{T^2} - \frac{1}{X^2} \right| \sin^2 \theta \cos^2 \theta = \frac{1}{\sigma_o^2} \quad (\text{II.5.B.8})$$

where Y, X, T are now tensile failure stress, transverse failure stress and in-plane shear failure stress respectively.

The maximum stress theory has been used by Cooper (32), Stowell and Liu (154), Kelly and Davies (82), and Jackson and Cratchley (74) for various systems. Grimes and Whitney (58) used the maximum strain theory for graphite fiber reinforced composite. Azzi and Tsai (8) and Agarwal and Narang (2) used the Tsai-Hill equation for glass fiber reinforced epoxy composites. Tsai (158) compared these theories for glass fiber reinforced composite and concluded that the fundamental difference between the Tsai-Hill criterion and others lies in the question of interactions among the failure modes. The maximum stress and strain theories assume there is no interaction among three failure modes and hence the Tsai-Hill criterion has found wider acceptability compared to the other two theories.

Rate process theories of fracture. As opposed to the phenomenological theories, rate process theories of fracture recognize the presence of discrete particles or elements forming the material body. Rate process theories intend to relate in a straightforward manner

breakage, displacement and reformation of these elements to deformation, defect development and fracture. Rate process theories of fracture were at first applied to the fracture of polymers. Independently from each other, Zhurkov et al. (168-176) in the Soviet Union and Bueche (21-23) in the United States expressed the idea that in fracture of polymers the breakage of primary bonds plays an important role. Using light scattering, infrared absorption, small angle X-ray scattering and electron spin resonance, they were able to show that polymer fracture occurs in three stages:

- 1) Formation of localized microsites of fracture with strongly overloaded interatomic bonds which results from non-uniform load distribution
- 2) Scission of overloaded bonds by thermal fluctuations with subsequent formation of submicrocracks
- 3) Coalescence of incipient microcracks into large main cracks, which leads to the eventual breakdown of a solid.

The detailed results on sizes and concentration of submicrocracks for different polymers before failure are summarized in Table 4 (169).

Rate process theories of fracture show that the time to fracture, t_f , under uniaxial stress σ_0 could be expressed by an exponential relationship involving three kinetic parameters:

$$t_f = t_0 \exp[(U_0 - \gamma\sigma_0)/kT] \quad (\text{II.5.B.9})$$

where t_0 = inverse of molecular oscillation frequency

U_0 = activation energy for bond scission

Table 4. Microvoids before Fracture (169)

Polymer	Diameter of Microvoids, μm	Concentration, per cubic cm
Nylon-6	0.009	9×10^{16}
Nylon-6, annealed at 220°C	0.022	5×10^{15}
Polypropylene	0.032	7×10^{14}
Polyethylene	0.015	6×10^{15}
Polyvinylchloride	0.30	1×10^{12}
Polyvinylbutyral	0.30	3×10^{12}
Polymethylmethacrylate	0.17	6×10^{12}
Acetobutyralcellulose	0.13	1×10^{12}

γ = frequency of thermal vibration of atoms

k = Boltzmann's constant

T = absolute testing temperature.

The above formula was applied to various fibrous composites (137), and it was shown that the formula to hold for composites within a certain stress and temperature range. Thus it was concluded that the fracture of composites, as that of other solids, should be considered as a thermally activated process of gradual accumulation of defects. More recently a somewhat different form of the above equation has been derived by Christensen (29), and it was applied to aramid composite strands with encouraging result, again indicating gradual crack growth within the composite.

II.5.C Small Angle X-Ray Scattering (SAXS)

Small angle scattering can yield valuable information on the size, amount and distribution of inhomogeneities. X-ray interference effects result from variations in electron density from one point to another in the material. If the atoms are regularly arranged according to a space lattice, the scattering angle 2θ is related to the interplanar spacing d by the Bragg equation:

$$n\lambda = 2d \sin\theta \quad (\text{II.5.C.1})$$

where n = order of reflection

λ = wavelength of the incident X-ray.

Because of the reciprocity between interatomic distance and $\sin\theta$, inhomogeneities of large dimensions generate X-ray interference scattering

at very small angle, typically less than 2° with $\text{CuK}\alpha$ X-ray. The two kinds of inhomogeneity that are responsible for small-angle X-ray scattering from solid polymers are (a) alternation of crystalline and amorphous regions (3) and (b) the presence of microvoids dispersed throughout the polymer (69, 149, 150). The former generally results in discrete scattering while the latter results in diffuse scattering with a maximum intensity at $\theta = 0^\circ$. The experimental requirements for SAXS experiments are very exacting in comparison with the requirement for wide-angle experiments, and they are discussed in references 3, 59 and 60.

For the interpretation of small-angle scattering, various types of ambiguities must be reckoned with. As a consequence of the Babinet principle of reciprocity it is not possible to distinguish the scattering by a system of particles in space from the scattering by a similar system of microvoids in a solid continuum. In addition it is not possible to differentiate without some degree of uncertainty the effects due to particle shape from those due to polydispersity. Finally, in dense systems interparticle interferences cannot be neglected. Thus the complete description of a dense system would require information with respect to size and shape of the particles, their size distribution, and their position and orientation with respect to each other (151). Consequently in all cases that have polydispersity or different shapes only an average quantity is obtainable, or possibly some rough approximation of shape or statistical size distribution can be determined.

It is well known that the diffraction pattern of a sample can be described in terms of a reciprocal space. If $\rho(\vec{x})$ is the electron density of the diffracting body at a point defined by the vector $\vec{x}$, then $A(\vec{k})$, the amplitude of the diffracted radiation is given by

$$A(\vec{k}) = \int \rho(\vec{x}) e^{-i\vec{k} \cdot \vec{x}} d\vec{x} \quad (\text{II.5.C.2})$$

where

$$\vec{k} = \frac{2\pi}{\lambda} (\vec{S} - \vec{S}_0).$$

λ is the wavelength of the radiation and $\vec{S}_0$ and $\vec{S}$ are unit vectors in the direction of the incident and diffracted rays, respectively (Figure 11). The scattered intensity is the product of the amplitude A and its complex conjugate A^*

$$I(\vec{k}) = A(\vec{k}) A^*(\vec{k}). \quad (\text{II.5.C.3})$$

However, as a consequence of collimation errors, exposure time, etc., only an average is observable (72).

For the theoretical treatment of SAXS, one must distinguish between dilute and dense systems. For dilute systems of identical randomly oriented particles, there is no interference between particles and the intensities diffracted by the various particles simply add. Thus, if ρ_0 is the electron density of the continuous medium, the scattering power per particle is given by

$$\overline{I(\vec{s})} = (\rho - \rho_0)^2 \overline{|\Sigma(\vec{s})|^2} \quad (\text{II.5.C.4})$$

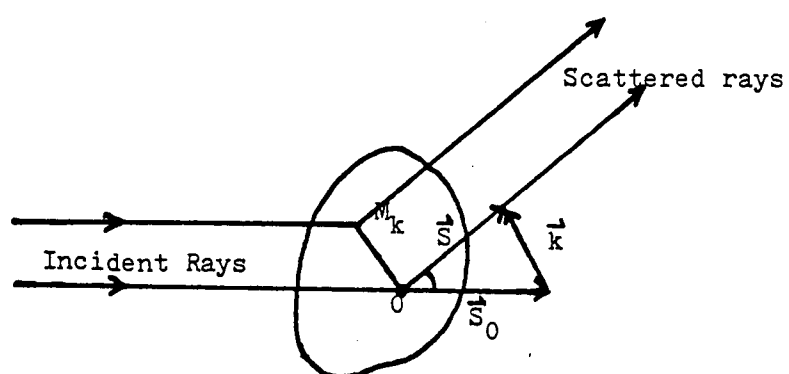


Figure 11. Diffraction by a single particle.

where $\vec{s} = (\vec{S} - \vec{S}_0)/2\pi$ and $|\vec{s}| = \frac{2 \sin \theta}{\lambda}$ and $\Sigma(\vec{s})$ is the Fourier transform of the form factor $\sigma(\vec{x})$ and is given by (59)

$$\Sigma(\vec{s}) = \int_V \exp(-2\pi i \vec{s} \cdot \vec{x}) dV_x.$$

$\overline{|\Sigma(\vec{s})|^2}$ means the average value of $|\Sigma(\vec{s})|^2$ over the sphere of radius $|\vec{s}|$.

For spherical particles of radius a , $I(s)$ becomes (59)

$$\overline{I(s)} = \left| (\rho - \rho_0) V \right|^2 \left| \frac{\text{Si}(4\pi sH)}{2\pi sH} - \frac{\sin^2(2\pi sH)}{(2\pi sH)^2} \right| \quad (\text{II.5.C.5})$$

For very thin cylinders of volume V and length $2H$, $I(s)$ becomes (59)

$$\overline{I(s)} = \left| (\rho - \rho_0) V \right|^2 \left| \frac{\text{Si}(4\pi sH)}{2\pi sH} - \frac{\sin^2(2\pi sH)}{(2\pi sH)^2} \right| \quad (\text{II.5.C.6})$$

where $\text{Si}(t) = (\sin t/t)$.

For disks of radius R and volume V , $I(s)$ becomes (59)

$$\overline{I(s)} = \left| (\rho - \rho_0) V \right|^2 \frac{2}{(2\pi sR)^2} \left| 1 - \frac{1}{2\pi sR} J_1(4\pi sR) \right| \quad (\text{II.5.C.7})$$

where J_1 is the Bessel function of first order.

For ellipsoids of revolution of volume V and axes a , a and va , $I(s)$ becomes (59)

$$\overline{I(s)} = \left| (\rho - \rho_0) V \right|^2 \int_0^{\pi} \frac{2\pi s a v}{\sqrt{\sin^2 \alpha + v^2 \cos^2 \alpha}} \cos \theta d\theta \quad (\text{II.5.C.8})$$

where $\phi(u) = 3 \frac{\sin u - u \cos u}{u^3}$, $u = 2\pi a s$ and $\alpha = \tan^{-1} (v \tan \theta)$.

According to Guiner (60), a Gaussian curve can be used as the first approximation for the scattering of particles of any shape near $s=0$, and hence if an approximation for $\Sigma(s)$ in the exponential form

$$\Sigma(s) = V \exp(-2\pi^2 s^2 R_D^2) \quad (\text{II.5.C.9})$$

where R_D is the average inertial distance, is used then an approximate formula for the scattering power per particle having definite orientation is given by

$$\overline{I(s)} = (\rho - \rho_0)^2 V^2 \exp(-4\pi^2 s^2 R_D^2) \quad (\text{II.5.C.10})$$

$$\overline{I(k)} = (\rho - \rho_0)^2 V^2 \exp(-k^2 R_D^2).$$

For a spherical particle of radius a , $R_D = a/\sqrt{5}$ and $\overline{I(s)}$ and $\overline{I(k)}$ are given by

$$\overline{I(s)} = (\rho - \rho_0)^2 V^2 \exp(-\frac{4}{5}\pi^2 a^2 s^2) \quad (\text{II.5.C.11})$$

$$\overline{I(k)} = (\rho - \rho_0)^2 V^2 \exp(-\frac{1}{5}a^2 k^2).$$

For ellipsoids of revolution of axes a , a , va irradiated perpendicular to their axes of revolution, R_D is $a/\sqrt{5}$ and $va/\sqrt{5}$ in the direction parallel and normal to these axes respectively and $\overline{I(s)}$ and $\overline{I(k)}$ are given by (Figure 12)

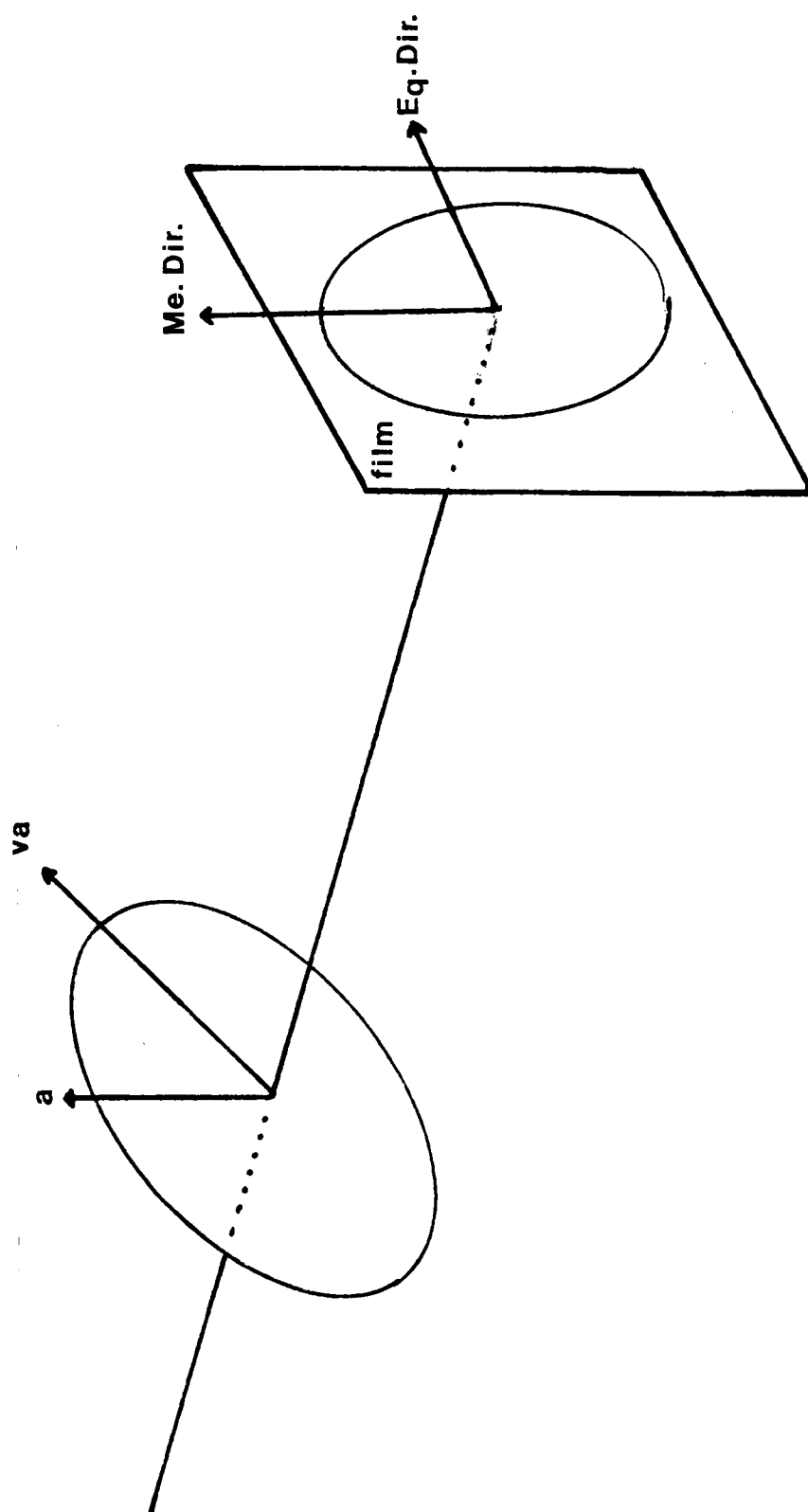


Figure 12. SAXS by an ellipsoid of revolution whose axis is perpendicular to the incident ray.

$$\overline{I(s)} = (\rho - \rho_o)^2 v^2 \exp(-\frac{4}{5}\pi^2 s^2 a^2) \quad (\text{II.5.C.12})$$

$$\overline{I(k)} = (\rho - \rho_o)^2 v^2 \exp(-\frac{1}{5}\pi^2 k^2)$$

for the equatorial direction and

$$\overline{I(s)} = (\rho - \rho_o)^2 v^2 \exp(-\frac{4}{5}\pi^2 s^2 v^2 a^2) \quad (\text{II.5.C.13})$$

$$\overline{I(k)} = (\rho - \rho_o)^2 v^2 \exp(-\frac{1}{5}\pi^2 a^2 k^2)$$

for the meridional direction.

When the particles have random orientations, R , the radius of gyration, defined by

$$R^2 = \frac{\int r^2 dV}{V} \quad (\text{II.5.C.14})$$

is used. Thus the average scattering power per particle in the case of random orientation is given by

$$\overline{I(s)} = (\rho - \rho_o)^2 v^2 \exp(-\frac{4\pi^2 R^2 s^2}{3}) \quad (\text{II.5.C.15})$$

$$\overline{I(k)} = (\rho - \rho_o)^2 v^2 \exp(-\frac{R^2 k^2}{3}).$$

For a spherical particle of radius a , $R = (3/5)^{1/2}a$ and for an ellipsoid of revolution with axes a, a, va , $R = ((2+v^2)/5)^{1/2}a$. By taking logarithms to the base 10 of both sides of equation (II.5.C.15),

$$\log \overline{I(s)} = \log \left| (\rho - \rho_o)^2 \right| V^2 - \frac{4\pi^2}{3} 0.4343 R^2 s^2 \quad (\text{II.5.C.16})$$

$$\log \overline{I(k)} = \log \left| (\rho - \rho_o)^2 \right| V^2 - \frac{1}{3} 0.4343 R^2 k^2$$

Thus if $\log I$ is plotted as a function of s^2 or k^2 , the curve tends to a straight line of slope

$$\alpha = - \frac{4\pi^2}{3} 0.4343 R^2 \quad (\text{II.5.C.17})$$

$$\alpha' = - \frac{1}{3} 0.4343 R^2.$$

It is to be noted here that if the particles are randomly oriented the resulting pattern is circularly symmetric regardless of the particle shape, hence the radius of gyration is the only precise parameter which can be measured. If the particles have a definite orientation the resulting pattern is no longer circularly symmetric and the determination of inertial distances for different orientations gives a good idea of the shape of the particles.

When the non-identical particles are separated widely enough, the particles are classified into groups of identical particles, and it is assumed that for each group the Guinier or exponential approximation is valid. If the i th group with n_i electrons per particle and with radius of gyration R_i is present with relative proportion g_i , the scattering power of the sample is then given by

$$\overline{I(s)} = \sum_i g_i n_i^2 \exp\left(-\frac{4\pi^2}{3} R_i^2 s^2\right) \quad (\text{II.5.C.18})$$

$$\overline{I(k)} = \sum_i g_i n_i^2 \exp\left(-\frac{1}{3} R_i^2 k^2\right).$$

For small s or k , expanding each of the exponents in a series, $\overline{I(s)}$ and $\overline{I(k)}$ become

$$\overline{I(s)} = \sum_i g_i n_i^2 \left(1 - \frac{4\pi^2 s^2}{3} \frac{\sum_i g_i n_i^2 R_i^2}{\sum_i g_i n_i^2} + \dots\right) \quad (\text{II.5.C.19})$$

$$\overline{I(k)} = \sum_i g_i n_i^2 \left(1 - \frac{k^2}{3} \frac{\sum_i g_i n_i^2 R_i^2}{\sum_i g_i n_i^2} + \dots\right).$$

A plot of $\ln I$ versus s^2 or $\ln I$ versus k^2 has a tangent as $s \rightarrow 0$ or $k \rightarrow 0$ with slope $-\frac{4\pi^2}{3} R_m^2$ or $-\frac{1}{3} R_m^2$ where

$$R_m^2 = \frac{\sum_i g_i n_i^2 R_i^2}{\sum_i g_i n_i^2}. \quad (\text{II.5.C.20})$$

R is an average radius of gyration of the particles. This equation shows that large radii of gyration are favored in the experimentally determined average.

Dense systems in general produce discrete interferences, diffuse scattering, or both at small angle and in interpreting the interparticle interference effects cannot be neglected. If discrete interferences appear in the small angle scattering patterns, they are usually observed in only one direction and the long spacing derived from the

first order reflection with the aid of Bragg's law is interpreted as the mean distance between centers of successively alternating high electron density regions.

On the other hand, if only diffuse scattering is observed from microvoids, the volume fraction of microvoids can be computed from the total integrated intensity scattered near the origin of reciprocal space. This integrated intensity is called the invariant, Q , of the scattered intensity and is given by

$$Q = 4\pi \int_0^\infty s^2 I(s) ds \quad (\text{II.5.C.21})$$

For a cylindrically symmetric distribution of scattered intensity, Q is given in terms of the intensities measured on the detector plane by (14)

$$Q_d = \frac{\int_0^\infty \int_{-\infty}^\infty 2\pi s_2 I(s_1, s_2) ds_2 ds_1}{I_0 \text{ (CT) (TM)}} \quad (\text{II.5.C.22})$$

and

$$Q = \frac{1}{(a\lambda)^3} \cdot Q_d \quad (\text{II.5.C.23})$$

where s_2 = the horizontal coordinate on the detector plane
perpendicular to the fiber axes of the fiber
sample
 s_1 = the vertical coordinate on the detector plane
parallel to the fiber axis

$I(s_2, s_1)$ = measured intensity at coordinate s_2, s_1

CT = fixed counting time

I_o = the intensity of the incident beam

TM = sample transmission factor

a = the specimen to detector distance

λ = the wavelength of radiation

According to Kratky and Miholic (89) the mean square fluctuation of the electron density is given by

$$\overline{(\rho - \rho_o)^2} = K Q_d \quad (\text{II.5.C.24})$$

where

$$K = \frac{1}{i_e N^2 t a \lambda^3}.$$

Here i_e is the Thomson scattering constant for a free electron ($7.94 \times 10^{-26} \text{ cm}^2$), N is the Avogadro's number, t is the specimen thickness in centimeters, a is the specimen to detector distance in centimeters, λ is the wavelength in centimeters.

For a system of two uniform phases a general expression for mean square electron density fluctuation is given (3) as

$$\overline{(\rho - \bar{\rho})^2} = (\rho - \rho_o)^2 w_1 w_o \quad (\text{II.5.C.25})$$

with $w_o + w_1 = 1$ where

ρ_o = electron density of phase 1

ρ = electron density of phase 2

$\bar{\rho}$ = average electron density of the system

w_o = volume fraction of phase 1

w_1 = volume fraction of phase 2

Since the chemical composition of each phase is uniform, the electron densities may be replaced by mass densities (105) as

$$\rho = \frac{d \cdot Z}{M.W.} \text{ (moles of electrons/cc)} \quad (\text{II.5.C.26})$$

where d = mass density (g/cm^3)

$M.W.$ = molecular weight (g/mole)

Z = atomic number.

CHAPTER III

EXPERIMENTAL PROCEDURES AND METHODS

III.1 MATERIALS

III.1.A Epoxy Resins

In the present research, two commercially available epoxy resins were studied. They were the diglycidyl ether of bisphenol A (EPON 828, DER 332) epoxies obtained from Shell Chemical Company and Dow Chemical Company. The EPON 828 has an average molecular weight of about 370-384 and a viscosity of about 120 centipoises at 25°C (145). It has the epoxy equivalent weight (WPE) of 190 (145). The DER 332 is a highly purified diglycidyl ether of bisphenol A with an average molecular weight of about 340-355 and a viscosity of about 4000-6400 centipoises at 25°C (133). It has the WPE of 172-178 (133).

The EPON 828 was cured with Nadic Methyl Anhydride (NMA) obtained from Shell Chemical Company. NMA whose chemical name is X-methyl-5-norborene-2,3-dicarboxylic anhydride is a light yellow liquid of viscosity of 2 poises at 25°C. N,N-dimethylbenzylamine (BDMA) from Aldrich Chemical Company is used as an accelerator. DER 332 was cured with m-phenylene diamine (MPDA) and diethylene triamine (DETA) both from Eastman Kodak Company.

All materials were used as received without any purification. The structures of these materials are presented in Table 5.

Table 5. Chemical Structures of Materials

Dyglycidyl Ether of Bisphenol A (EPON 828)	
Nadic Methyl Anhydride (NMA)	
Benzyltrimethylamine (BDMA)	
Dyglycidyl Ether of Bisphenol A (DER 332)	
m-Phenylene Diamine (MPDA)	
Diethylene Triamine (DETA)	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$

III.1.B Kevlar^R Fibers

Kevlar^R 49 and Kevlar^R 29 fiber yarns were obtained from Du Pont Chemical Company. Kevlar^R was 1140 denier yarn and used without any further treatment.

Three degraded Kevlar^R 49 fibers were furnished by the Lawrence Livermore Laboratory for small angle X-ray scattering studies. The degradation procedures are presented in Table 6.

III.2 SAMPLE PREPARATION AND CHARACTERIZATION

III.2.A Sample Preparation

Epoxy resins. The cure conditions and the weight percent of curing agents are presented in Table 7.

EPON 828/NMA samples were prepared with three different amounts of NMA. EPON 828 was measured and heated to 60°C and then was immediately mixed with NMA. The accelerator BDMA was added to this mixture. The mixture was stirred for five minutes using a mechanical stirrer and then degassed in a vacuum chamber for ten minutes. The mixture was poured into a warm aluminum mold (3"x4"x $\frac{1}{4}$ ") (Figure 13) sprayed with mold releasing agent and then cured in a compression molding machine.

DER 332/MPDA samples were prepared by heating the resin and curing agent separately to 80°C then combined and mixed thoroughly with a mechanical stirrer for five minutes while being maintained at 80°C. The warm mixture was degassed for ten minutes in a vacuum chamber then poured into the mold and cured.

Table 6. Degradation Procedures for Kevlar^R 49 Fibers

Degraded Kevlar ^R 49 #1	Degraded at 125° C, 100% R. H. for 40 days
Degraded Kevlar ^R 49 #2	Degraded at 150° C, 100% R. H. for 14 days
Degraded Kevlar ^R 49 #4	Degraded at 200° C, 100% R. H. for 2 days

Table 7. Cure Conditions

Epoxy Resin	Curing Agent	Wt. % of Curing Agent	Cure Condition
Dyglycidyl Ether Bisphenol A (EPON 828)	NMA BDMA	48 (90*) 0.5	1 hr 93°C 4 hr 120°C 3 hr 150°C
Dyglycidyl Ether Bisphenol A (EPON 828)	NMA BDMA	41 (70*) 0.5	1 hr 93°C 4 hr 120°C 3 hr 150°C
Dyglycidyl Ether Bisphenol A (EPON 828)	NMA BDMA	52 (110*) 0.5	1 hr 93°C 4 hr 120°C 3 hr 150°C
Dyglycidyl Ether Bisphenol A (DER 332)	MPDA	14 (16*)	2 hr 85°C 24 hr 160°C
Dyglycidyl Ether Bisphenol A (DER 332)	DETA	11 (12*)	24 hr 23°C 24 hr 150°C

* Per hundred part epoxy resin.

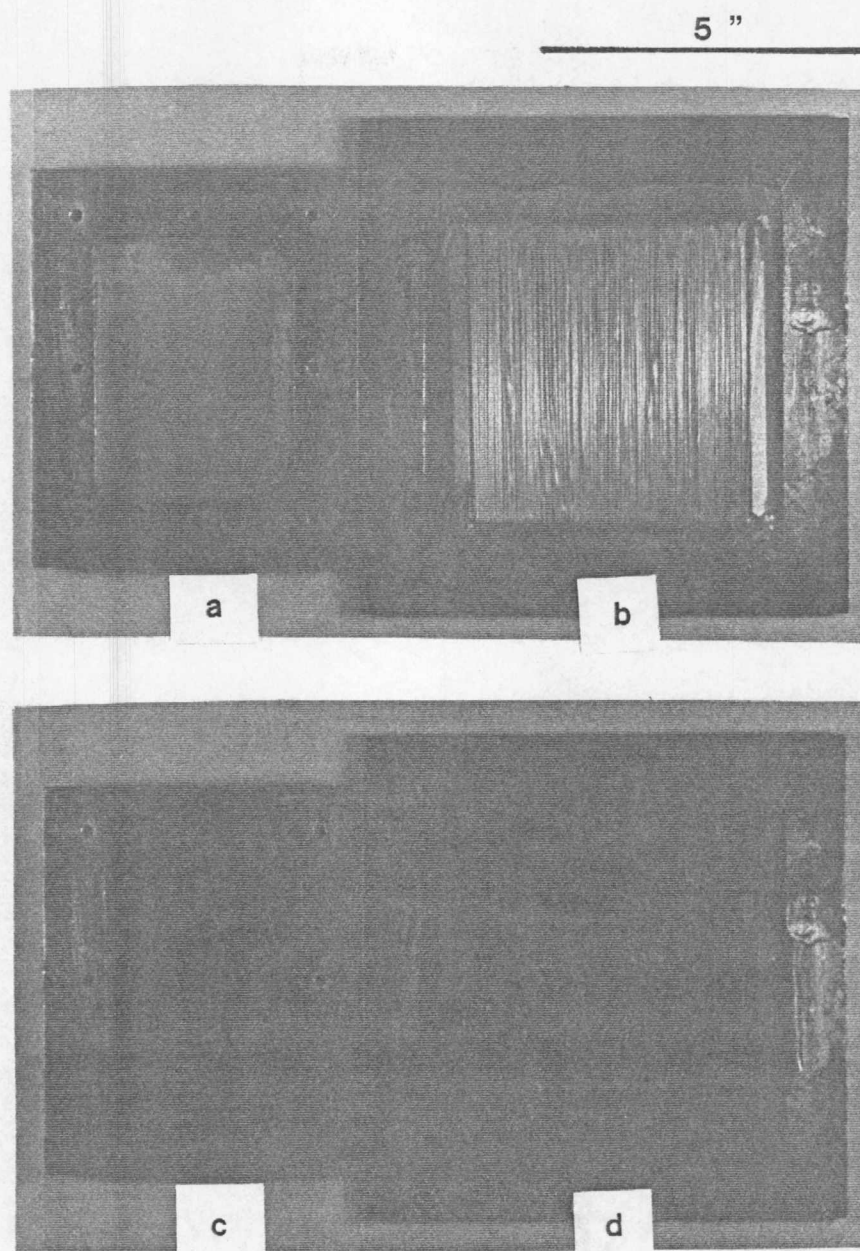


Figure 13. Molds a) for epoxy resins, b) for Kevlar^R fiber composites, c) after curing, d) after curing.

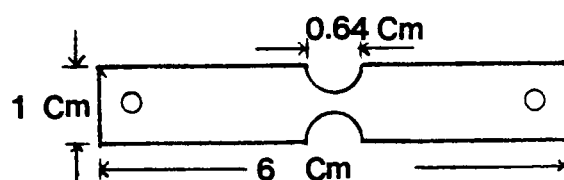
Composites. Kevlar^R 49 fiber yarns were wound uniaxially around an aluminum frame (Figure 13) washed with acetone. In order to study the dependence on the volume fractions of fibers, two different composites were prepared by varying the amount of fibers. The Kevlar^R 49 fiber wound aluminum frame was placed in an aluminum mold ($5\frac{1}{2}" \times 5\frac{1}{2}" \times \frac{1}{8}"$) (Figure 13), and epoxy resin was poured making sure all the fibers were immersed in the resin. Then the resin was cured following the same schedule as in Table 7.

III.2.B Sample Characterization

Tensile testing of epoxies and composites. The behavior of epoxies and Kevlar^R fiber reinforced epoxies with various fiber orientations have been studied under tensile load. Tensile tests provide the data necessary for the study of the stress-strain behavior, the elastic modulus and the strengths.

Dogbone-shaped tensile bar samples were cut from the cured epoxies and composites. The dimensions of the tensile bars are shown in Figure 14. For epoxies five tensile bars per sample were tested using an Instron Tensile Tester at room temperature. For composites tensile bars with four different fiber angles (0° , 30° , 45° , 90°) were cut from a single molded sheet. Three tensile bars for each angle were tested using the Instron. The tensile tests were performed using a crosshead speed of $0.05"/\text{min}$ in all cases. The force-elongation curves were used to evaluate Young's modulus, ultimate tensile strength and ultimate elongation. Young's modulus (E) is given by the following equation

a. For Small Angle X-Ray Experiments



b. For Mechanical Experiments

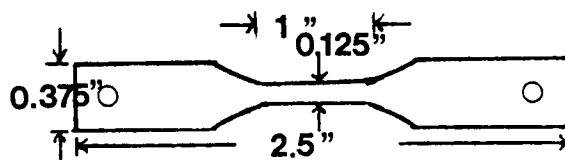


Figure 14. The dimensions of the tensile bars.

$$E = \frac{\sigma}{\epsilon}$$

and was calculated from the initial slope of the force-elongation curve.

The ultimate tensile strength (σ) was calculated from the expression

$$\sigma = \frac{F}{A_0}$$

where F is the force at break and A_0 is the initial cross sectional area. The ultimate elongation (%) on the sample (ϵ) was determined from the following equation:

$$\epsilon = \frac{\Delta L}{L_0} = 100 \times \frac{(\text{Crosshead Speed}) \times (\text{Chart Distance})}{(\text{Chart Speed}) \times L_0}$$

where L_0 is the initial gauge length of the specimen.

Density measurement. Densities of degraded Kevlar^R fibers, epoxies and composites were measured in a density gradient column made of sodium bromide-water solution in the range of density of 1.180 to 1.300 g/cm³ at 25°C. The techniques of constructing a linear density gradient column are described by Tung and Taylor (160) and Wiley (168). The samples were dropped into the column for at least twenty-four hours beforehand to reach their final levels of displacement.

Morphological characterization. The morphologies of Kevlar^R fibers, epoxies and composites were studied using an AMR Model 900 high resolution Scanning Electron Microscope and a Leitz Optical Microscope. The epoxy and composite SEM samples were prepared by cutting

the fractured specimens near their fractured surface and mounting on aluminum sample holders using a commercial rapid cure epoxy. The Kevlar^R fiber SEM samples were prepared by cutting the fibers using a sharp razor blade and then mounting on double-stick adhesive tape. After the samples were mounted, they were metalized with gold-palladium in a vacuum chamber.

III.3 SMALL ANGLE X-RAY SCATTERING (SAXS)

EXPERIMENTAL PROCEDURE

III.3.A Sample Preparation

The most important dimension of the sample in SAXS experiment is the thickness. Therefore the linear absorption coefficient determination of epoxy was carried out at the outset, and it was determined to be 7.3 cm^{-1} . The optimum thickness of the epoxy is then about 0.14 cm. The optimum thickness of the composites is assumed to be close to this value. Once the thickness is set, the width is determined from both the maximum loading available to the sample and the sample's breaking stress. The maximum loading available to the sample by the existing hydraulic system in the NCSASR SAXS facility is 533 N. Using a breaking stress of $8.00 \times 10^7 \text{ Pa}$, the width of the sample should be less than 0.45 cm. Since the width of the X-ray beam is 0.1 cm, this dimension is tolerable.

The thickness of the molded and cut tensile bars was 0.32 cm, and hence it was necessary to slice the tensile bars into two thinner pieces. This was carried out using the Buehler ISOMET^R Low Speed Saw. The surfaces of the sliced tensile bars were then smoothened using

ultra-fine sandpaper grinder and then washed thoroughly with water and dried in air.

The nature of the inhomogeneities in cured epoxies was studied by obtaining SAXS patterns for liquid epoxy. This was carried out by using a sample holder with a $\frac{1}{4}$ " diameter hole in the middle (Figure 15). Both ends of the hole were sealed tight using two thin Mylar^R films. A scattering pattern was then obtained from Mylar^R films only. One end of the hole was then peeled off and liquid epoxy was filled into the hole. The open end was then sealed with the same piece of Mylar^R film, and a scattering pattern was obtained and corrected for background by subtracting the scattering patterns of the Mylar^R films.

In order to study the dynamic scattering behavior of Kevlar^R fibers a special fiber straining device (Figure 16) was designed and used.

III.3.B NCSASR SAXS Facility

The NCSASR SAXS apparatus, including the newly installed dynamic deformation device used in this work, has been described in detail in the literature (67, 68, 166). A brief summary of important characteristics nevertheless is presented here.

An overall view and a schematic drawing of the SAXS device is shown in Figure 17. Here the important components of the device will be described.

X-ray Generator: The X-ray generator is a 6.0 KW Rigaku-Denki rotating anode type. When operating at 40 KV and 40 mA with a source to sample distance of 1.6 meters, the CuK α intensity can be as high as 2.5×10^6 photons per square millimeter per second.

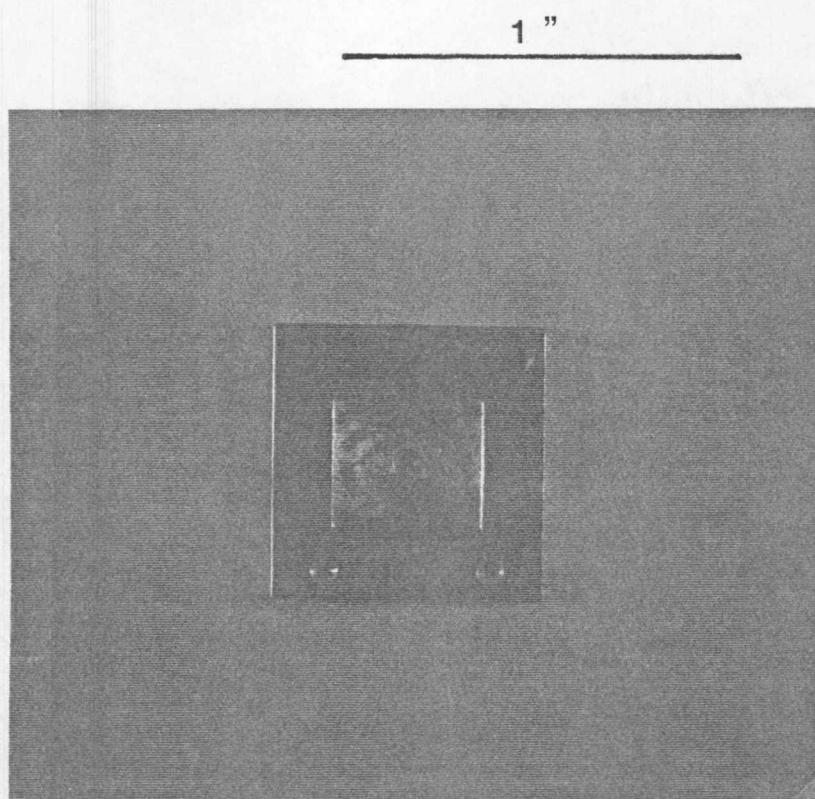


Figure 15. Sample holder for liquid epoxy SAXS experiments.

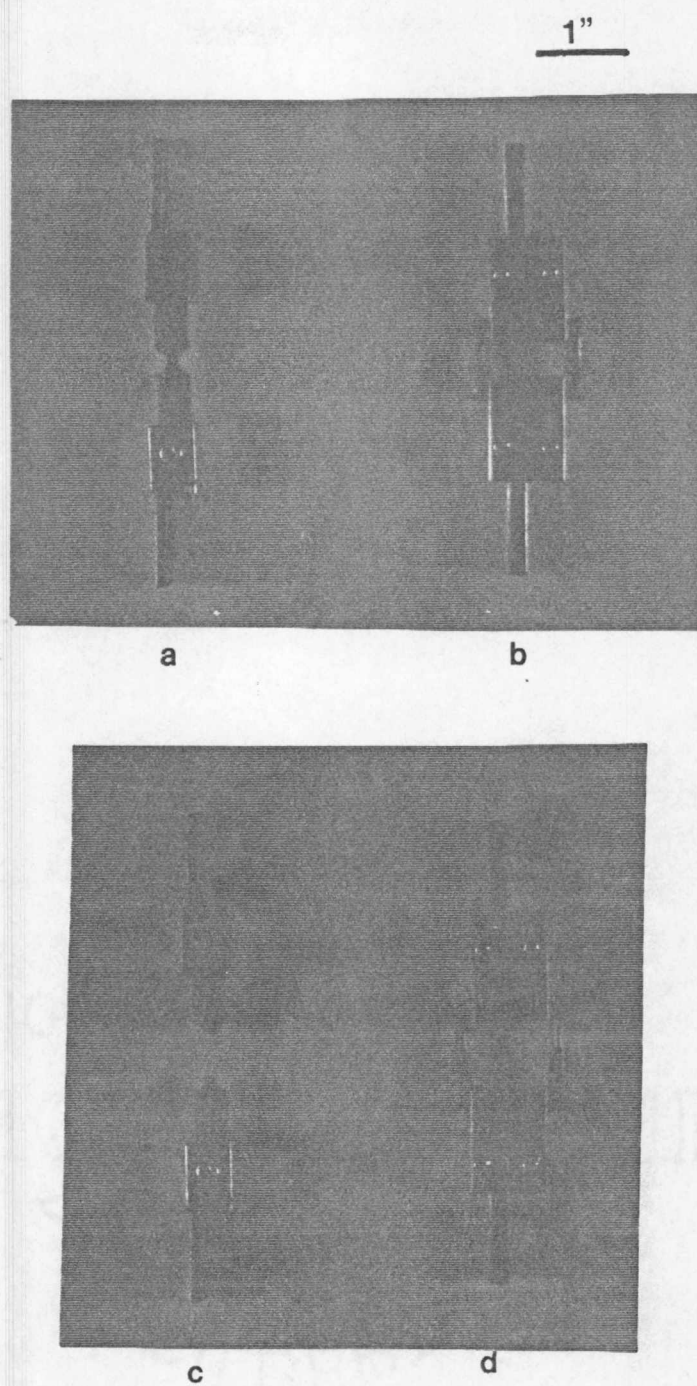


Figure 16. SAXS sample straining devices.

- a) for epoxy resins and composites.
- b) for Kevlar^R fibers
- c) after epoxy sample has failed
- d) after the Kevlar^R fibers have failed

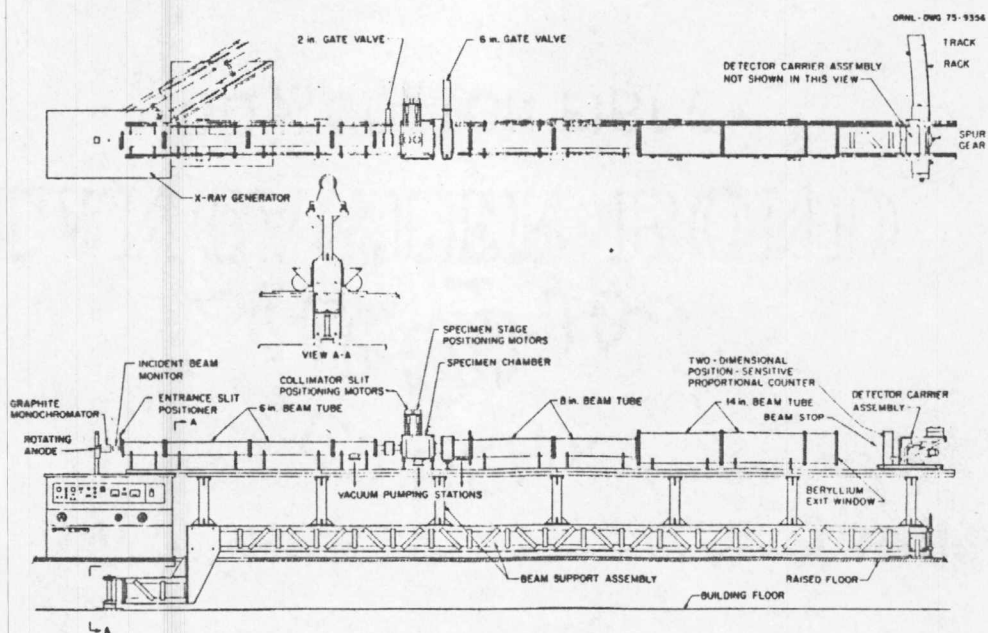


Figure 17. Overall view and schematic drawing of SAXS facility.

Monochromator and Collimation: The incident beam monochromator is a small, flat piece of pyrolytic graphite. The angle of the X-ray from the generator with respect to the collimation apparatus is set so that $\text{CuK}\alpha$ ($\lambda = 1.54\text{\AA}$) radiation is used. The collimation system consists of two 1 mm^2 pinholes separated by 1.6 meters. The pinhole geometry is used in order to avoid a deconvolution step in the desmearing of scattering data.

Sample Chamber: The sample chamber (Figure 18) consists of a 30x30x35 cm vacuum chamber containing externally operated x-y positioning devices for the specimen stage. A piece of glassy carbon is installed on a sliding mechanism and by use of a motor equipped with an eccentric cam, the glassy carbon can be reproducibly moved into the incident beam. Its attenuation is measured to determine the transmission coefficient of the sample.

Sample Holder: The sample holder pullrods are equipped with a hydraulic system which allows up to 533 N tensile force to be applied to the sample. The hydraulic system is operated by a function generator with servo control. It was designed to operate with sinusoidal or other cyclic loadings. However, in this study the frequency response was too low to obtain meaningful data and hence a step loading was chosen (Figure 19). Deformation of the sample was accomplished by movement of the upper pullrod, while the lower pullrod remains stationary.

Detector: The detector is a two-dimensional position-sensitive proportional counter. It consists of two parallel grids of 75 μm wires.

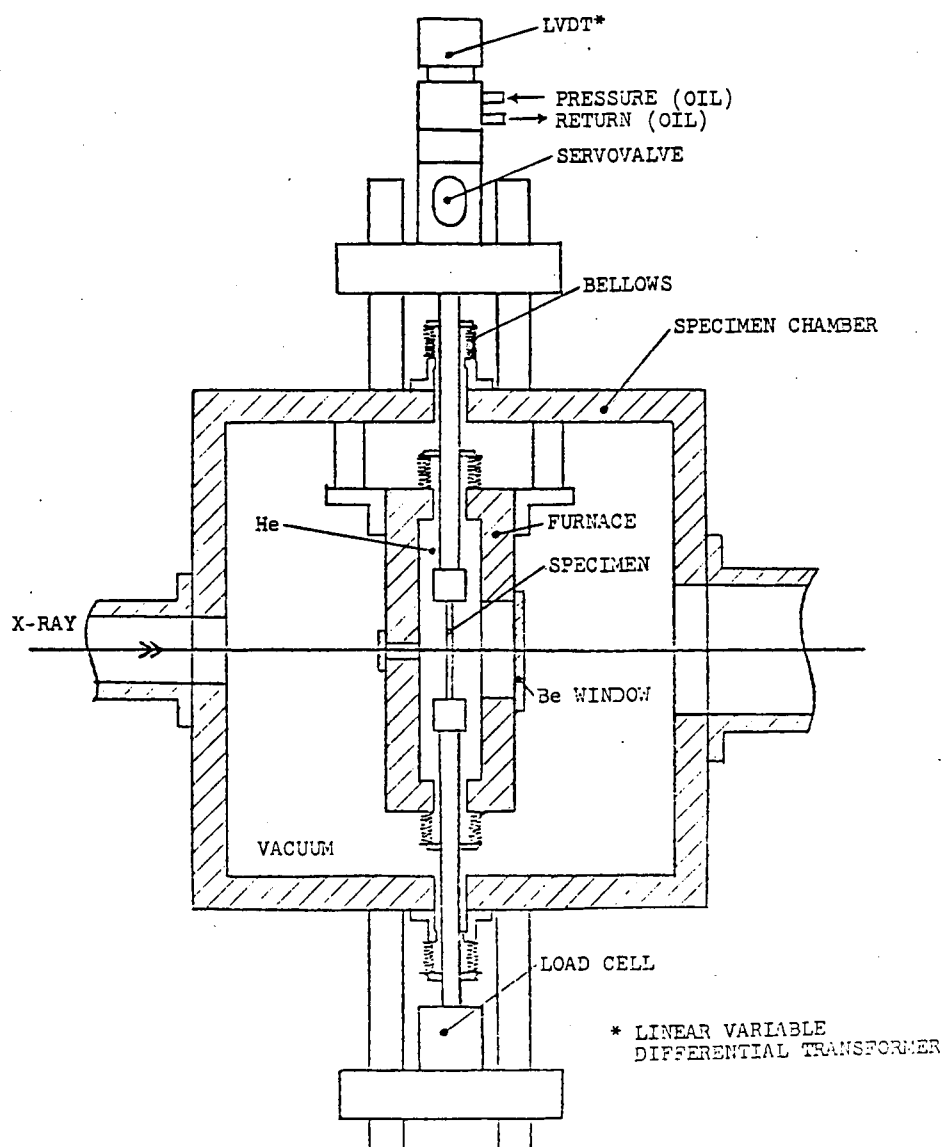


Figure 18. Schematic drawing of the sample chamber of the dynamic SAXS device.

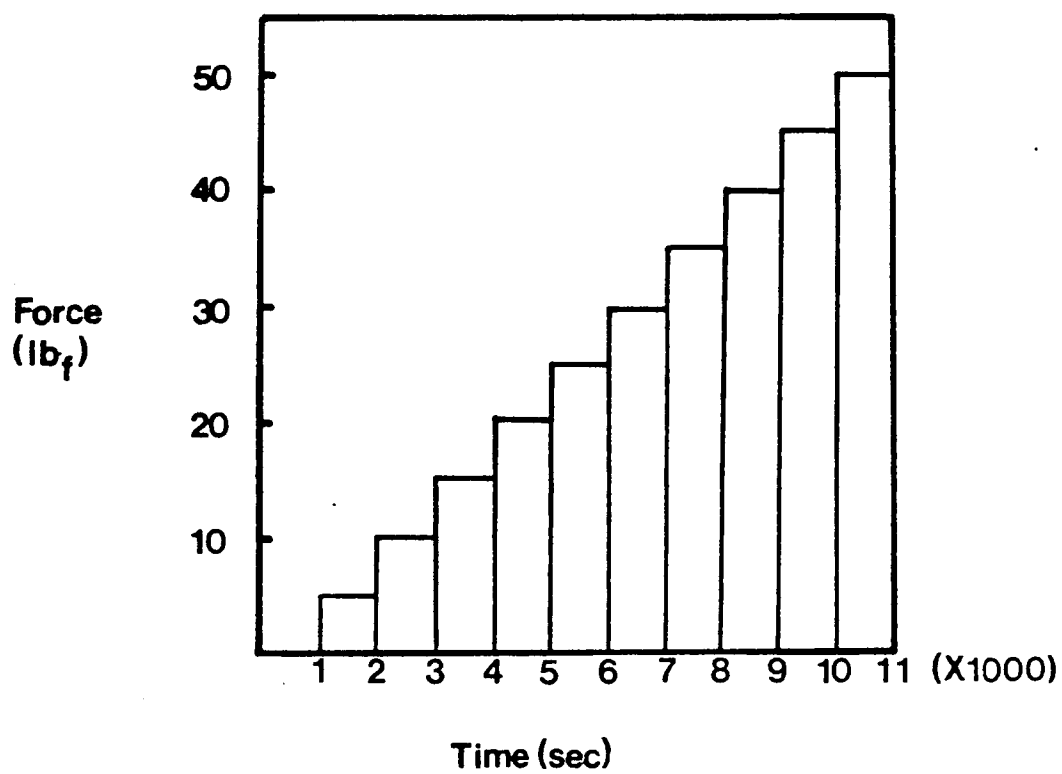


Figure 19. Histogram of sample deformation.

The grid is divided into 64×64 elements based on the detector resolution and the limitation of the computer memory capacity. The size of each detector element is 0.309×0.309 cm making the size of the detector 20.0×20.0 cm. The intensity measured by each detector element is position encoded and directed by the microprocessor to store in a unique address in the computer memory. The detector can be moved about to make the distance between sample holder and the detector from one meter to five meters thus enabling one to control the available angular resolution.

Computer: The major functions of the computer system are the collection, manipulation and display of the data recorded by the detector. The collection is accomplished by allocating specific locations in memory for each detector element and sample information. Sample information is stored in a designated block called header record. The header record contains such information as the experiment number, equipment geometry, absolute intensity and sample constants, etc. The computer uses the header information when executing data correction and reduction. Data correction is accomplished by subtracting background radiation and normalizing for detector sensitivity and transmission coefficient of the sample.

Software: The computer software enables the collection, correction and reduction of data. For data acquisition, a high-priority foreground task SAX is employed. The program SAX is a user-oriented interactive program. Its various directives provide complete control of the camera functions among which are: start and stop data acquisition,

zero data array, save data on disk, move motors, and print experimental status.

Analysis Programs: A summary of some important programs for data analysis is given.

FILE is to fetch and store two-dimensional data from disk storage to working memory.

BKG, BKC are two routines for subtracting background intensity while normalizing for detector sensitivity, transmission coefficient, absolute intensity, etc. BKC is used for samples with a low signal to noise ratio.

COUNTOUR displays the corrected two dimensional data in contour plot form. Subroutine CEN allows one to establish the center of the contour plot with a cursor and stores that position in the header record. Subroutine RAD and AVE reduces the two-dimensional data to a one-dimensional form by performing circular or linear averages respectively. VUE lets the user make various plots.

MANAGER manipulates data sets which are stored on the archive disks. One can read from, or write on to the disk, delete data, alter header records, etc.

DIFFER calculates the differences in intensity between two runs after both have been corrected for background.

VUERDL examines and plots the radially averaged intensity data. It also enables the user to make a linear regression analysis on some of the plots.

INVAR calculates the total absolute integrated intensity and the mean square electron density fluctuation of a sample background corrected scattering data.

III.3.C SAXS Experimental Procedure

Alignment. Due to the large size of the SAXS camera, extreme care must be taken to insure maximum performance of the device. The most important diagnostic tool used in the alignment of the SAXS camera is the detector. Contour plots obtained at strategic times during the alignment will tell the operator how much and in what direction to move. Other important tools used during the alignment procedure include an oscilloscope, the counters and a fluorescent screen.

First both pinholes are removed from the machine. In this case, the X-ray beam results in high intensity at the detector. Therefore low power of 10 KV and 2 mA is used. The sample chamber air locks are closed whenever possible to prevent damage to the detector.

Crystal Monochromator. The alignment procedure begins with the removal of the crystal monochromator chamber from the X-ray generator and then positioning it in the center of the incident X-ray beam hole. The projection of the crystal must occupy the maximum area of the incident X-ray beam hole. Adjustment of the angle of the crystal monochromator with respect to the incident beam is made using a fluorescent screen. Here it is important to obtain a sharp focus. Next, the exit slit of the monochromator chamber is adjusted so that it is approximately in the center of the opening of the collimating slit.

Pinhole collimators. The detector is used to align the first and second pinholes. The second pinhole stage has a one-inch diameter hole where the pinhole assembly is attached. The stage and the pinhole assembly are designed so that when the pinhole is mounted, it is located precisely at the center of the hole. Therefore, the second pinhole stage is accurately positioned with the pinhole assembly by locating the position of the stage yielding the maximum count rate and a symmetric contour pattern. If a dynamic SAXS experiment is to be carried out, there is one more restriction on the location of the second pinhole. Since the X-ray beam must intersect the line of action of the pullrods, the horizontal position of the second pinhole is limited. This position is accomplished by measuring the horizontal distance between the pullrods and a reference point and equating it with the distance between the pinhole and the same reference point. The vertical position of the second pinhole is set simultaneously with the tilt monochromator and the pivot crank. Usually, several iterations of these settings are done to achieve a symmetrical contour pattern, maximum count rate, and a centrally located pattern. When the stage alignment is complete, the second pinhole assembly is mounted on its stage. By taking low intensity patterns, the central location of the detector can be found. After all this is done, the first pinhole is installed with the aid of an oscilloscope to locate its position. The position of the first pinhole is located at the spot of maximum transmitted intensity as indicated by the oscilloscope.

Beamstop. The beamstop is attached with wax on the exterior of the beryllium exit window. The size of the beamstop can be calculated from the divergence of the main beam. A crude approximation of the proper location for the beamstop may be obtained by measuring the center of the detector. Accurate location for the beamstop is found by a lower power contour pattern showing a perfectly symmetrical background pattern (Figure 20). The background contour pattern is a cross shape due to the square cross sectional collimation.

Shielding. The system is now completely aligned and ready for calibration. However, in order to cut down the cosmic radiation reaching the detector, a large lead shield is placed around the exterior of the detector. Also a lead shield equipped with a small hole in the center is placed in the sample chamber just in front of the second pin-hole to minimize stray radiation.

Calibration. In order to calibrate the SAXS camera, the following experiments need to be carried out: absolute intensity measurement, detector sensitivity determination, background intensity and dark current intensity determination and transmission coefficient measurements.

Absolute intensity determination. The absolute intensity of a SAXS experiment is the ratio of the scattered intensity to that of the primary beam. The intensity of the primary beam is defined as the rate of photon bombardment per cross-sectional area of the sample in a given time. An absolute intensity measurement is required for calculations involving the absolute determination of the scattering particle size distribution and their volume fraction. Several methods are

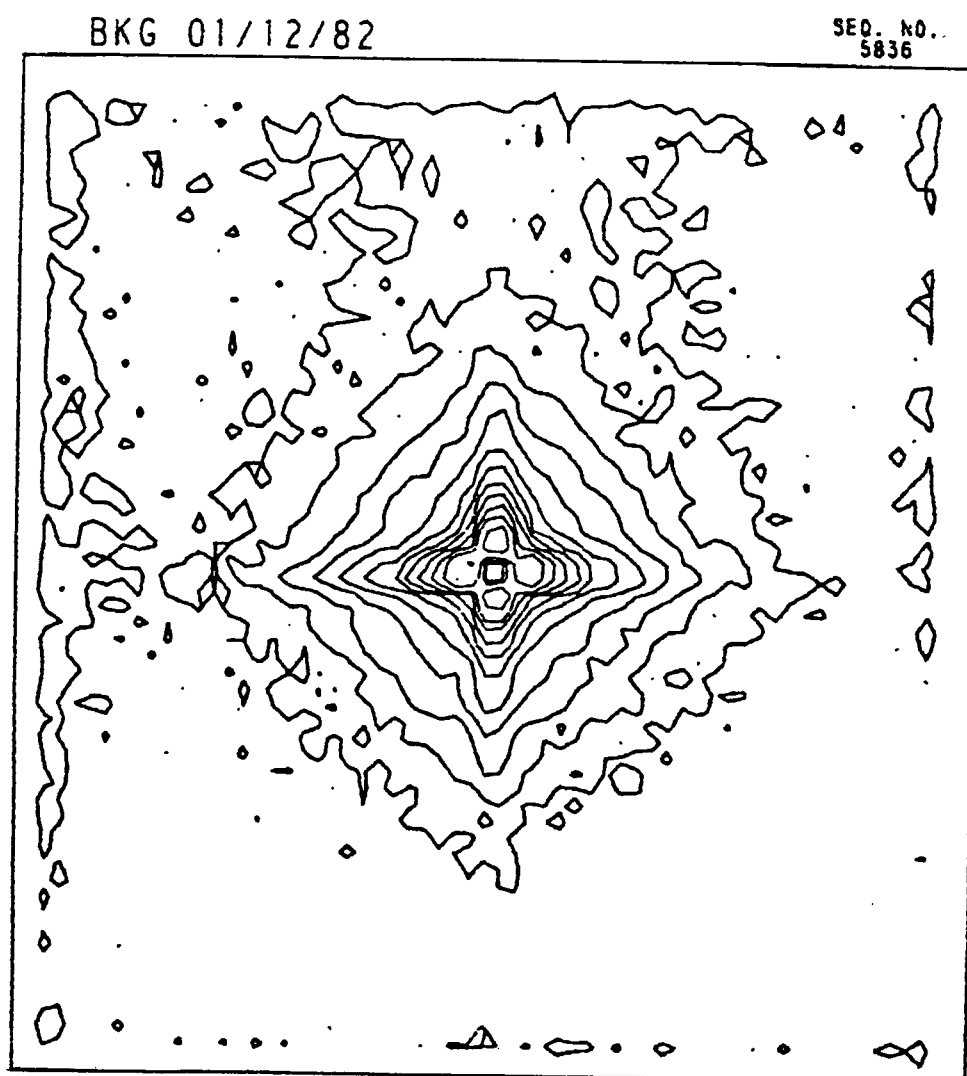


Figure 20. Isointensity contour plot of background.

available (103, 131, 132). However, the multiple nickel foil and Lupolen methods (131, 132) are used here because of their ease of application.

The nickel foil method involves attenuating the X-ray beam with layers of nickel foil, then plotting the transmitted intensity versus nickel foil thickness in a semi-logarithmic scale and extrapolating to zero thickness. The intensity value extrapolated to zero nickel thickness is the absolute intensity of the primary beam. This follows from

$$I_{\text{trans}} = I_o (\exp (-\mu t))$$

where I_{trans} = transmitted intensity

I_o = incident beam intensity

μ = linear absorption coefficient of nickel

t = thickness of nickel foil.

However, there is the detector dead time delay and hence true transmitted intensity, I_{true} , is given by

$$I_{\text{true}} = (I_{\text{obs}} - I_{\text{dc}}) / [1 - \tau \cdot (I_{\text{obs}} - I_{\text{dc}})]$$

where I_{obs} = observed intensity in counts/sec

τ = deadtime of 7 μ s associated with detection system

I_{dc} = dark current intensity.

Once the absolute intensity has been determined by the nickel foil method or other methods, the scattering from a standard sample is used to calculate the absolute intensity at any time by a comparative measurement. Lupolen is one of these standard samples. Lupolen is a

heat-treated polyethylene fabricated by Badische Anilin und Sodafabrik whose microstructure is stable. Its SAXS pattern consists of an isotropic halo with the maximum intensity at approximately 0.003 radian. The quantitative features of the scattering pattern vary only with the primary beam power. Hence, a radial average around the beamstop of the Lupolen scattering pattern is analyzed by recording the intensity at a specified angle ($2\theta = 0.0103$ rad) where the scattered intensity is linear and then by getting a ratio of the values of the Lupolen intensities at two different times and multiplying by the original absolute intensity.

Detector sensitivity determination. Each individual detector element may have a different sensitivity to radiation than others. This may be due to the following: portions of the detector are partially blocked by the beamstop or beryllium window support frame, variation in detector wires due to unequal damaging rates, or non-uniform material processing properties (166). Thus to calibrate the detector for these effects, a totally uniform radiation source is placed in the sample holder. Iron 55 is used as such a source and the sensitivity measurement is made until several million counts are recorded. This allows the computer to normalize detector sensitivity.

Background and dark current intensity determination. A significant background intensity exists due to the second pinhole collimator. The pinhole has a square cross-sectional area, thus the background scattering appears as a cross (Figure 20). This background intensity

is subtracted from the scattering pattern. Dark current refers to the counts registered by the detector even when no X-rays are admitted to the detector. Its primary causes are cosmic radiation and electronic noise. Although this intensity is low, it must be subtracted from low scattering intensity samples. A dark current experiment is carried out by closing the sample chamber gates and recording stray intensity for 1000 seconds at 40 KV and 40 mA.

Transmission coefficient measurement. The transmission coefficient is a function of the sample thickness, absorption coefficient and mass density. The transmission coefficient is calculated for a sample using the following equation:

$$T_C = \frac{I_{CSAM} - I_{DC}}{I_C - I_{DC}} \quad \text{at 20 KV and 10 mA}$$

where T_C = transmission coefficient of the sample

I_{CSAM} = scattered intensity with glassy carbon and sample in the beam

I_C = scattered intensity with glassy carbon in the beam

I_{DC} = dark current intensity.

III.3.D Collection and Reduction of Data

Collection of data. In static runs, after calibration procedures are completed, the sample is placed in the chamber and the chamber is pumped to vacuum. Then the beam path is pumped to vacuum. After

reaching sufficient vacuum, the valves blocking the X-ray beam are open and collection of data begins.

In dynamic runs, the samples are gripped in the sample holders and stressed in a stepwise manner. The stress is held constant during the collection of data. The stress is raised by changing the setpoint on the servo controller to the hydraulic system. The first scattering pattern for each sample is carried out under zero stress and this is later used as the background scattering intensity by the DIFFER analysis program. This is a direct consequence of the valid assumption that any excess scattering originating from the samples under stresses is due to changing structures within the samples under applied stresses. Thus by studying these excess scattering patterns as a function of the applied stresses or time, structural changes may be evaluated.

Reduction of data. A two-dimensional contour plot is generated by the computer after each run has been corrected for background scattering and dark current and normalized for the detector sensitivity in the following manner:

$$I_{\text{SAM}} = \left(I_{\text{SAM}} - I_{\text{DC}} \times \frac{\text{SMON}}{\text{CMON}} \right) \times T_{\text{C}} - \frac{\text{SMON}}{\text{BMON}} \left(I_{\text{BAC}} - I_{\text{DC}} \times \frac{\text{BCOM}}{\text{CMON}} \right)$$

where I_{SAM} = total scattered intensity with the sample in the beam
 T_{C} = transmission coefficient of the sample
 SMON = sample run monitor count

CMON = dark current run monitor count

BMON = background run monitor count

I_{BAC} = total background scattered intensity.

This contour plot is useful for qualitative study. To quantify data, the averaged intensity slices of specific angles may be calculated using a subroutine AVE in the CONTOUR program. For isotropic scattering patterns, radial averages of the scattering intensity may be calculated by the computer using the RADIAL program. Various plots such as the Guinier plots, the Porod plots, etc., may be obtained for any specific angles directly from the computer. Such reduction of data yields an average dimension of the scattering centers in each major axes. With absolute intensity calibrations, the volume fraction of two phases in materials may be calculated.

CHAPTER IV

SAXS STUDY OF STRUCTURES

In this chapter, the results of the experimental investigation using SAXS methods are presented and discussed. The dependence of the scattering patterns on the applied stress levels is illustrated.

IV.1 ABSOLUTE INTENSITY MEASUREMENT

Absolute intensity measurements of the X-ray beam were made using the nickel foil and the Lupolen methods. For the sample to detector distance of 1020 mm the initial intensity was found to be 2.11×10^6 photons/mm² per second at an X-ray power of 40 KV and 40 mA. Subsequent calibrations were made using the Lupolen after instrumental changes. The summary of absolute intensity calibrations for this configuration using Lupolen is shown in Figure 21. The big jump in absolute intensity may be due to a change of the filament in the X-ray generator.

IV.2 EPOXY RESINS

IV.2.A Static Experiments

The scattering behavior of EPON 828/NMA/BDMA systems at varying curing agent concentrations was studied. Figure 22 shows the contour plots of scattered intensities for the EPON 828/NMA (70 phr)/BDMA, EPON 828/NMA (90 phr)/BDMA and EPON 828/NMA (110 phr)/BDMA systems, respectively. They show isotropic scattering patterns. Figure 23 shows the observed variations of intensity with scattering vector k .

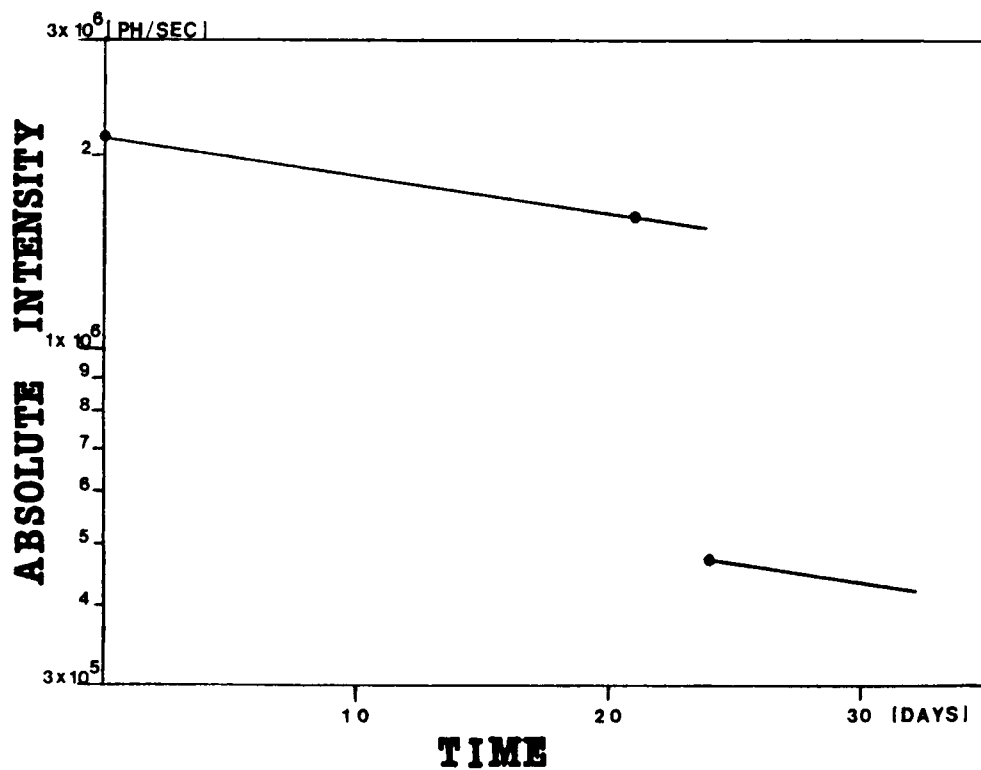


Figure 21. Summary of Absolute Intensity Calibration for the sample to detector distance of 1020 mm.

Figure 22. Two-dimensional isointensity contour plots of EPON 828 cured with various amounts of NMA. The outermost contour represents an intensity of 16 photons per channel with inner contours increasing by $\times 2$ at each level.

- a) 70 phr NMA
- b) 90 phr NMA
- c) 110 phr NMA

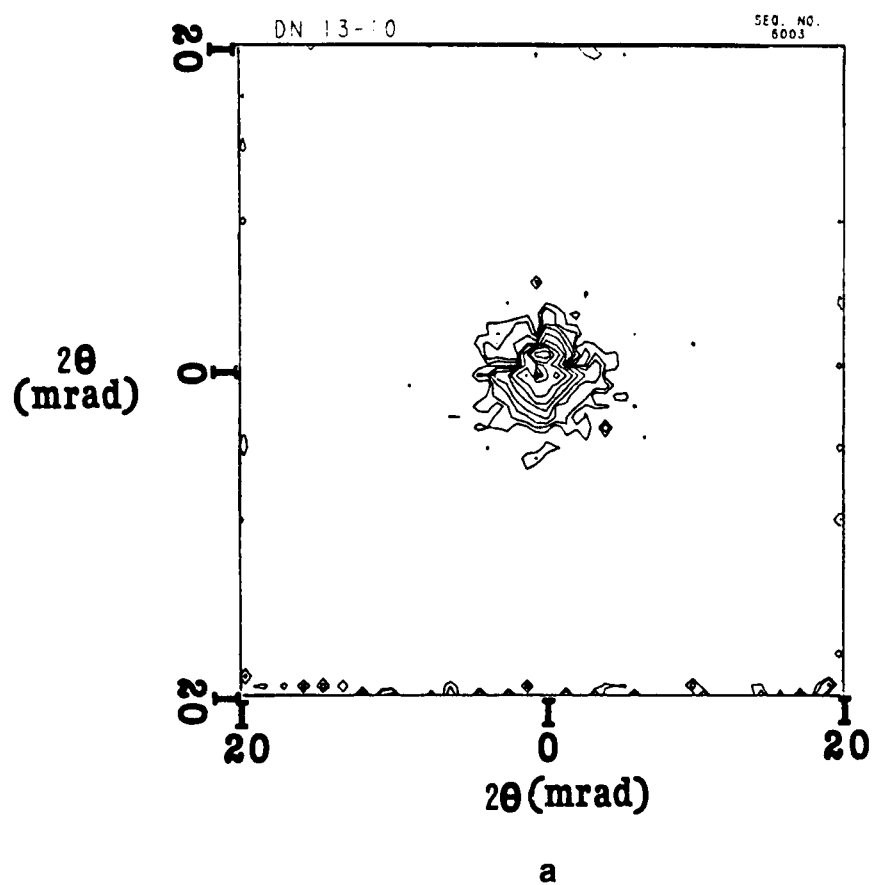


Figure 22

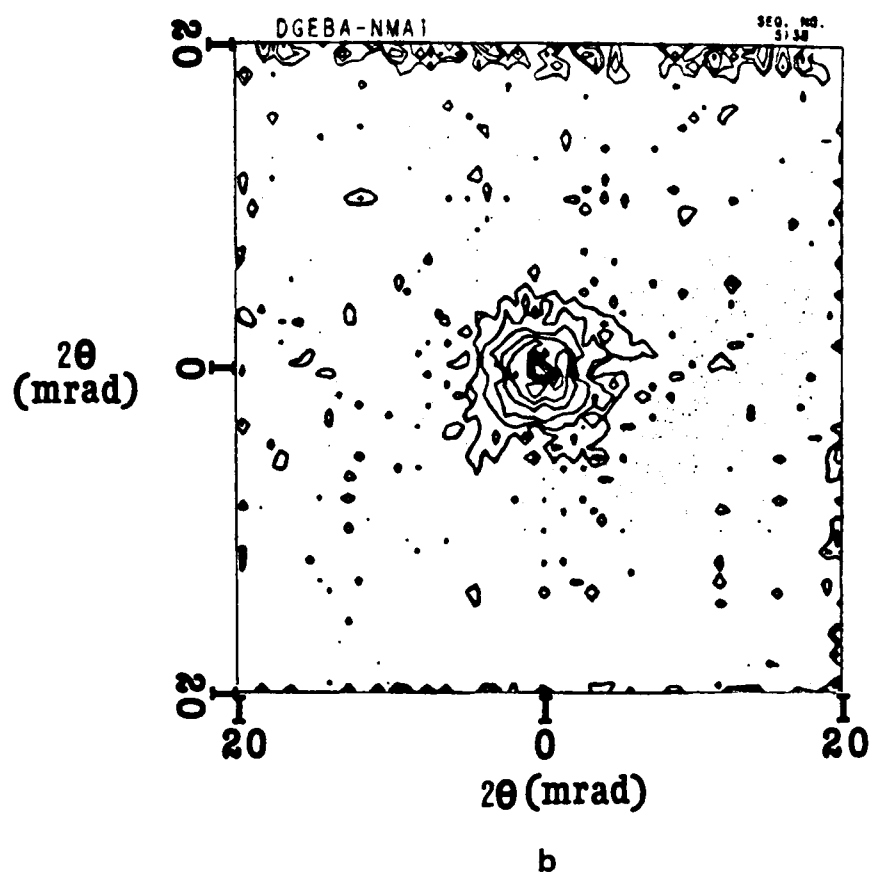


Figure 22 (Continued)

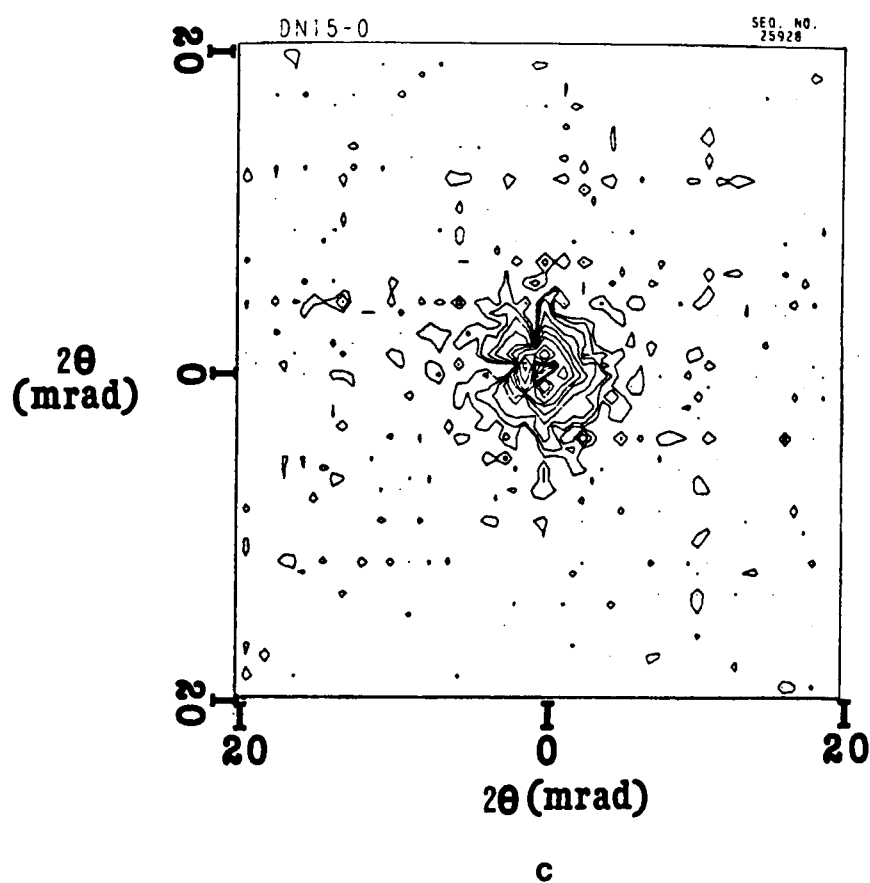


Figure 22 (Continued)

Figure 23. Variations of intensity for EPON 828 cured with various amounts of NMA.

- a) 70 phr NMA
- b) 90 phr NMA
- c) 110 phr NMA

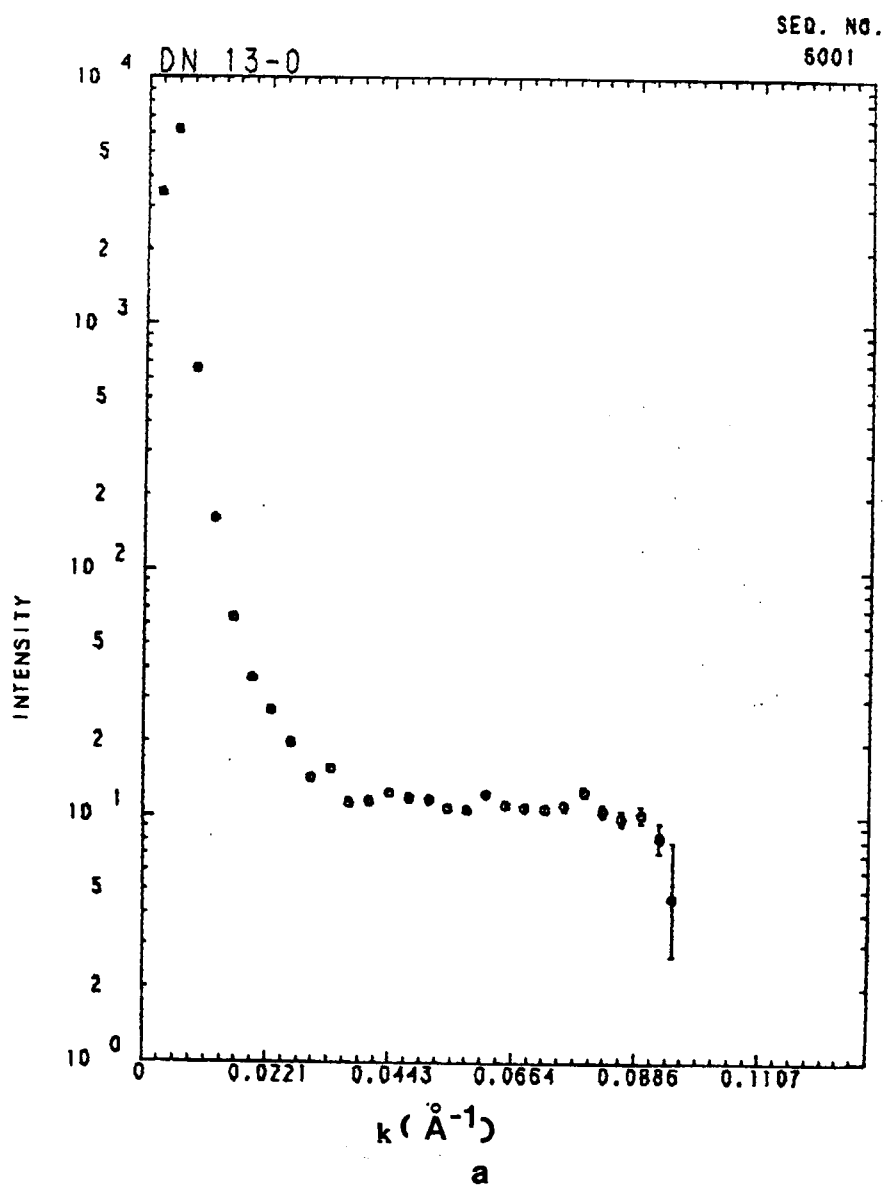


Figure 23

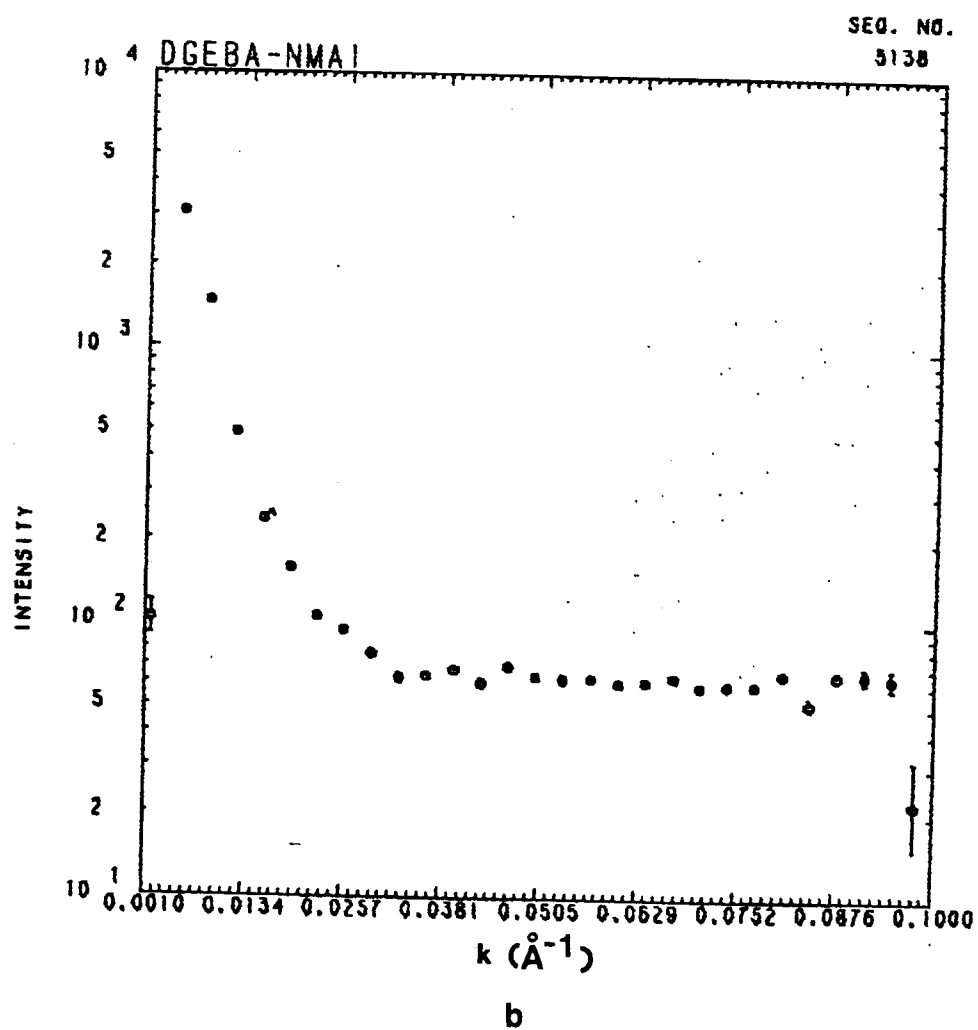


Figure 23 (Continued)

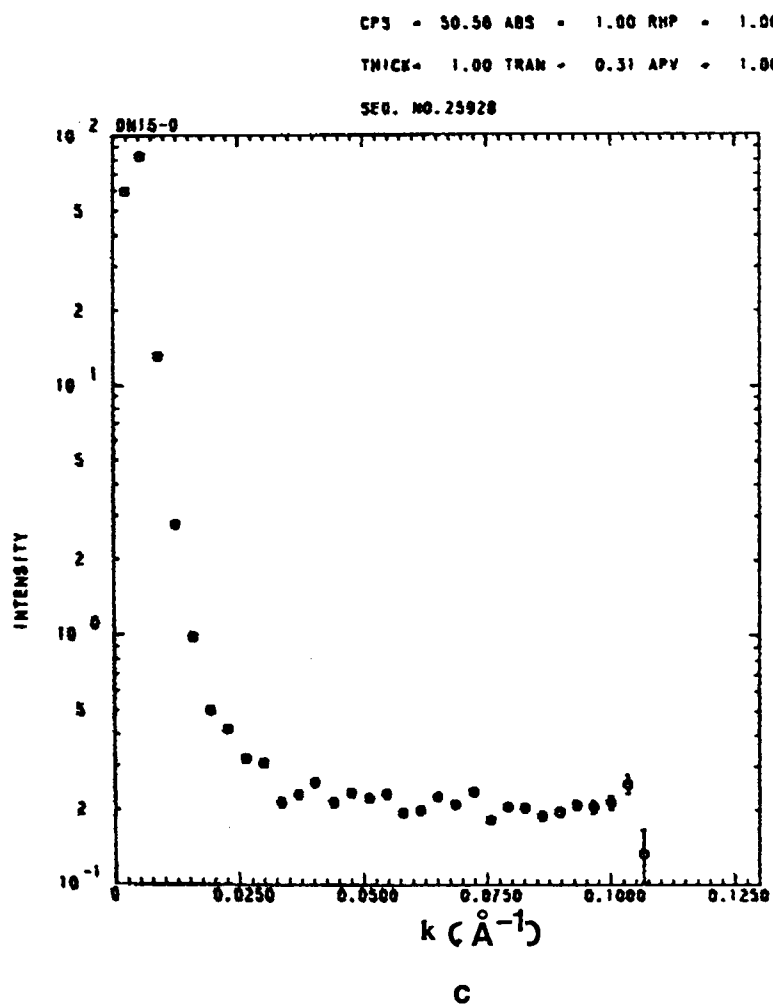


Figure 23 (Continued)

The intensity decreases strongly with increasing angle between $0.0057 \text{ \AA}^{-1}$ (0.7 mrad) and $0.022 \text{ \AA}^{-1}$ (2.7 mrad) and reaches a nearly constant asymptotic value at larger angles. The scattering curves for the three epoxy systems are qualitatively similar to each other and to those obtained from other amorphous polymers. Isotropic scattering patterns indicate the material has either a broad or a multimodal distribution of inhomogeneities in the relatively large size scattering centers of $100 \text{ \AA}$ or more. The high angle flat scattering may be attributed to the tail of a broad Bragg diffraction which occurs at higher angles, or it may be short-range-order diffuse scattering expected for an ideal liquid or glass because of the presence of thermal fluctuations in density or composition. In the low k range, no discrete scattering is observed except for the decrease in intensity at very small angle due to the beamstop. This indicates that the inhomogeneities are essentially randomly distributed and in such cases the radii of gyration can be calculated using the Guinier approximation (Eq. II.5.C.18). The calculated radii of gyration are $240 \text{ \AA}$, $270 \text{ \AA}$ and $260 \text{ \AA}$ for 70, 90 and 110 phr NMA cured EPON 828 epoxies, respectively. SAXS scattering patterns from DER 332/MPDA (16 phr) epoxies cured under vacuum have resulted in similar patterns as shown in Figure 24.

In order to study the nature of these inhomogeneities, SAXS patterns were obtained for liquid DER 332/MPDA (16 phr) system. A typical contour plot is presented in Figure 25. Note that the pattern is obtained for shorter sample to detector distance of 2120 mm and hence covers larger scattering angle. Figure 26 shows the observed variations

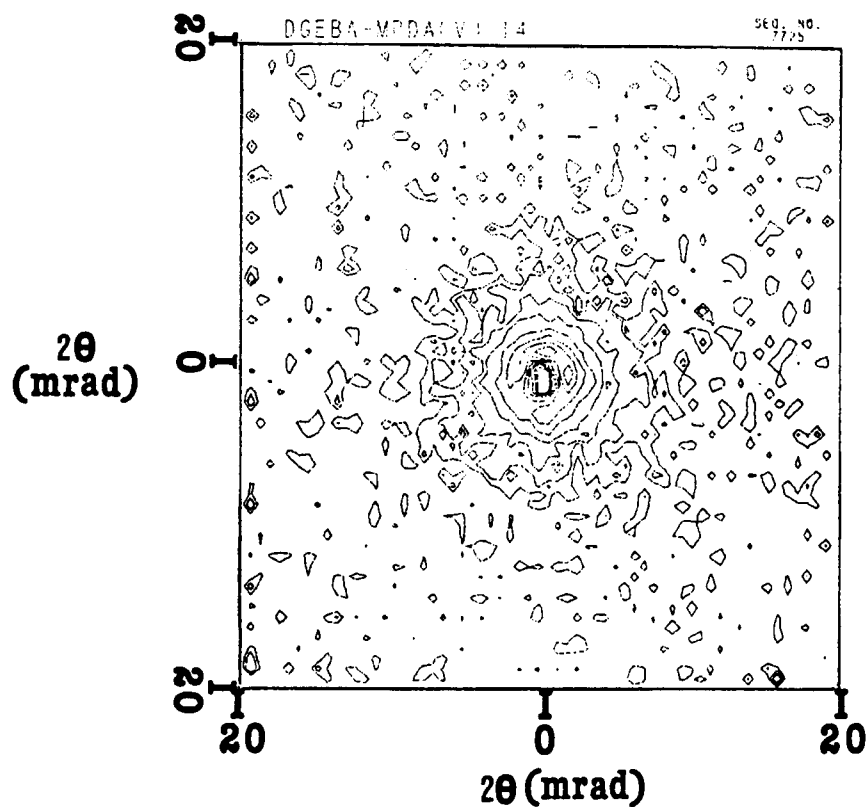


Figure 24. Two-dimensional isointensity contour plots of DER 332/MPDA (16 phr) cured under vacuum. The outermost contour represents an intensity of 16 photons per channel with inner contours increasing by $\times 2$ at each level.

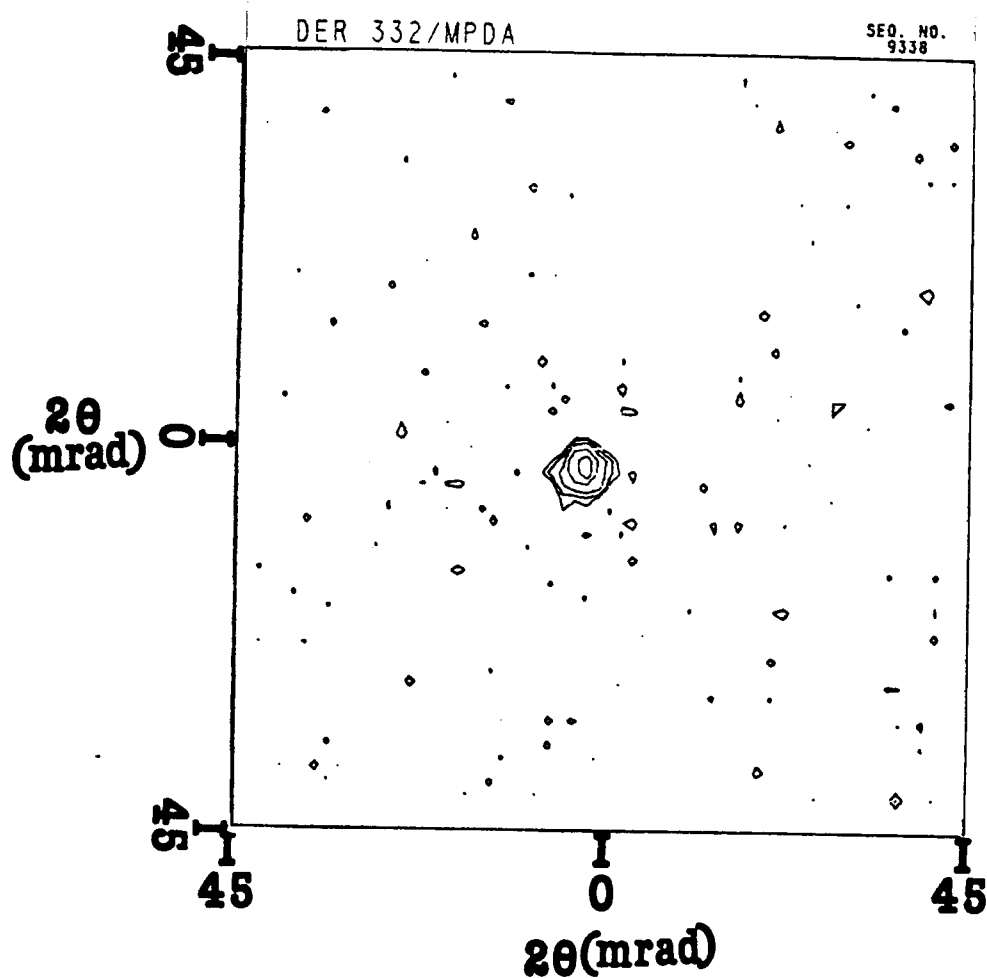


Figure 25. Two-dimensional isointensity contour plot of liquid DER 332/MPDA (16 phr) epoxy resin. The outermost contour represents an intensity of 16 photons per channel with inner contours increasing by $\times 2$ at each level.

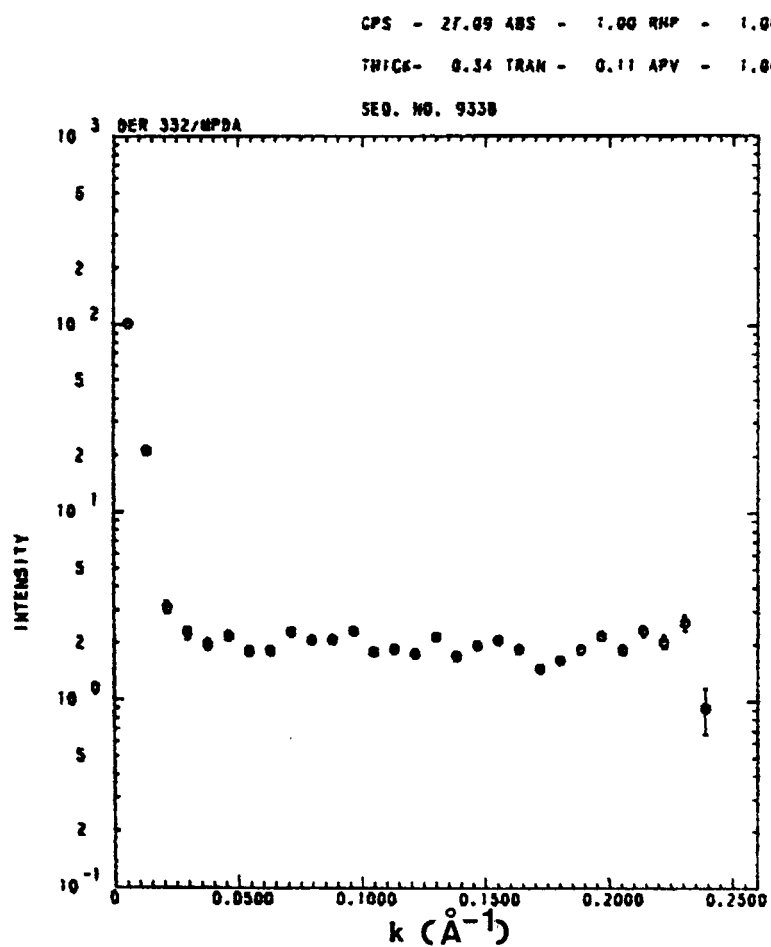


Figure 26. Variations of intensity for liquid DER 332/MPDA (16 phr) epoxy resin.

of intensity with scattering vector k . The intensity decreases strongly with increasing angle between $0.0049 \text{ \AA}^{-1}$ (0.6 mrad) and $0.20 \text{ \AA}^{-1}$ (2.5 mrad) and reaches a nearly constant asymptotic value at larger angles. The scattering curves for the liquid DER 332/MPDA are qualitatively similar to those for cured epoxy system. The radius of gyration calculated using the Guinier approximation (Eq. II.5.C.18) is $165 \text{ \AA}$. The present results indicate that the sharp increase in intensity at very small angle between $(0.0041 \text{ \AA}^{-1} \text{ (0.5 mrad) to } 0.020 \text{ \AA}^{-1} \text{ (2.5 mrad)})$ is mainly due to heterogeneities extrinsic to the polymer, such as gas bubbles introduced during curing of the resins, dirt imbedded in cured resins, etc. Curing the resins under vacuum does not eliminate such scattering. The present results are inconsistent with the presence of two-phase structures in cured epoxy. If such two-phase structures are present in cured epoxy due to curing mechanism resulting in high cross-link density region imbedded in a less crosslinked matrix, the curing process should be accompanied by noticeable changes in scattered intensity from that of the uncured resin.

II.2.B Dynamic Experiments

The EPON 828/NMA (70 phr)/BDMA, EPON 828/NMA (90 phr)/BDMA and EPON 828/NMA (110 phr)/BDMA systems were studied dynamically by collecting SAXS data while the samples were stressed in a stepwise manner. The resulting scattering patterns for 110 phr NMA resin are shown in Figure 27. These patterns show very little change as the stress level is increased. $\text{Log}(I(k))$ versus k^2 plots for three stress levels are presented in Figure 28. There is a very slight increase in the

Figure 27. Dynamic two-dimensional isointensity contour plots for EPON 828/NMA (110 phr)/BDMA epoxy resin. The outermost contour represents an intensity of 16 photons per channel with inner contours increasing by x2 at each level.

- a) 0 psi
- b) 850 psi
- c) 1750 psi
- d) 3270 psi
- e) 4590 psi
- f) 7300 psi
- g) after fractured

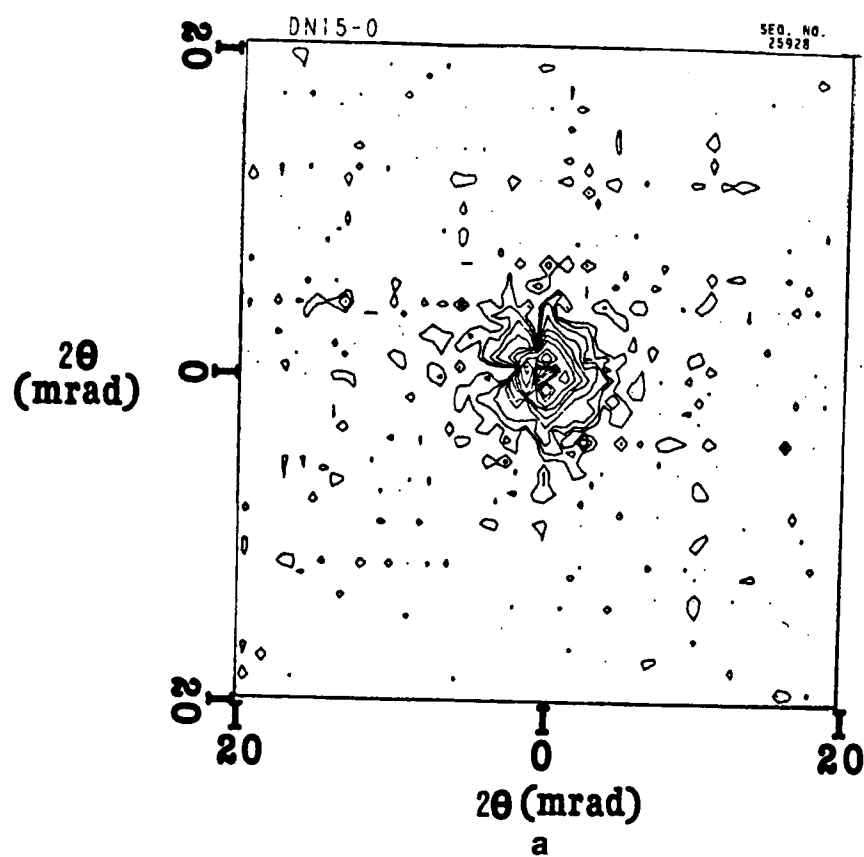


Figure 27

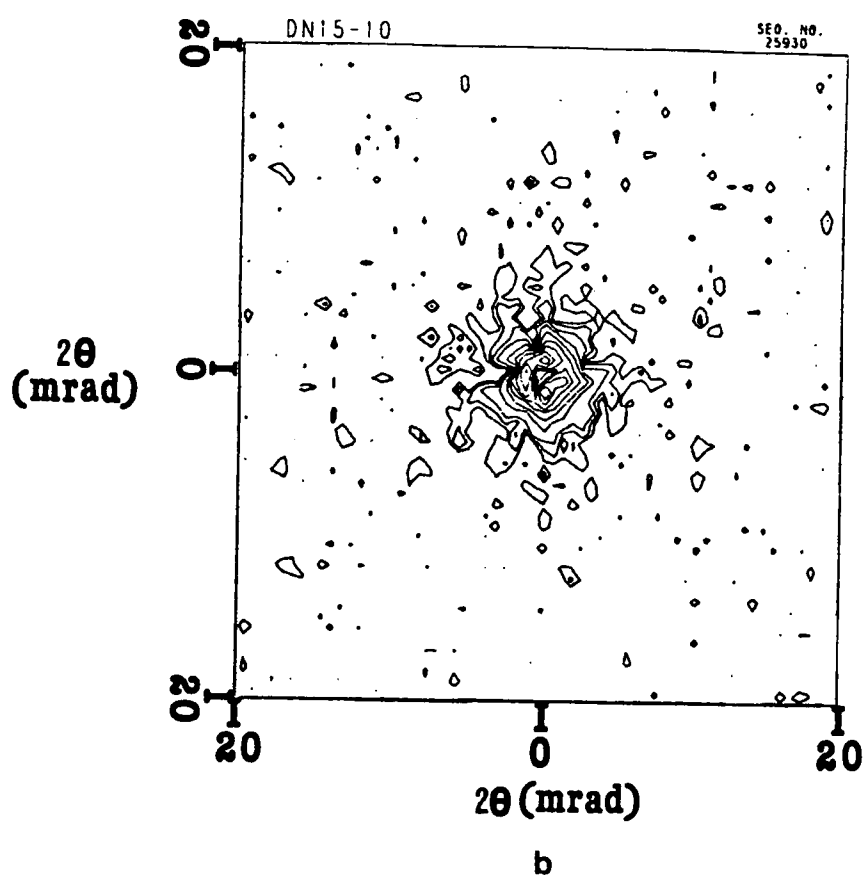


Figure 27 (Continued)

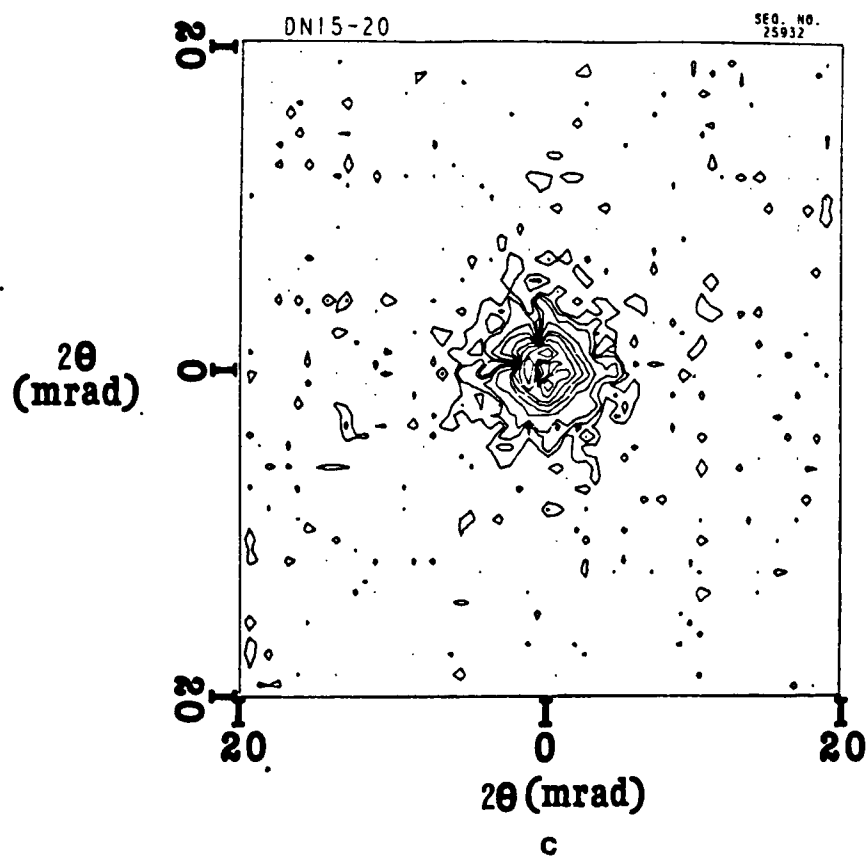


Figure 27 (Continued)

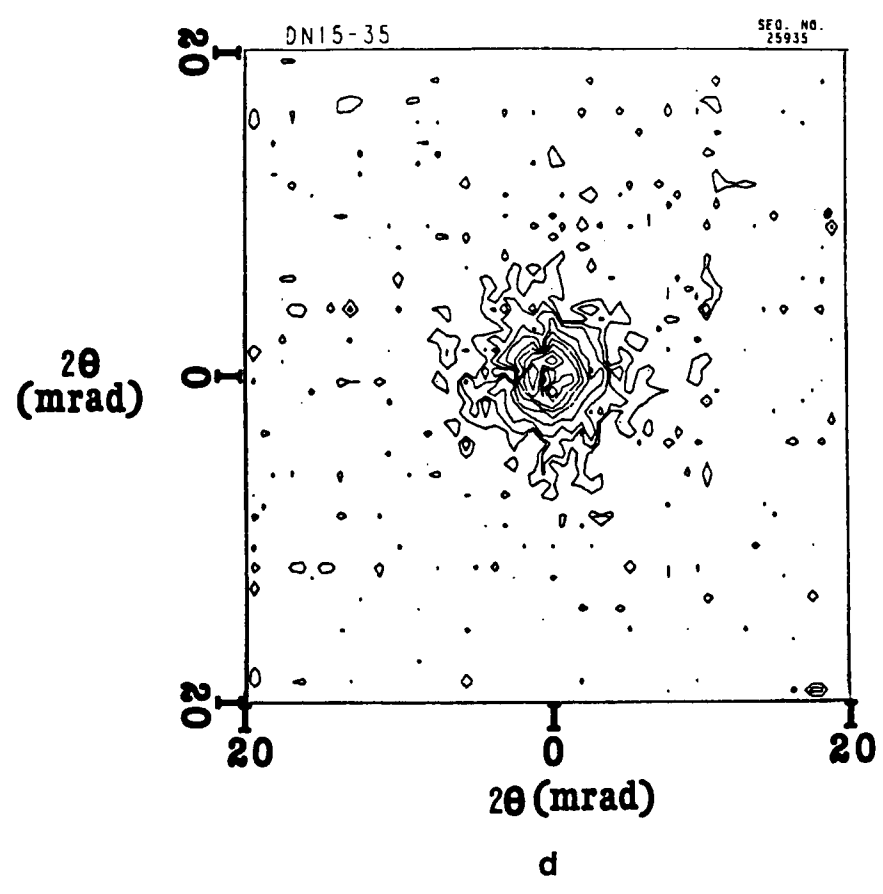


Figure 27 (Continued)

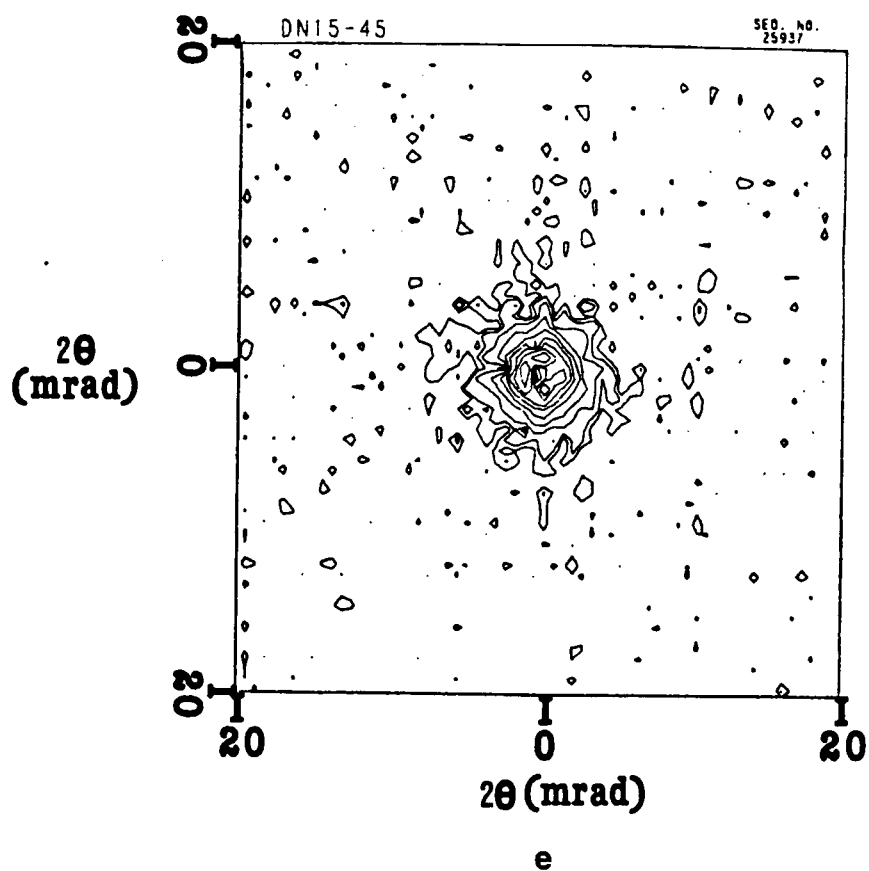


Figure 27 (Continued)

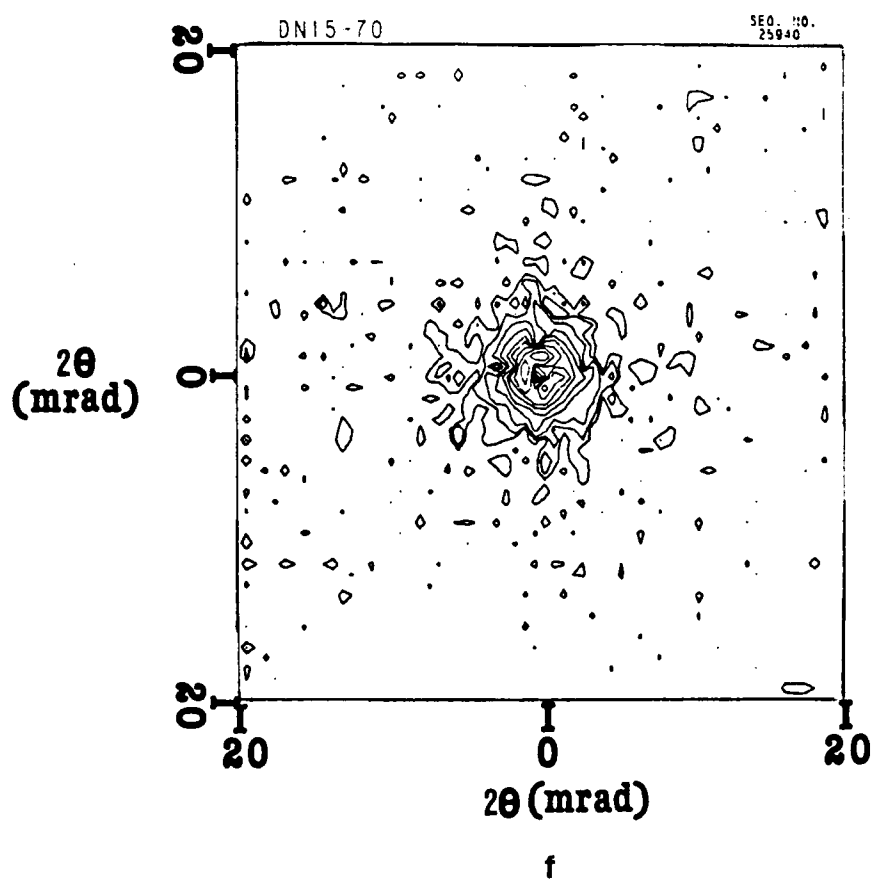


Figure 27 (Continued)

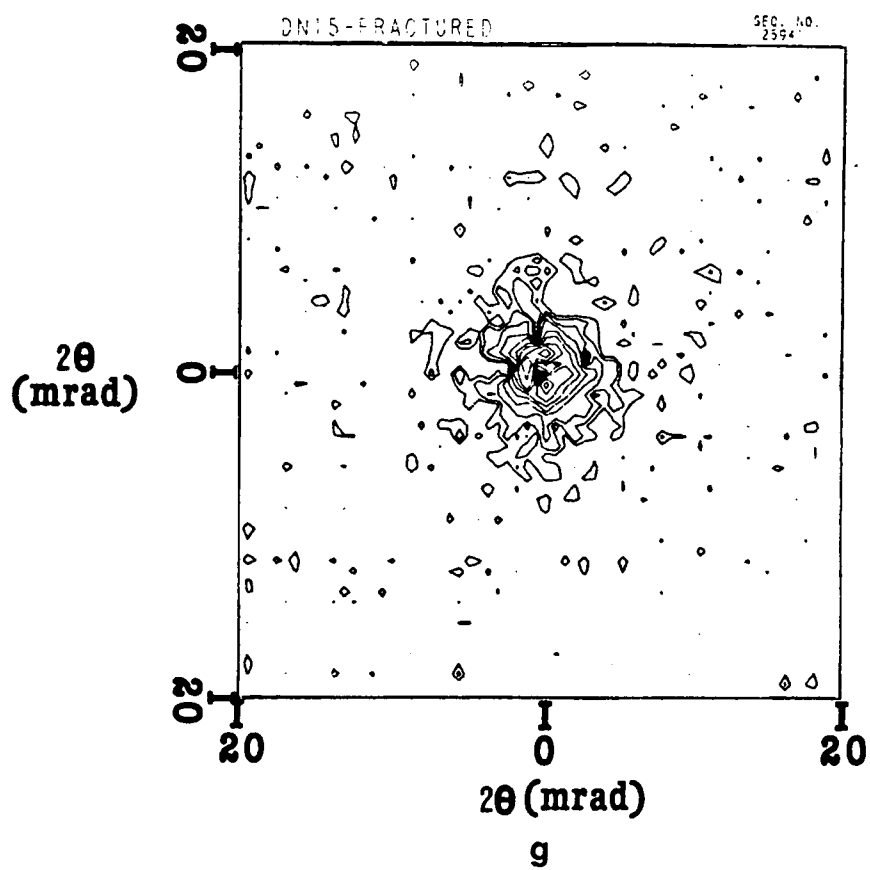


Figure 27 (Continued)

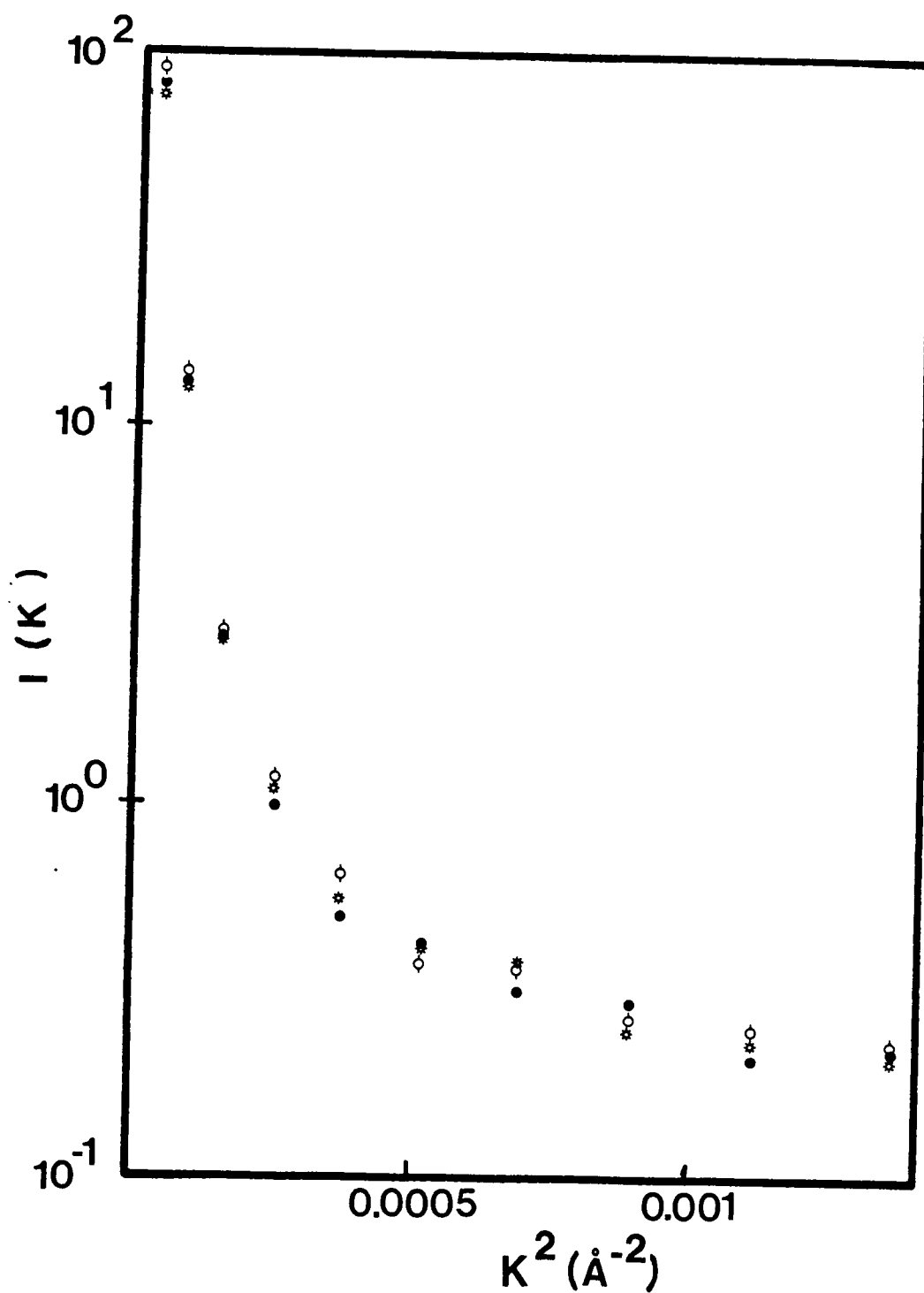


Figure 28. Relative scattering intensity $I(k)$ vs k^2 for EPON 828/NMA (110 phr)/BDMA epoxy resin. ● 0 psi, ○ 7300 psi, ☆ after fracture.

intensity for the highly stressed sample compared to the unstressed sample and a little change in the intensity for the fractured sample.

In order to obtain a better qualitative picture, the scattering from unstressed sample is subtracted from the scattering from each stressed sample using the DIFFER program. The net scattering patterns at the increasing stress levels are presented in Figure 29. Evidently there is very little stress induced scattering until the final failure. The same behavior is observed for 70 phr NMA resin as shown in Figure 30. $\text{Log}(I(k))$ versus k^2 plots for 90 phr NMA resin and 70 phr NMA resin are presented in Figure 31 and in Figure 32, and they show same results as that of the 110 phr NMA resin.

The present results of dynamic SAXS experiments show no evidence of crazing. For comparison the SAXS result from crazed polystyrene is presented in Figure 33. It shows a very strong anisotropy with a strong intensity streak in the direction parallel to the tensile direction. Westbrook (166) contends this anisotropic scattering is due to reflection phenomenon of X-ray. Regardless of the cause of such scattering, all the crazed polystyrene samples showed this feature.

Furthermore, the present results are not in accordance with the rate process theories of fracture discussed in section II.5.B. According to these theories, failures in glassy polymers are initiated by growth of microvoids or microcracks followed by coalescence thus leading to fracture. Such theories have not been applied to epoxies and the present results indicate that such theories do not apply to the epoxies under consideration here. There is very little change in

Figure 29. Net dynamic two-dimensional isointensity contour plots of EPON 828/NMA (110 phr)/BDMA epoxy resin. The outermost contour represents an intensity of 16 photons per channel with inner contours increasing by x2 at each level. The scattering from unstressed sample is subtracted as background from each scattering plot.

- a) 850 psi
- b) 1750 psi
- c) 3270 psi
- d) 4590 psi
- e) 7300 psi
- f) after fractured

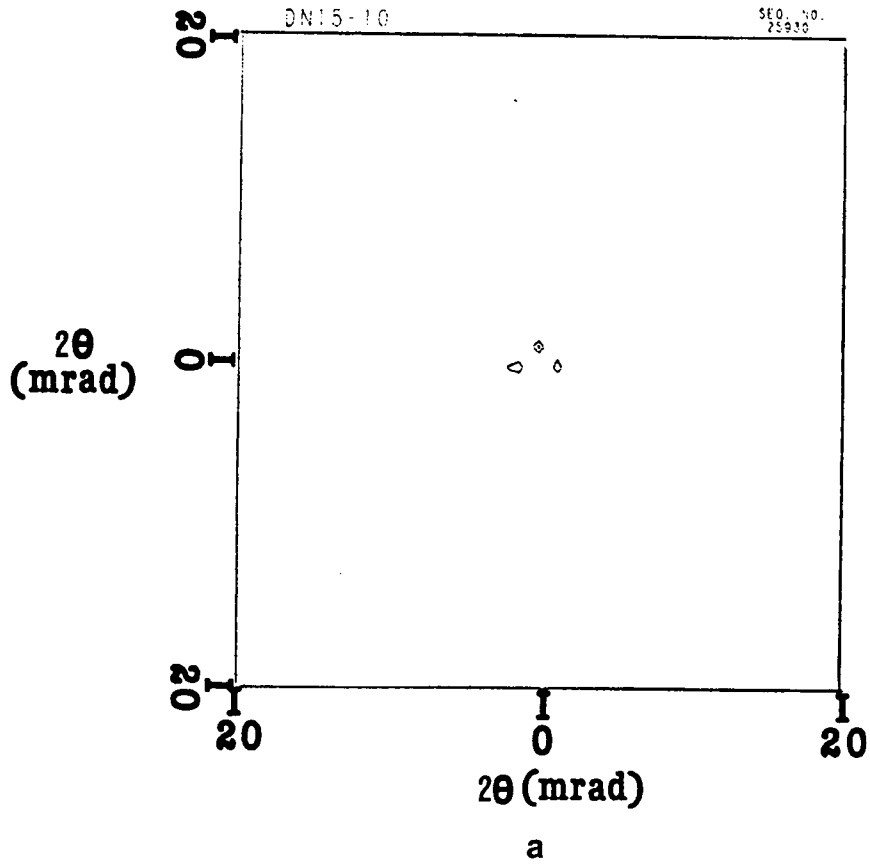


Figure 29

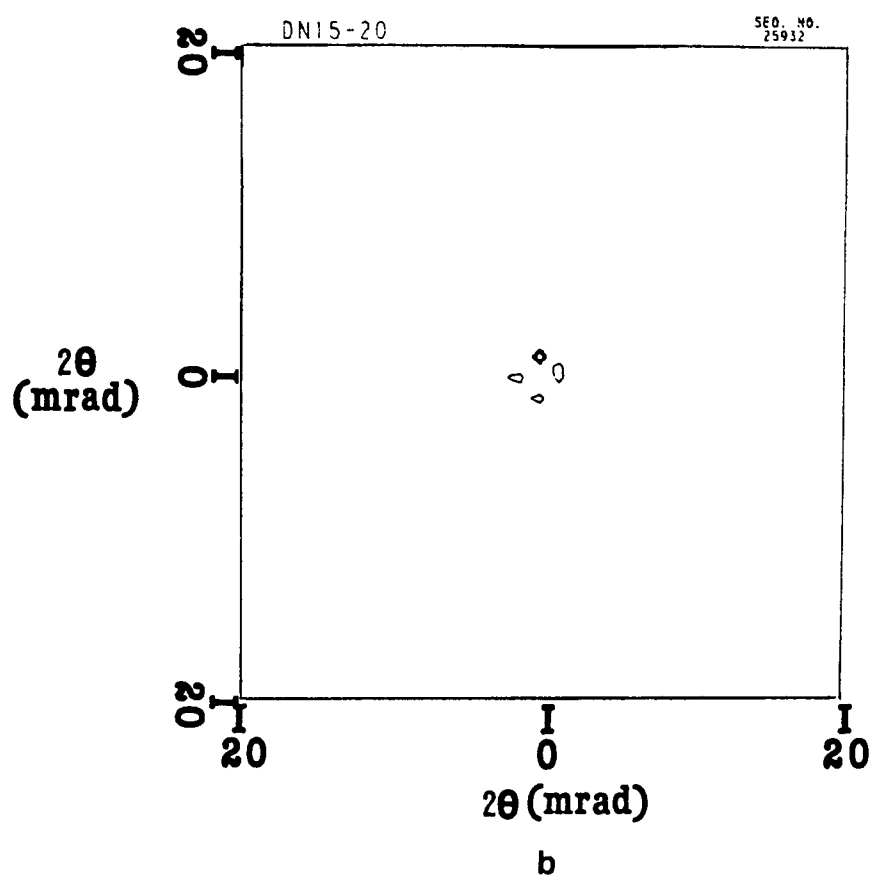


Figure 29 (Continued)

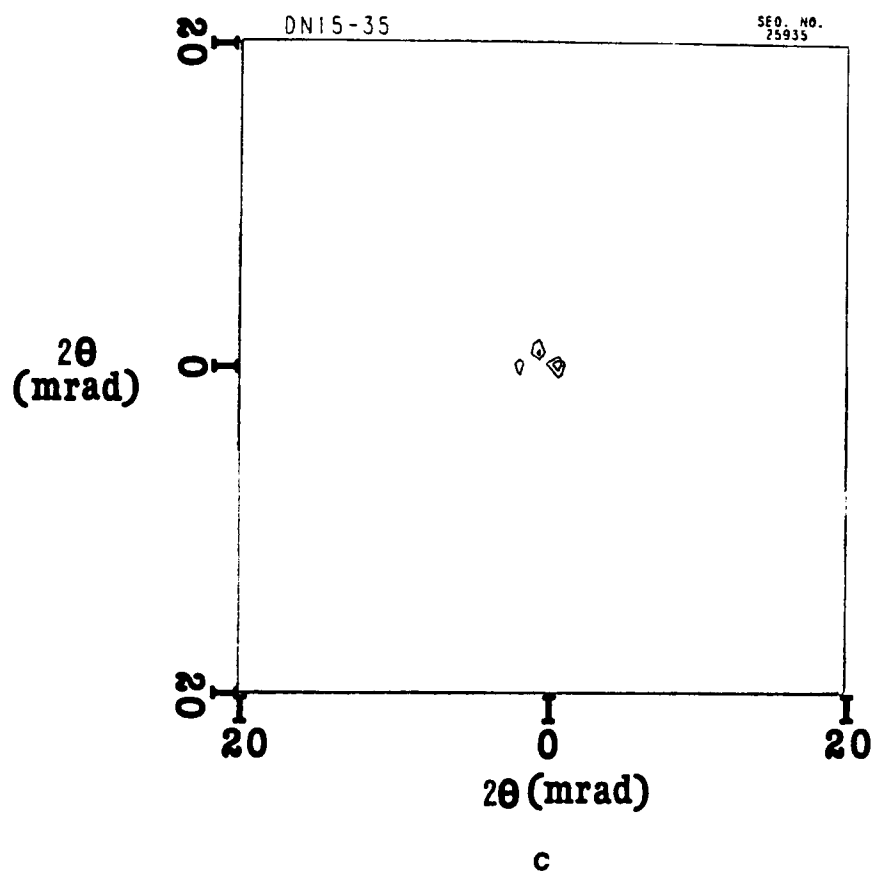


Figure 29 (Continued)

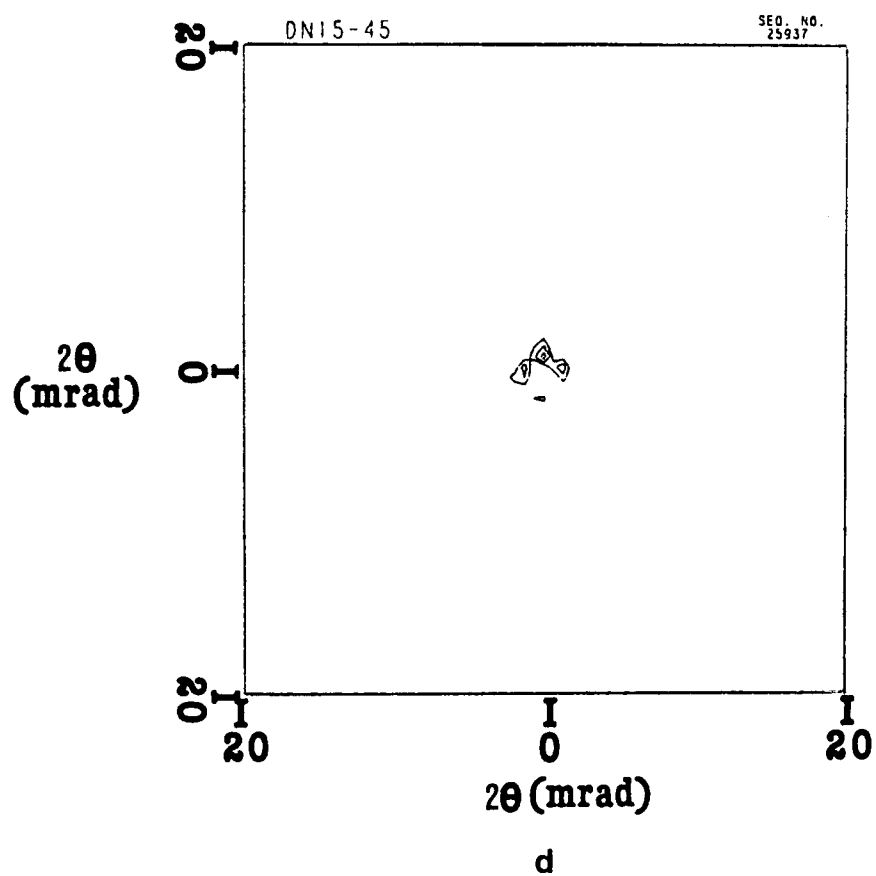


Figure 29 (Continued)

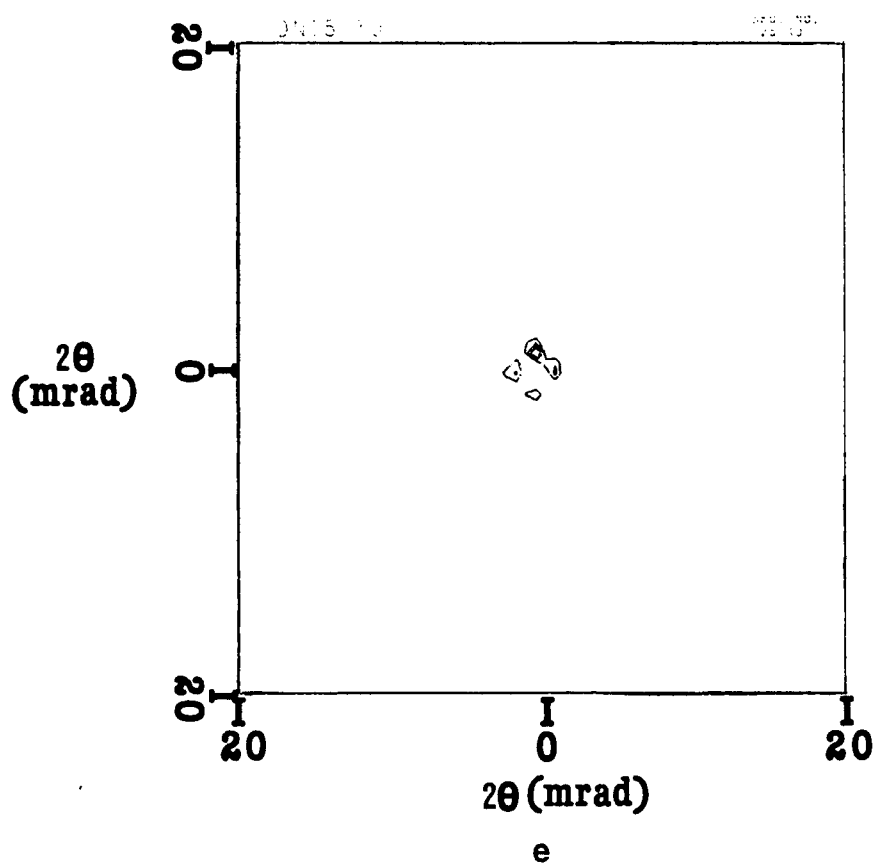


Figure 29 (Continued)

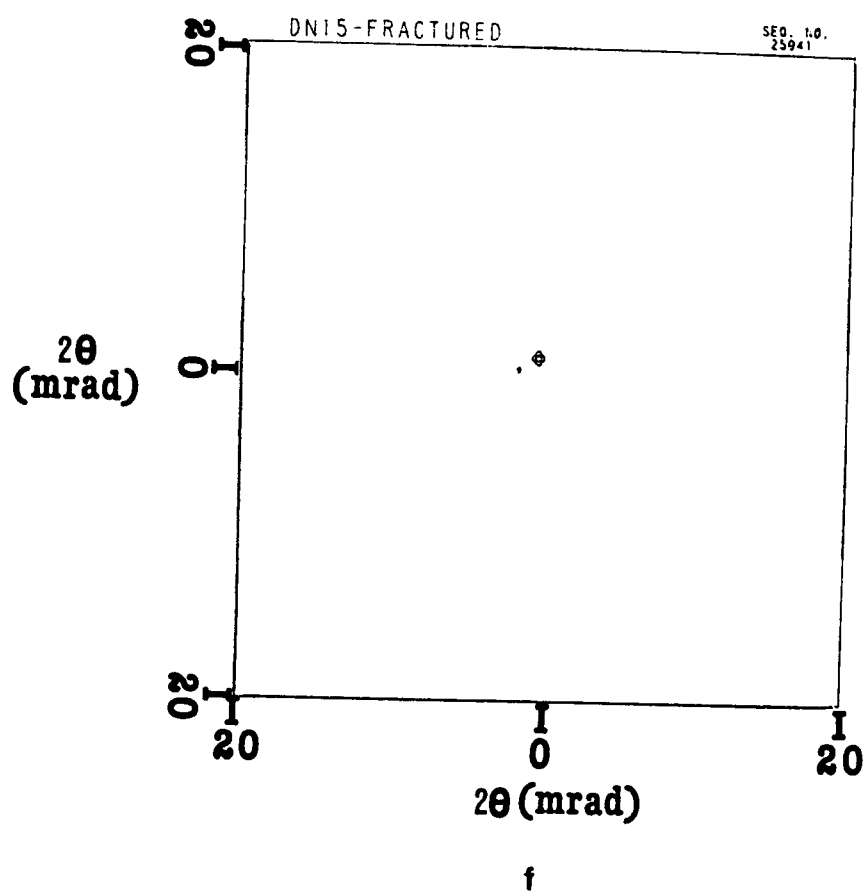


Figure 29 (Continued)

Figure 30. Net dynamic two-dimensional isointensity contour plots of EPON 828/NMA (70 phr)/BDMA epoxy resin. The outermost contour represents an intensity of 16 photons per channel with inner contours increasing by x2 at each level. The scattering from unstressed sample is subtracted as background from each scattering plot.

- a) 1420 psi
- b) 2120 psi
- c) 2830 psi
- d) 3540 psi
- e) 4250 psi

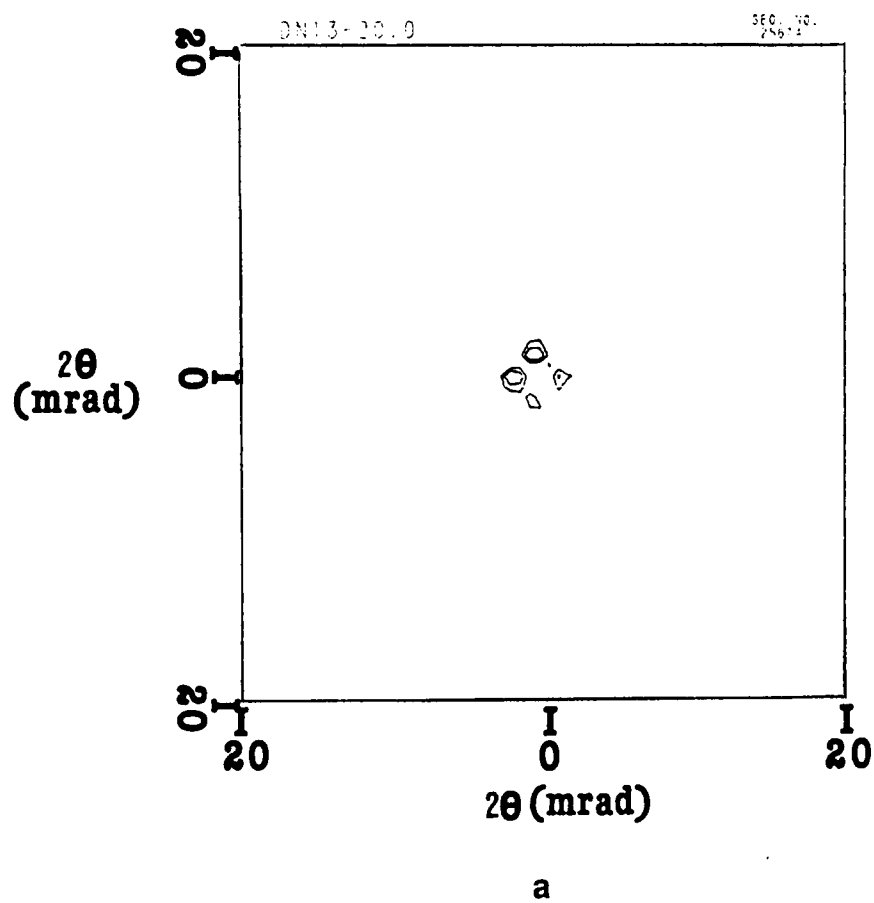


Figure 30

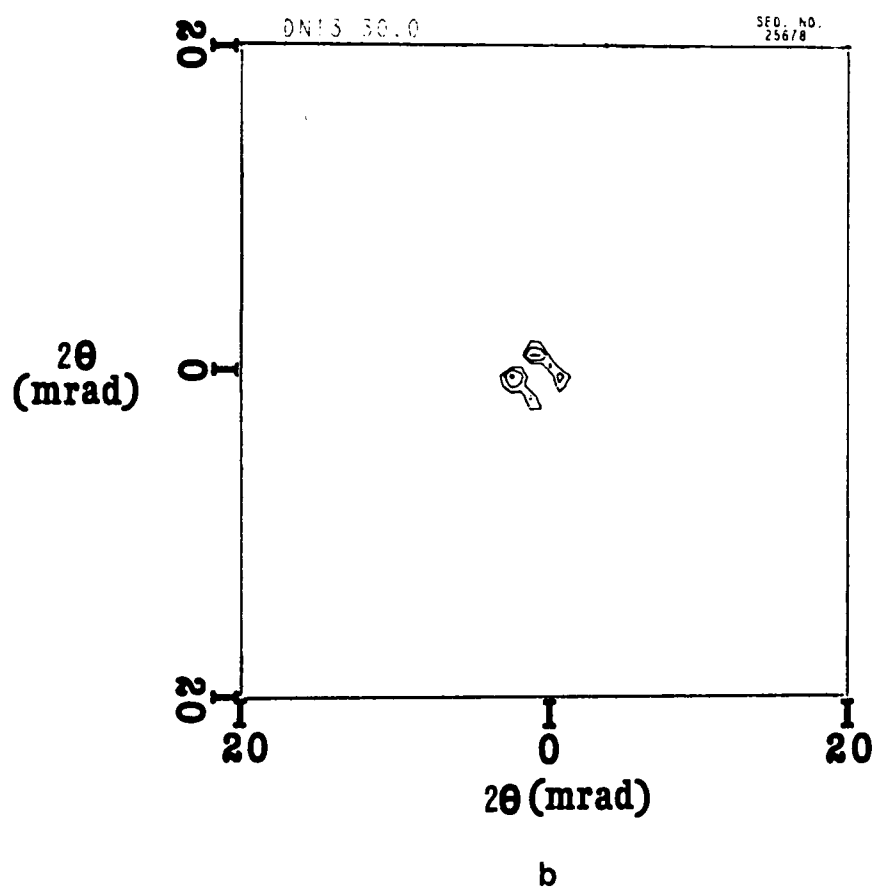


Figure 30 (Continued)

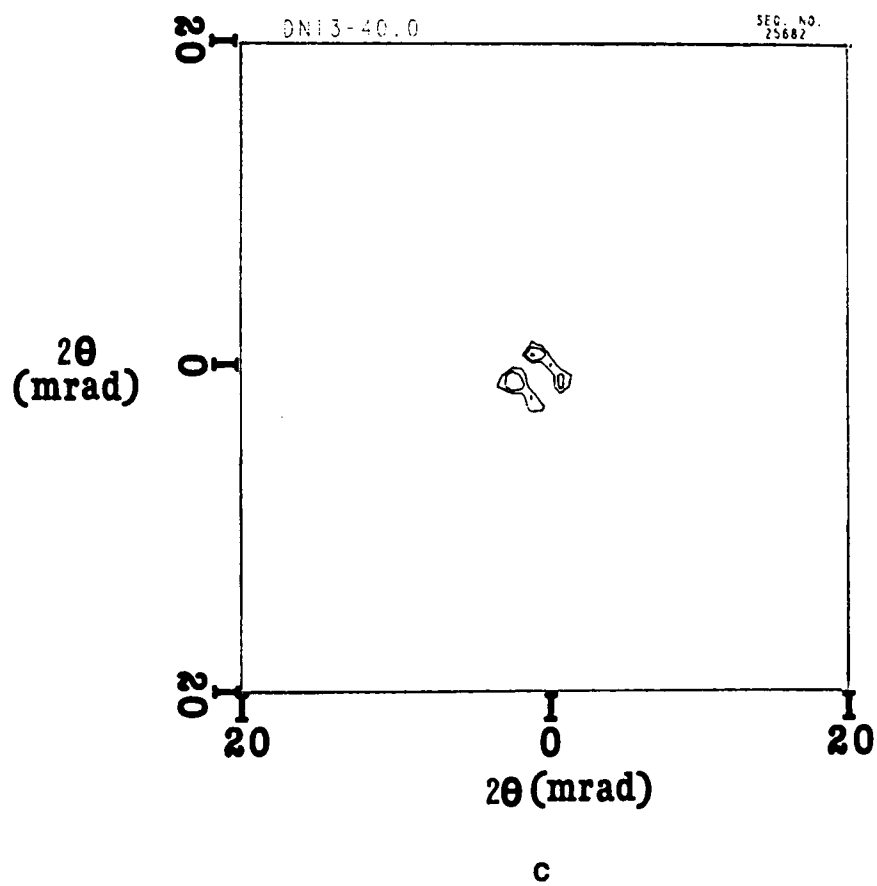


Figure 30 (Continued)

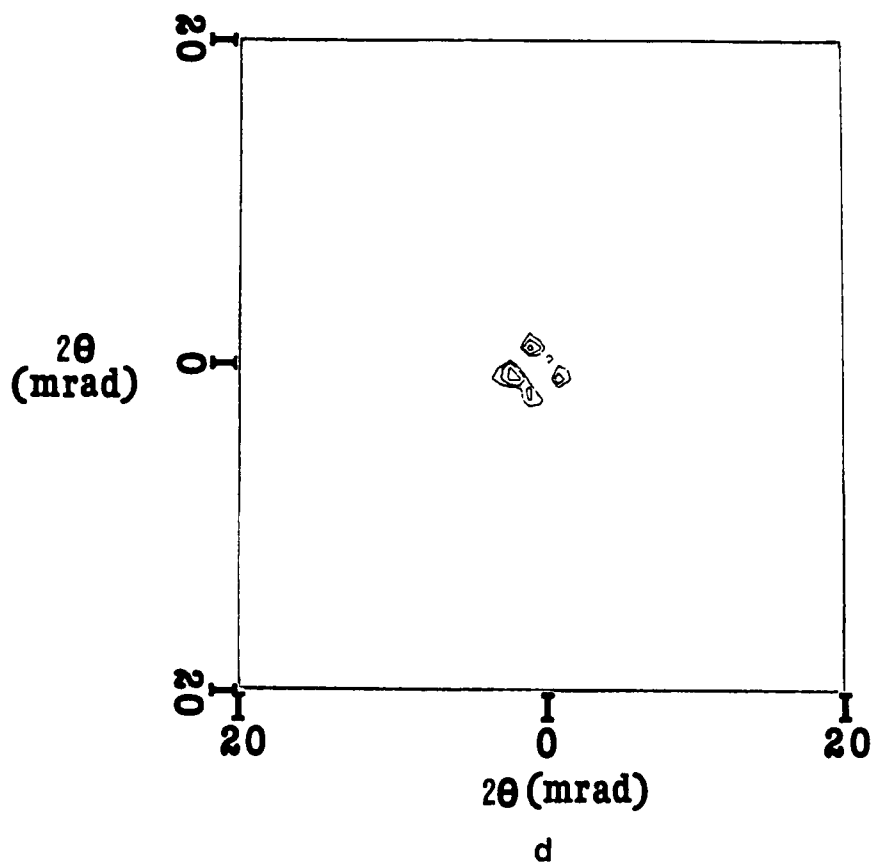


Figure 30 (Continued)

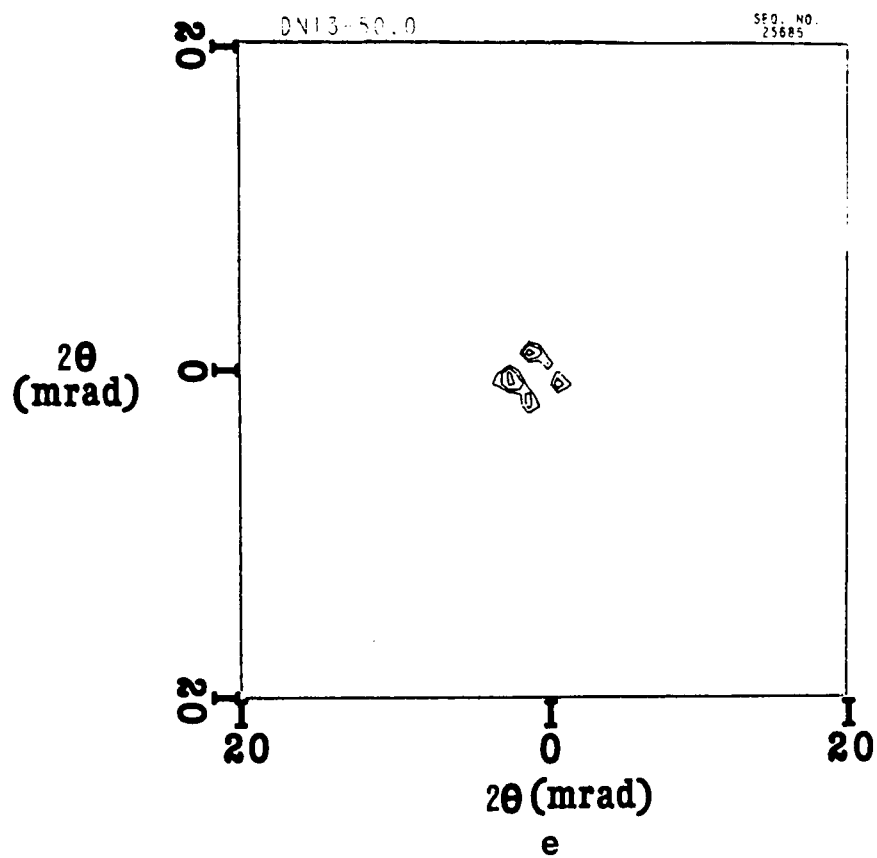


Figure 30 (Continued)

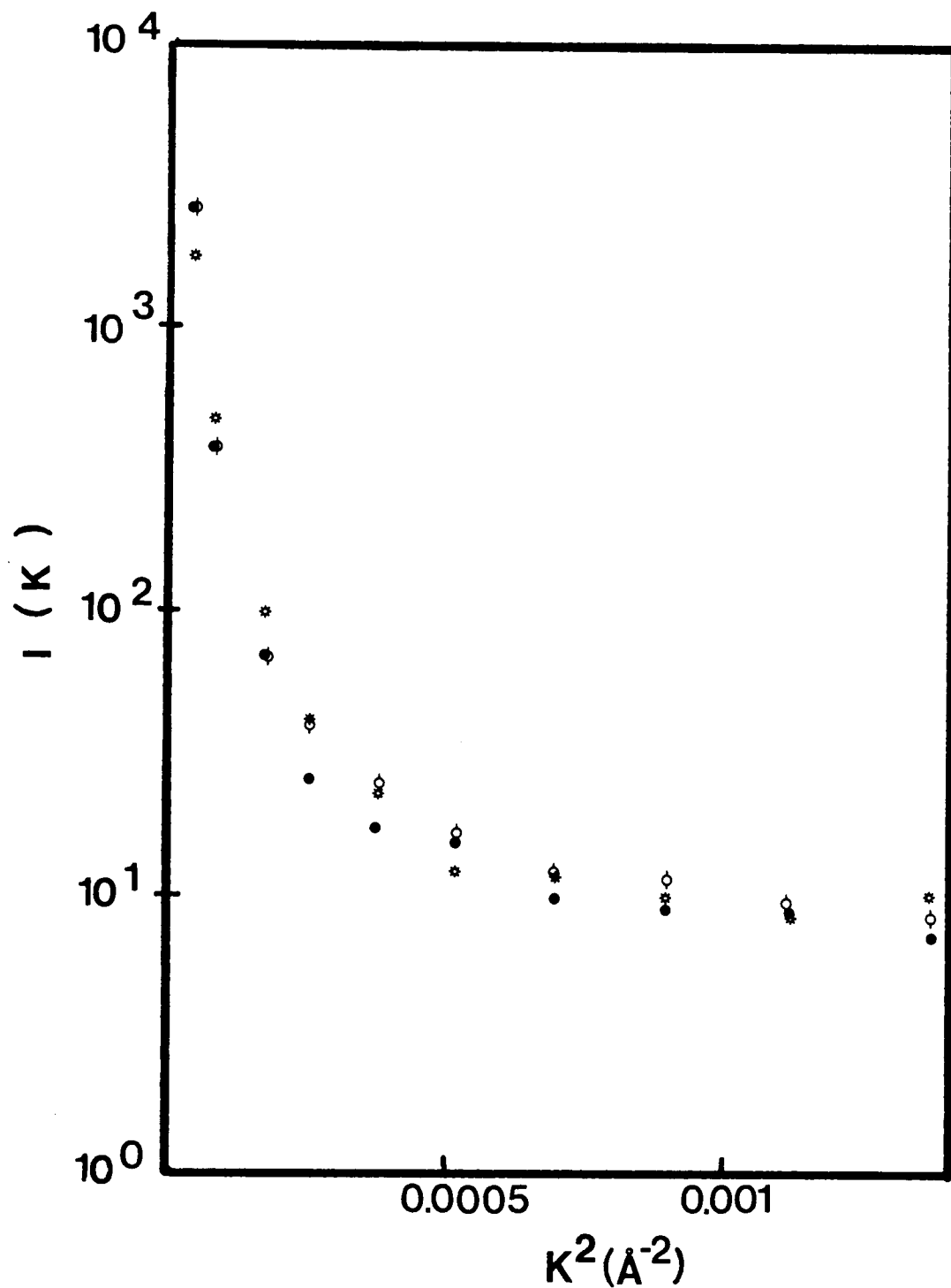


Figure 31. Relative scattering intensity $I(k)$ vs k^2 for EPON 828/NMA (90 phr)/BDMA epoxy resin. ● 0 psi, ○ 400 psi, * 5500 psi.

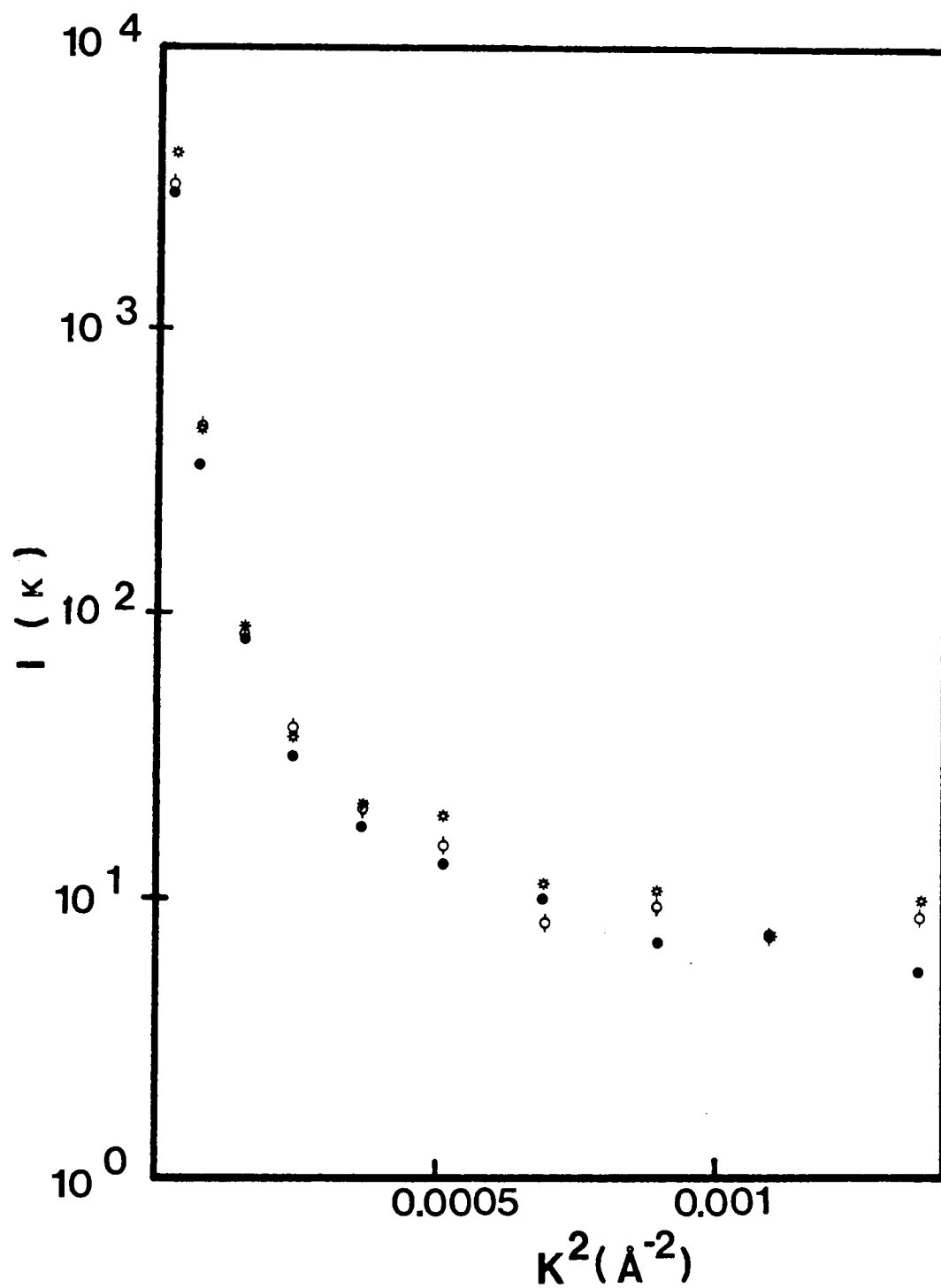


Figure 32. Relative scattering intensity $I(k)$ vs k^2 for EPON 828/NMA (70 phr)/BDMA epoxy resin. $\bullet$ 0 psi, $\circ$ 1090 psi, $\ast$ 5240 psi.

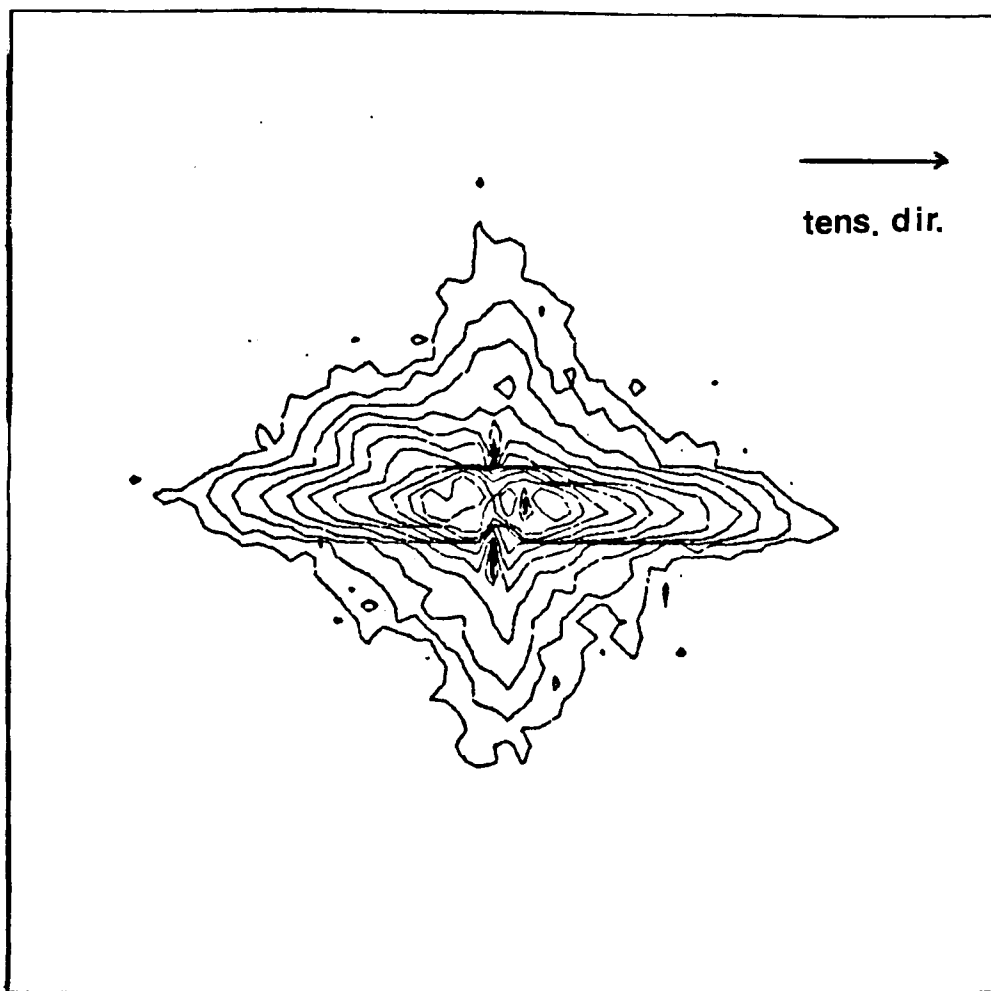


Figure 33. Typical polystyrene craze scattering pattern under a stress of 4200 psi. $\overline{M}_n = 200,000$, PD = 1.1 (166).

scattering intensity as stress is increased and growth of microvoids is not evident. Rather it is more reasonable to regard the failure process in epoxy as a catastrophic dynamic process. The crack propagates very fast across the whole sample leading to complete failure in a very short time.

IV.3 KEVLAR^R FIBERS

Kevlar^R 49, Kevlar^R 29 and degraded Kevlar^R 49 fibers have been studied using SAXS.

IV.3.A Static Experiments

Kevlar^R 49 fibers were wound on a specially designed frame (Figure 16, p. 78) and placed in the beam. Figure 34 shows the contour plot of the scattered intensity for Kevlar^R 49 fibers. The scattering is anisotropic, i.e. the scattering is elongated in the equatorial direction. Figure 35 shows the observed variation of intensity with scattering angle 2θ along the equatorial direction. There is an intensity maximum at about 5 mrad and at larger angles the intensity shows a smoothly changing curvature. The observed intensity maximum could be due to the beam stop. The inertial distances for different direction can be calculated using eq. II.5.C.12. SAXS patterns from the cross section of a bundle of Kevlar^R 49 fibers were obtained by aligning the fiber axis along the beam. Figure 36 shows the contour plots of the scattered intensity. It shows an isotropic scattering pattern. From these observations the scattering centers were deduced to be ellipsoidal shapes with their major axis along the fiber axis direction.

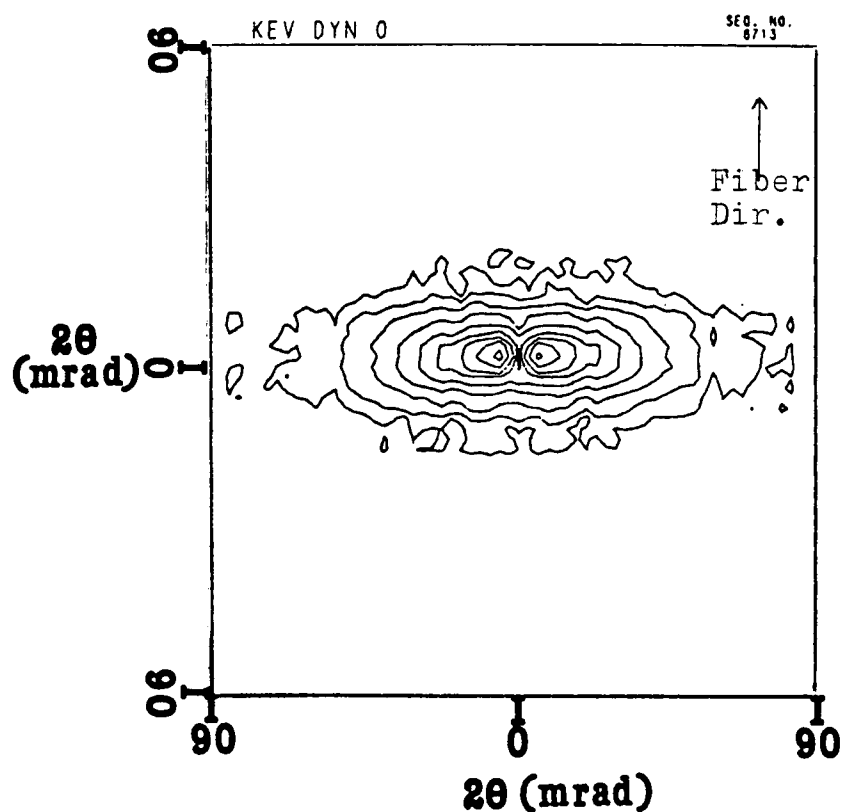


Figure 34. Two-dimensional isointensity contour plots of Kevlar^R 49. The outermost contour represents an intensity of 100 photons per channel with inner contours increasing by $\times 2$ at each level.

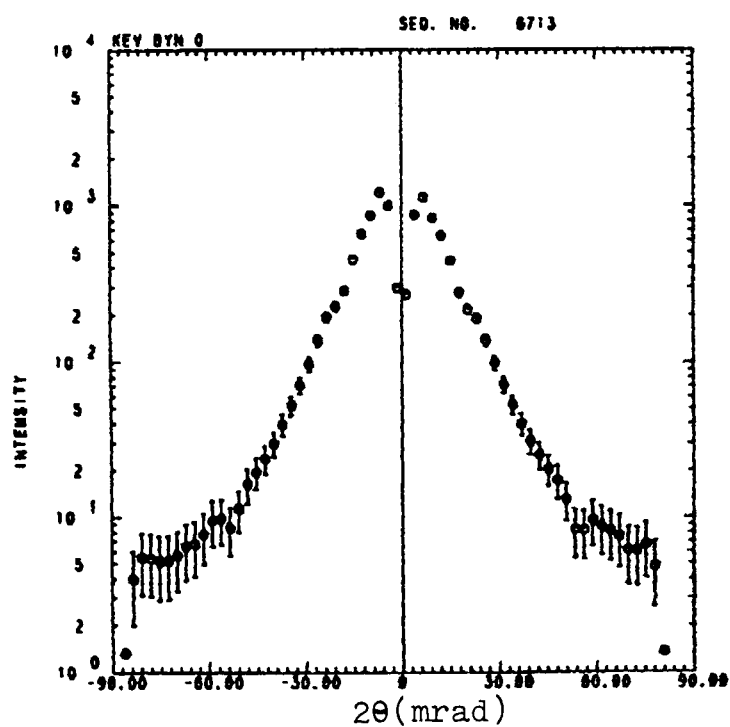


Figure 35. Observed scattering intensity variation with scattering angle 2θ along the equatorial direction.

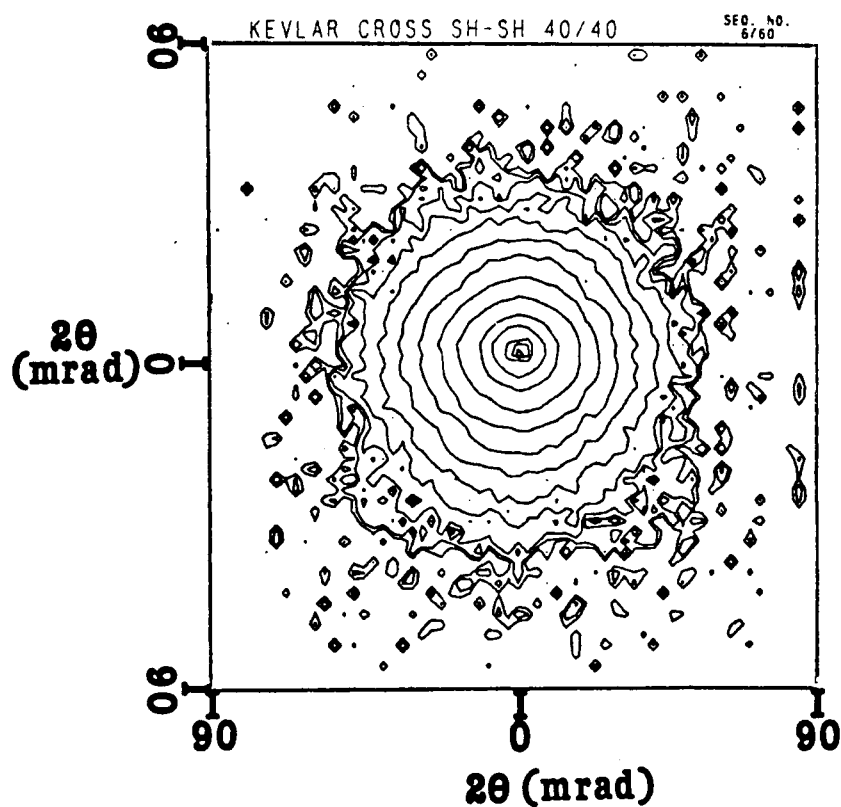


Figure 36. Two-dimensional isointensity contour plot of the cross section of Kevlar^R 49. The outermost contour represents an intensity of 16 photons with inner contours increasing by x2 at each level.

In order to identify the nature of the scattering centers, Kevlar^R 49 fibers were wound on an aluminum frame and soaked in EPON 828 at approximately 80°C for 48 hours and then the SAXS patterns were obtained. Figure 37 shows the observed contour plot of scattered intensity. The soaked Kevlar^R 49 fibers produced isotropic scattering. Dobb et al. (39) attributed the anisotropic scattering to microvoids in the fibers and the present results indeed indicate that the scattering is due to microvoids in the fibers and these microvoids can be partially filled by liquid such as EPON 828.

The scattering pattern was also obtained for Kevlar^R 29 fibers for comparison purposes, and it is presented in Figure 38. The scattering is anisotropic. The scattering patterns for three degraded Kevlar^R 49 fibers were obtained and presented in Figures 39 to 41. They are qualitatively similar to those of Kevlar^R 49 and Kevlar^R 29. Using the Guinier approximation (Eq. II.5.C.12 and Eq. II.5.C.13) and assuming that the microvoids are ellipsoidal, the average inertial distances of microvoids can be determined, and they are presented in Table 8. For weaker Kevlar^R fibers such as Kevlar^R 29, and degraded Kevlar^R 49 fibers, void widths are larger than that of Kevlar^R 49.

The volume fraction of microvoids is calculated for Kevlar^R 49 fibers using the INVAR program. INVAR calculates the fluctuations between phases in two-phase system. The volume fraction of microvoids in Kevlar^R 49 fibers was calculated to be 0.82 percent. If one compares this value to the volume fraction of microvoids calculated using the theoretical density of 1.48 g/cm³ (125) and reported density (125) of

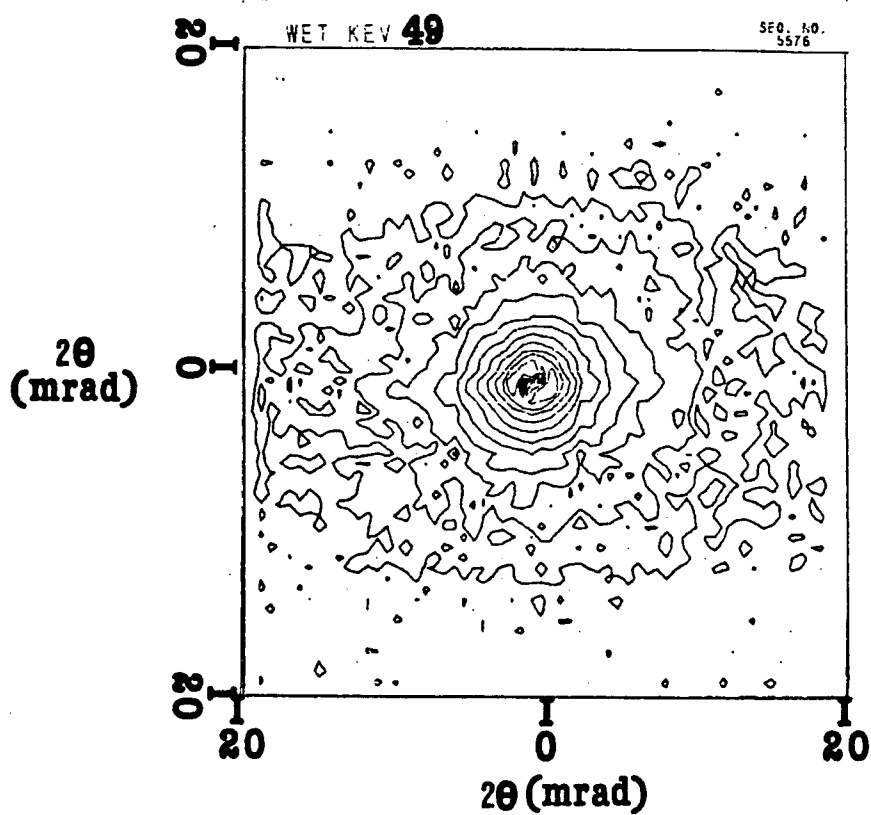


Figure 37. Two-dimensional isointensity contour plot of soaked Kevlar^R 49. The outermost contour represents an intensity of 16 photons with inner contours increasing by x2 at each level.

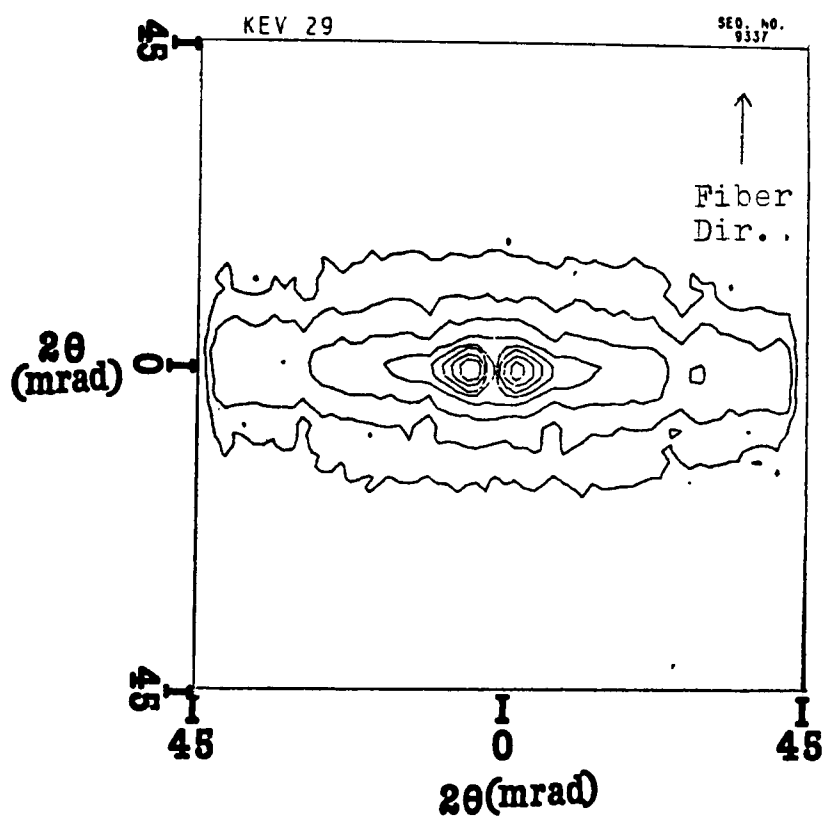


Figure 38. Two-dimensional isointensity contour plot of Kevlar^R 29. The outermost contour represents an intensity of 100 photons with inner contours increasing by $\times 2$ at each level.

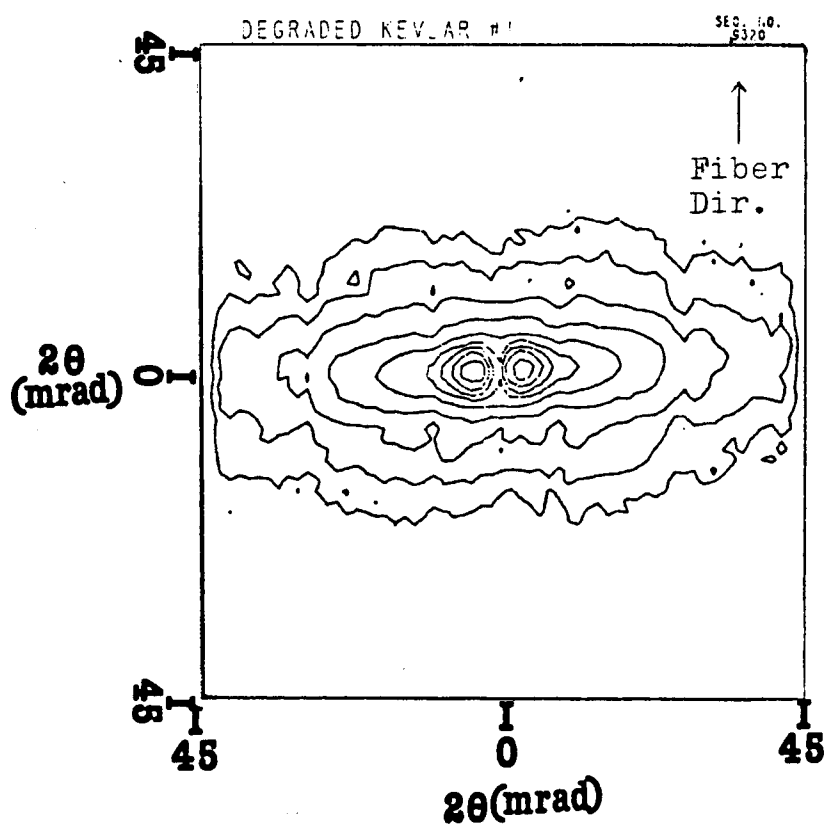


Figure 39. Two-dimensional isointensity contour plot of Kevlar^R 49 degraded at 125°C, 100% R.H. for 40 days. The outermost contour represents an intensity of 100 photons per channel with inner contours increasing x2 at each level.

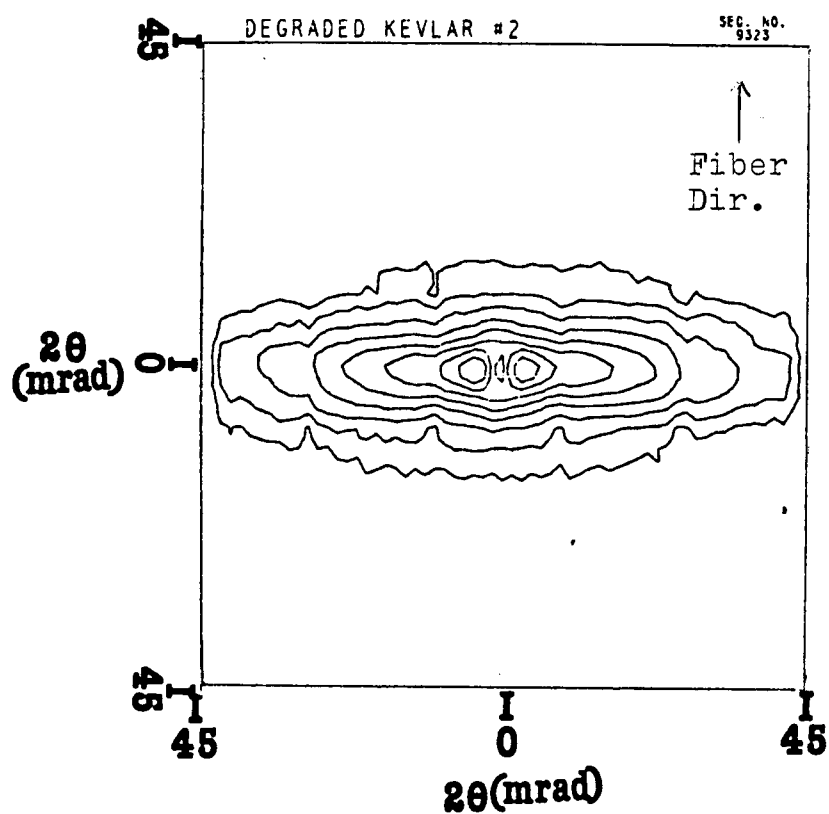


Figure 40. Two-dimensional isointensity contour plot of Kevlar^R 49 degraded at 150°C, 100% R.H. for 14 days. The outermost contour represents an intensity of 100 photons per channel with inner contours increasing $\times 2$ at each level.

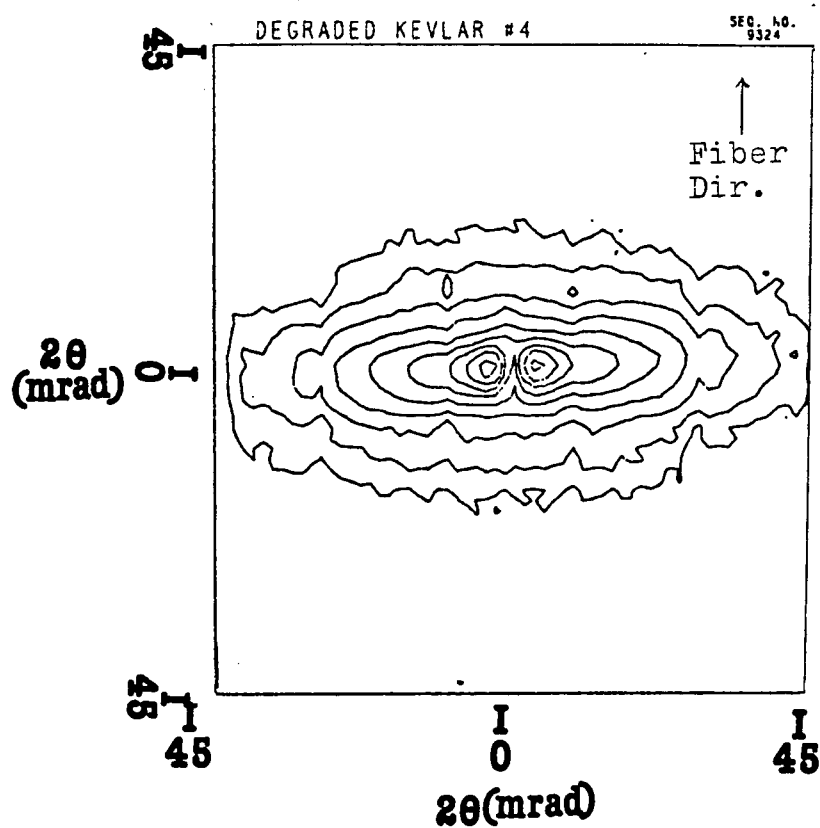


Figure 41. Two-dimensional isointensity contour plot of Kevlar^R 49 degraded at 200°C, 100% R.H. for 2 days. The outermost contour represents an intensity of 100 photons per channel with inner contours increasing x2 at each level.

Table 8. Void Dimensions Determined by SAXS

	Void Width (nm)	Void Length (nm)
Kevlar ^R 49	4.7	10.7
Kevlar ^R 29	10.8	10.6
Degraded Kevlar ^R 49 #1	10.0	10.8
Degraded Kevlar ^R 49 #2	7.6	11.0
Degraded Kevlar ^R 49 #4	9.8	8.0

1.43 g/cm³--3.38 percent--there is large discrepancy. These results can be understood if only one-fourth of the total microvoids consists of sufficiently small voids to affect the accessible small-angle-scattering range. Therefore, it is reasonable to presume there are microvoids much larger than a few hundred angstroms.

IV.3.B Dynamic Experiments

A Kevlar^R 49 fiber bundle was studied dynamically by collecting the SAXS patterns while the bundle was being stressed in a stepwise manner and the resulting net scattering patterns are shown in Figure 42. It is evident from these patterns that unlike the scattering patterns of epoxies there are gradual changes in the scattering patterns induced by the application of stresses. The net scattering patterns are anisotropic. The gradual changes are more clearly shown in Figure 43 which

Figure 42. Net dynamic two-dimensional isointensity contour plots of Kevlar^R 49 stressed in a stepwise manner. The outermost contour represents an intensity of 16 photons per channel with inner contours increasing by x2 at each level. The scattering from the unstressed sample is subtracted as background from each scattering plot.

- a) 7.90 lb_f
- b) 11.0 lb_f
- c) 16.0 lb_f
- d) 22.0 lb_f
- e) 28.0 lb_f
- f) 32.0 lb_f
- g) 37.0 lb_f
- h) 42.0 lb_f
- i) 46.0 lb_f
- j) 75.0 lb_f

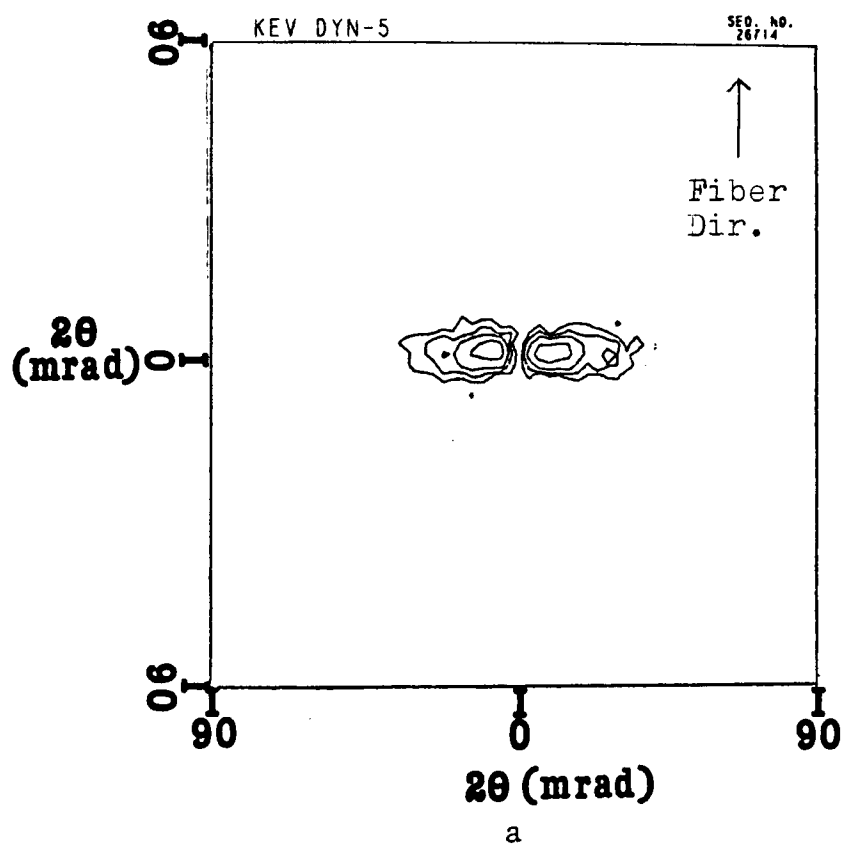


Figure 42

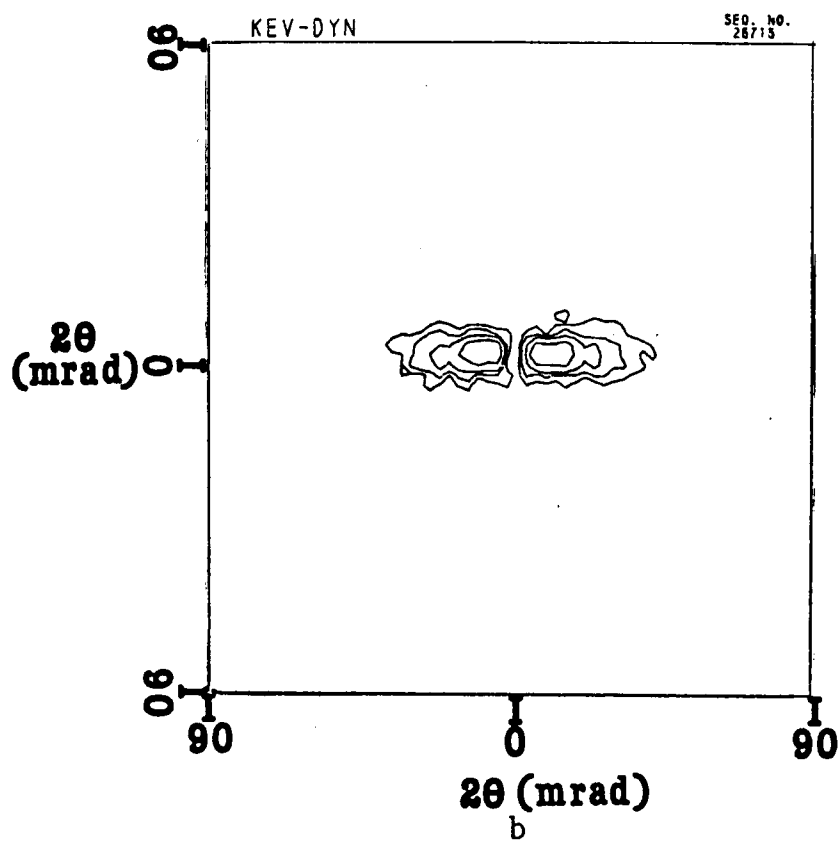


Figure 42 (Continued)

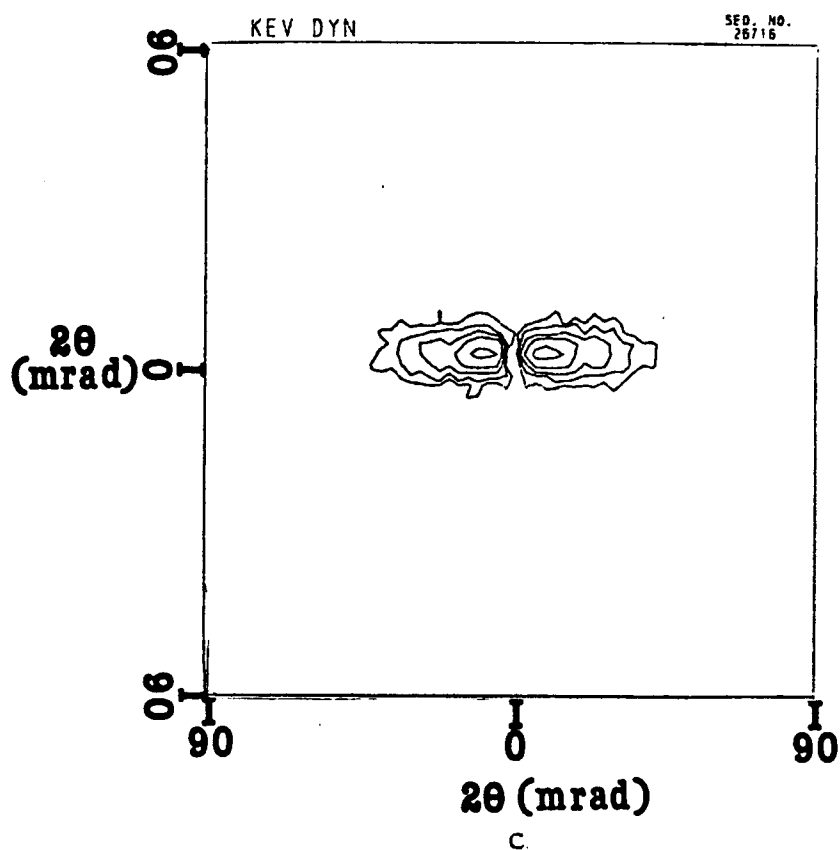


Figure 42 (Continued)

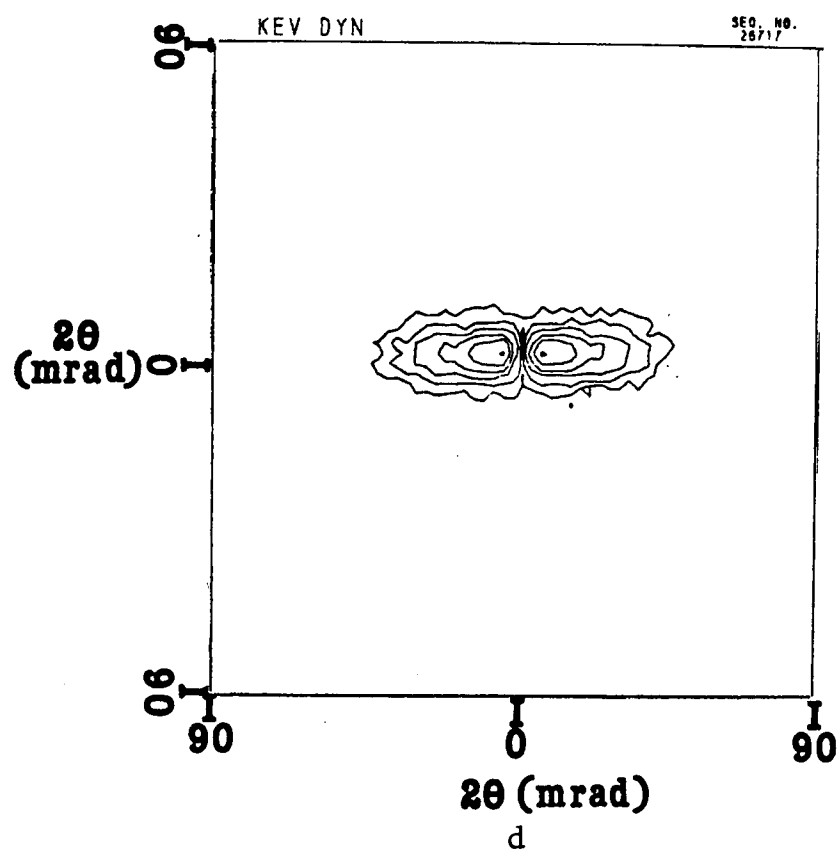


Figure 42 (Continued)

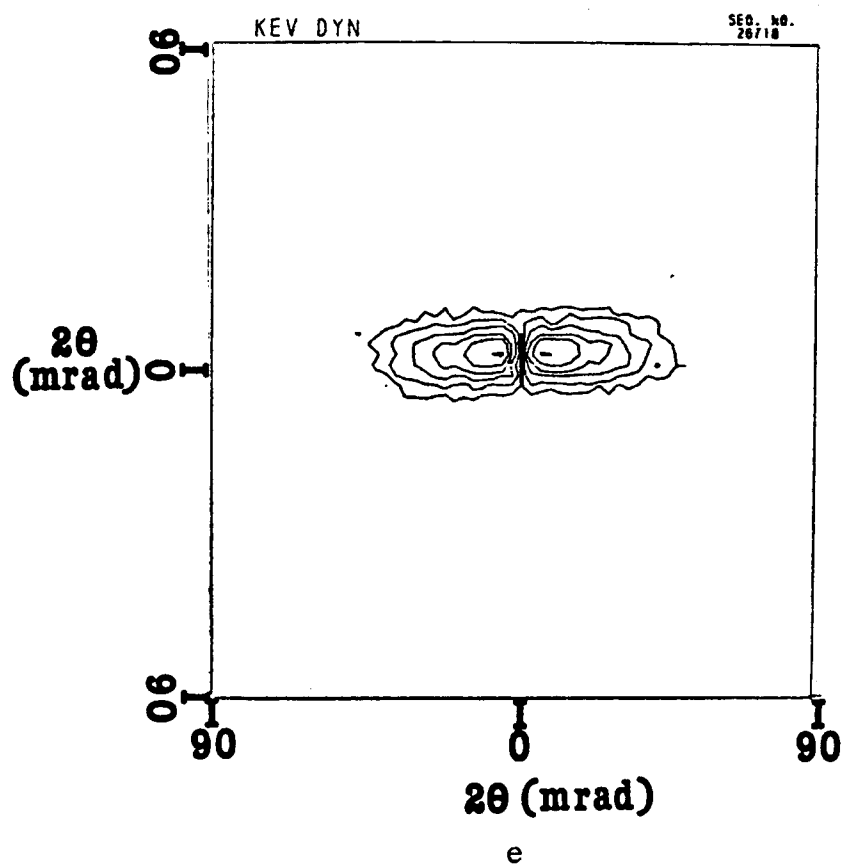


Figure 42 (Continued)

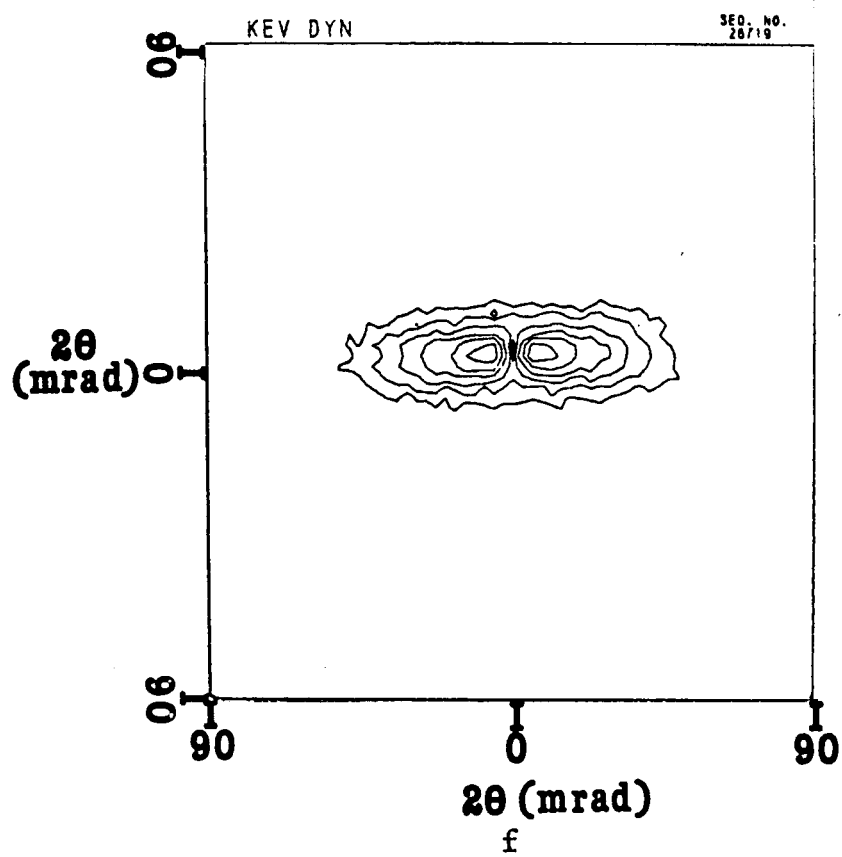


Figure 42 (Continued)

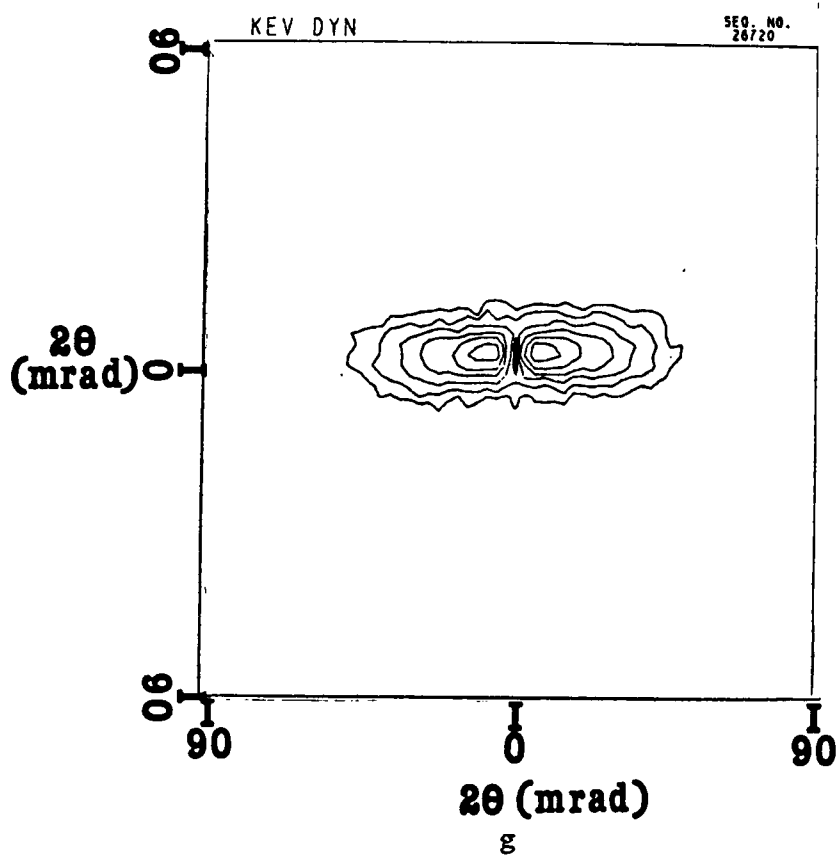


Figure 42 (Continued)

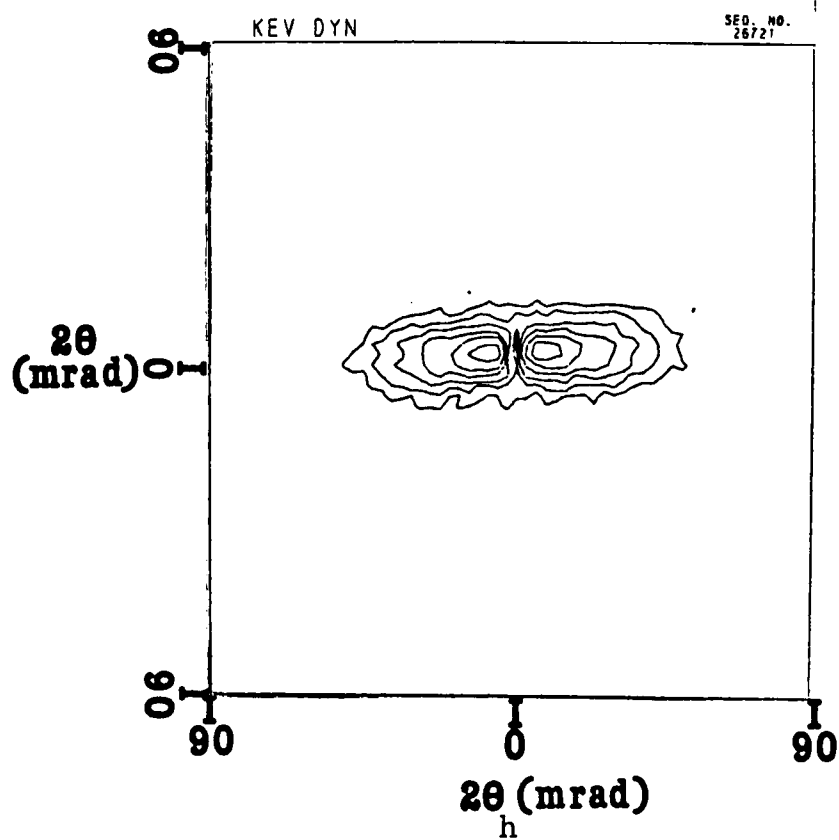


Figure 42 (Continued)

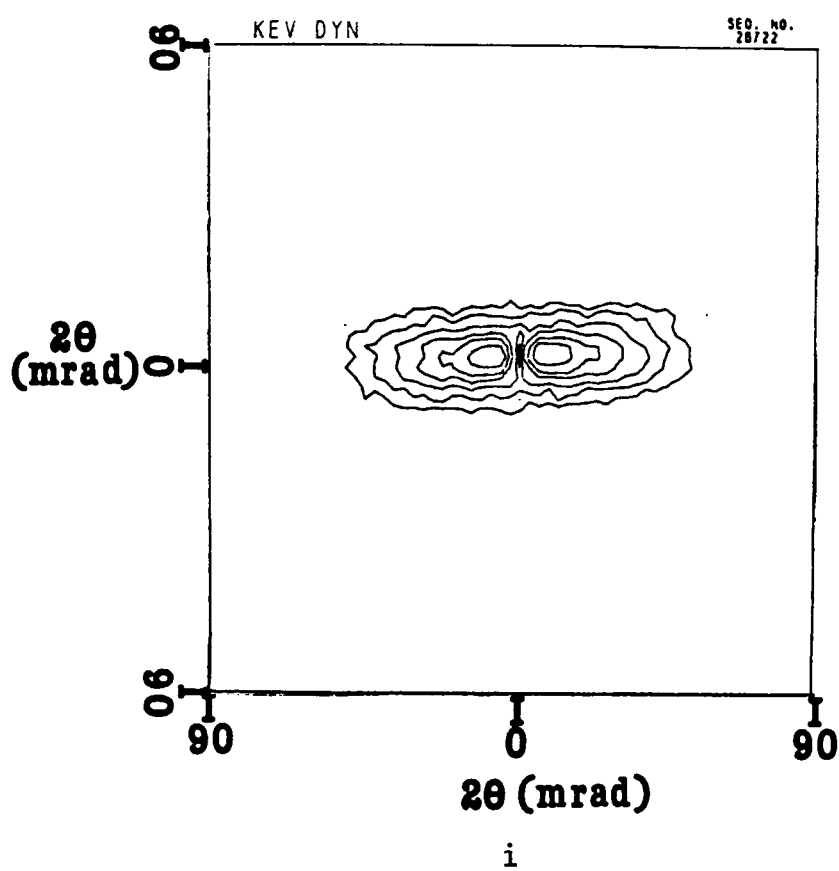


Figure 42 (Continued)

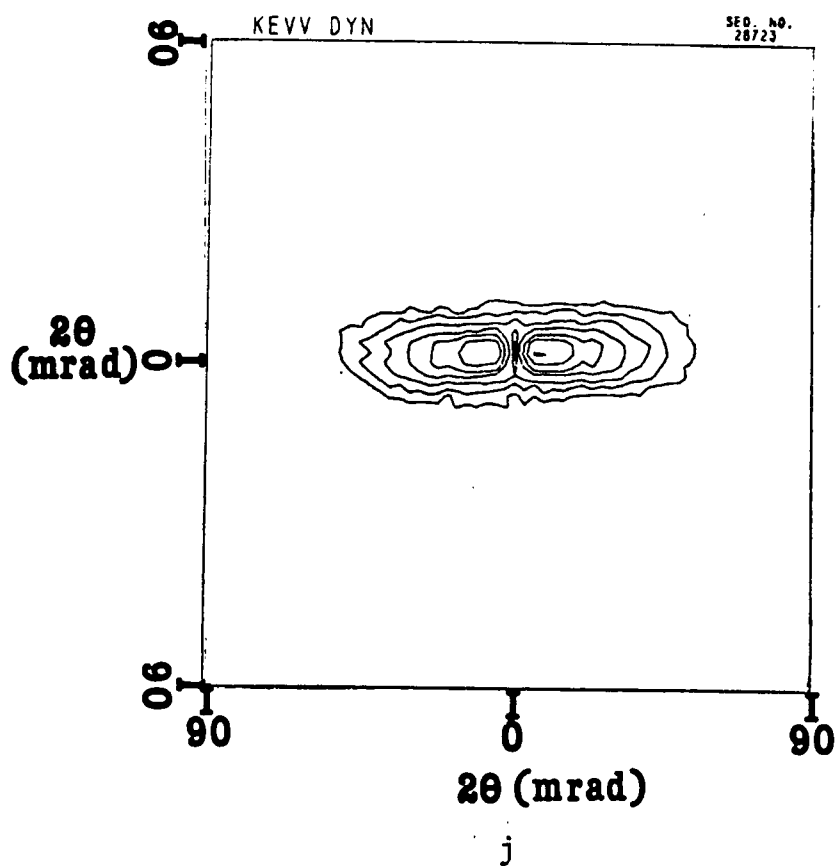


Figure 42 (Continued)

Figure 43. Incremental dynamic two-dimensional isointensity contour plots of Kevlar^R 49 stressed in a stepwise manner. The outermost contour represents an intensity of 16 photons per channel with inner contours increasing by x2 at each level. The scattering from previously stressed sample is subtracted as background from each scattering plot.

- a) 11.0 lb_f - 7.90 lb_f
- b) 16.0 lb_f - 11.0 lb_f
- c) 22.0 lb_f - 16.0 lb_f
- d) 28.0 lb_f - 22.0 lb_f
- e) 32.0 lb_f - 28.0 lb_f
- f) 37.0 lb_f - 32.0 lb_f
- g) 42.0 lb_f - 37.0 lb_f
- h) 46.0 lb_f - 42.0 lb_f
- i) 75.0 lb_f - 46.0 lb_f

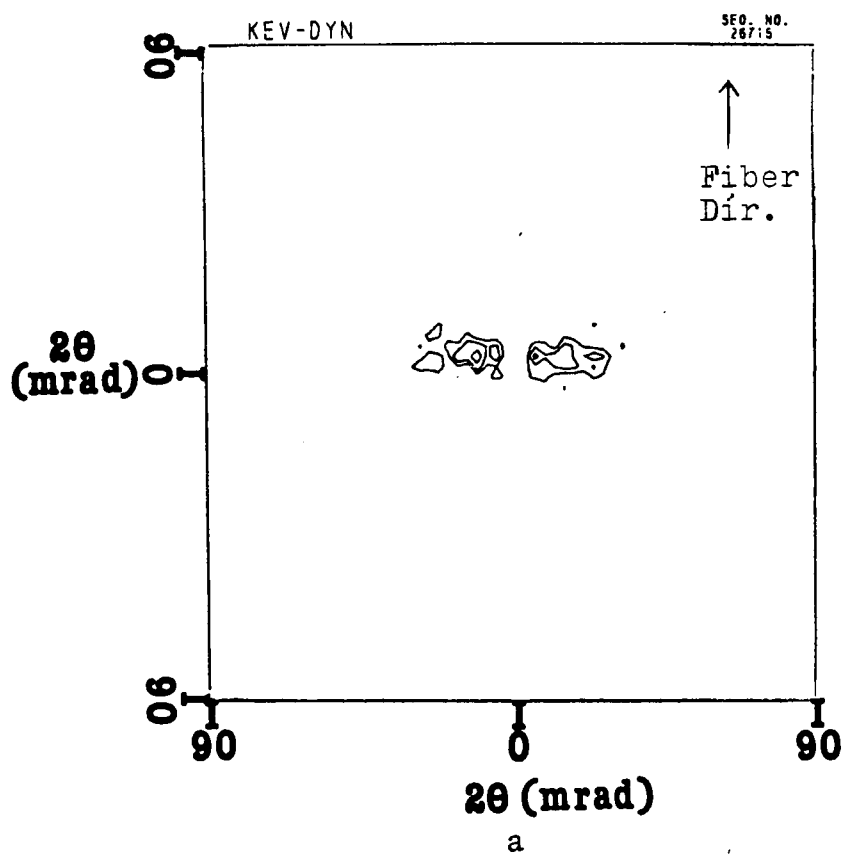


Figure 43

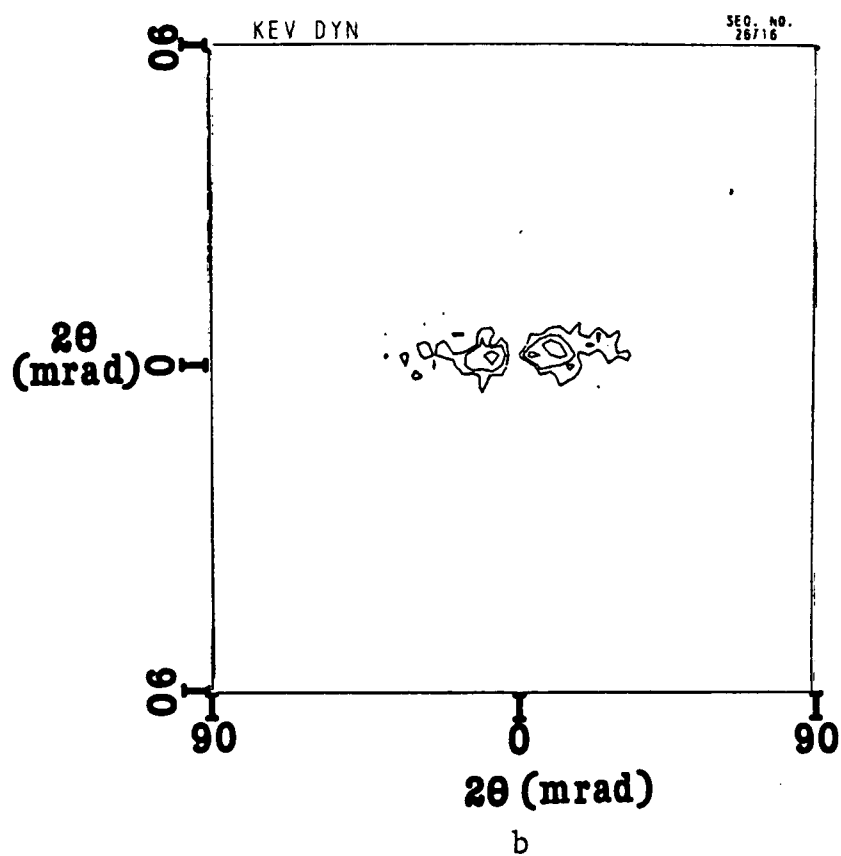


Figure 43 (Continued)

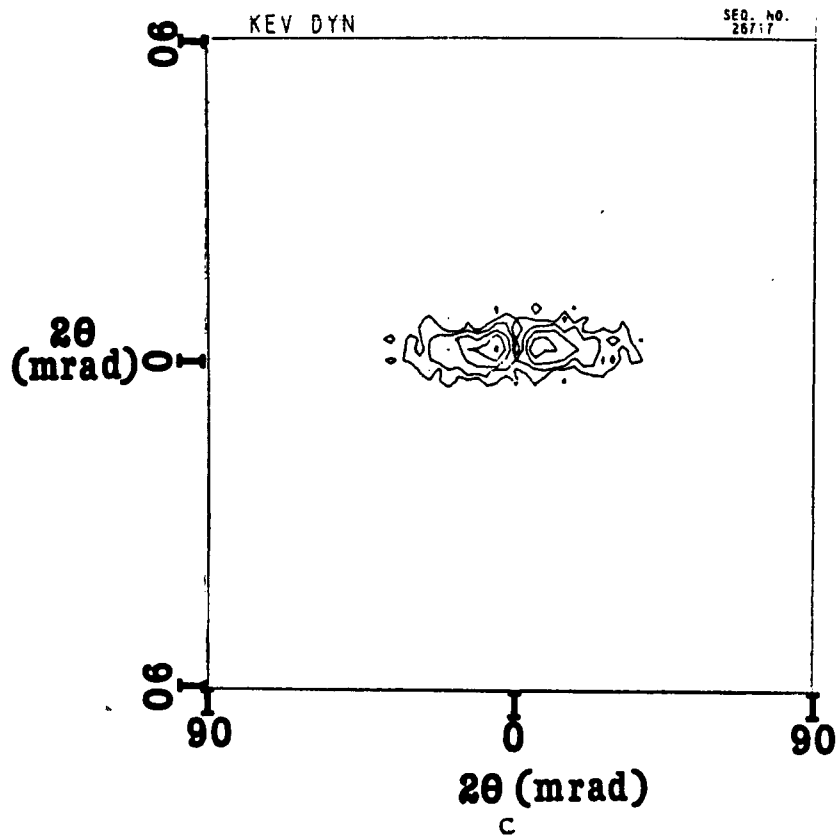


Figure 43 (Continued)

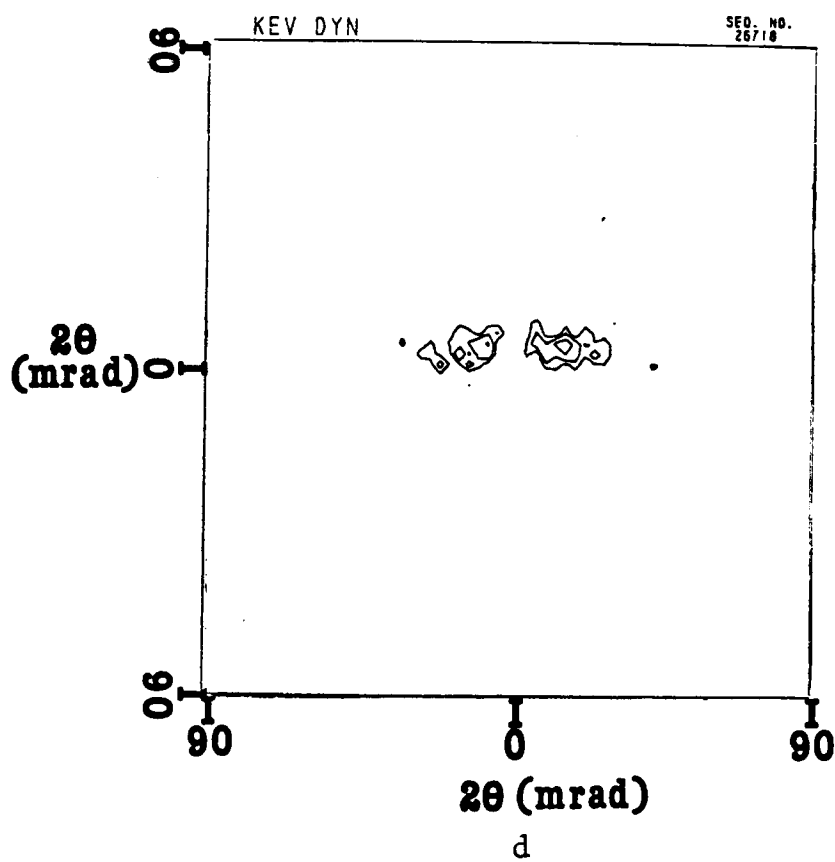


Figure 43 (Continued)

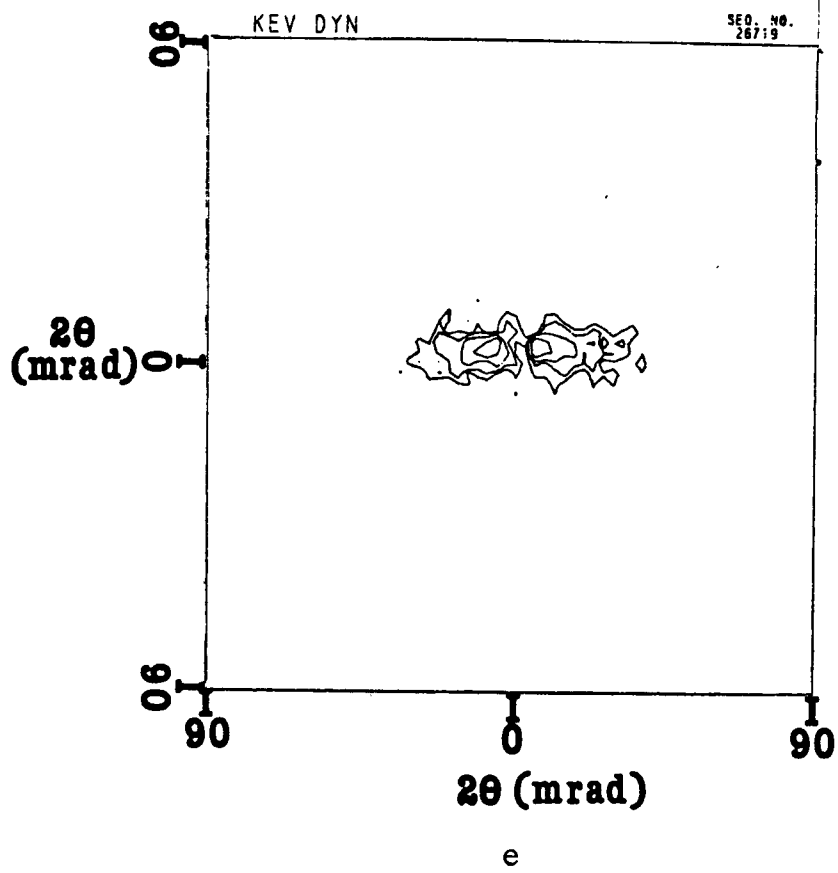


Figure 43 (Continued)

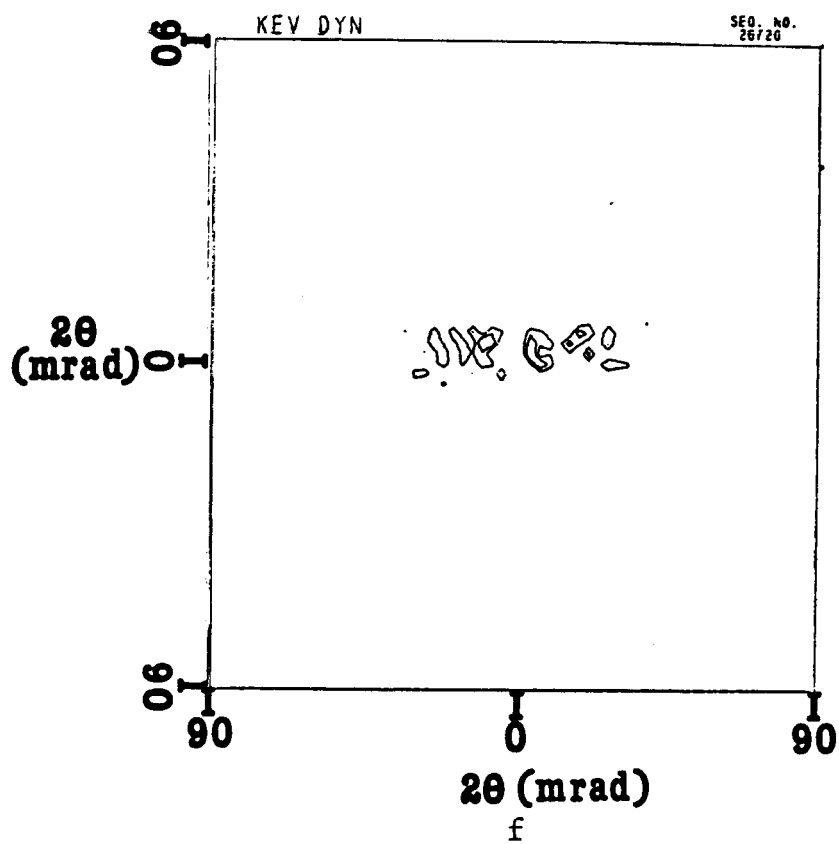


Figure 43 (Continued)

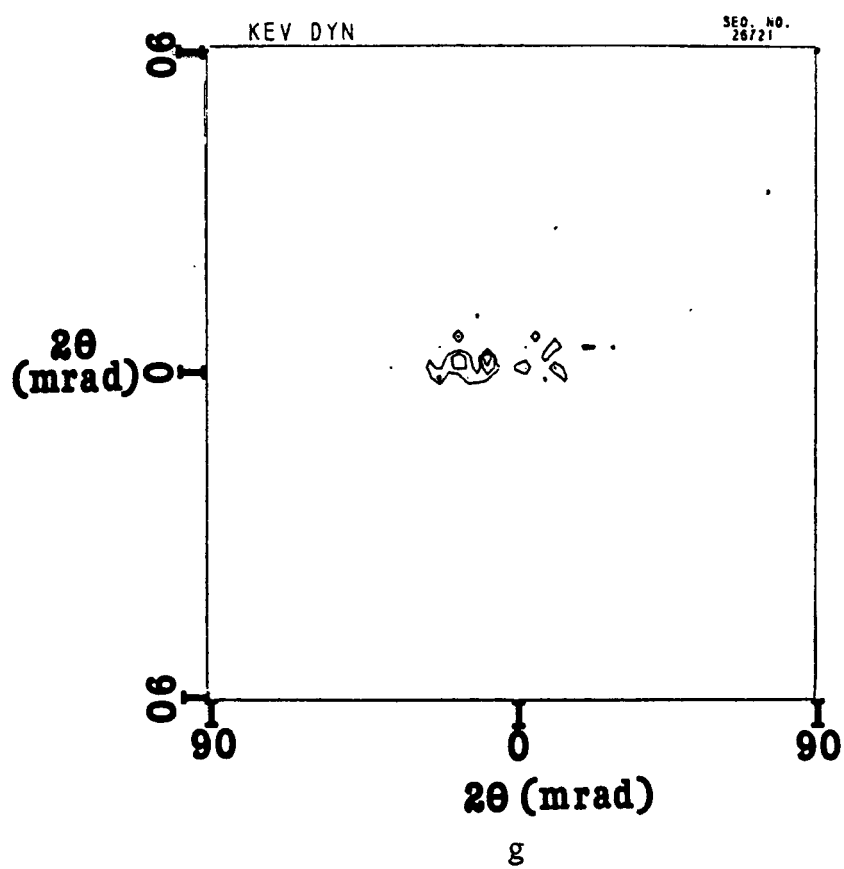


Figure 43 (Continued)

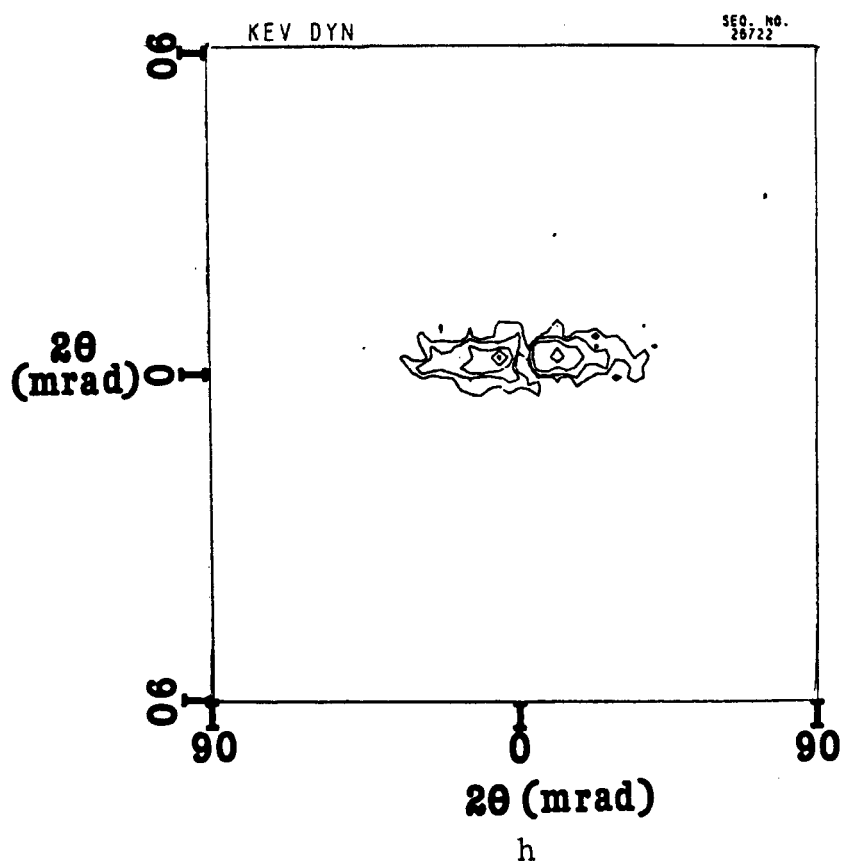


Figure 43 (Continued)

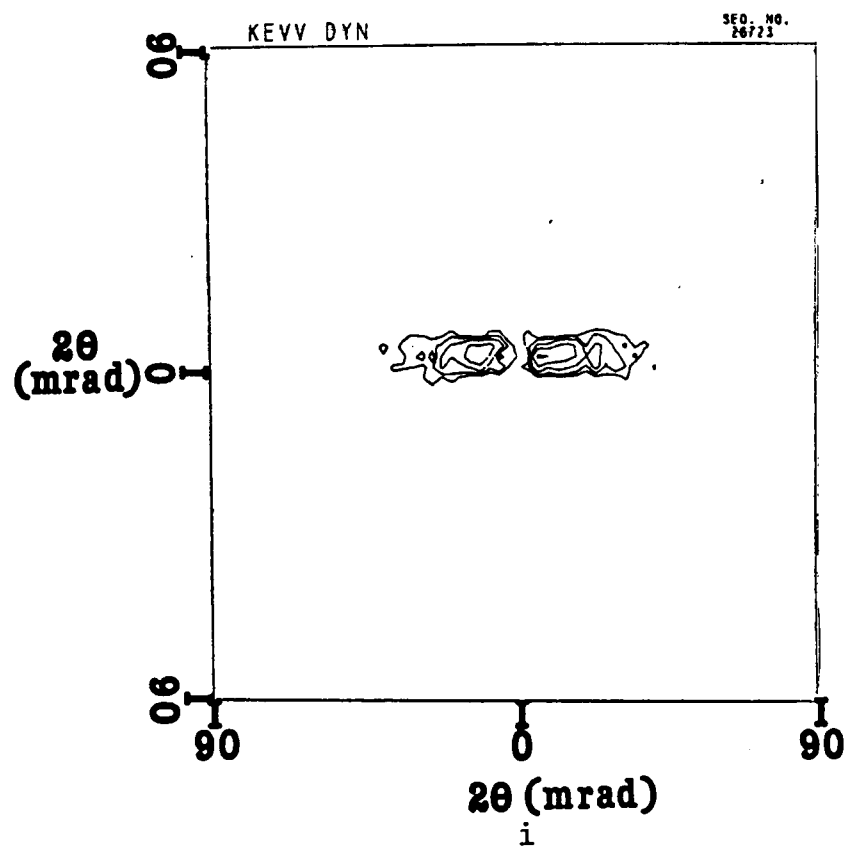


Figure 43 (Continued)

shows the net incremental scattering patterns, i.e. scattering due only to incremental stress application. The intensity variation with the square of scattering vector k^2 shown in Figure 44 clearly demonstrates the increasing intensity in the equatorial direction with the increasing stress levels. This clearly contrasts with the results obtained for epoxies. A soaked Kevlar^R fiber bundle was also studied dynamically and the resulting net scattering patterns are shown in Figure 45. There are once again gradual changes induced by the application of stresses.

The failure process of Kevlar^R 49 fibers has been studied by Konopasek and Hearle (88). However, their study is limited in the sense that their failure mechanism is macroscopic, and they deduced the failure mechanisms from the electron microscopic observations of failed fibers. The present study has been able to present direct evidence of the failure process in Kevlar^R 49 fibers. Looking at Figure 44, the slopes of the intensity curve in the Guinier range remain nearly constant, and from this it can be inferred that the increase in intensity is mostly due to an increase in the volume fraction of microvoids and not in the increase in sizes of the individual microvoids. A further evidence of this finding is presented in Table 9 which shows the increase in volume fraction of microvoids, w_1 , with increased applied stresses. The results of dynamic experiments on soaked Kevlar^R fiber bundle presented in Figure 45, however, shows the microvoids are being enlarged along the fiber axis direction. These two results are not contradictory to each other when one considers two different sizes of microvoids--one in the order of 100 Å's and the other much larger sizes.

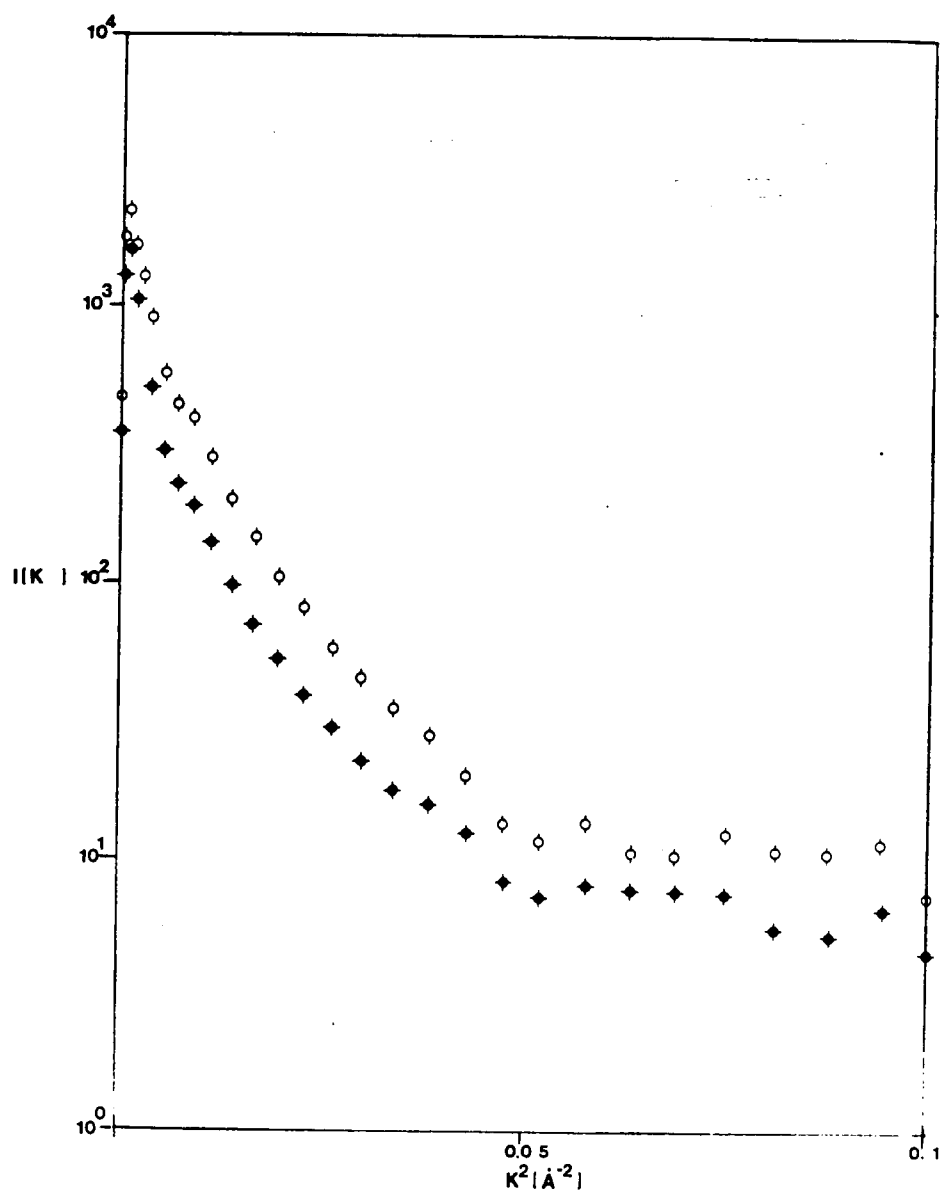


Figure 44. Relative intensity $I(k)$ vs k^2 for Kevlar^R 49. ◆ 0 lb_f ,
 O 46 lb_f .

Figure 45. Net dynamic two-dimensional isointensity contour plots for soaked Kevlar^R 49 fibers stressed in a stepwise manner. The outermost contour represents an intensity of 16 photons per channel with inner contours increasing by x2 at each level.

- a) 4.0 lb_f
- b) 7.2 lb_f
- c) 12 lb_f
- d) 17 lb_f
- e) 28 lb_f
- f) 39 lb_f
- g) 46 lb_f

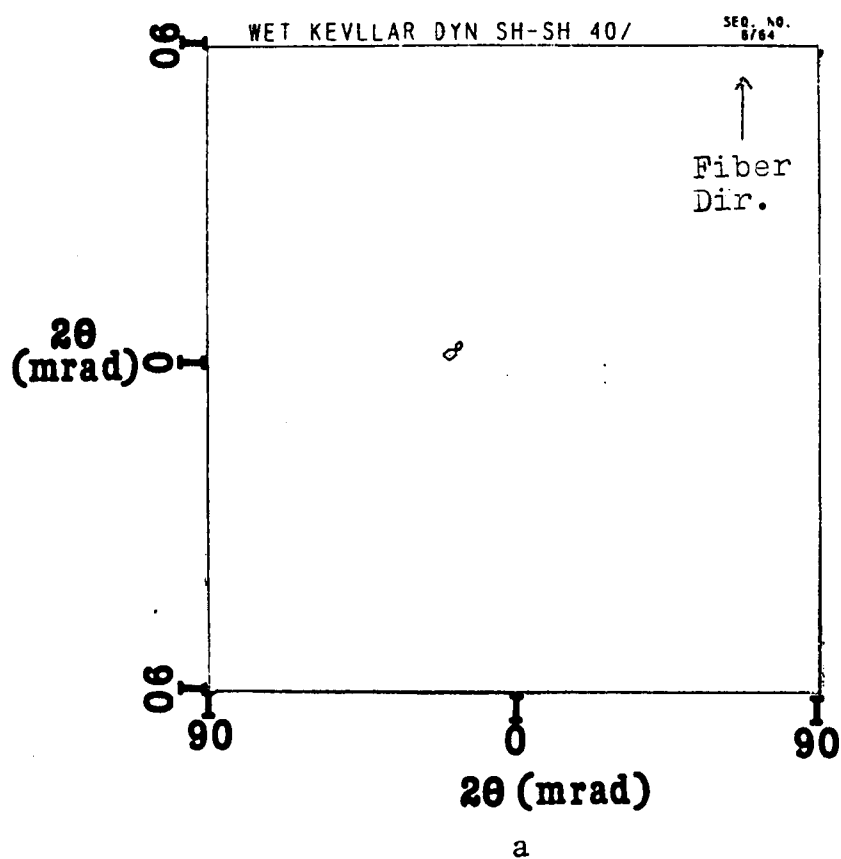


Figure 45

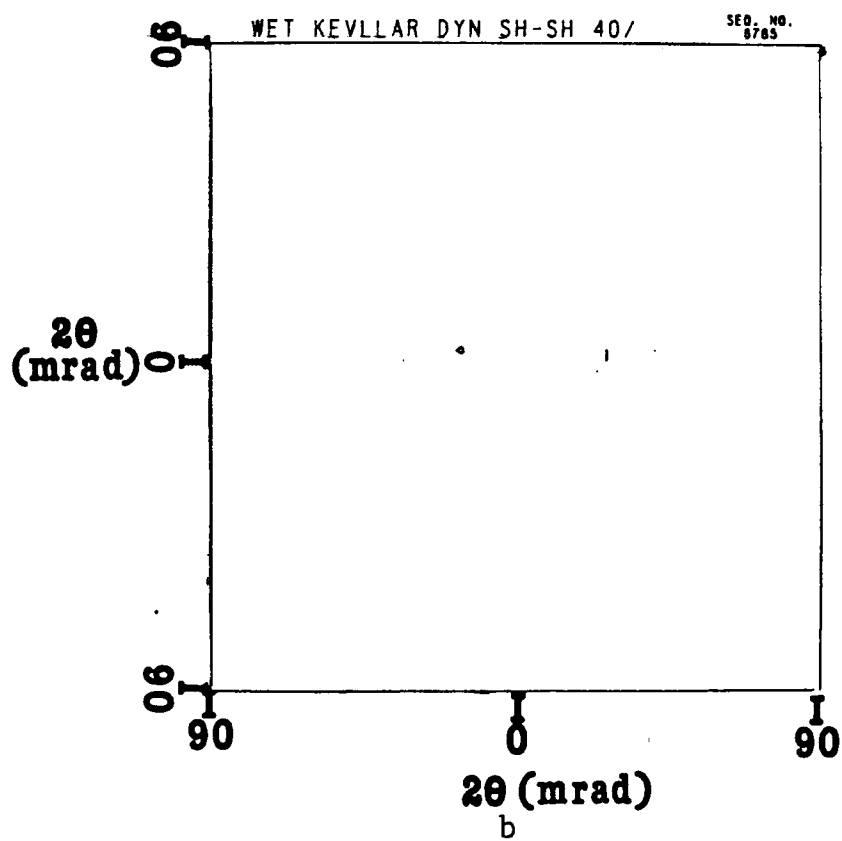


Figure 45 (Continued)

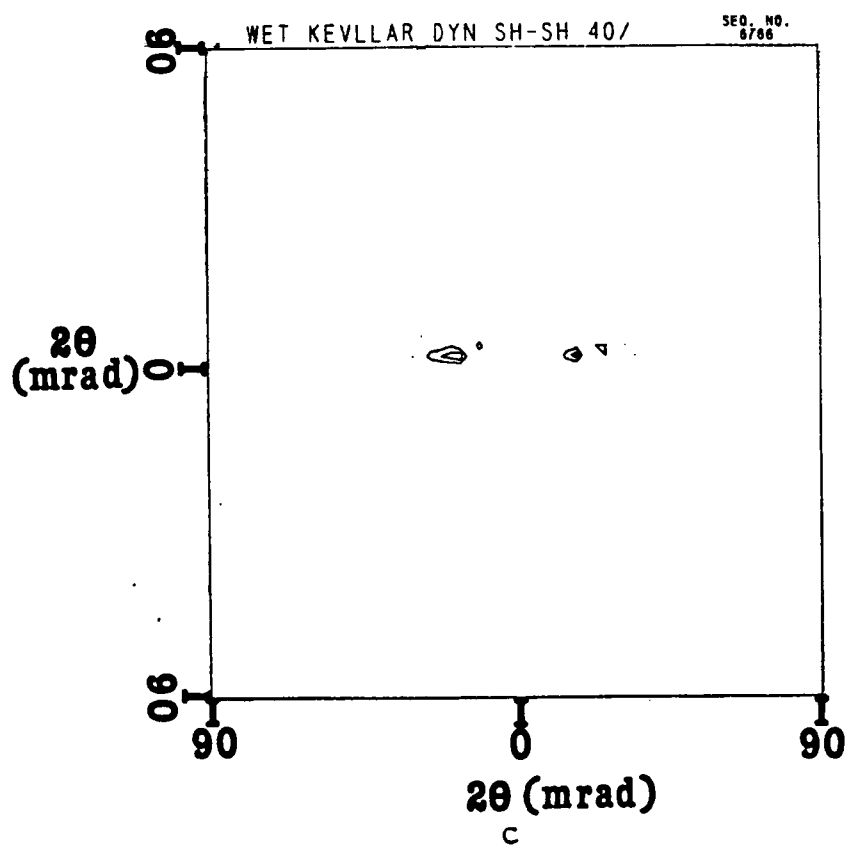


Figure 45 (Continued)

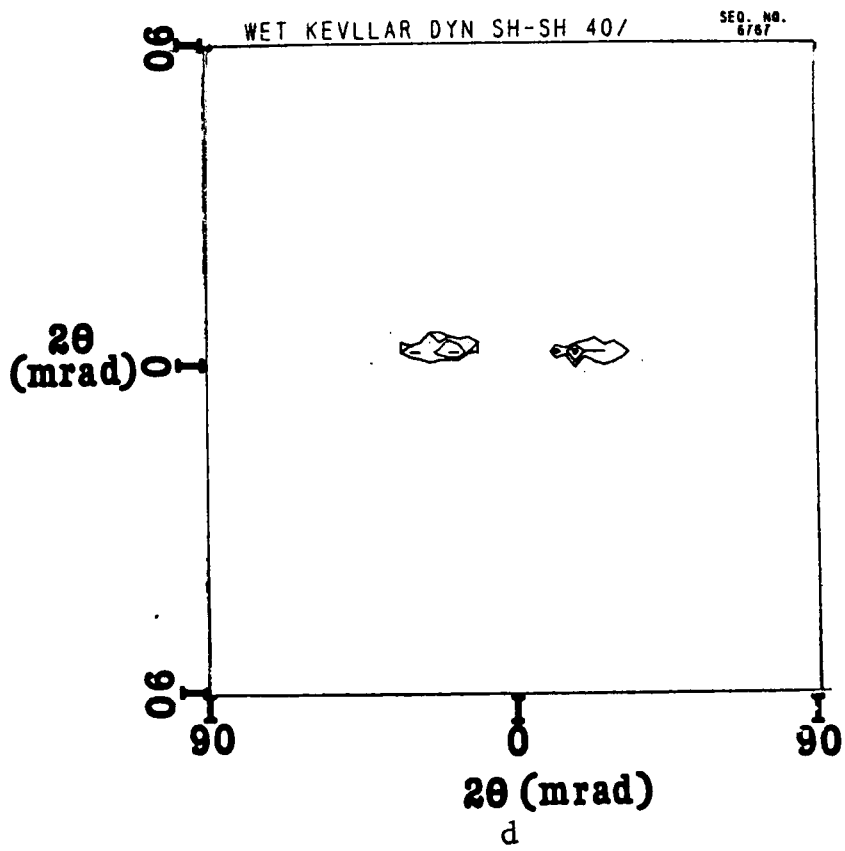


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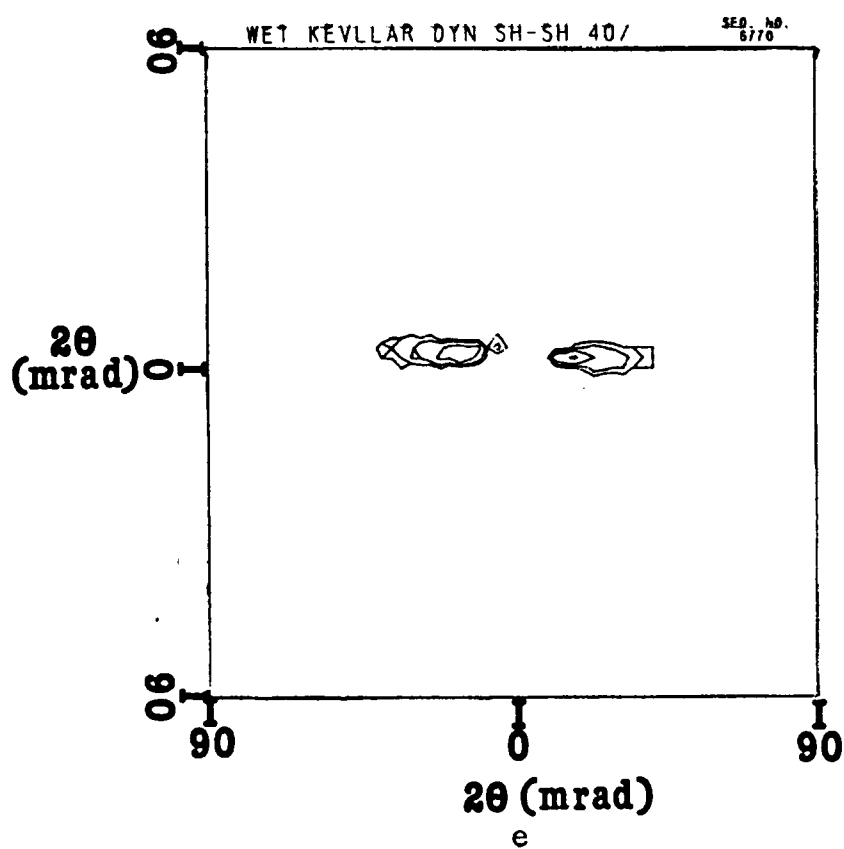


Figure 45 (Continued)

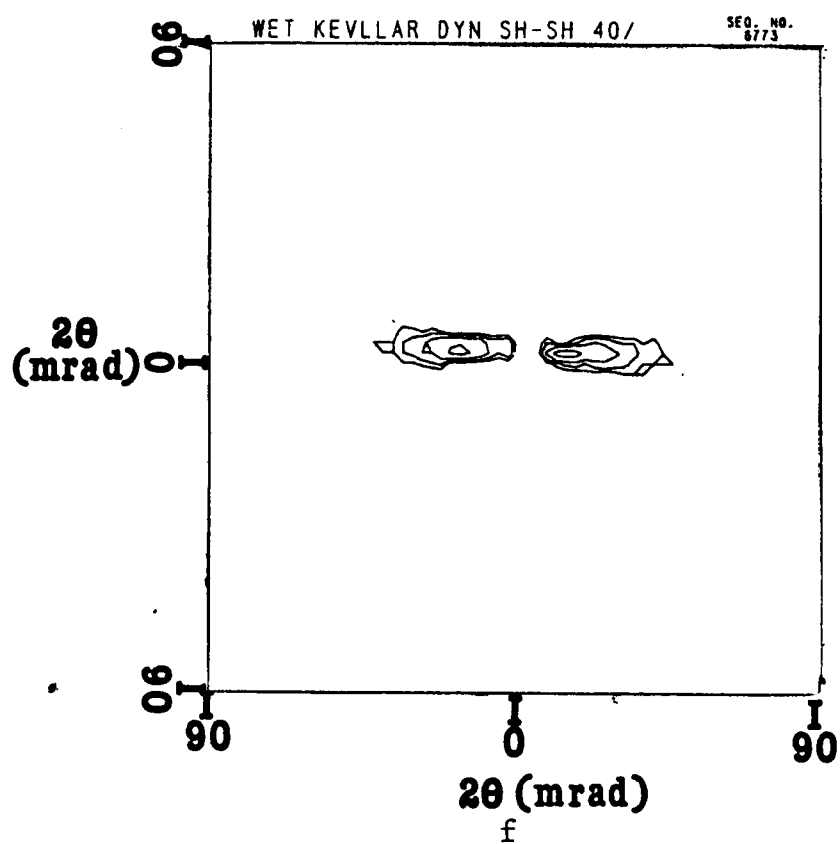


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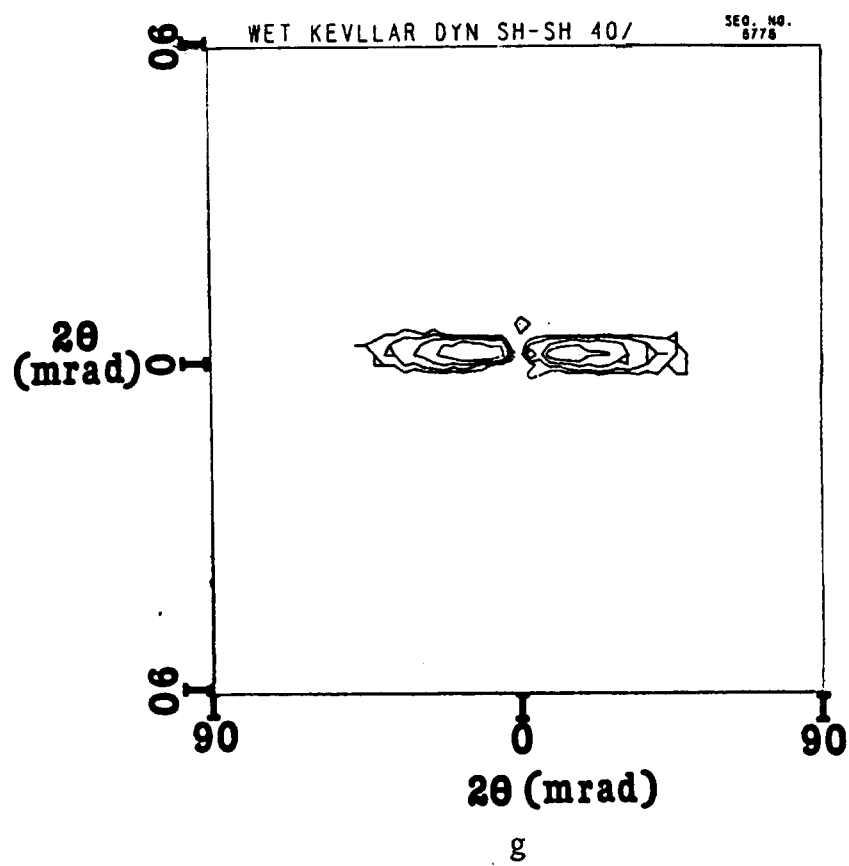


Figure 45 (Continued)

Table 9. Void Fractions for Kevlar^R 49 Fibers Stressed in a Stepwise Manner Calculated from SAXS Invariant Analysis

Force (lb _f)	Q (cm)	MS EDF (moles of electrons/cm ⁶)	w ₁
0.0	0.9253x10 ⁻³	0.4557x10 ⁻²	0.0082
7.9	0.1052x10 ⁻²	0.5184x10 ⁻²	0.0093
11.4	0.1110x10 ⁻²	0.5468x10 ⁻²	0.0098
16.2	0.1185x10 ⁻²	0.5835x10 ⁻²	0.0105
22.0	0.1292x10 ⁻²	0.6364x10 ⁻²	0.0115
28.0	0.1373x10 ⁻²	0.6764x10 ⁻²	0.0122
32.4	0.1465x10 ⁻²	0.7216x10 ⁻²	0.0130
37.3	0.1528x10 ⁻²	0.7525x10 ⁻²	0.0136
42.2	0.1566x10 ⁻²	0.7712x10 ⁻²	0.0139
46.2	0.1620x10 ⁻²	0.7978x10 ⁻²	0.0144
74.6	0.1700x10 ⁻²	0.8374x10 ⁻²	0.0151

Larger microvoids are presumably masked by soaking and when stress is applied these large microvoids enlarge. Therefore, the failure mechanisms in Kevlar^R fibers postulated based on the present results are: small microvoids grow in number while larger microvoids grow in size along the fiber axis direction when stress is applied. Small microvoids may coalesce to form larger microvoids when the applied stress is high.

IV.4 COMPOSITES

Uniaxially reinforced Kevlar^R fiber/epoxy composites were studied using SAXS. The epoxy resins were EPON 828 cured with NMA with BDMA as the accelerator. The volume fraction of fibers was 2.9 percent determined by the density column method. In order to study the orientation effects of fibers in failure behaviors, tensile bars with four different (0° , 30° , 45° and 90°) angled fiber composites were cut from a single molded composite sheet. Composites with fiber angle 90° were stressed along the fiber axis direction while composites with fiber angle 0° were stressed perpendicular to the fiber axis direction. The angle between tensile stress direction and the fiber axis direction in 30° and 45° composites were therefore 60° and 45° , respectively.

IV.4.A Dynamic Experiments

The samples were loaded on to the pullrods in the sample chamber of the SAXS camera and stressed in a stepwise manner using the servo controller. Figure 46, Figure 47, and Figure 48 show the contour plots

Figure 46. Dynamic two-dimensional isointensity contour plots of Kevlar^K 49 fiber reinforced EPON 828/NMA (90 phr)/BDMA composite with fiber angle 90 degrees. The outermost contour represents an intensity of 2 photons per channel with inner contours increasing by x2 at each level.

- a) 0 psi
- b) 590 psi
- c) 1100 psi
- d) 1800 psi
- e) 2750 psi
- f) 3400 psi
- g) 5400 psi

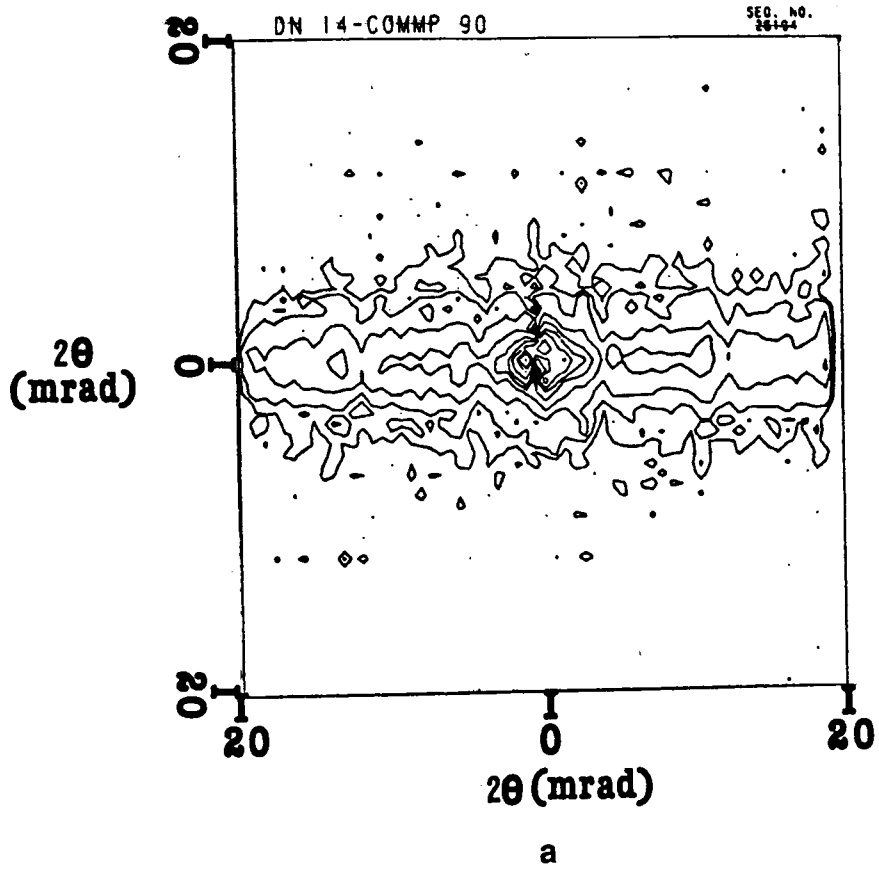


Figure 46

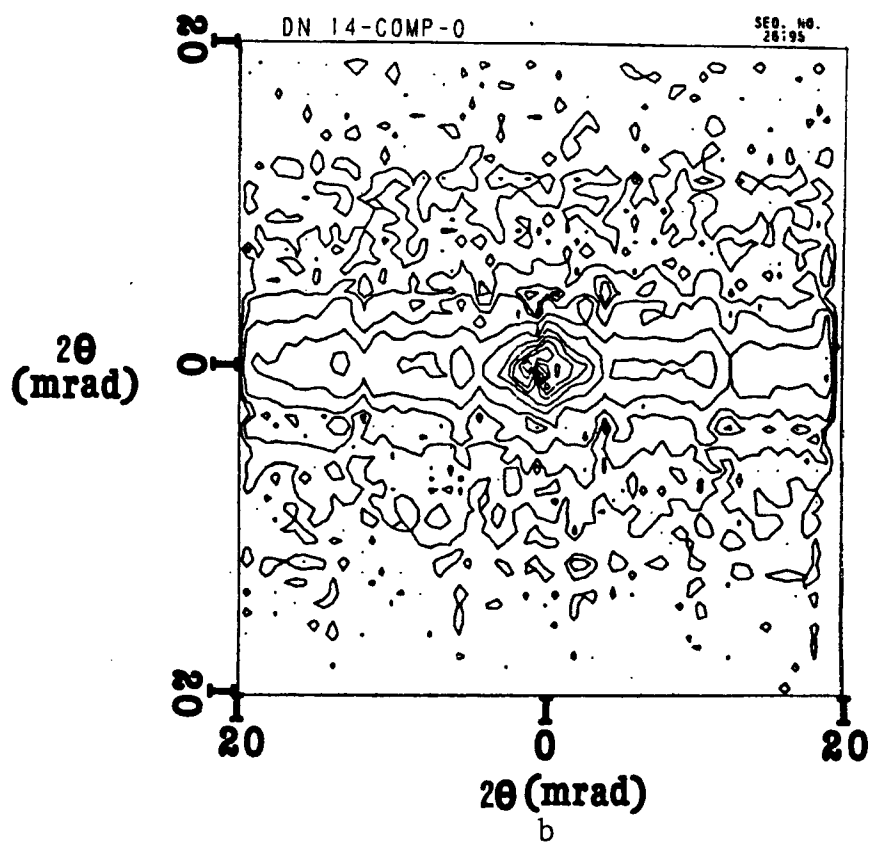


Figure 46 (Continued)

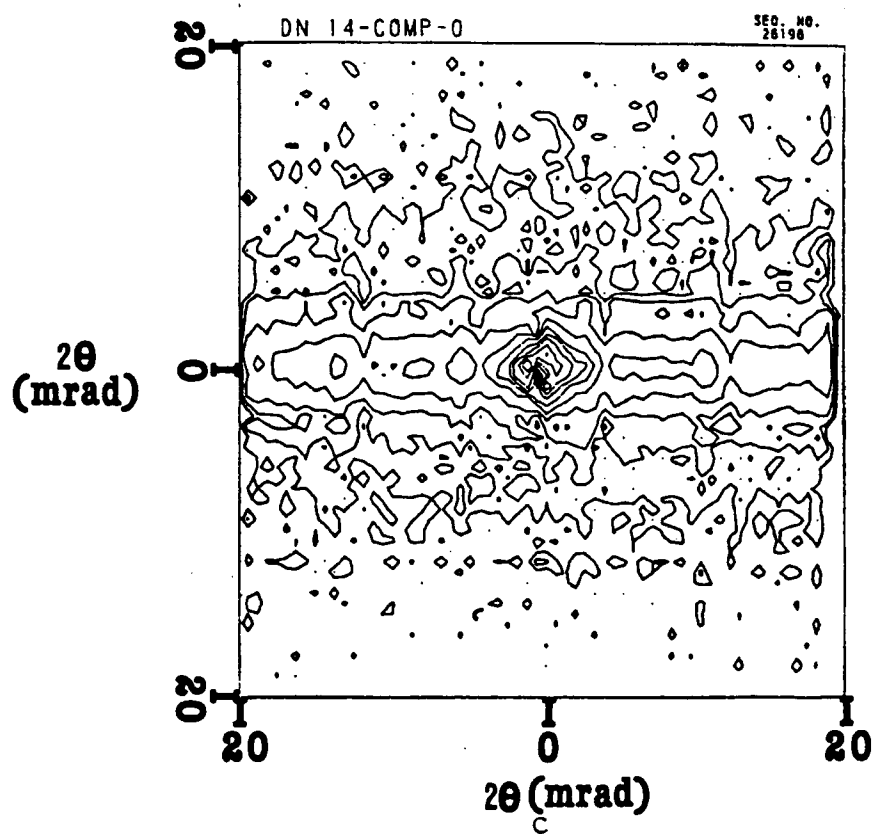


Figure 46 (Continued)

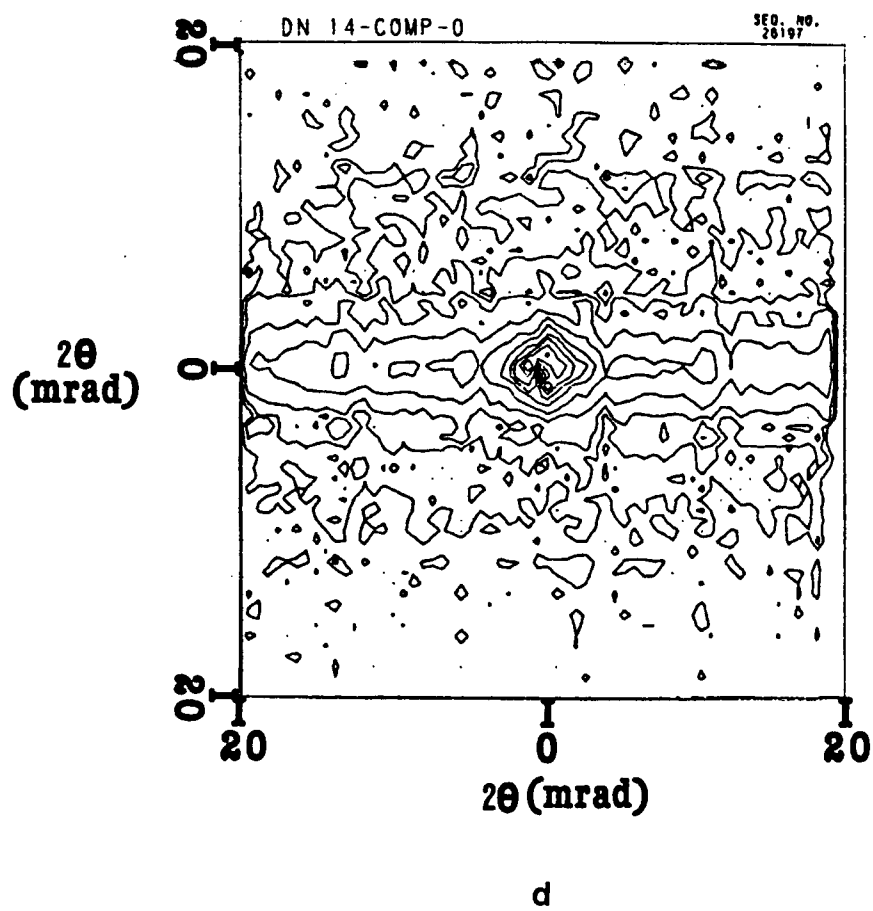


Figure 46 (Continued)

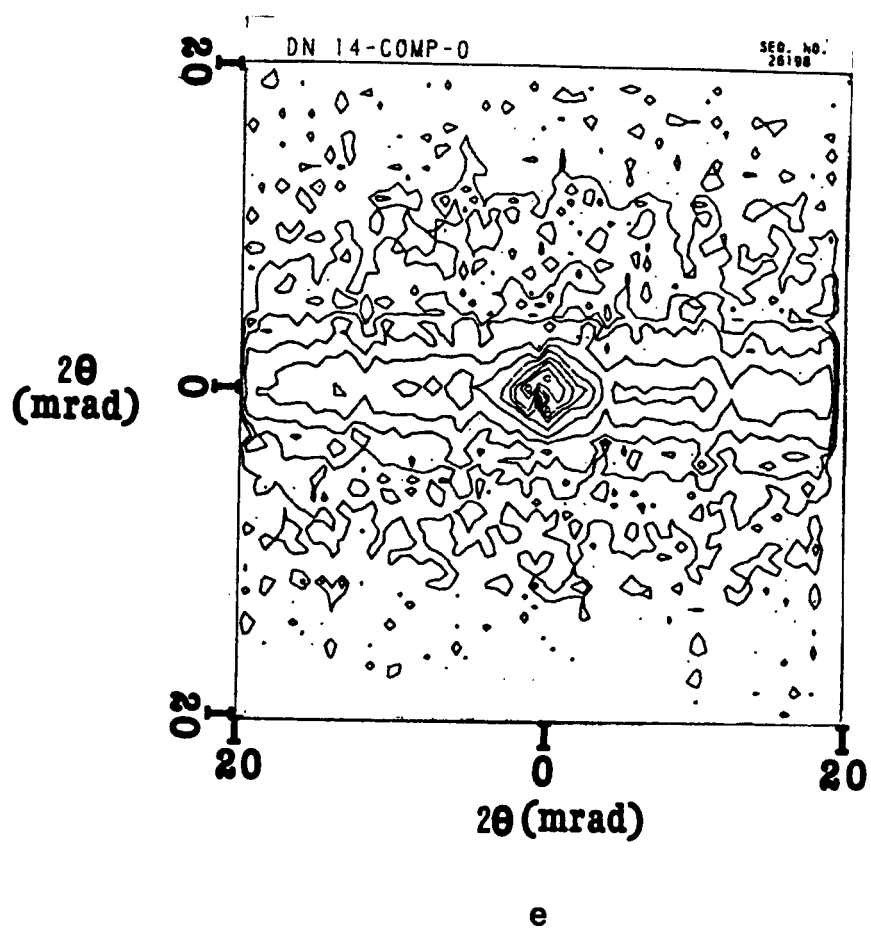


Figure 46 (Continued)

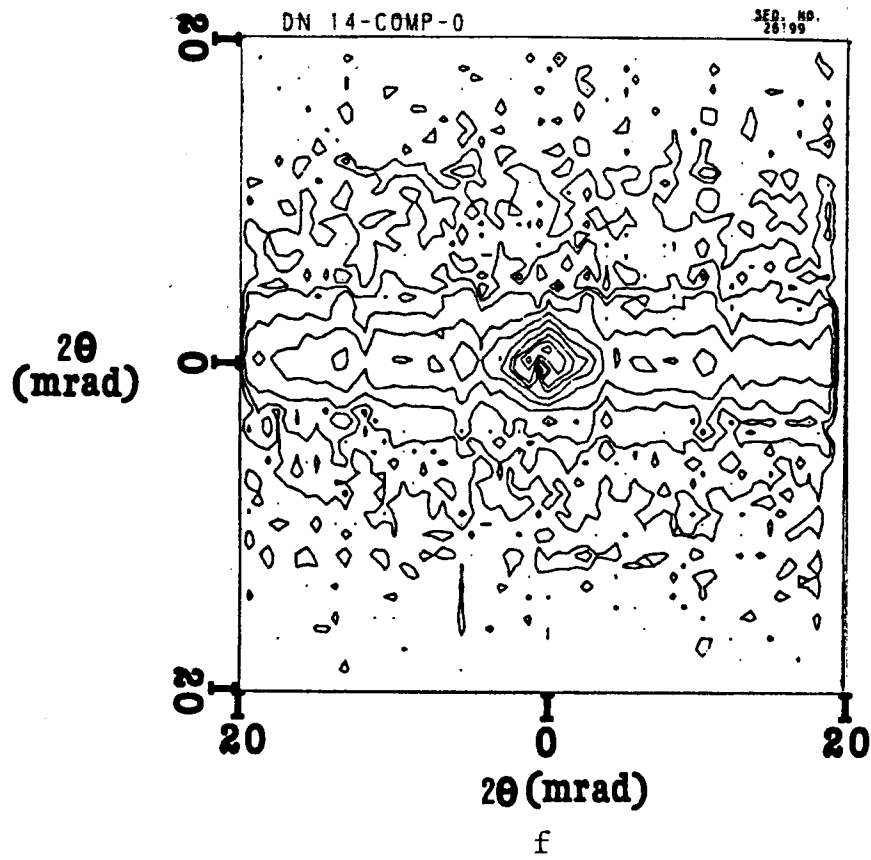


Figure 46 (Continued)

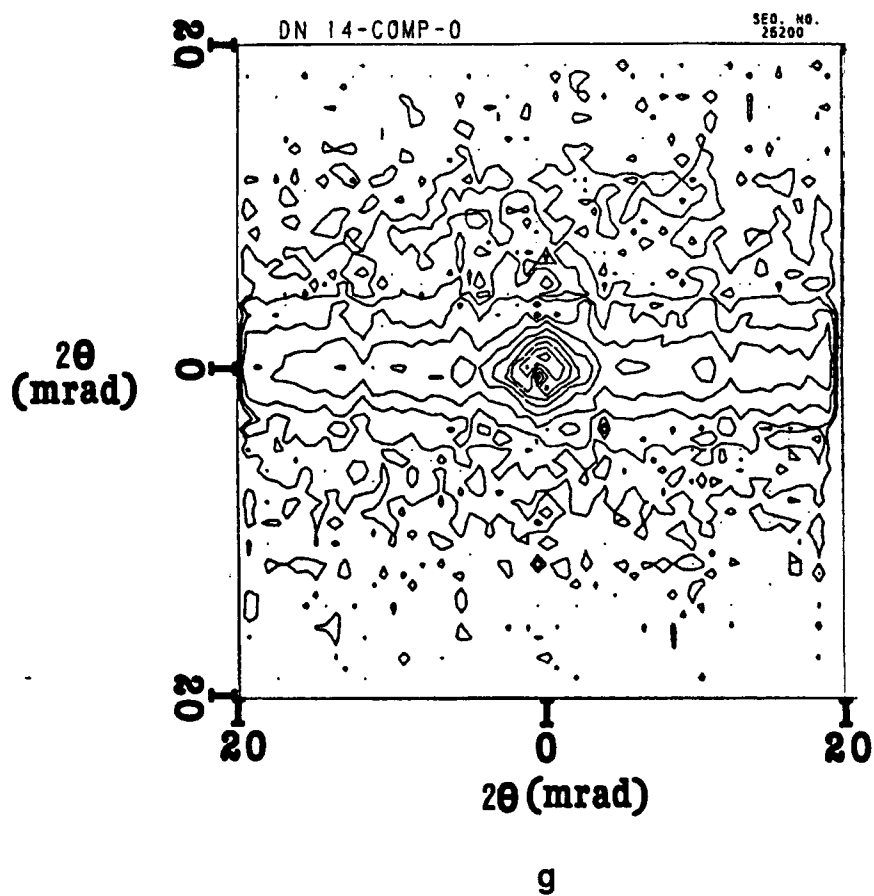


Figure 46 (Continued)

Figure 47. Dynamic two-dimensional isointensity contour plots of Kevlar^R 49 fiber reinforced EPON 828/NMA (110 phr)/BDMA composite with fiber angle 0 degree. The outermost contour represents an intensity of 2 photons per channel with inner contours increasing by x2 at each level.

- a) 0 psi
- b) 680 psi
- c) 1100 psi
- d) 1500 psi
- e) 1780 psi
- f) 2300 psi
- g) 2800 psi

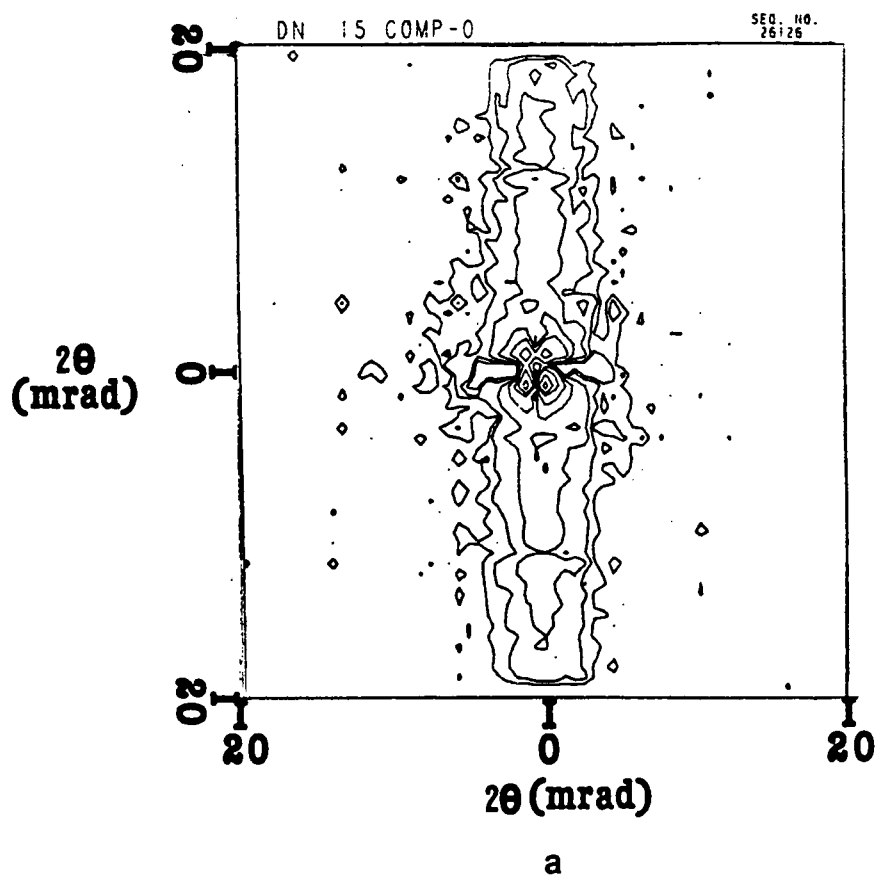


Figure 47

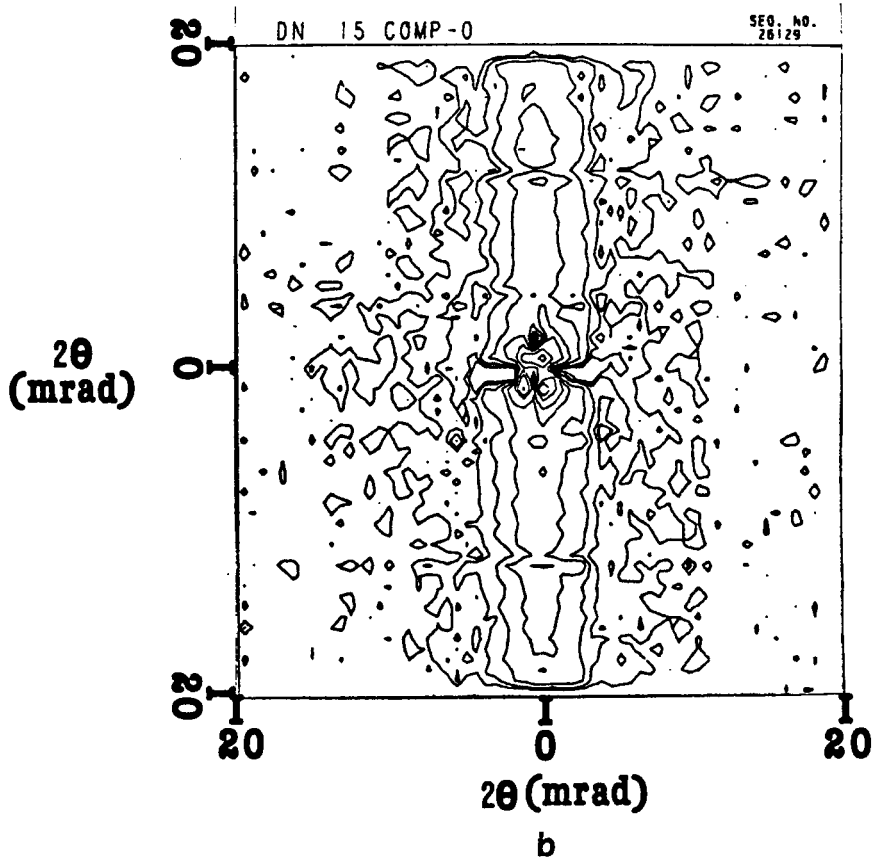


Figure 47 (Continued)

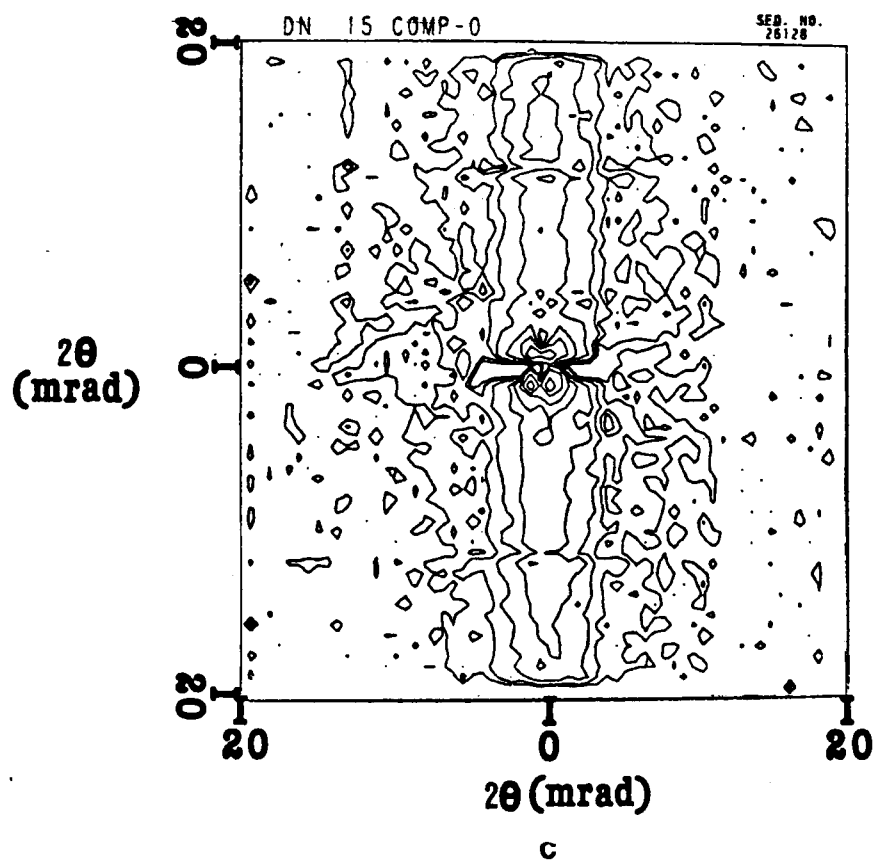


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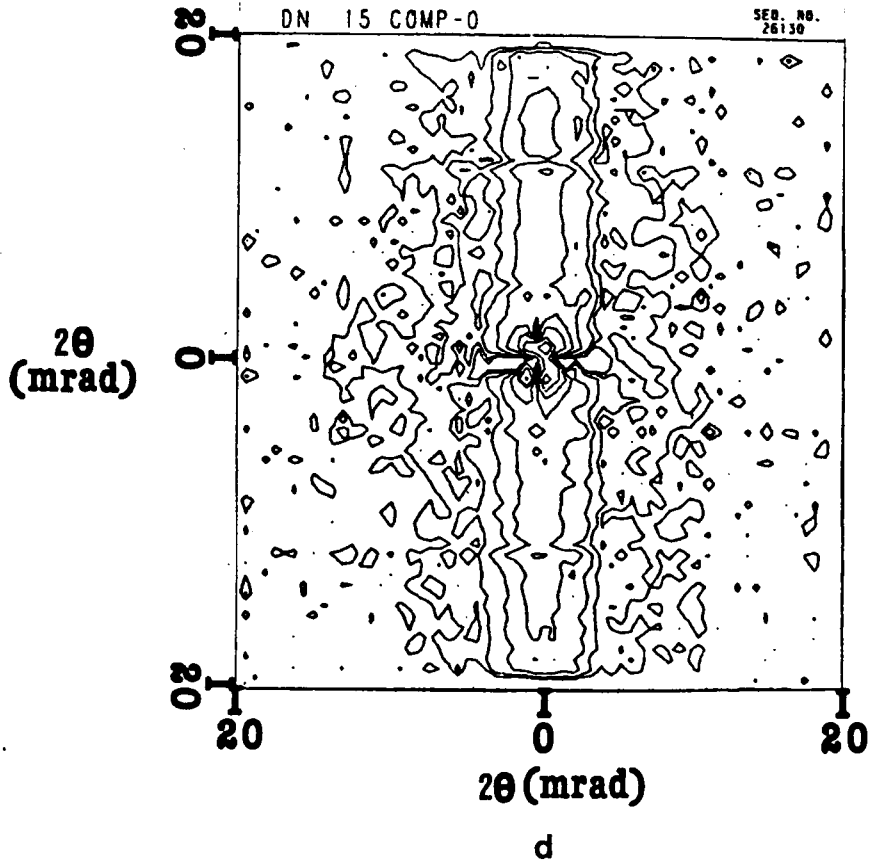


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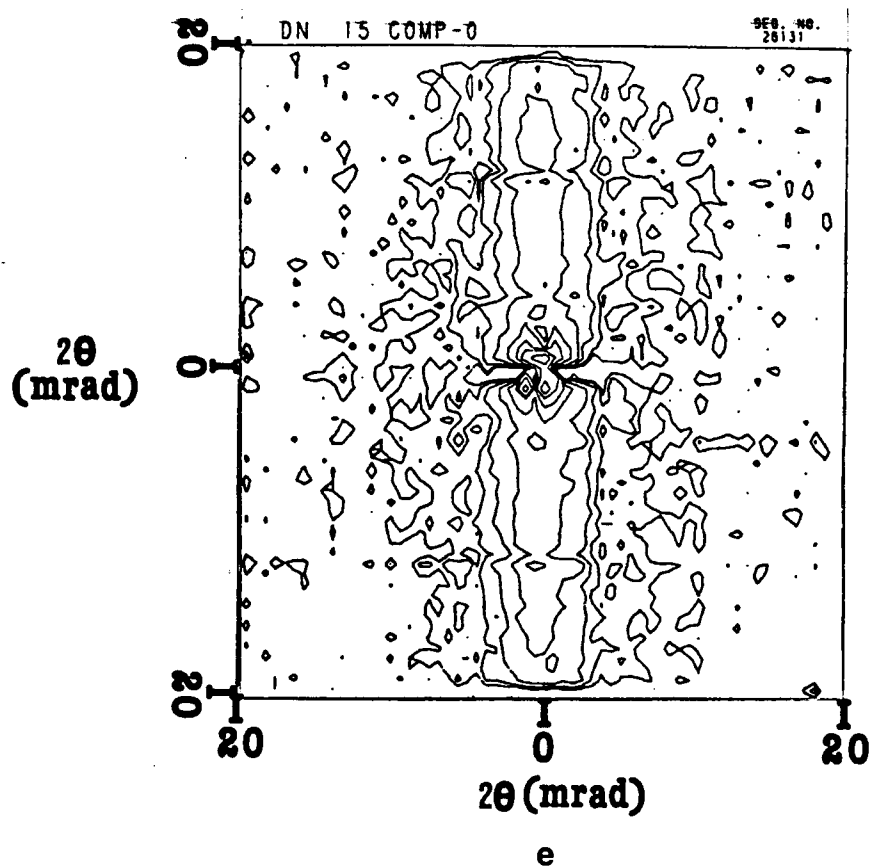


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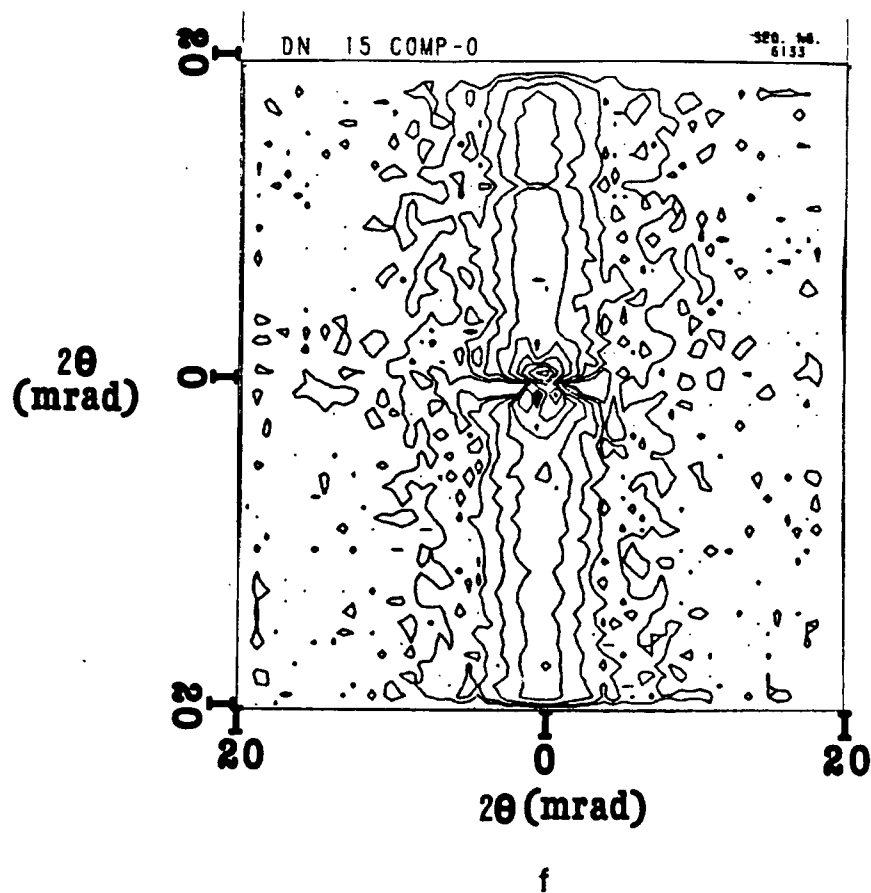


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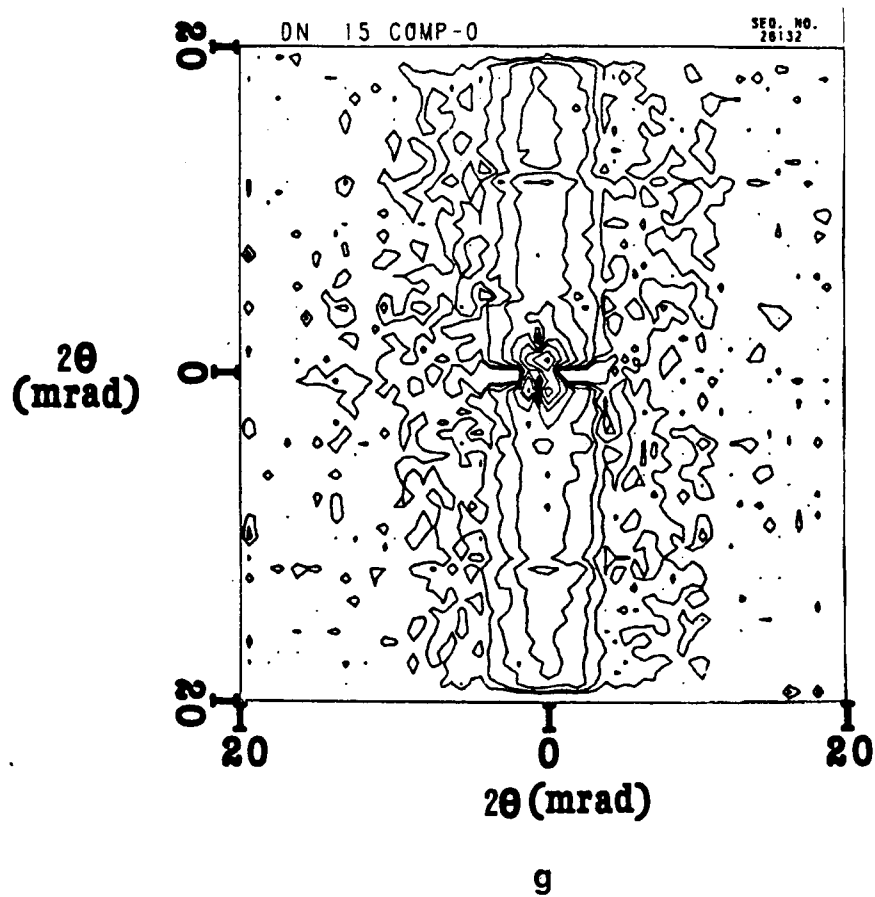


Figure 47 (Continued)

Figure 48. Dynamic two-dimensional isointensity contour plots of Kevlar^R 49 fiber reinforced EPON 828/NMA (110 phr) composite with fiber angle 30 degrees. The outermost contour represents an intensity of 2 photons per channel with inner contours increasing by x2 at each level.

- a) 0 psi
- b) 920 psi
- c) 1650 psi
- d) 2350 psi
- e) 3200 psi

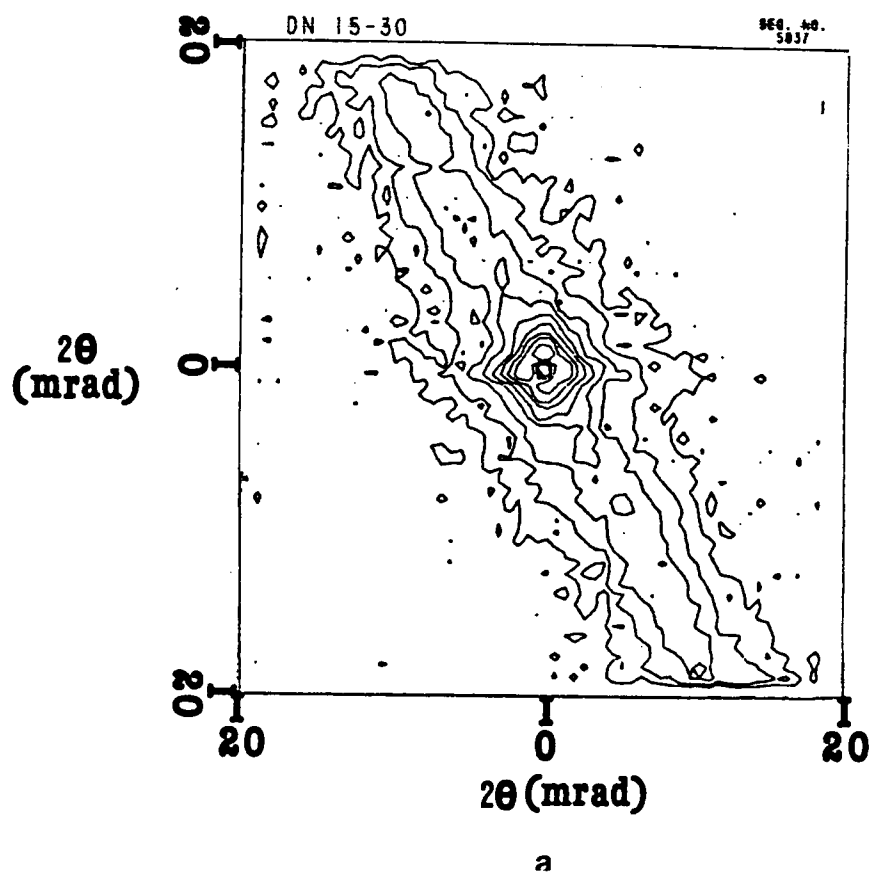


Figure 48

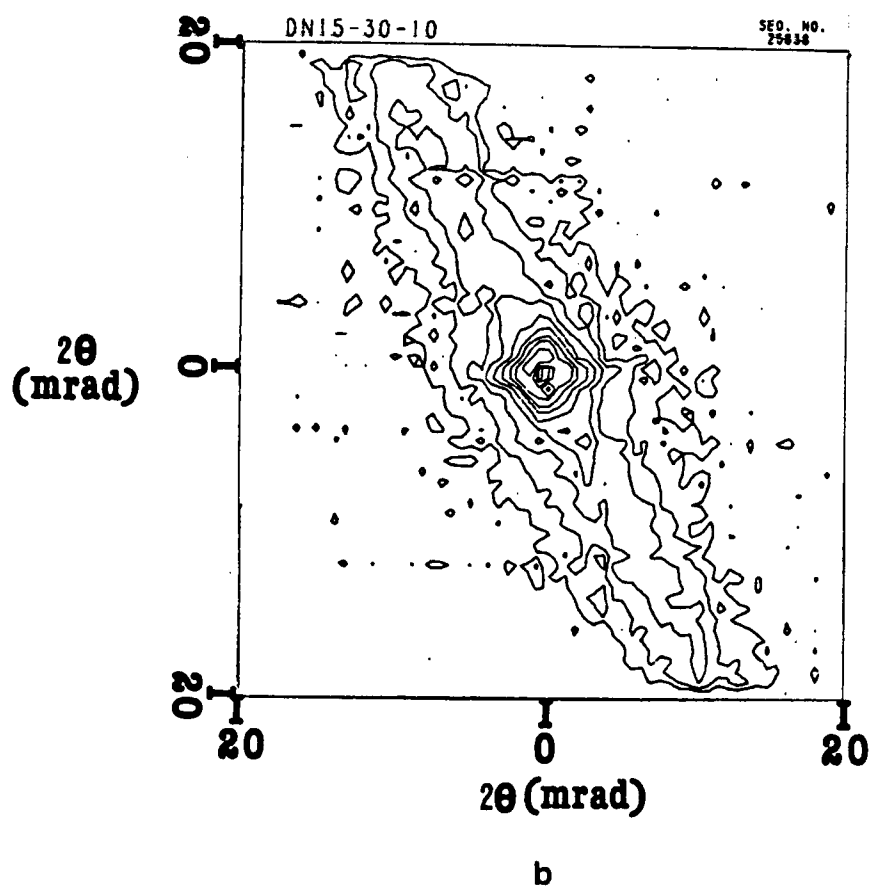


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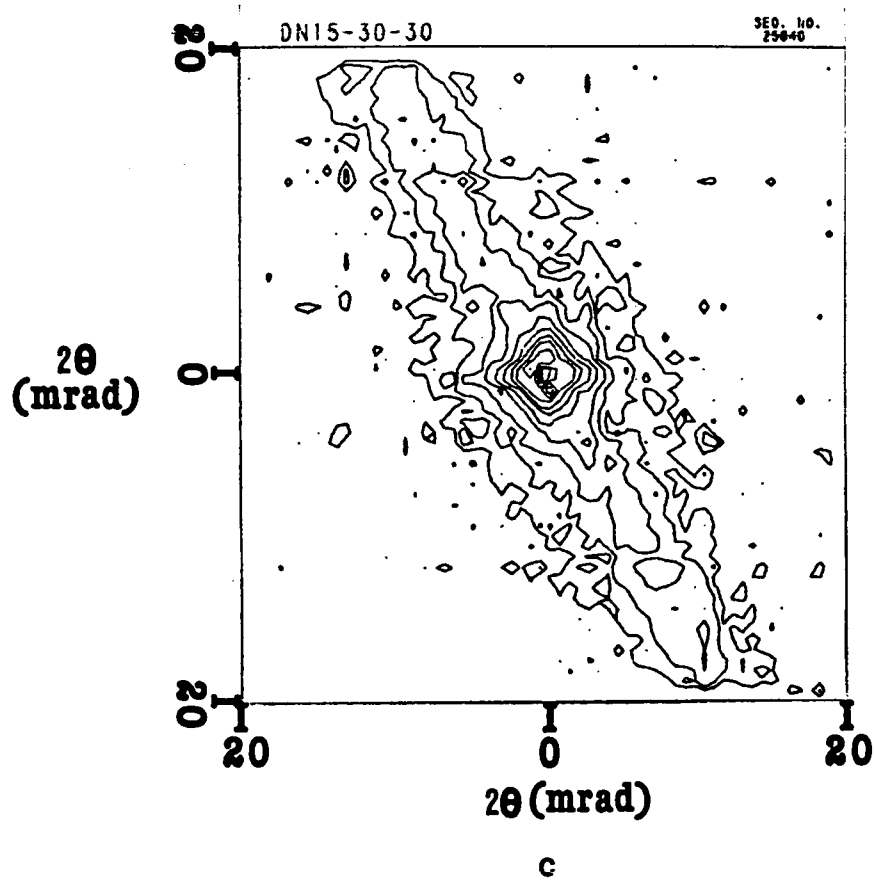


Figure 48 (Continued)

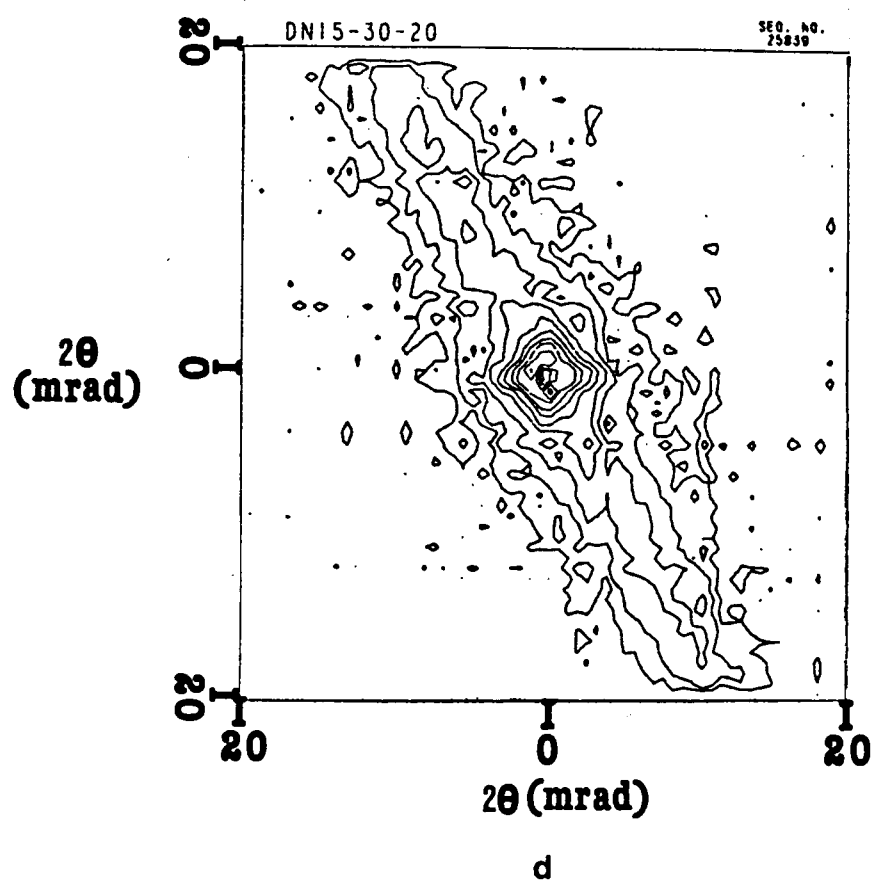


Figure 48 (Continued)

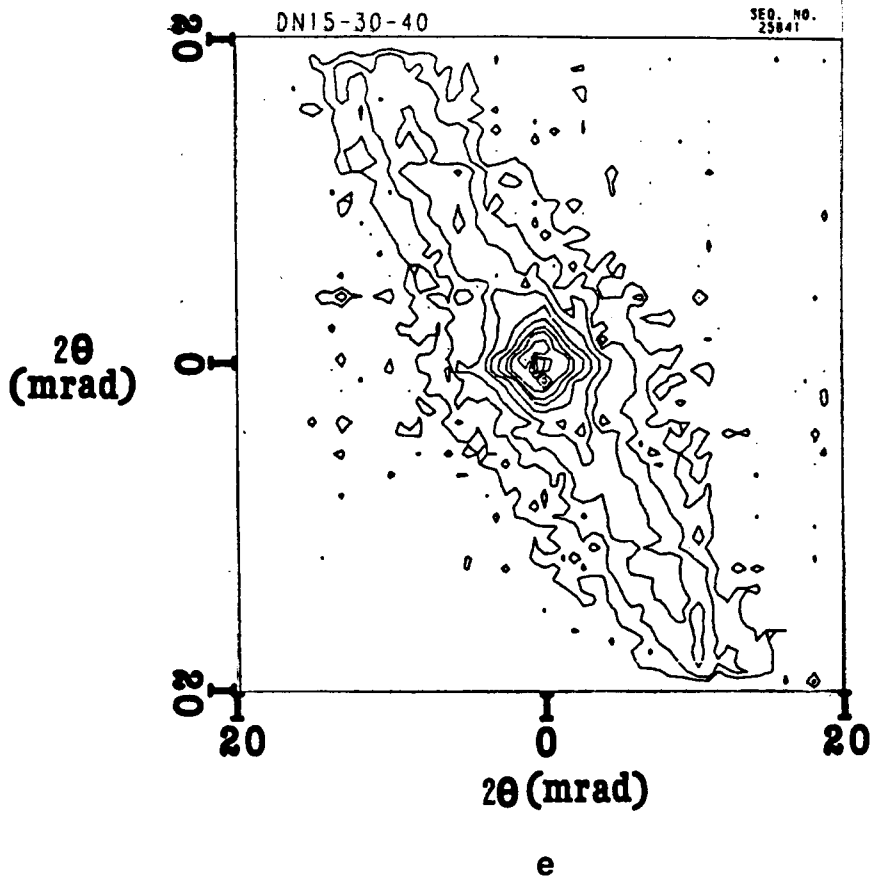


Figure 48 (Continued)

of scattered intensities for 90° EPON 828/NMA (90 phr)/BDMA composite, 0° EPON 828/NMA (110 phr)/BDMA composite and 30° EPON 828/NMA (110 phr)/BDMA composite, respectively. They show the anisotropic scattering patterns elongated in the direction perpendicular to the fiber axis direction, and the scattering is believed to be due to microvoids within the Kevlar^R 49 fibers. Another possible source of the scattered intensities is the microvoids formed at the interfaces between the fibers and the matrix during processing. Yet another possible source may be the reflections of X-ray from the fiber surfaces or fibrillated fibers due to compressive force during curing of the epoxy resins. From the present results, differentiating between these various sources is not possible. The scattered intensity patterns show very little change as the stress level is increased. In order to obtain a better qualitative picture, the net scattering patterns for 90° EPON 828/NMA (90 phr)/BDMA composite, 0° EPON 828/NMA (110 phr)/BDMA composite and 30° EPON 828/NMA (110 phr)/BDMA composite are presented in Figure 49, Figure 50 and Figure 51, respectively. Evidently there is very little stress induced scatterings in all cases. The net scattering patterns are very similar to ones observed for the epoxy resins, and thus it is deduced that failures of composites occur within the matrix and not in the fibers nor at the interface. For the 0° composite there is some net scattering along the meridional direction, i.e. along the fiber axis direction and hence some interfacial debonding seems to occur. Figure 52, Figure 53 and Figure 54 show the $\log(I(k))$ versus k^2 plot for 90° EPON 828/NMA (90 phr)/BDMA composite, 0° EPON 828/NMA (110 phr)/BDMA composite and

Figure 49. Net dynamic two-dimensional isointensity contour plots of Kevlar^R 49 fiber reinforced EPON 828/NMA (90 phr)/BDMA composite with fiber angle 90 degrees. The outermost contour represents an intensity of 2 photons per channel with inner contours increasing by x2 at each level. The scattering from unstressed sample is subtracted as background from each scattering plot.

- a) 590 psi
- b) 1100 psi
- c) 1800 psi
- d) 2750 psi
- e) 3400 psi
- f) 5400 psi

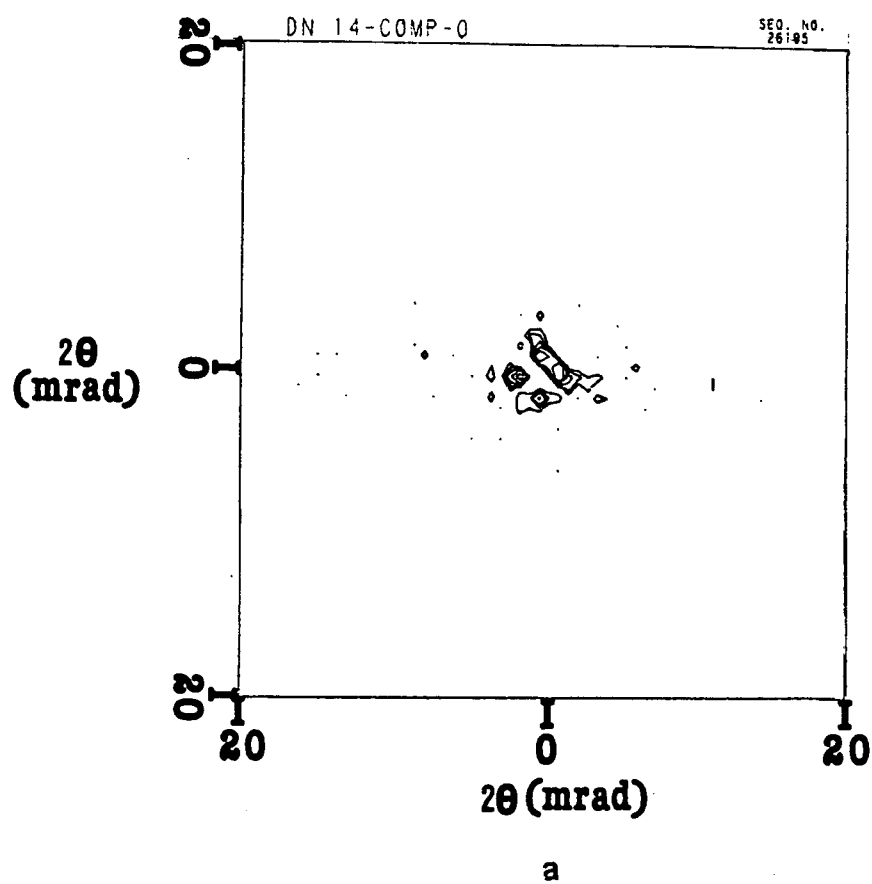


Figure 49

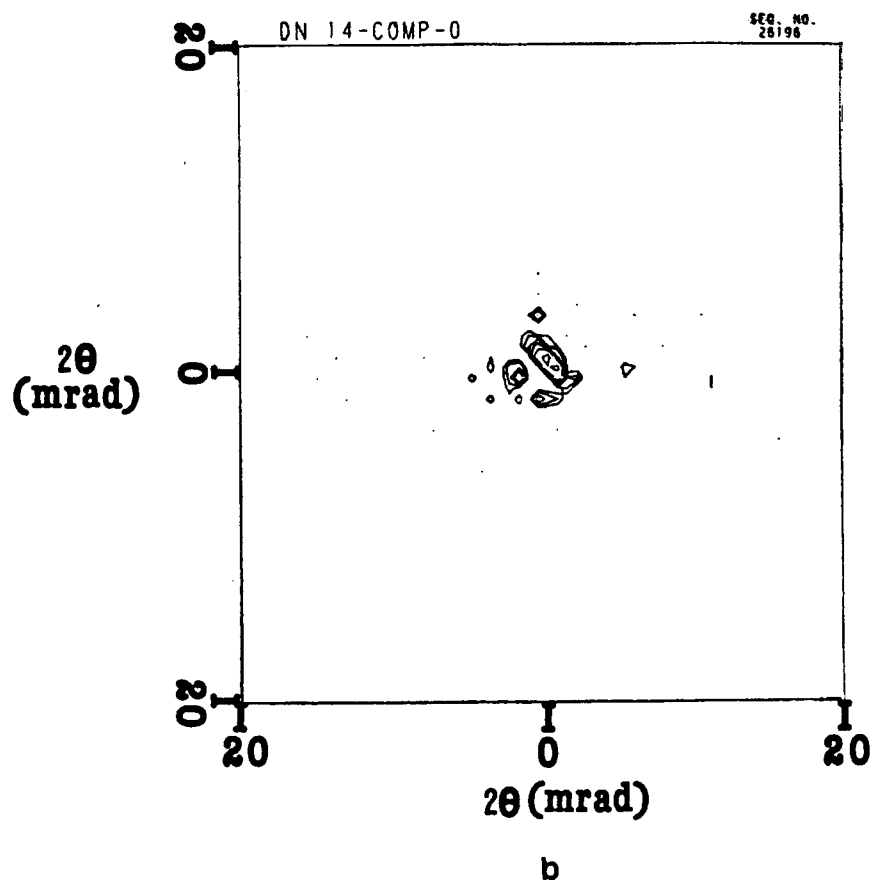


Figure 49 (Continued)

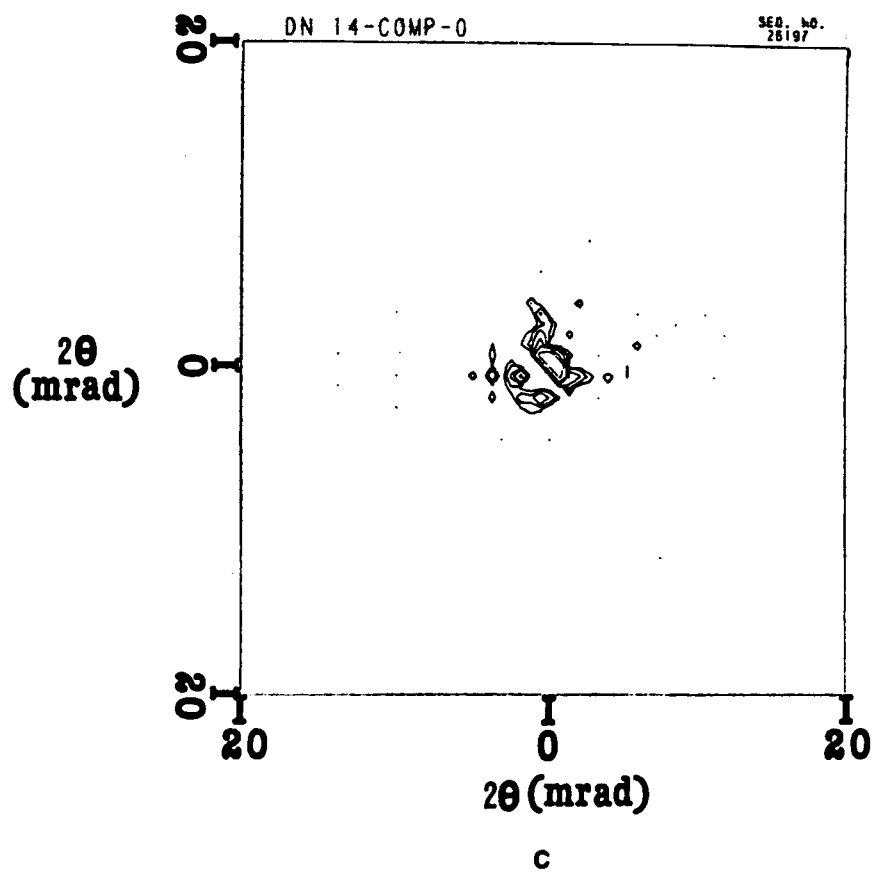


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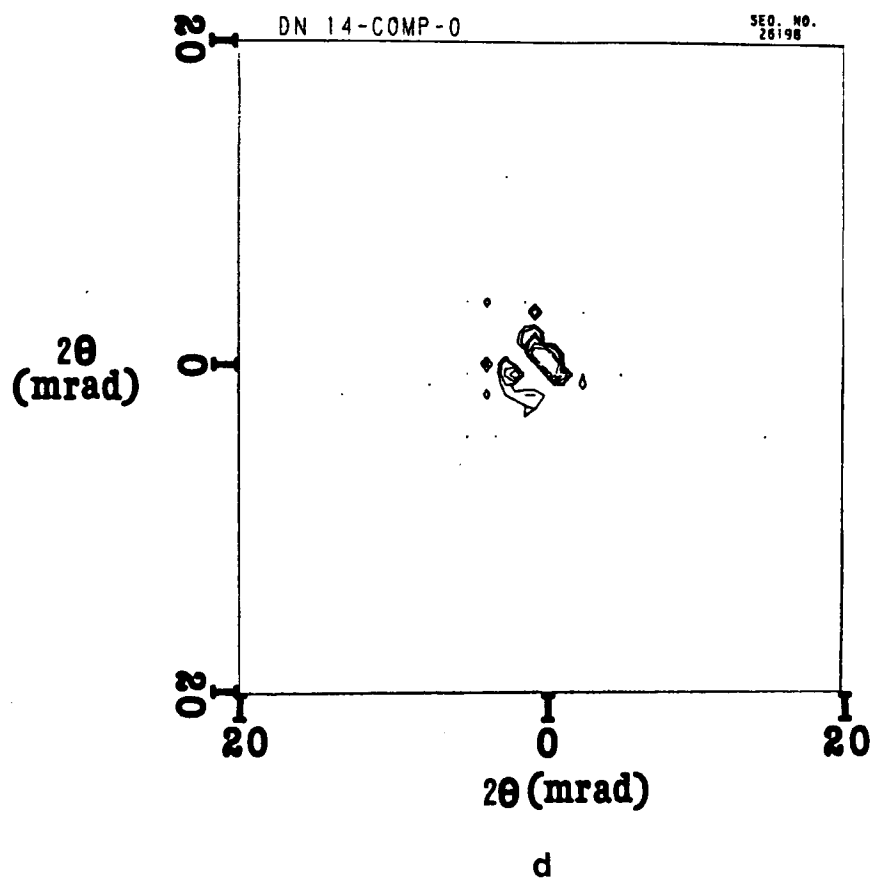


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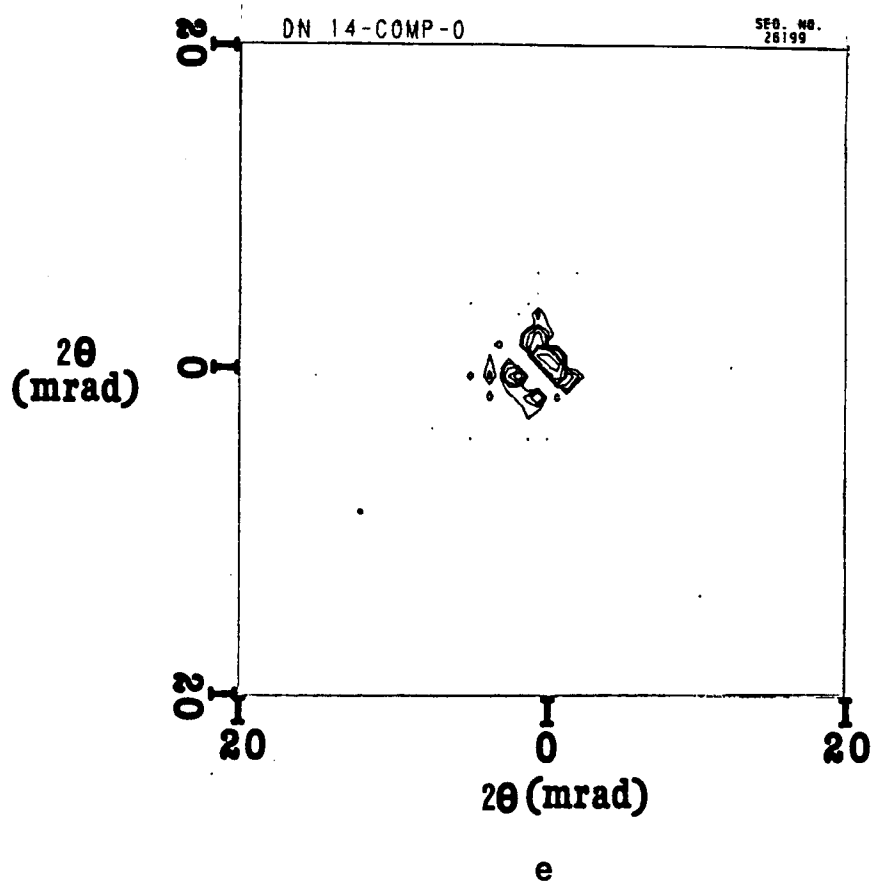


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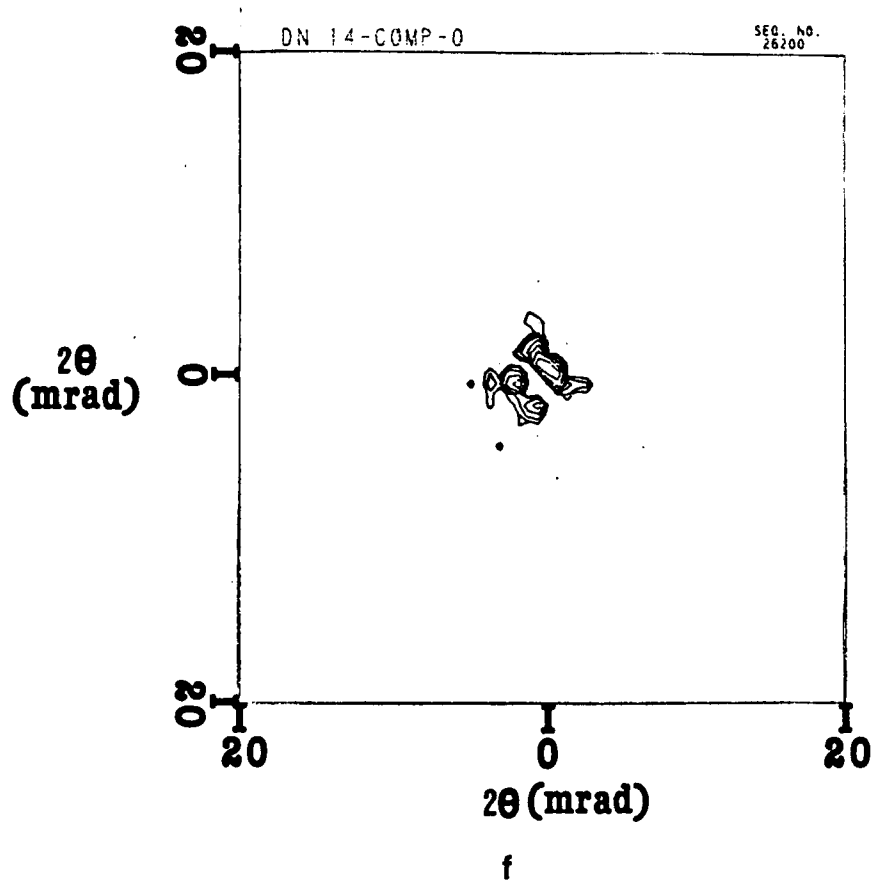


Figure 49 (Continued)

Figure 50. Net dynamic two-dimensional isointensity contour plots of Kevlar^R 49 reinforced EPON 828/NMA (110 phr)/BDMA composite with fiber angle 0 degree. The outermost contour represents an intensity of 2 photons per channel with inner contours increasing by x2 at each level. The scattering from unstressed sample is subtracted as background from each scattering plot.

- a) 680 psi
- b) 1100 psi
- c) 1500 psi
- d) 1780 psi
- e) 2300 psi
- f) 2800 psi
- g) after fractured

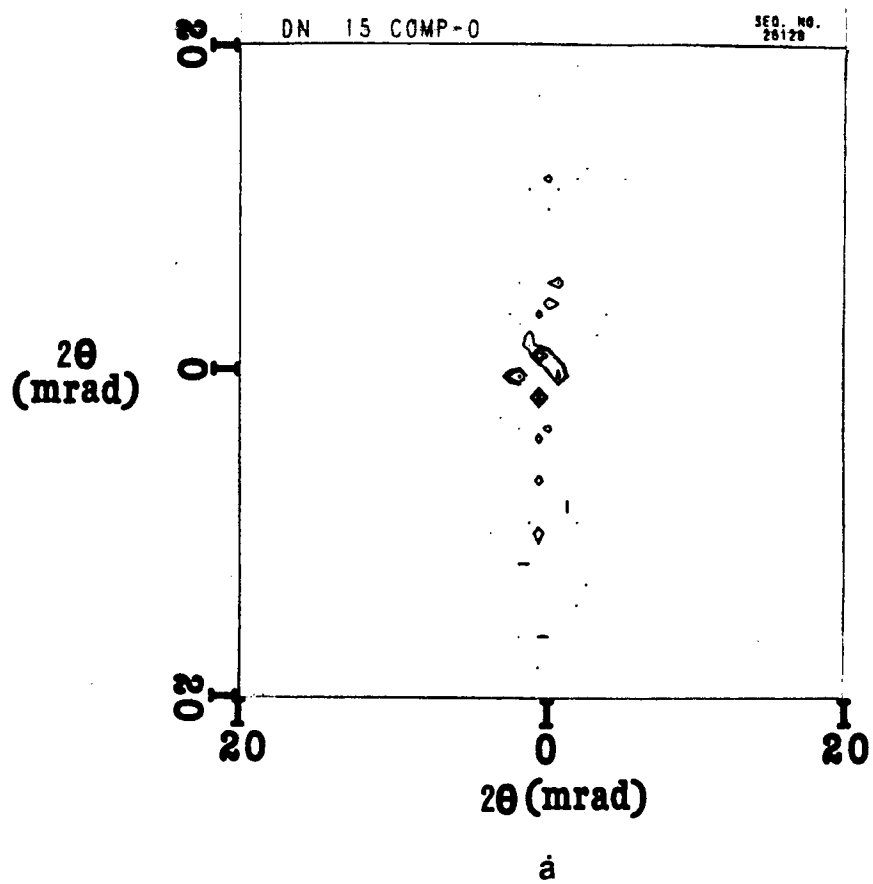


Figure 50

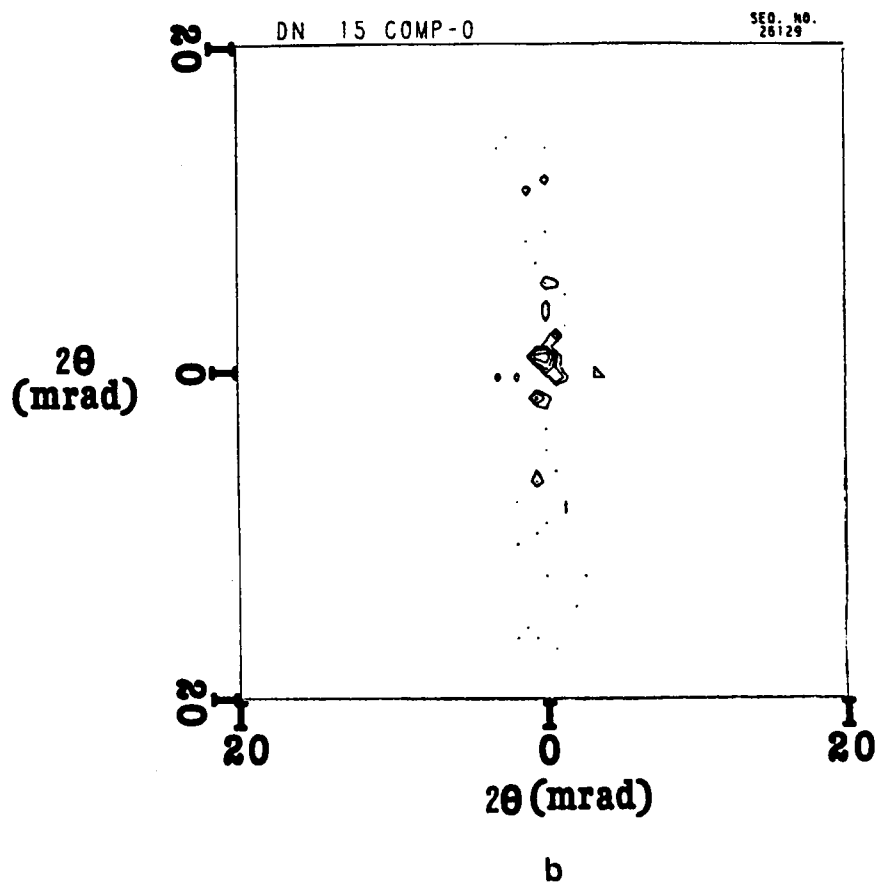


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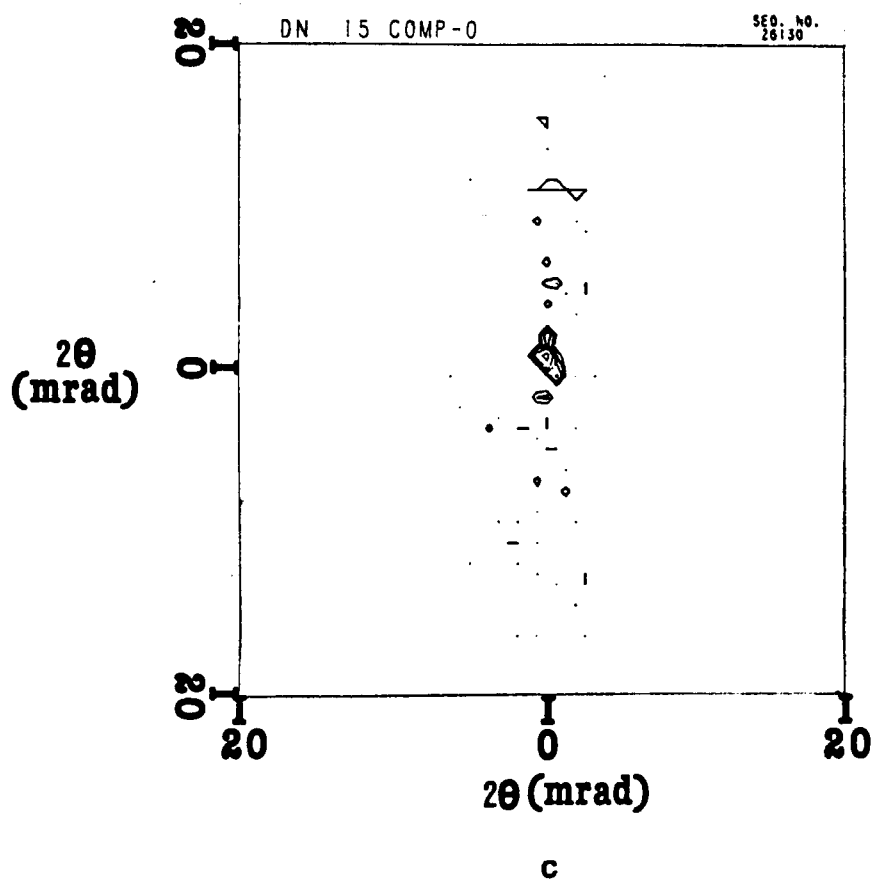


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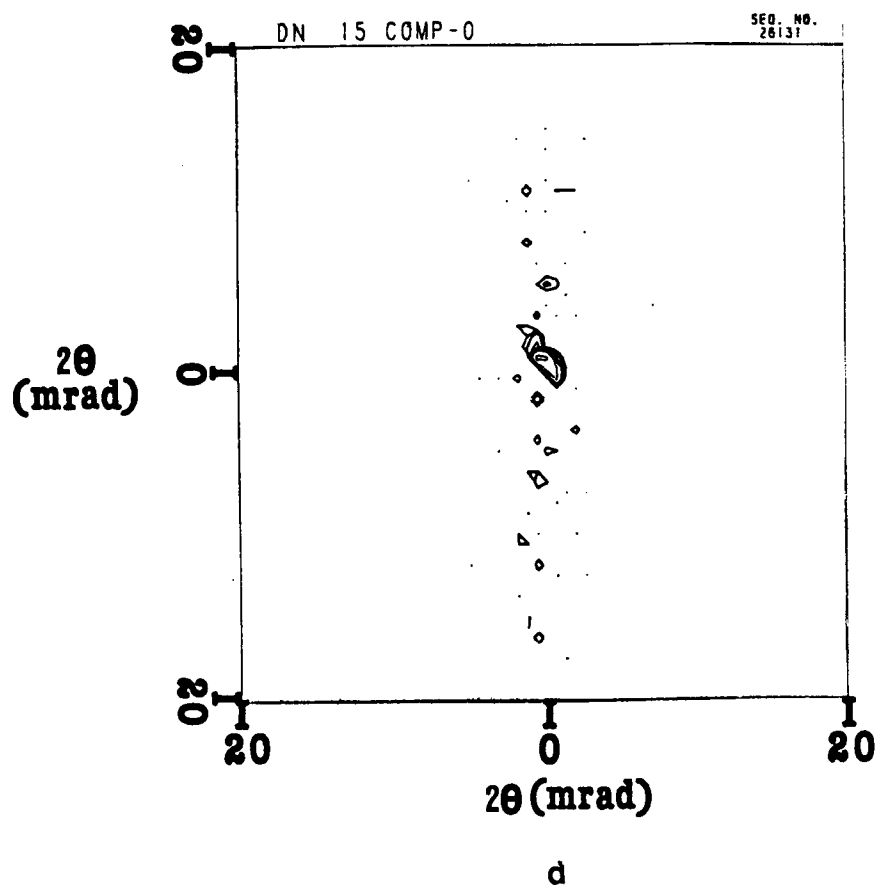


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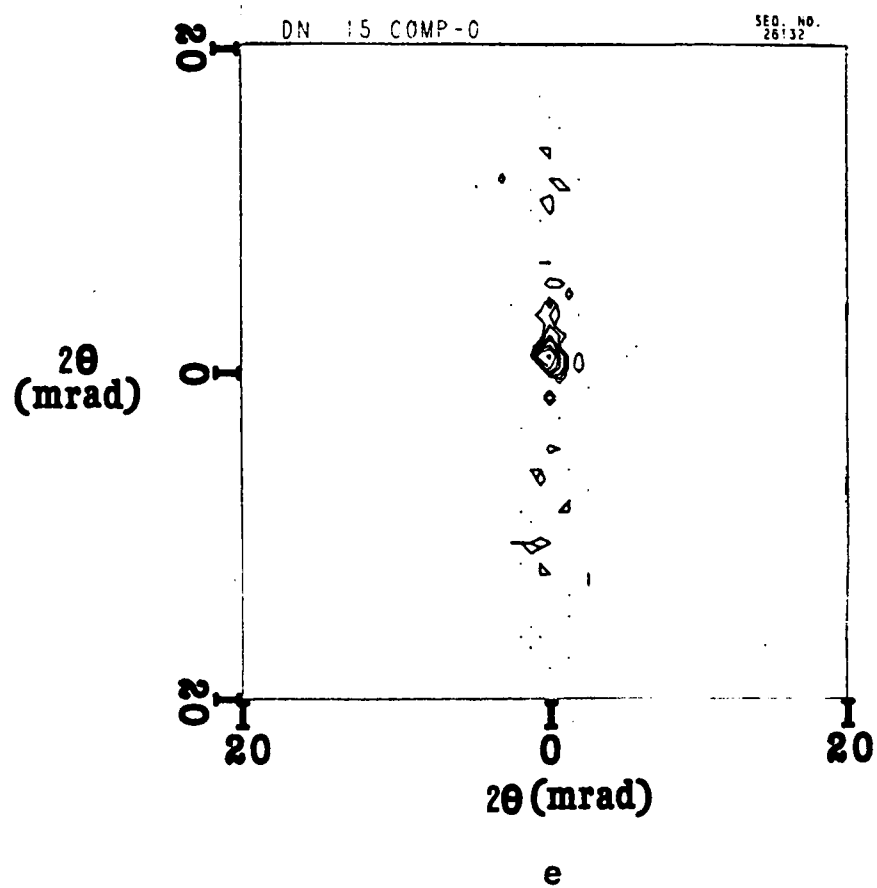


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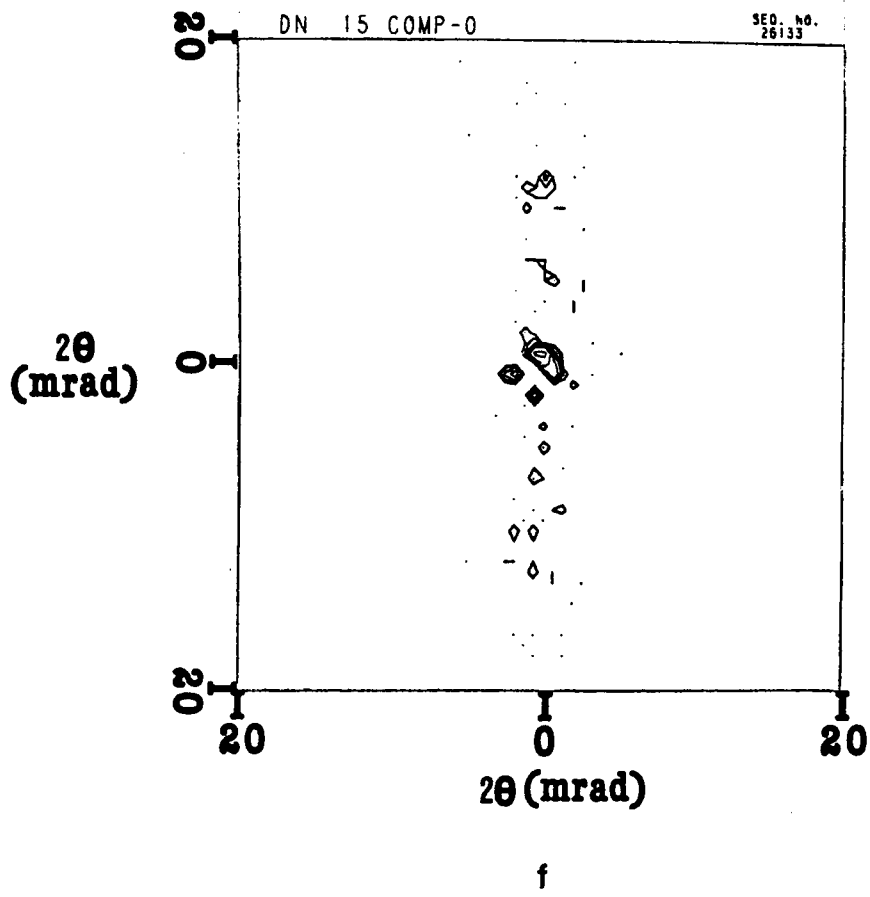


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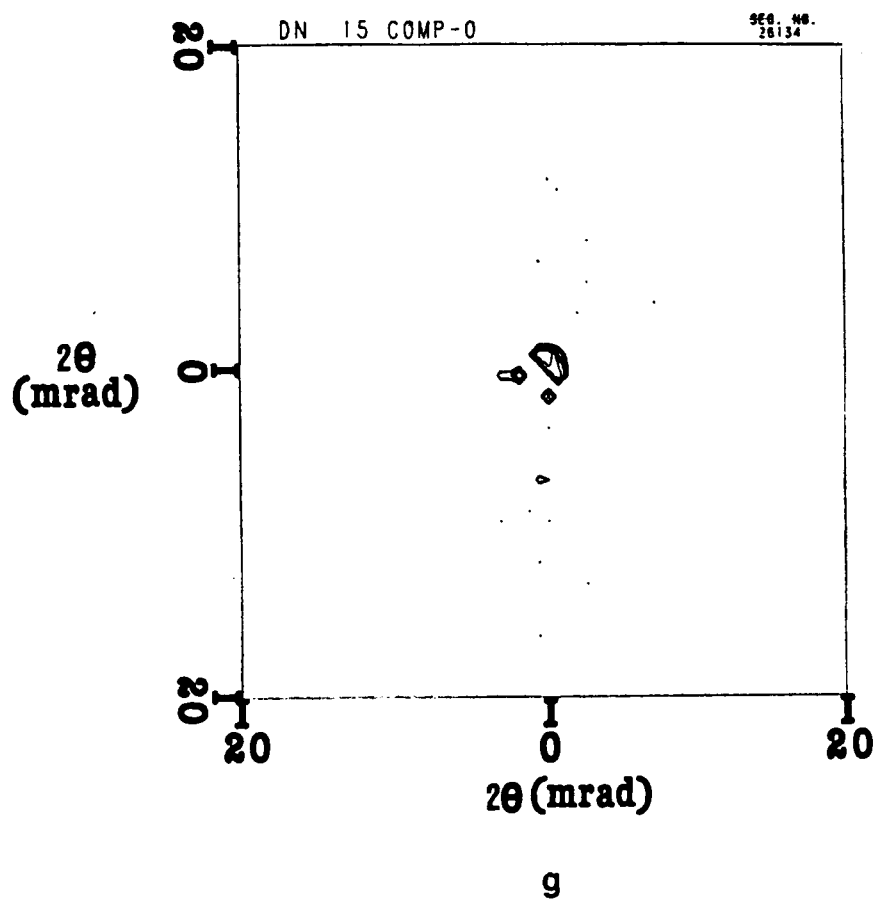
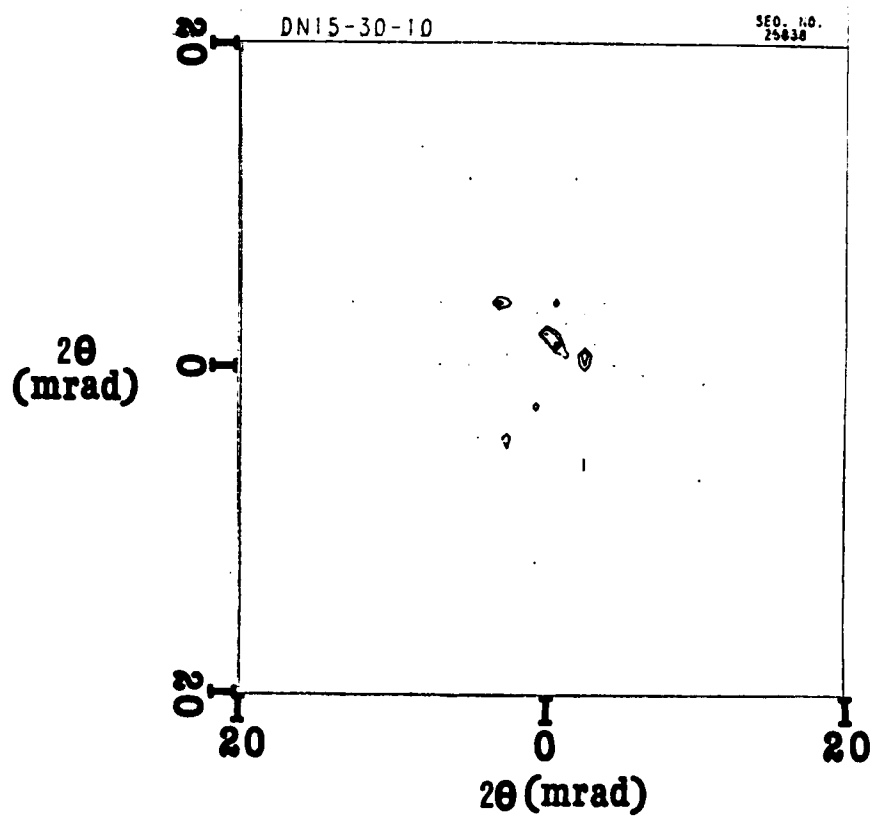


Figure 50 (Continued)

Figure 51. Net dynamic two-dimensional isointensity contour plots of Kevlar^R 49 reinforced EPON 828/NMA (110 phr)/BDMA composite with fiber angle 30 degrees. The outermost contour represents an intensity of 2 photons per channel with inner contours increasing by x2 at each level. The scattering from unstressed sample is subtracted as background from each scattering plot.

- a) 920 psi
- b) 1650 psi
- c) 2350 psi
- d) 3200 psi



a

Figure 51

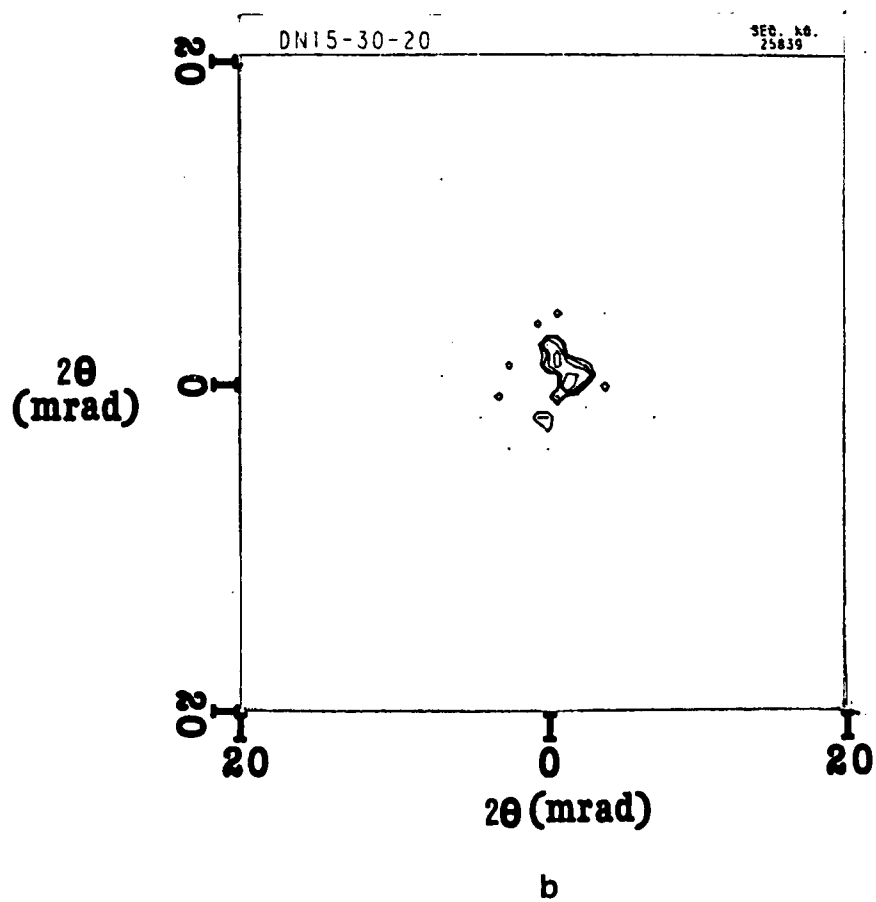


Figure 51 (Continued)

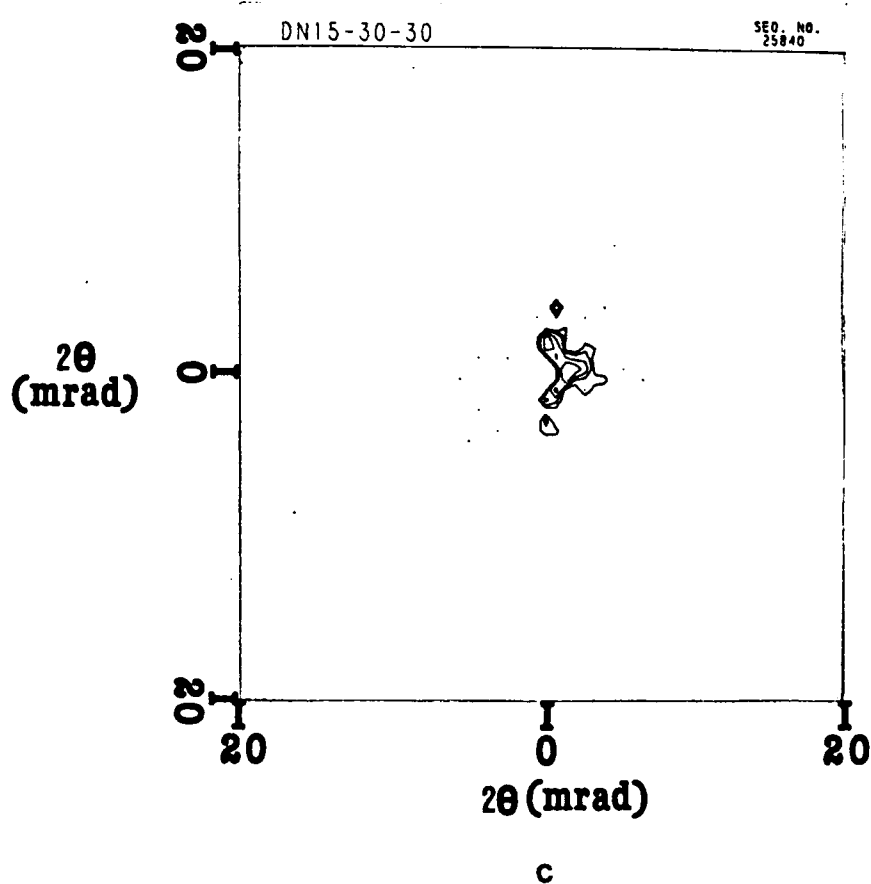


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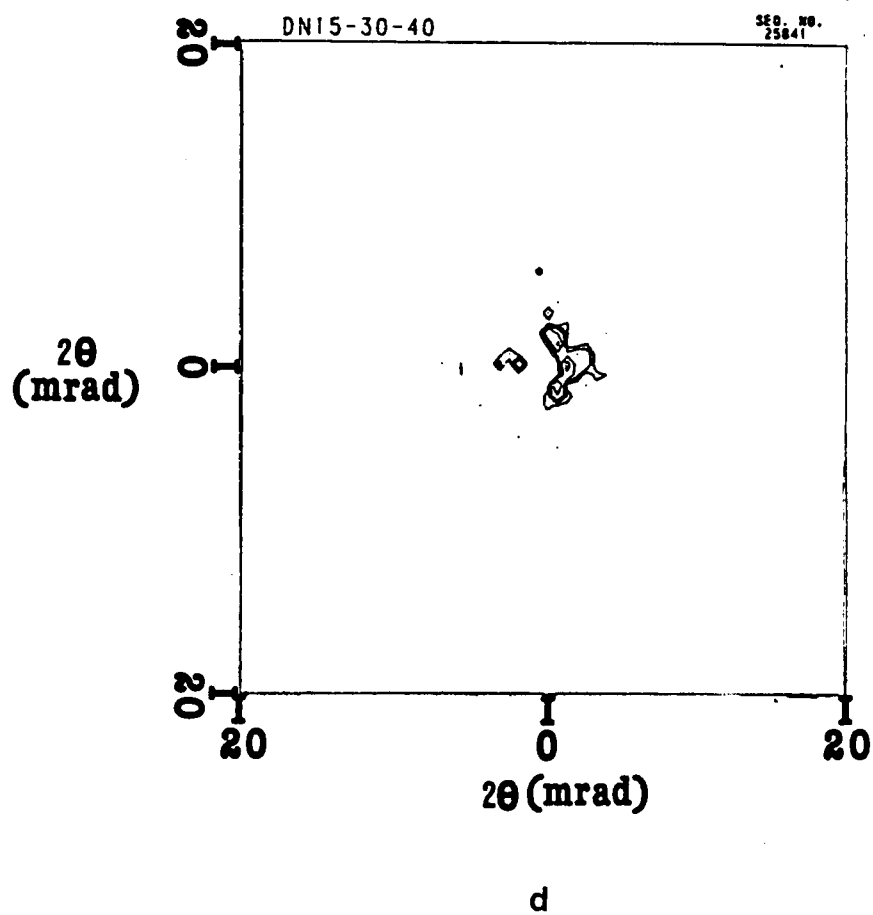


Figure 51 (Continued)

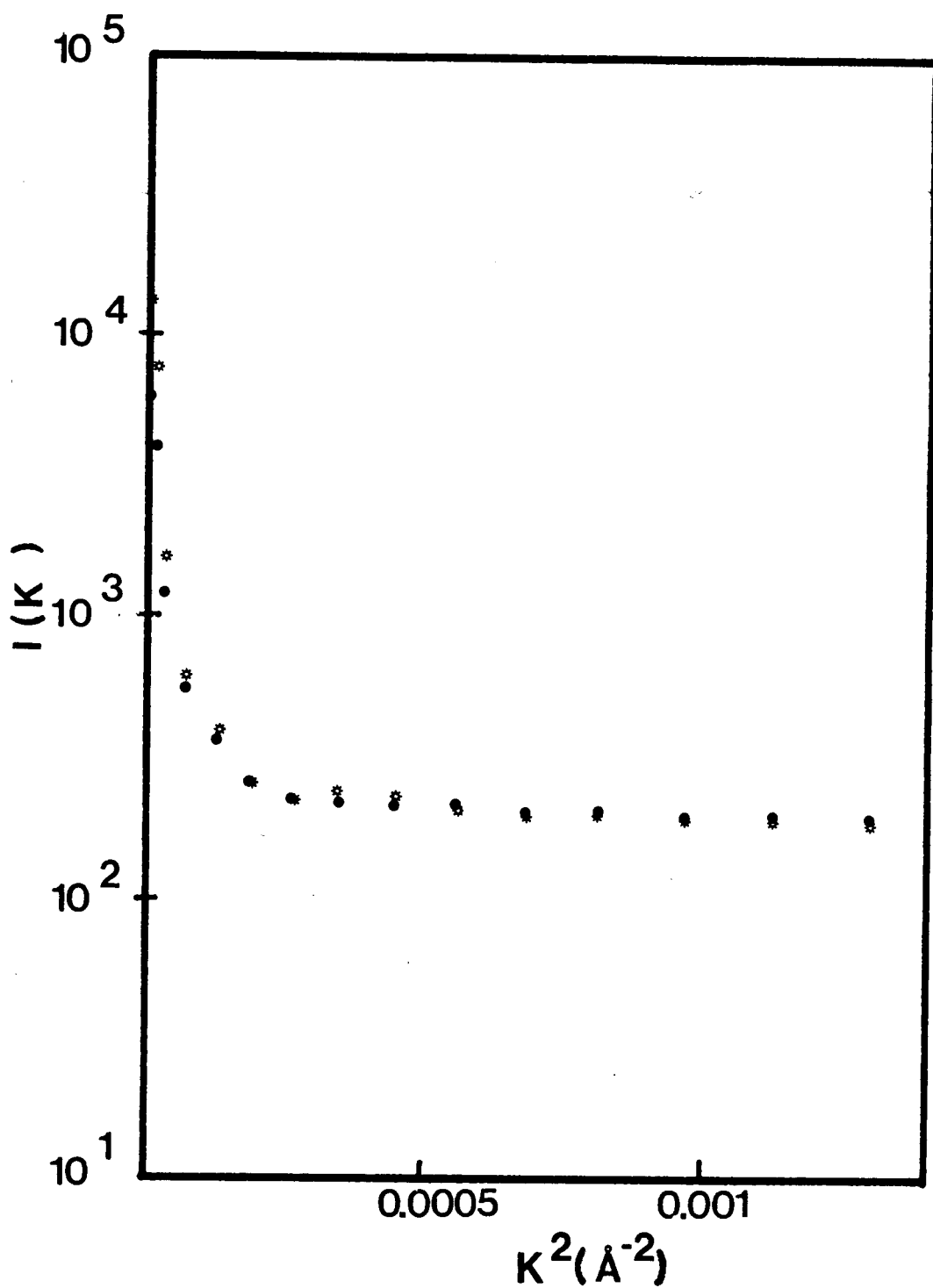


Figure 52. Relative scattering intensity $I(k)$ vs k^2 for Kevlar^R 49 reinforced EPON 828/NMA (90 phr)/BDMA composite with fiber angle 90 degrees. ● 0 psi, * 5420 psi.

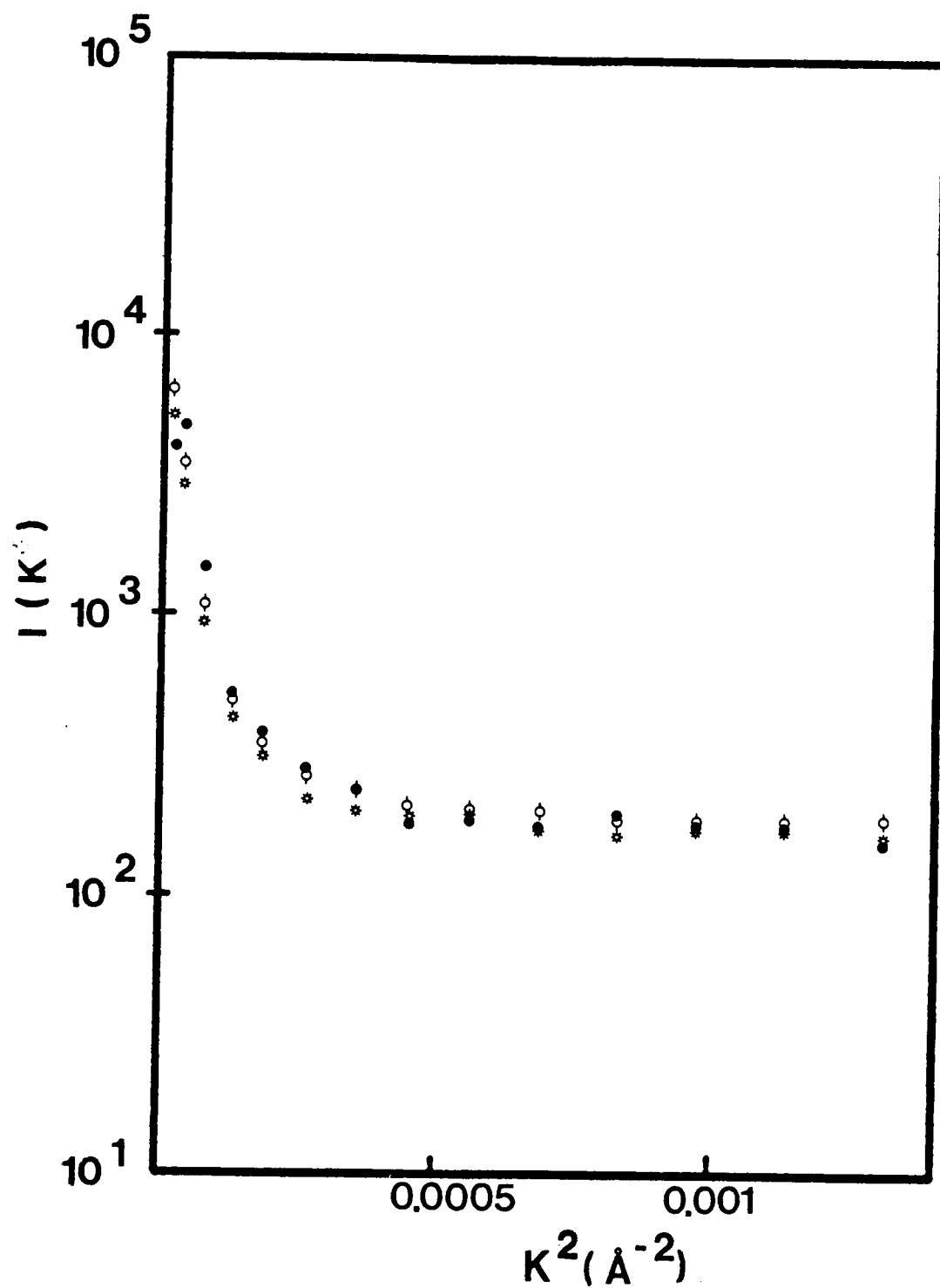


Figure 53. Relative scattering intensity $I(k)$ vs k^2 for Kevlar^R 49 reinforced EPON 828/NMA (110 phr) composite with fiber angle 0 degree. ● 0 psi, * 2790 psi, ○ after fracture.

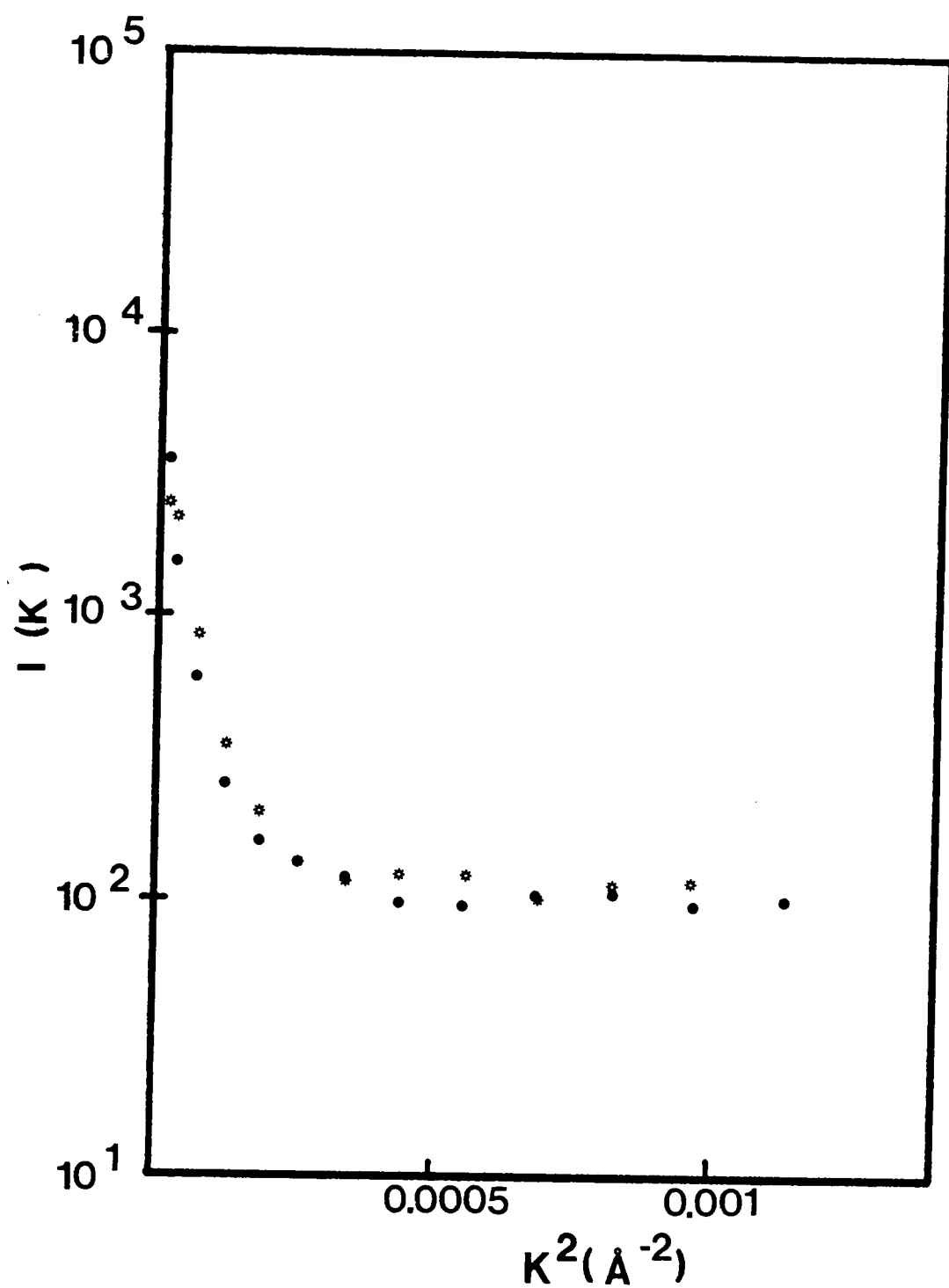


Figure 54. Relative scattering intensity $I(k)$ vs k^2 for Kevlar^R 49 reinforced EPON 828/NMA (110 phr)/BDMA composite with fiber angle 30 degrees. ● 0 psi, * 3210 psi.

30° EPON 828/NMA (110 phr)/BDMA composite respectively at various stress levels, and it is evident, as in the case of epoxy resins, there is very little stress induced scattering. Therefore, the failure mechanism in the low volume fraction (2.9 percent) Kevlar^R fiber reinforced epoxy composites is regarded as a catastrophic dynamic process with incipient failure occurring in the matrix. For 0° fiber reinforced composites, there is evidence of interfacial debonding at the very early stages of failure. Also the present study has shown the importance of the matrix material in composite processing.

CHAPTER V

MORPHOLOGICAL CHARACTERIZATION

In this chapter, the results of the experimental investigations using density column, scanning electron microscope (SEM) and optical microscope are presented and discussed.

V.1 DENSITY COLUMN MEASUREMENT

The densities of degraded Kevlar^R 49 fibers, epoxies and composites were determined using a sodium bromide-water density column at 25°C. They were added into the column for approximately twenty-four hours to reach their final level of displacement. The results are presented in Table 10. The void fractions of degraded Kevlar^R 49 fibers were calculated using the theoretical density of 1.48 g/cm³ (125). The degraded Kevlar^R 49 fibers apparently have much higher volume fractions of microvoids than Kevlar^R 49 fibers. Of the epoxy systems studied, the EPON 828/NMA (14 phr)/BDMA system has the highest density followed by the DER 332/MPDA (16 phr) system and then by the DER 332/DETA (12 phr) system. The apparent volume fractions of fibers, $\bar{X}$, in composites were calculated, assuming the absence of voids, using

$$\bar{X} = \frac{\rho_c - \rho_m}{\rho_f - \rho_m}$$

Table 10. Void Fraction and Volume Fraction Determined by Density Measurement

	Density (g/cc)	Void fraction (%)	Volume fraction of fibers (%)
Kevlar ^R 49	1.43*	3.38	
Degraded Kevlar ^R 49 #1	1.23	17.1	
Degraded Kevlar ^R 49 #2	1.16	21.4	
Degraded Kevlar ^R 49 #4	1.20	19.0	
EPON 828/NMA (14 phr)/BDMA	1.23		
DER 332/MPDA (16 phr)	1.22		
DER 332/DETA (12 phr)	1.21		
EPON 828/NMA (14 phr) high volume fraction composite	1.25		8.60
EPON 828/NMA (14 phr) low volume fraction composite	1.23		2.88
DER 332/MPDA (16 phr) low volume fraction composite	1.22		2.62
DER 332/DETA (12 phr) high volume fraction composite	1.21		6.57

*From reference 125.

where ρ_c = the density of the composite
 ρ_m = the density of the matrix
 ρ_f = the density of the Kevlar^R fibers (1.43 g/cm³).

V.2 SEM STUDY OF FRACTURED SURFACES

V.2.A Kevlar^R Fibers

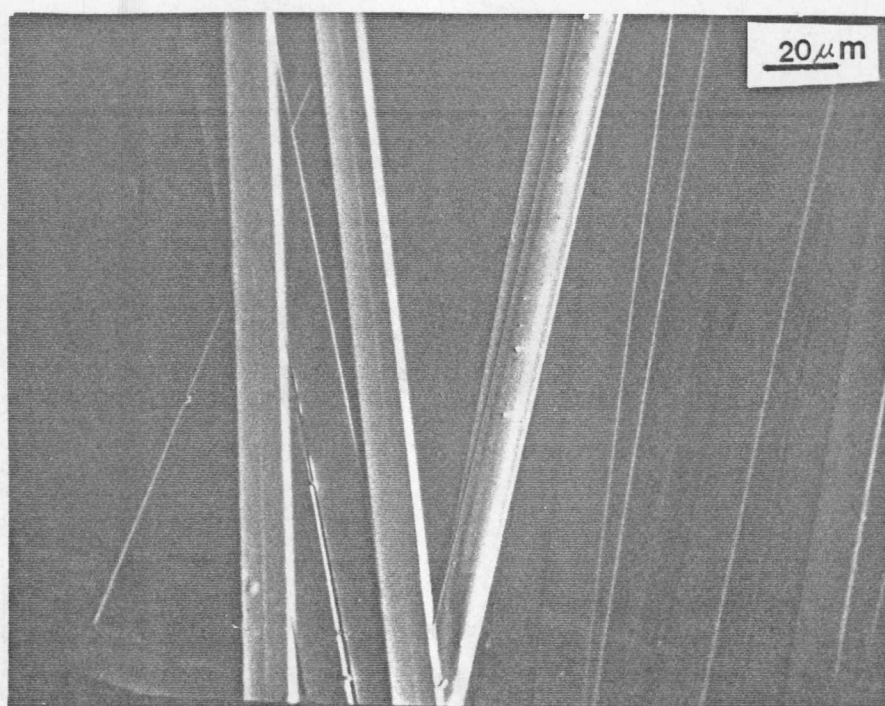
The scanning electron micrographs of the virgin Kevlar^R 49 fibers, the Kevlar^R 29 fibers, the degraded Kevlar^R 49 fibers and the Kevlar^R 49 fibers fractured under tension were taken to investigate the external and internal structures of the fibers, and they are presented in Figure 55. The diameters of a single filament are measured to be approximately 12 μm for all the fibers. The skin of the Kevlar^R 49 and the Kevlar^R 29 fibers is smooth while the skin of the degraded Kevlar^R 49 fibers is rough. This is more clearly evident in the magnified micrographs shown in Figure 56. These surface defects are believed to be the probable cause of lowering of the tensile strength. Figure 57 shows some of the structural defects found in the virgin Kevlar^R 49 fibers. Looking at Figure 57c, it is evident that extensive splitting could occur readily near the broken end of the fiber.

V.2.B Epoxy Resins

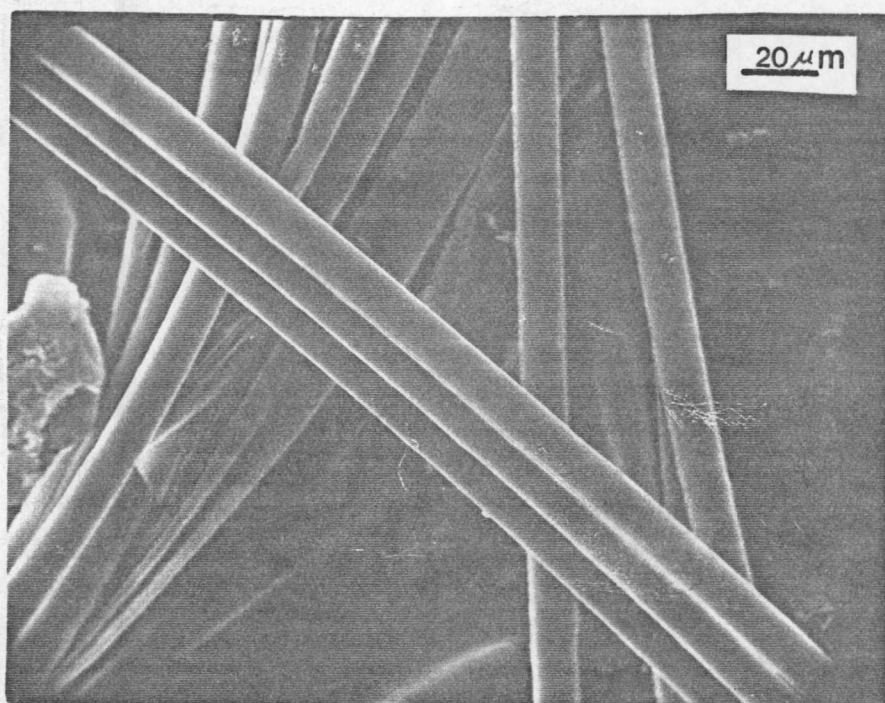
The scanning electron micrographs of various epoxy resins fractured under tension were taken. The SEM micrographs of EPON 828/NMA (90 phr)/BDMA, EPON 828/NMA (70 phr)/BDMA and DER 332/DETA (12 phr) are presented in Figure 58. It may be noted that the fractured surface is

Figure 55. The scanning electron micrographs of Kevlar^R fibers.

- a) Kevlar^R 49 fibers
- b) Kevlar^R 29 fibers
- c) Degraded Kevlar^R 49 fibers #1
- d) Degraded Kevlar^R 49 fibers #2
- e) Degraded Kevlar^R 49 fibers #4

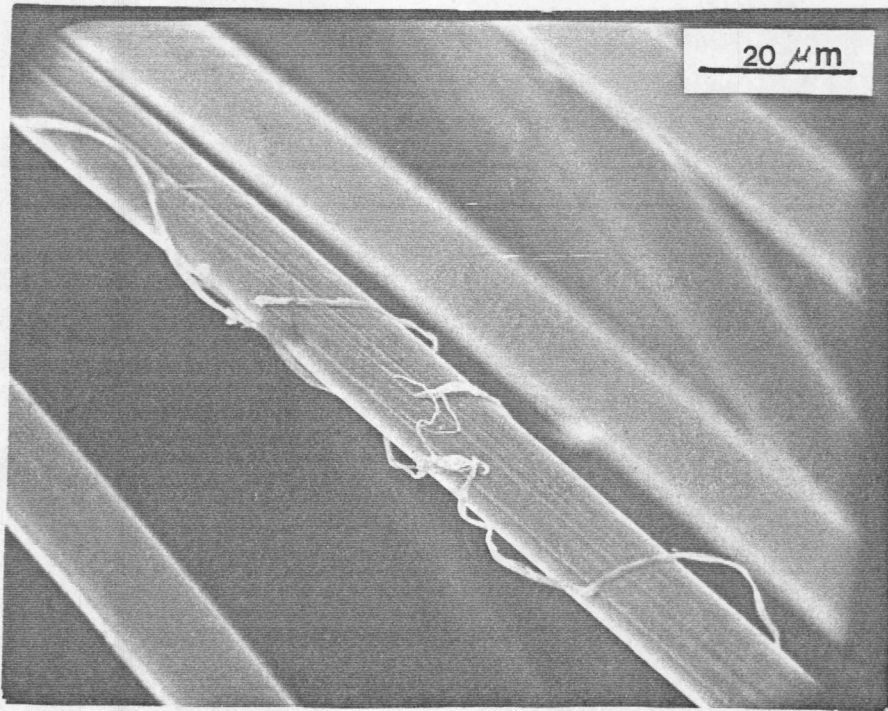


a

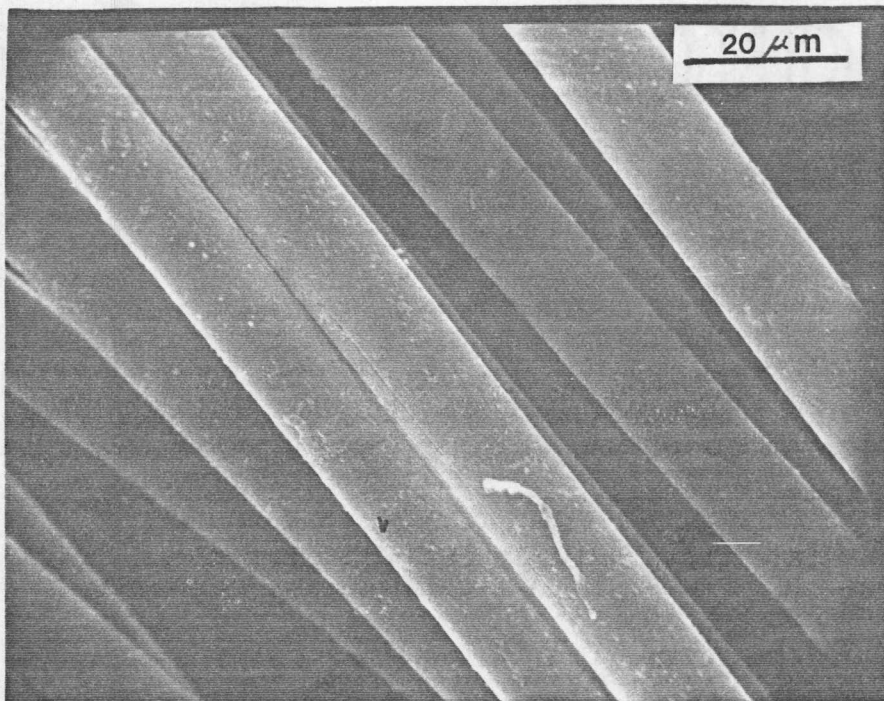


b

Figure 55

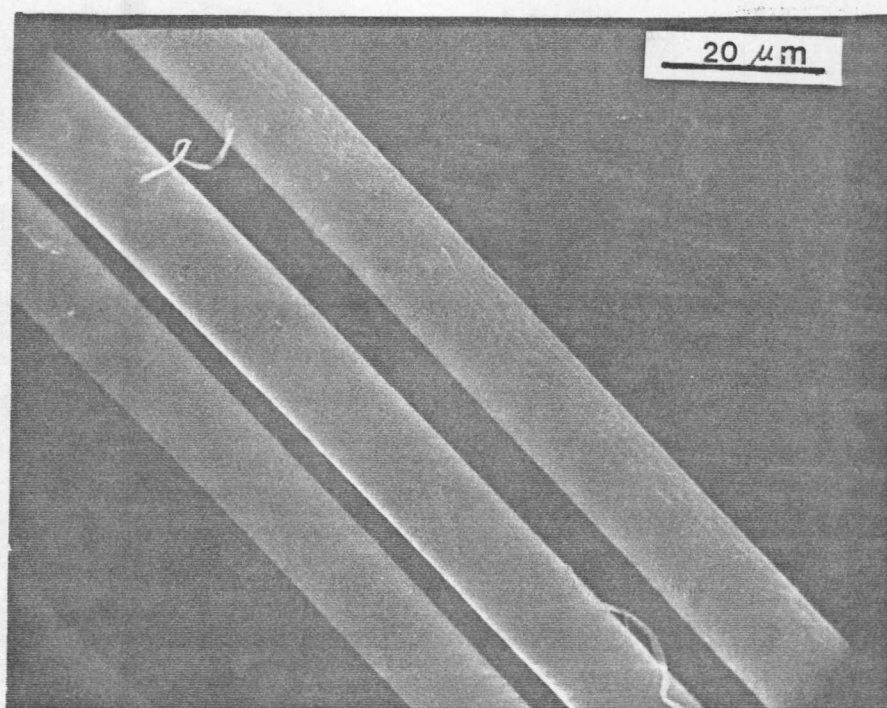


c



d

Figure 55 (Continued)

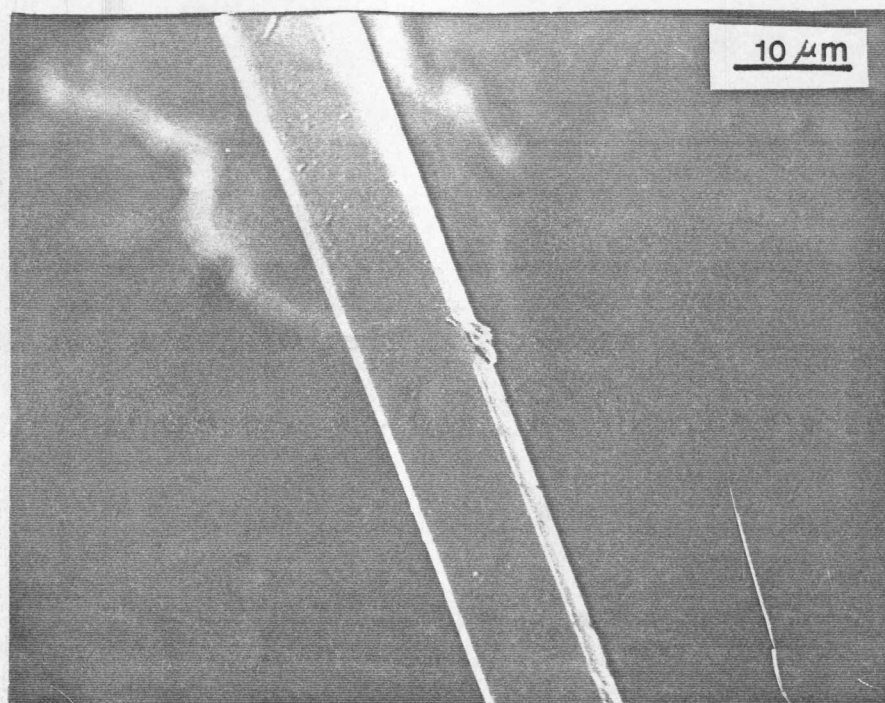


e

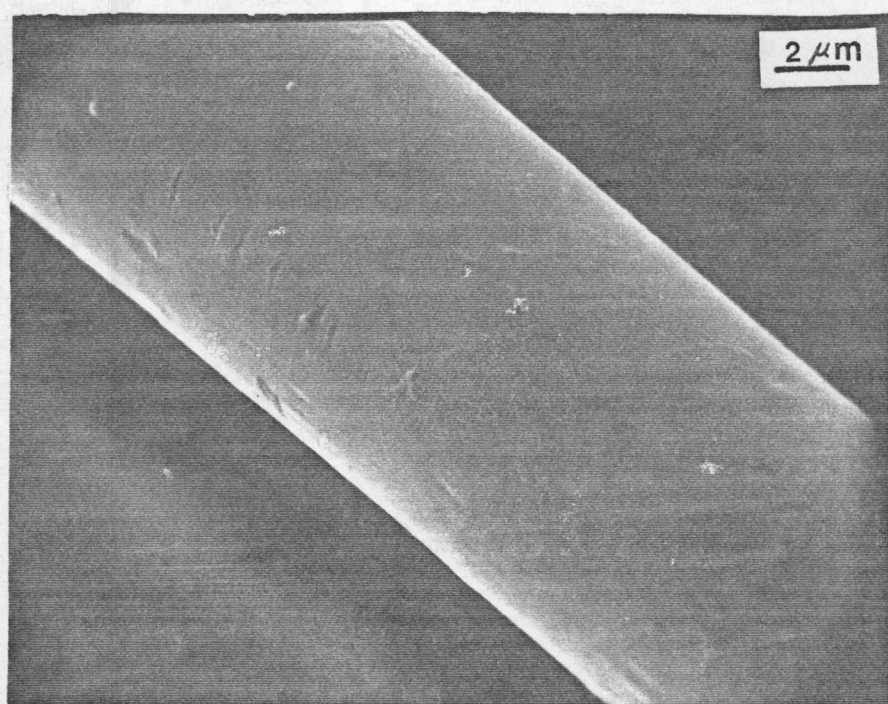
Figure 55 (Continued)

Figure 56. The scanning electron micrographs of Kevlar^R fibers at high magnification.

- a) Kevlar^R 49 fibers
- b) Degraded Kevlar^R 49 fibers #1
- c) Degraded Kevlar^R 49 fibers #2
- d) Degraded Kevlar^R 49 fibers #4

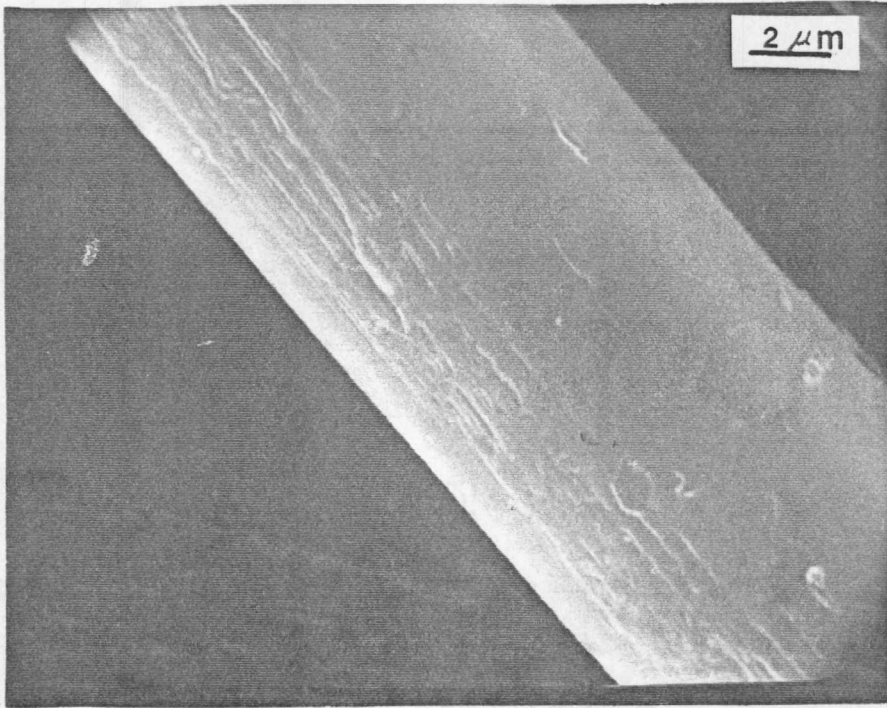


a

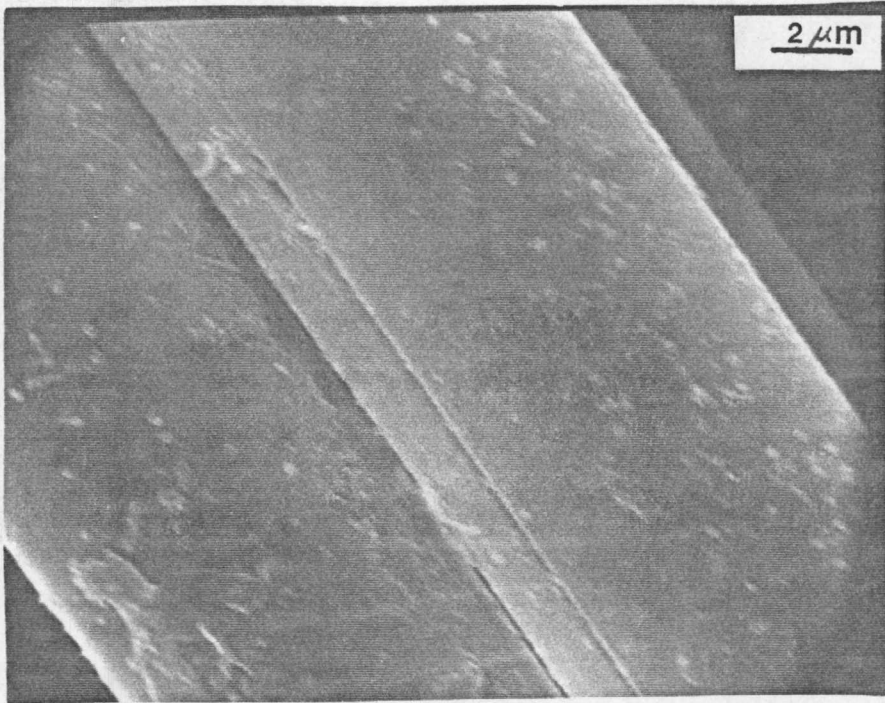


b

Figure 56



c



d

Figure 56 (Continued)

Figure 57. The scanning electron micrographs of structural defects found on Kevlar^R 49 fibers.

- a) Non-uniform surface profile
- b) Wrinkling
- c) Splitting near the broken end

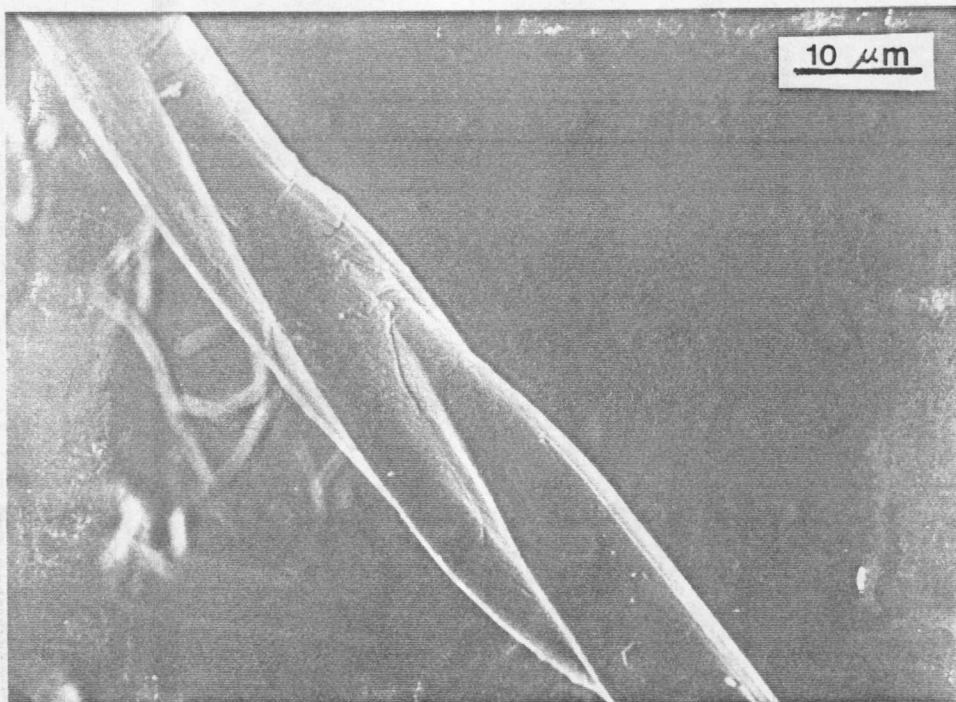
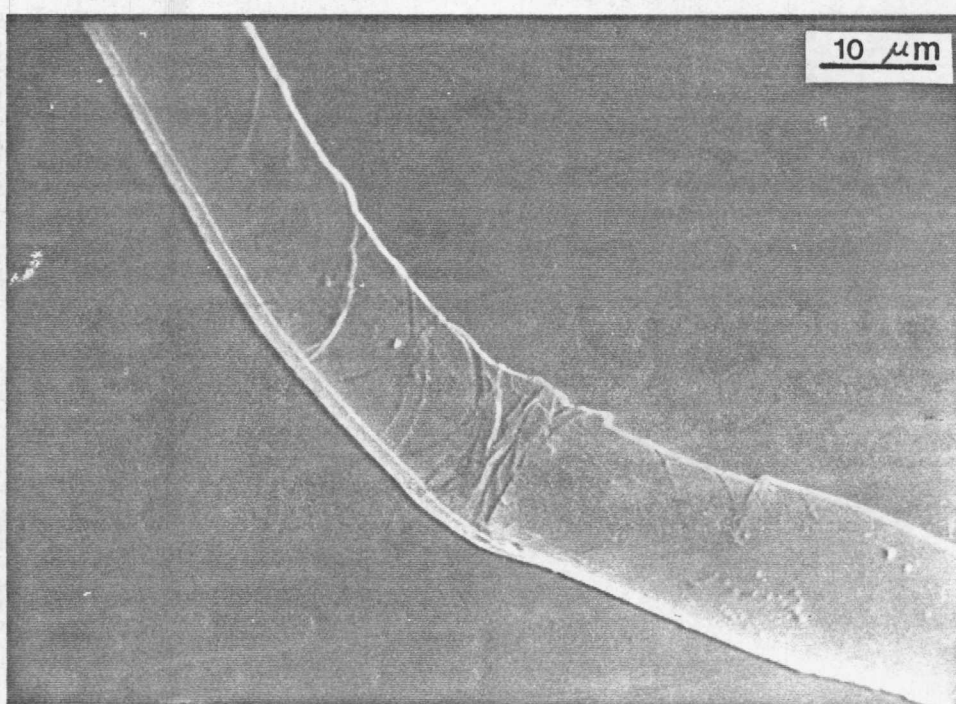
**a****b**

Figure 57

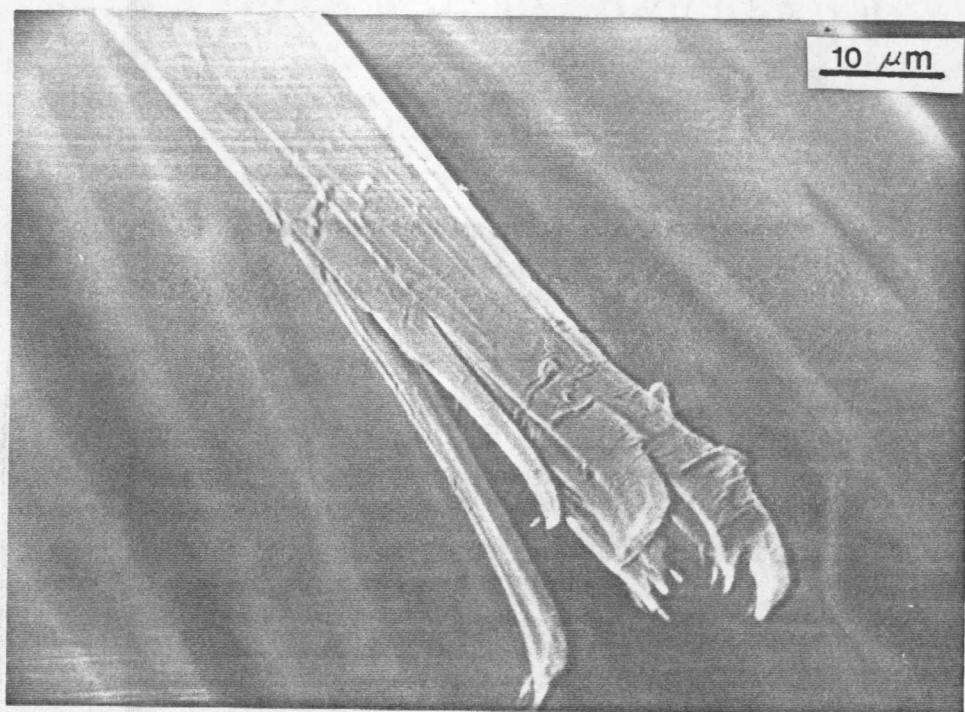
**C**

Figure 57 (Continued)

Figure 58. The scanning electron micrographs of epoxies failed under tension.

- a) EPON 828/NMA (90 phr)/BDMA
- b) EPON 828/NMA (70 phr)/BDMA
- c) DER 332/DETA (12 phr)

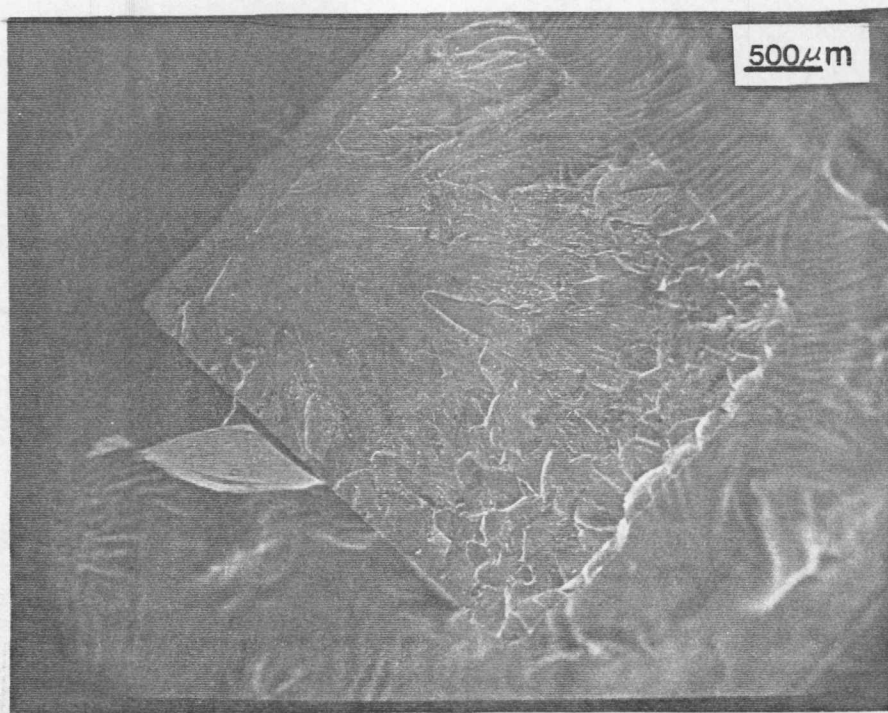
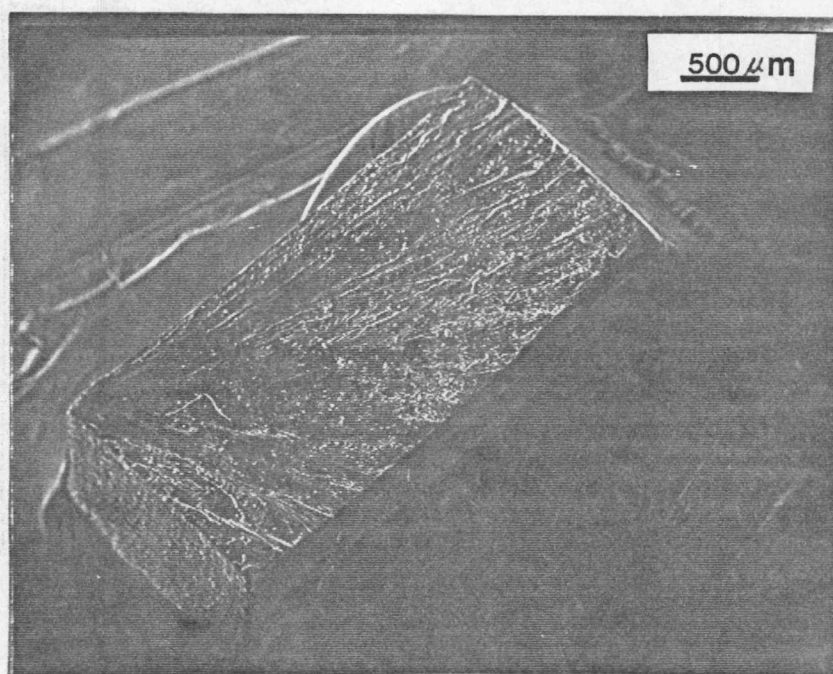
**a****b**

Figure 58

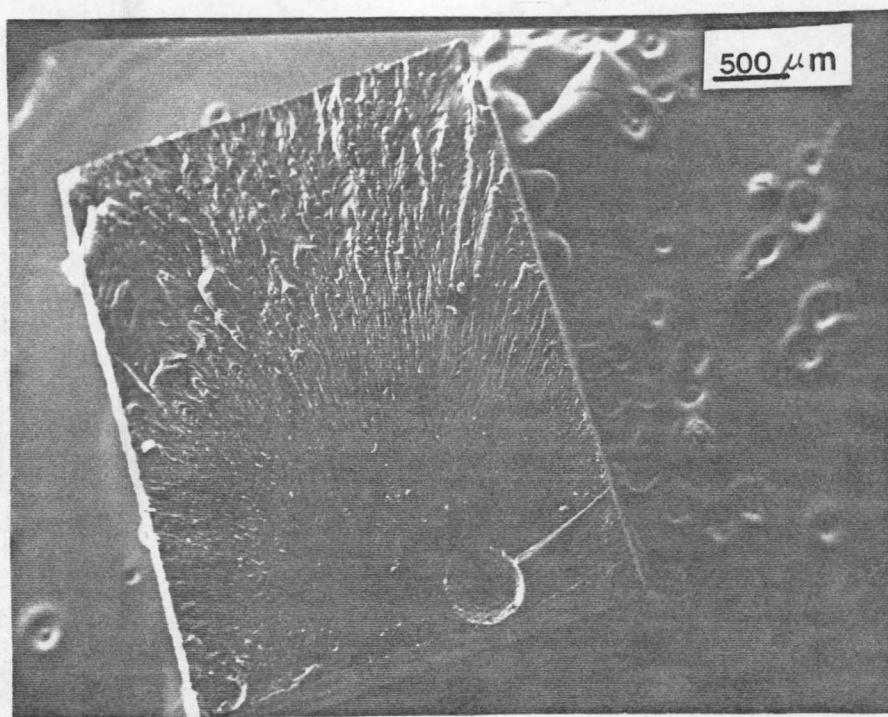


Figure 58 (Continued)

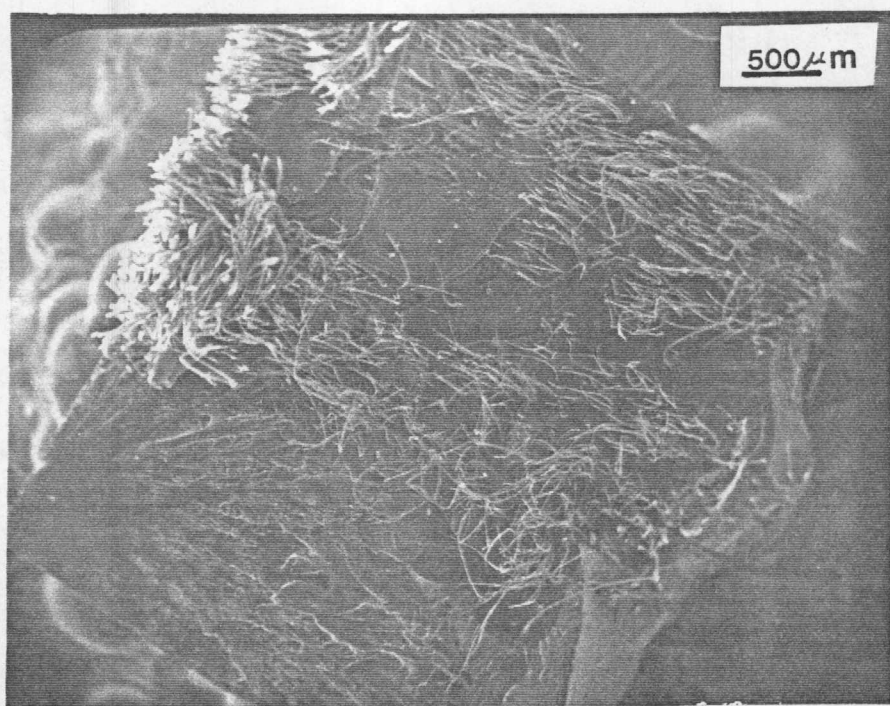
roughly divided into two morphologically distinct regions in all three specimens. One encompasses a smaller area and shows a smooth surface. The other encompasses a much larger area and shows a rough surface. In EPON 828/NMA (70 phr)/BDMA and DER 332/DETA (12 phr) the latter region shows evidence of plastic flow and crack branching. Observations of the direction of the propagation of the cracks indicate the former is the initiation region. From the present results it can be deduced that the fracture has initiated from either surface defects or a large air bubble which may be imbedded in the matrix during curing.

V.2.C Composites

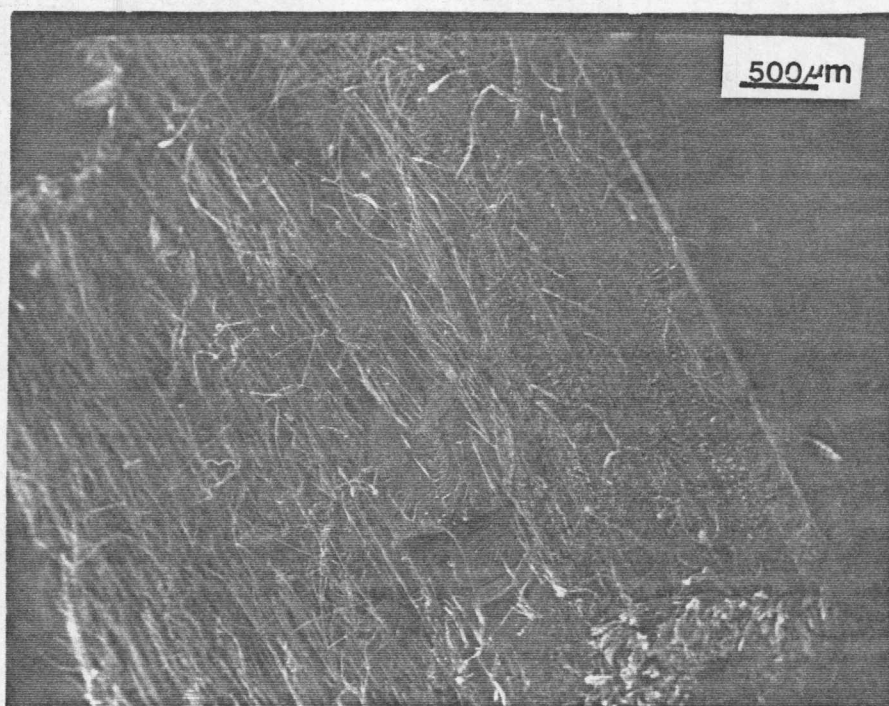
The scanning electron micrographs of composites failed under tension were taken and presented in Figure 59. Figure 59 shows an interesting feature. It shows the fracture initiation of the matrix and from this it can be deduced that the failure had initiated in the matrix. Had the fibers failed first and the crack had initiated from the fiber breaks, the direction of crack propagation should be opposite to that shown--running radially outward from each fiber break. Figures 60-63 show the details of the failed composites. The fiber reinforcement angle is 90° and 0° in Figure 60 and in Figure 61, respectively. Figure 60 reveals an interesting morphology. The fibers show severe splitting. The holes from which the fibers have pulled out are visible in the matrix. A split piece of fiber may sometimes be seen adhering to the hole as shown in Figure 60d. The matrix crack as shown in Figures 60c and 60d is running across the fibers and not initiating from the holes

Figure 59. The scanning electron micrographs of the composites failed under tension.

- a) EPON 828/NMA (90 phr)/BDMA with fiber angle 60 degrees (low volume fraction)
- b) EPON 828/NMA (90 phr)/BDMA with fiber angle 60 degrees (high volume fraction)
- c) DER 332/DETA (12 phr) with fiber angle 90 degrees (high volume fraction)
- d) DER 332/DETA (12 phr) with fiber angle 0 degree (high volume fraction)
- e) DER 332/DETA (12 phr) with fiber angle 60 degrees (high volume fraction)

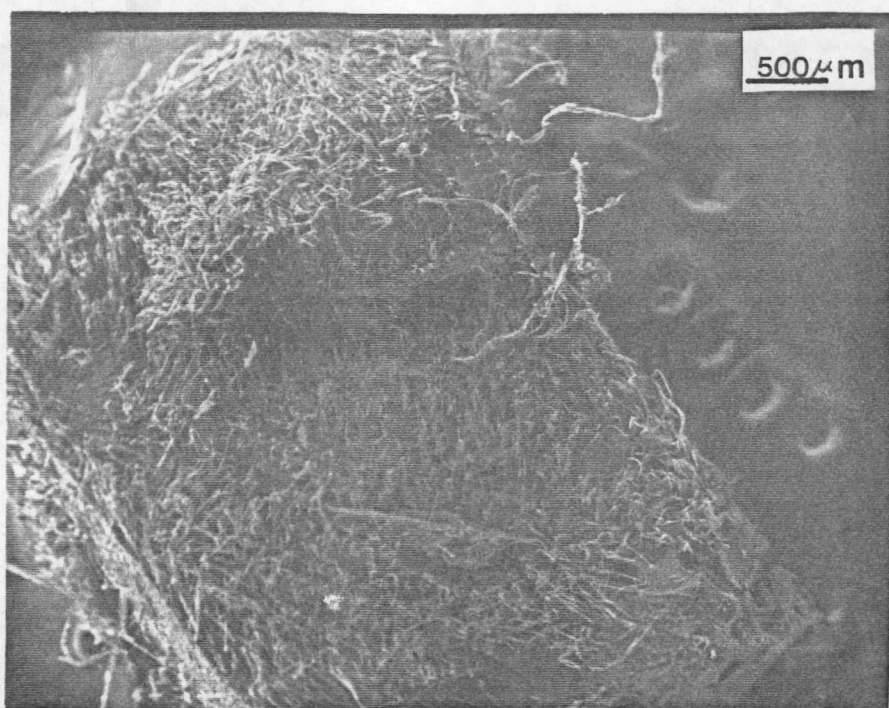


a

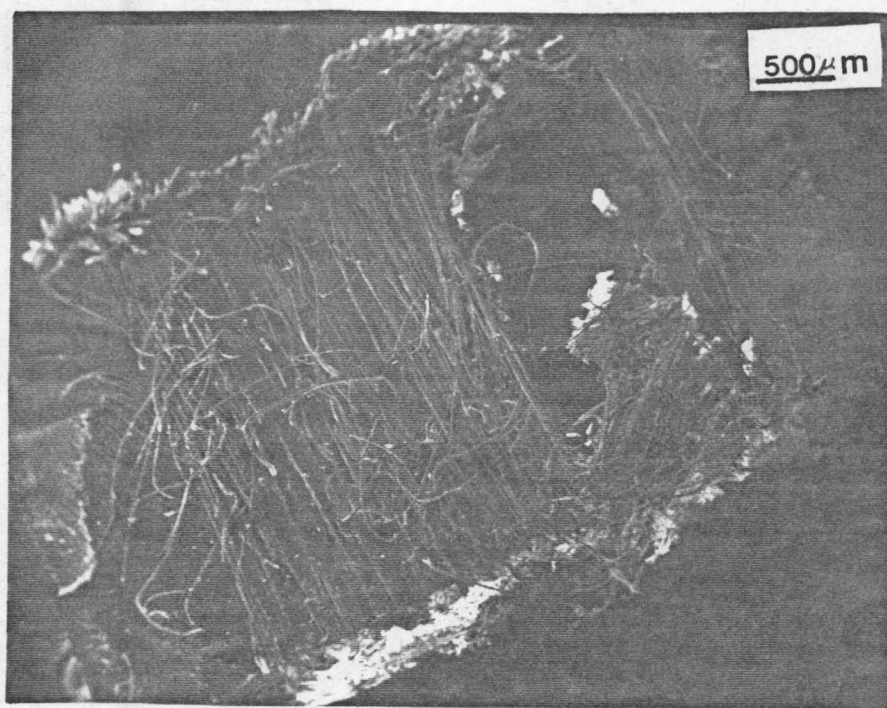


b

Figure 59

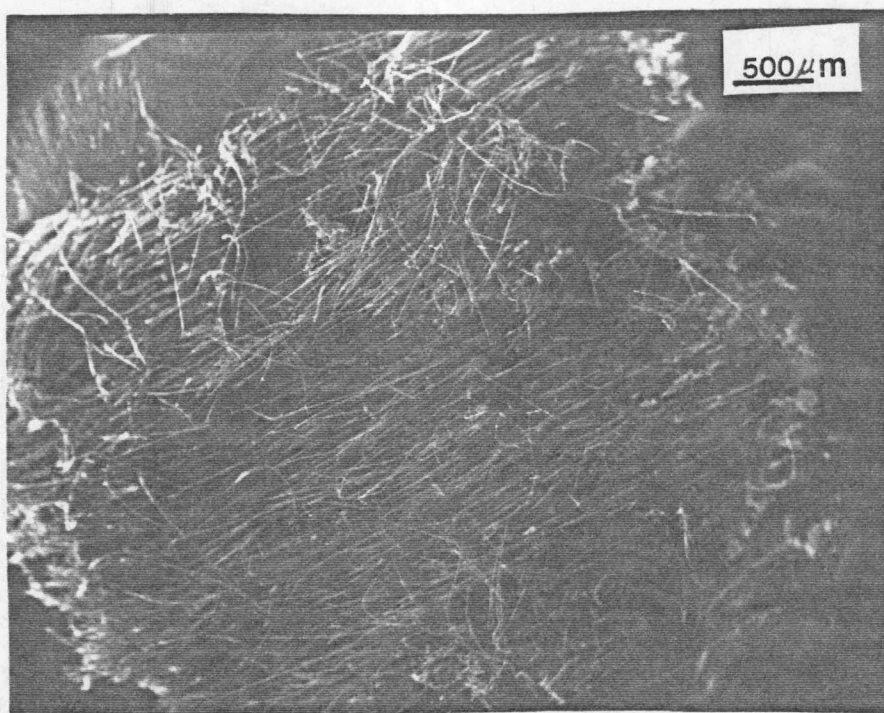


c



d

Figure 59 (Continued)

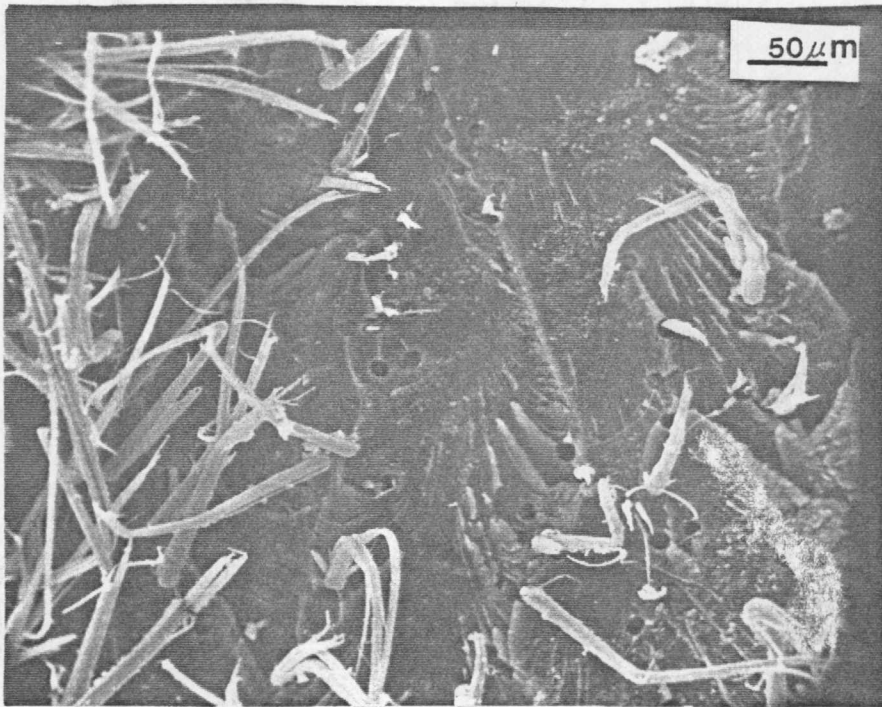


e

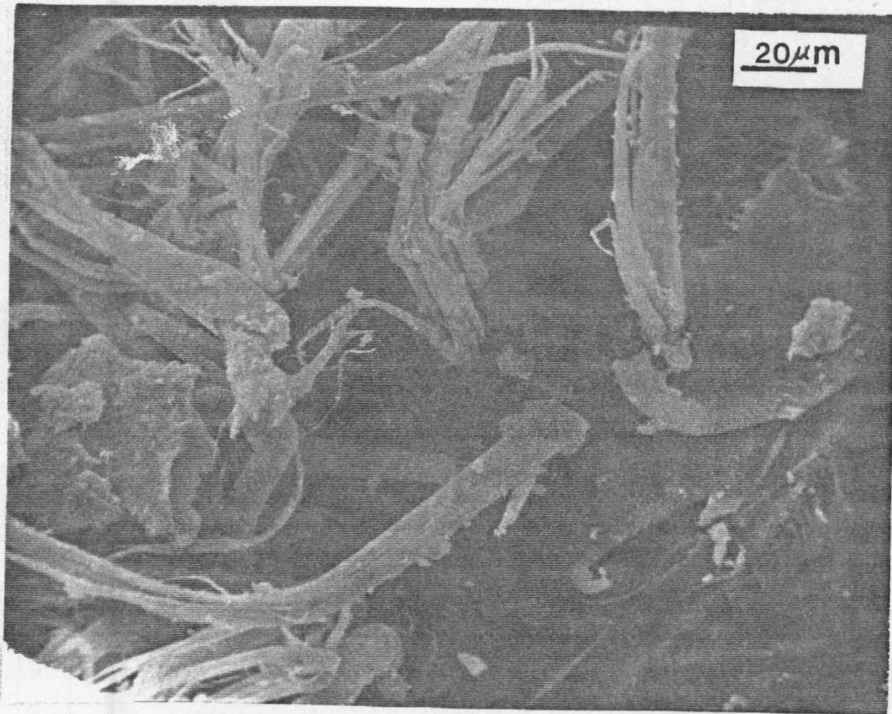
Figure 59 (Continued)

Figure 60. Details of EPON 828/NMA (90 phr)/BDMA composite with fiber angle 90 degrees failed under tension.

- a) x200
- b) x500
- c) x2000
- d) x5000



a

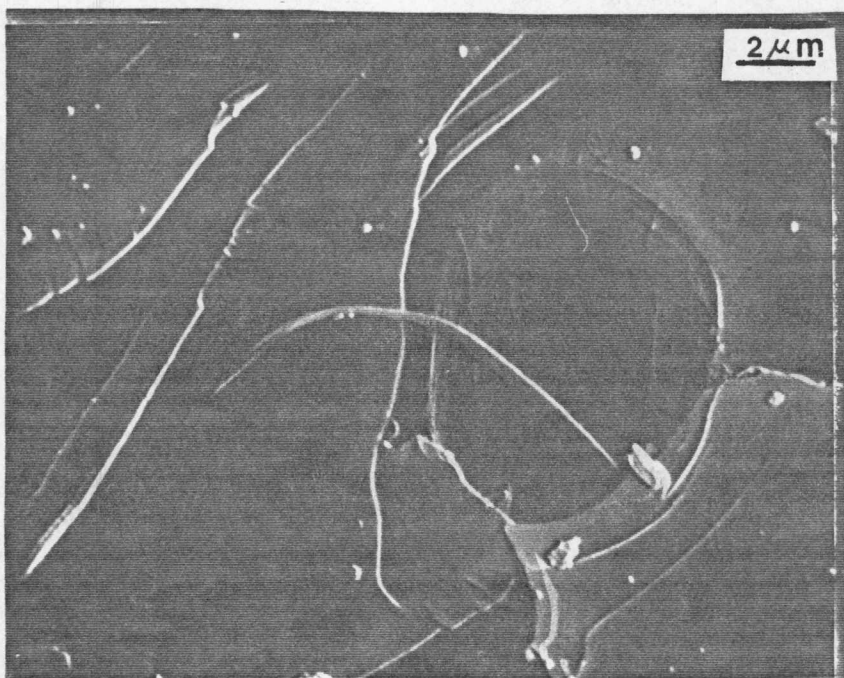


b

Figure 60



c

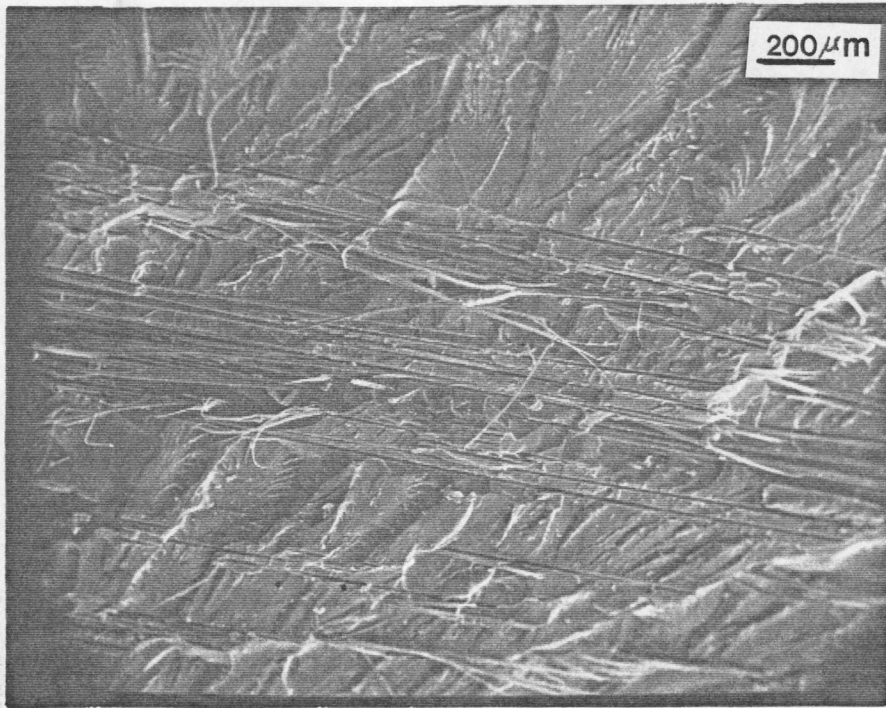


d

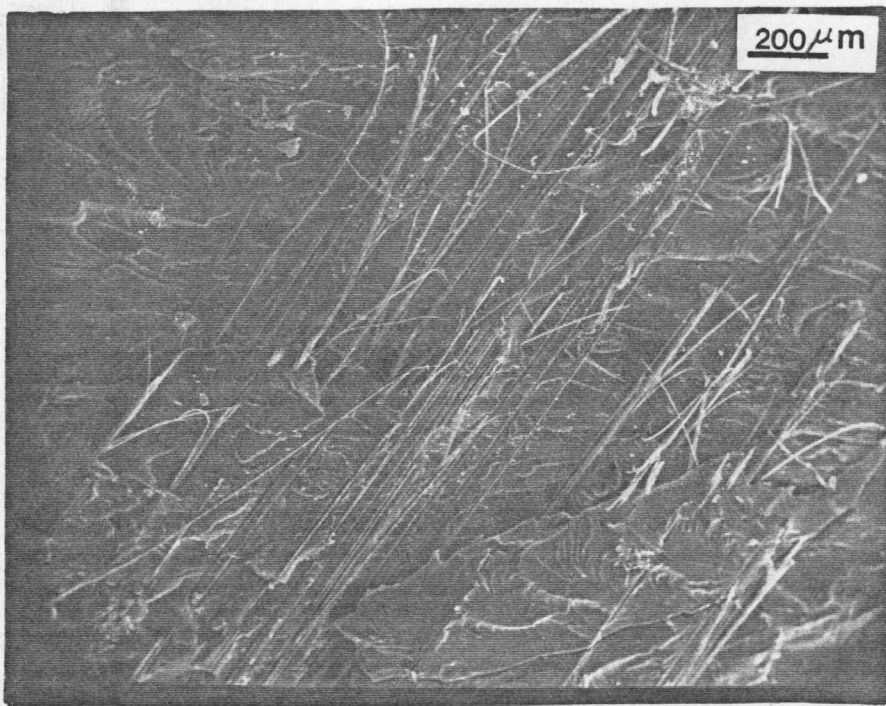
Figure 60 (Continued)

Figure 61. Details of EPON 828/NMA (90 phr) BDMA composite with fiber angle 0 degrees failed under tension.

- a) x50
- b) x50
- c) x200
- d) x500

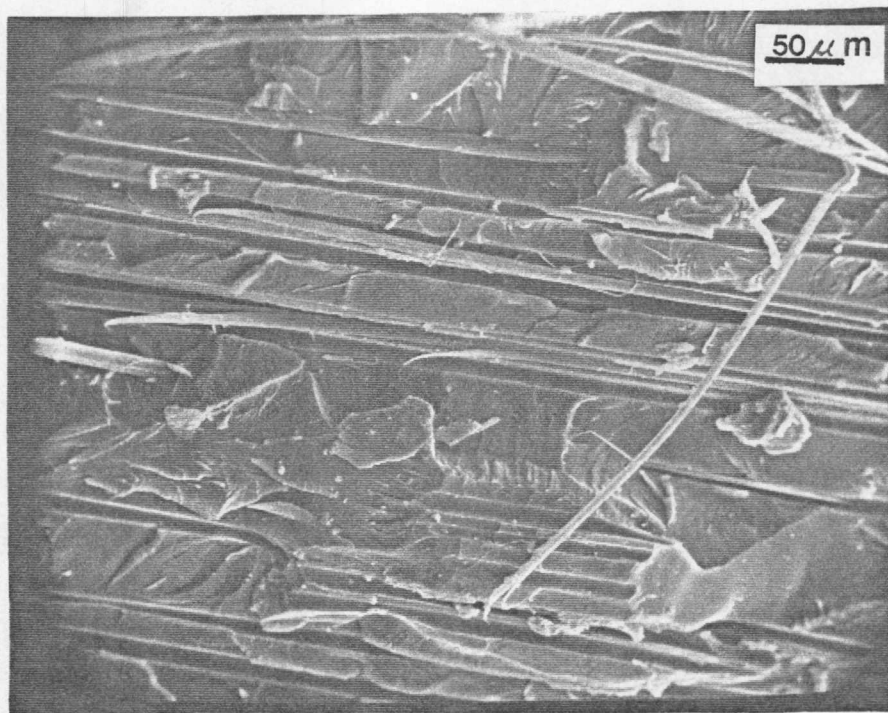


a

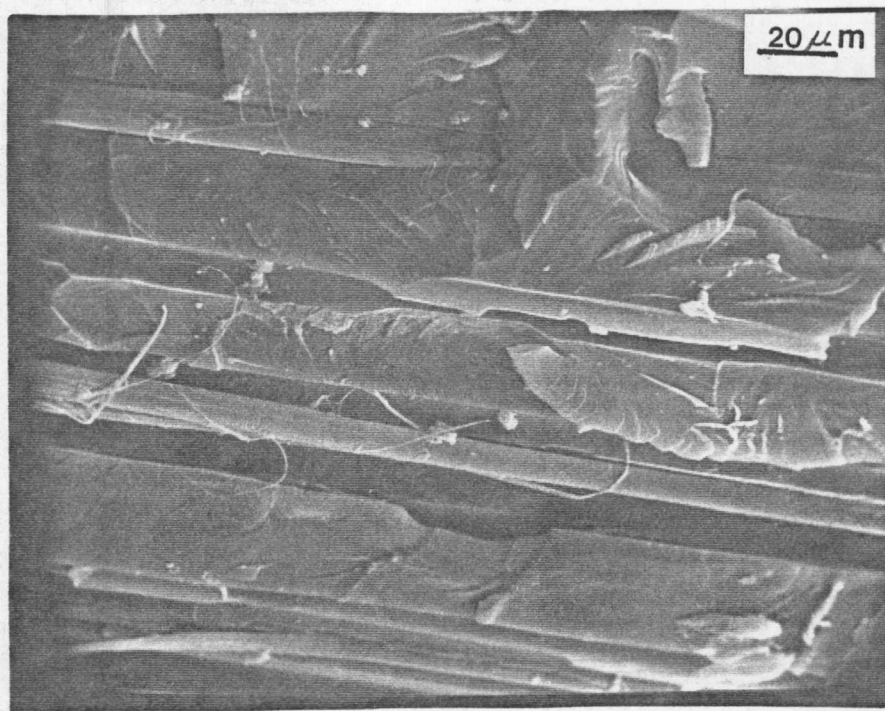


b

Figure 61



c



d

Figure 61 (Continued)

Figure 62. Details of EPON 828/NMA (90 phr)/BDMA composite with fiber angle 60 degrees failed under tension.

- a) fibers
- b) matrix
- c) holes within the matrix

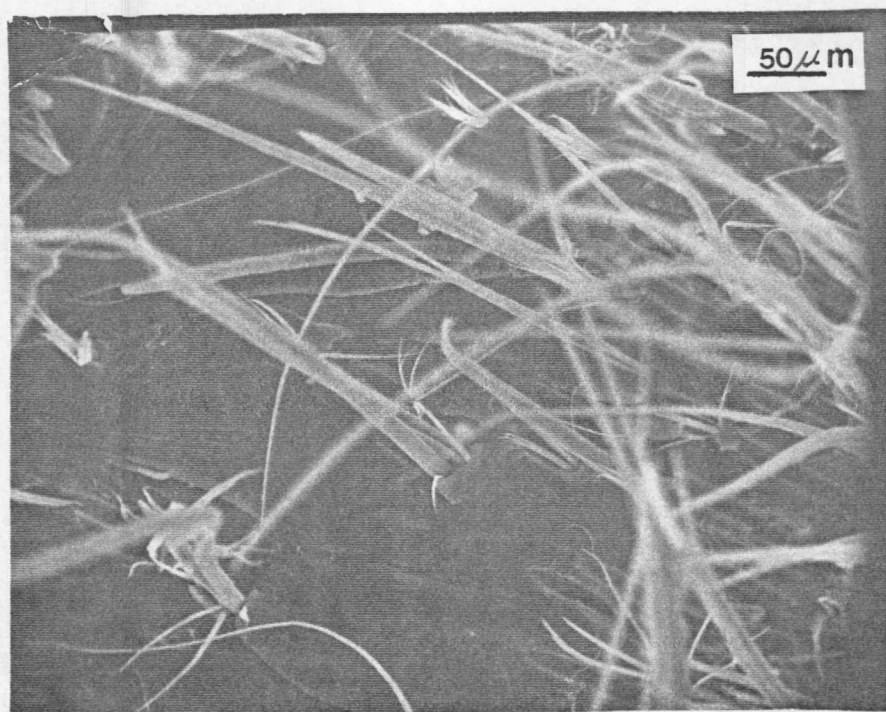
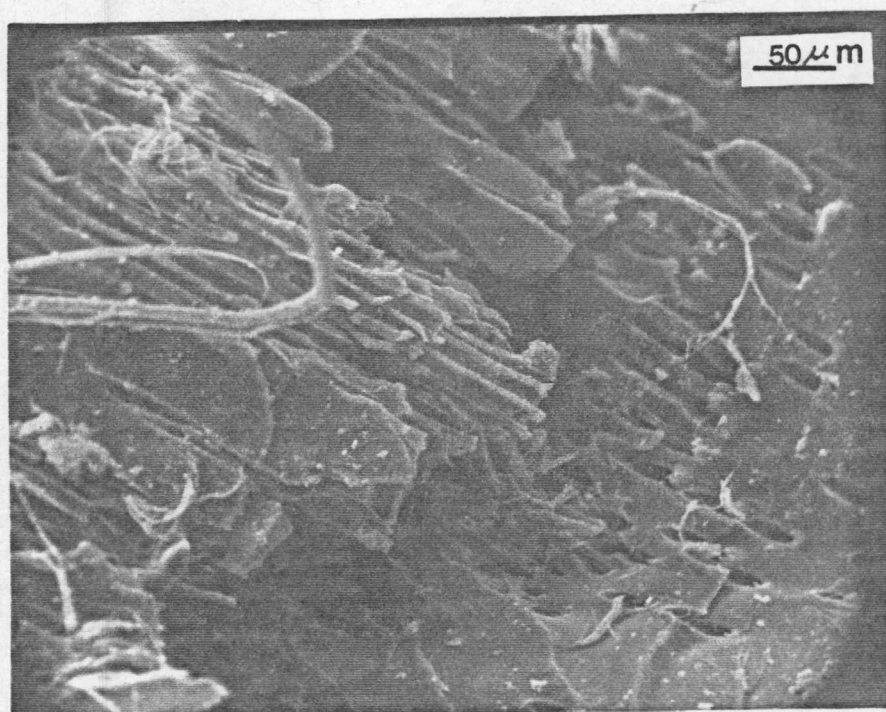
**a****b**

Figure 62

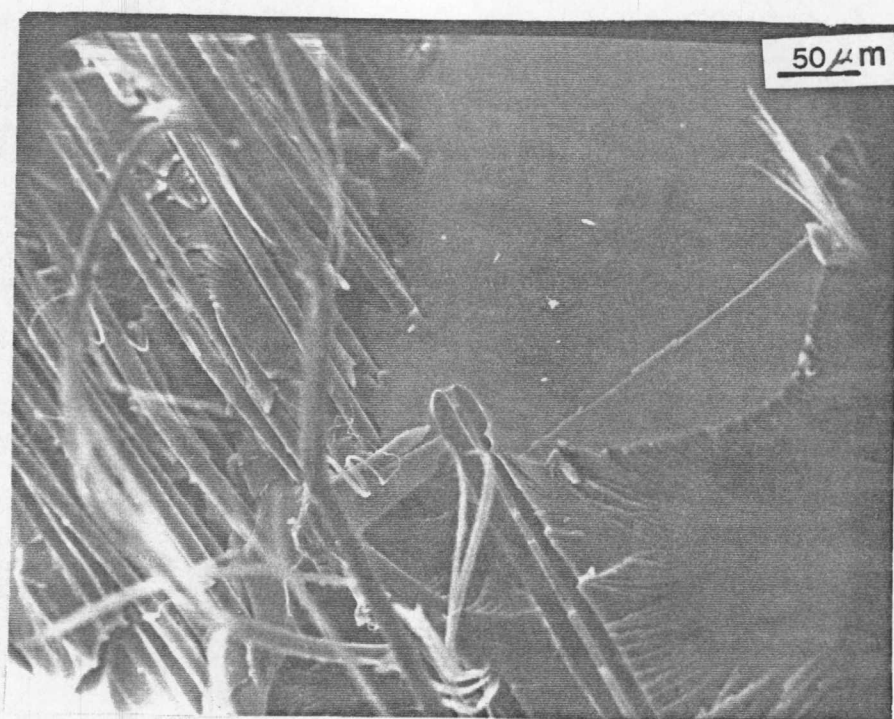
**c**

Figure 62 (Continued)

Figure 63. Details of Kevlar^R fiber reinforced DER 332/DETA (12 phr) composites failed under tension.

- a) fiber angle 90 degrees
- b) fiber angle 0 degree
- c) fiber angle 60 degrees

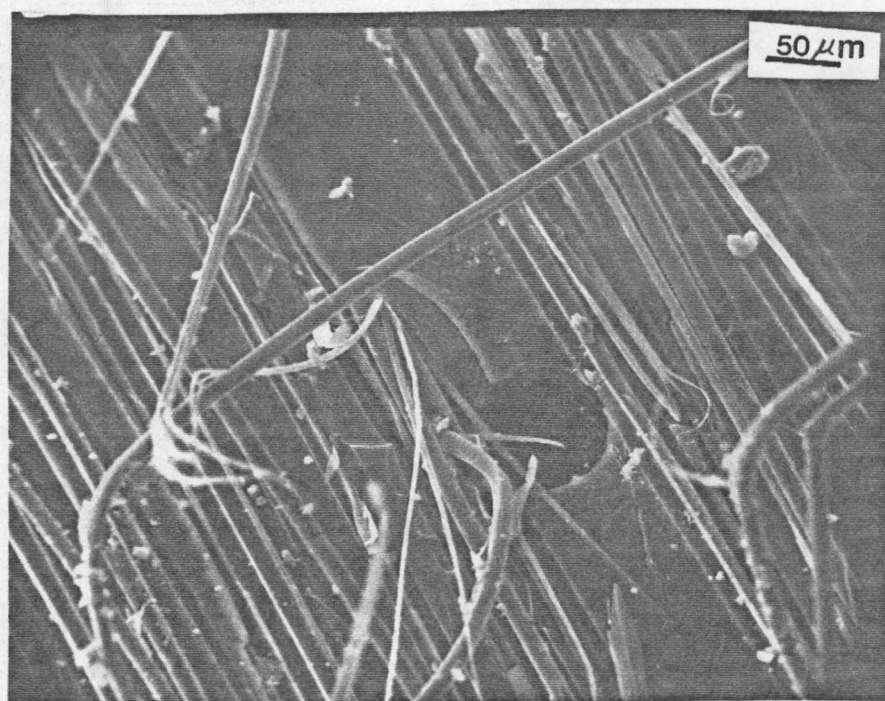
**a****b**

Figure 63

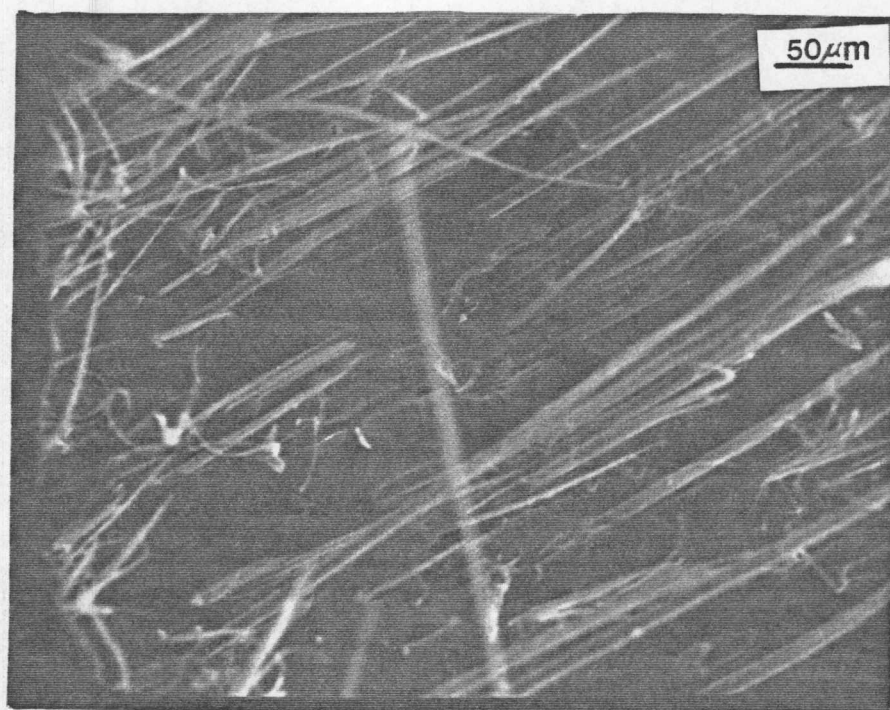
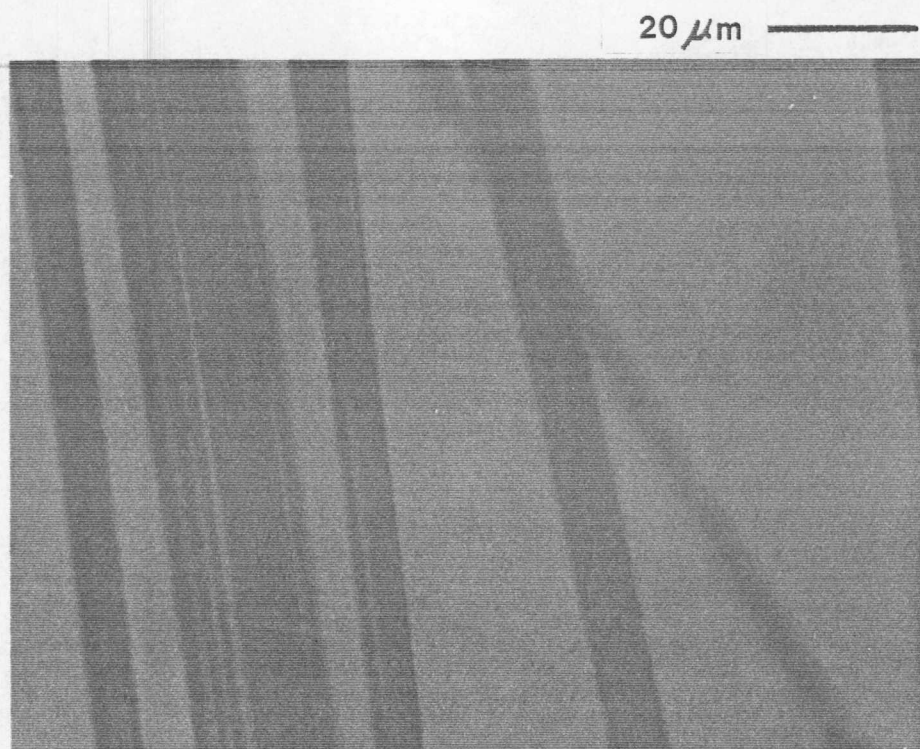
**c**

Figure 63 (Continued)

or the fiber breakages. Figure 61, p. 250, shows the top and bottom pieces of the same specimen failed under tension. It is obvious from Figure 61 that fibers are adhering to both the top and bottom pieces. The magnifications show fibers being pulled apart giving rise the wedge-shaped fiber-splits. Within the matrix, the regions where the fibers used to be are clearly visible. The matrix fractures show complex morphologies. In Figure 62, p. 253, the composites whose fiber reinforcement angle is 60° are presented. The fibers are being lifted from the matrix at an angle, leaving clear wedge shaped markings in the matrix. The split ends of fibers are also visible. At the region where the matrix fracture has taken place, long holes where the fibers used to be are visible. The composites with the fiber reinforcement angle of 45° show similar morphologies. In Figure 63 the Kevlar^R fiber reinforced DER 332/DETA (12 phr) composites failed under tension are presented. They show similar morphologies as the Kevlar^R fiber reinforced EPON 828/NMA (90 phr)/BDMA composites.

V.3 OPTICAL MICROSCOPIC OBSERVATION

The virgin Kevlar^R 49 fibers observed under the unpolarized and polarized optical microscope show smooth round filaments as presented in Figure 64. The fibers imbedded in the matrix examined under the polarized optical microscope show the crisscross patterns of dark lines as shown in Figure 65. The origin of such lines is not clearly understood. It is possible that the curing process put the skin of the fiber in a compressive stress and caused such patterns to appear. Konosasek and Hearle (88) had reported seeing such lines in Kevlar^R 29.



a

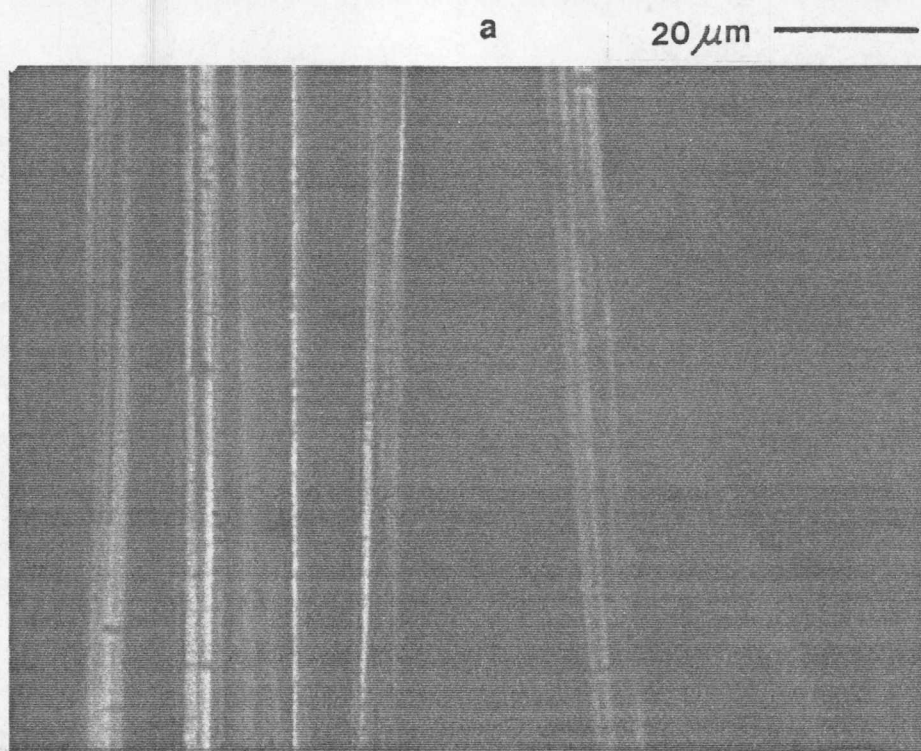


Figure 64. Kevlar^R 49 fibers examined under an optical microscope.

- a) unpolarized
- b) polarized

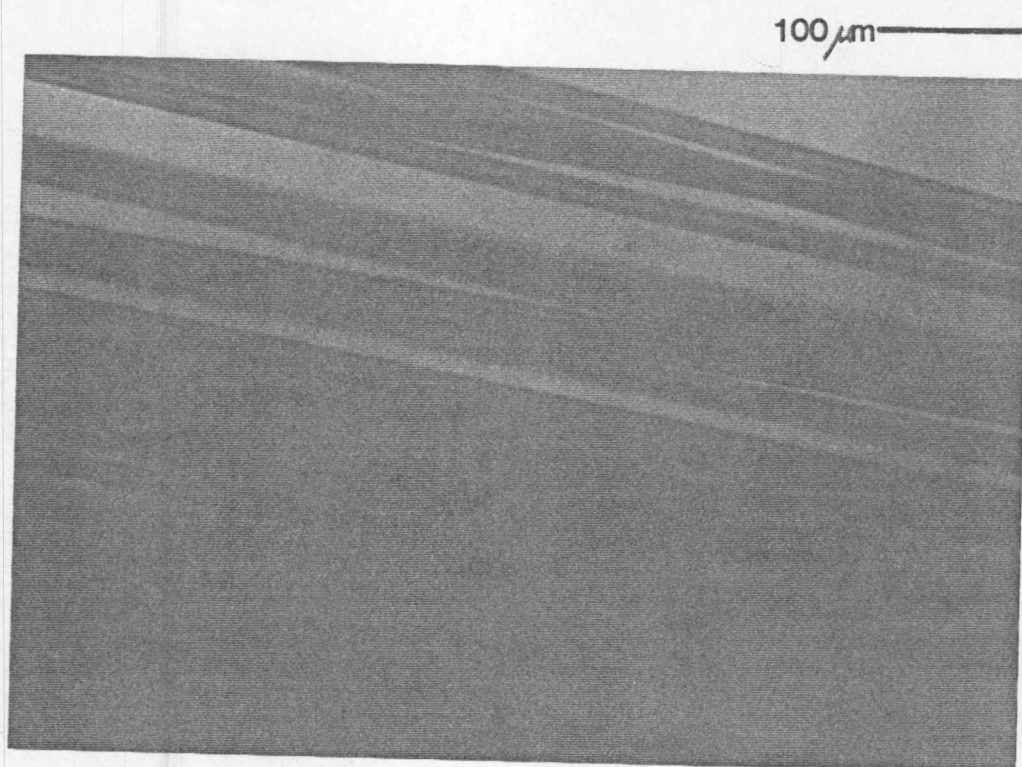


Figure 65. An optical microscopic observation of Kevlar^R 49 fibers imbedded in epoxy resin.

CHAPTER VI

MECHANICAL PROPERTIES

In this chapter the behavior of specimens of uniaxial Kevlar^R fiber reinforced epoxy with various fiber orientations has been studied under tensile load.

The angular dependence of the composite failure is shown in Figures 66 and 67, respectively, for 2.88 volume percent and 8.60 volume percent Kevlar^R fiber reinforced EPON 828/NMA (90 phr)/BDMA composites. It may be noted the propagation of fracture takes place along the direction of the fibers.

The angular dependence of the composite modulus is shown in Figure 68. The modulus continuously decreases as the angle between the fibers and loading axis increases or as θ decreases. This decrease is sharp for large θ but becomes small as θ becomes less than 45 degrees. It is also evident that the modulus is higher for high volume fraction fiber composites at large θ than low volume fraction composites but the difference becomes small at small θ . The moduli of the EPON 828/NMA (90 phr) BDMA epoxy resin and the DER 332/DETA (12 phr) epoxy resins were 105000 - 130000 psi (720 - 900 MPa) and 96000 - 105000 psi (660 - 720 MPa), respectively, and hence below about $\theta = 50^\circ$ the composite modulus is approximately same as the modulus of epoxy resins.

The modulus of unidirectional fibrous composites can be calculated by Halpin and Tsai formula (Section II.5.A):

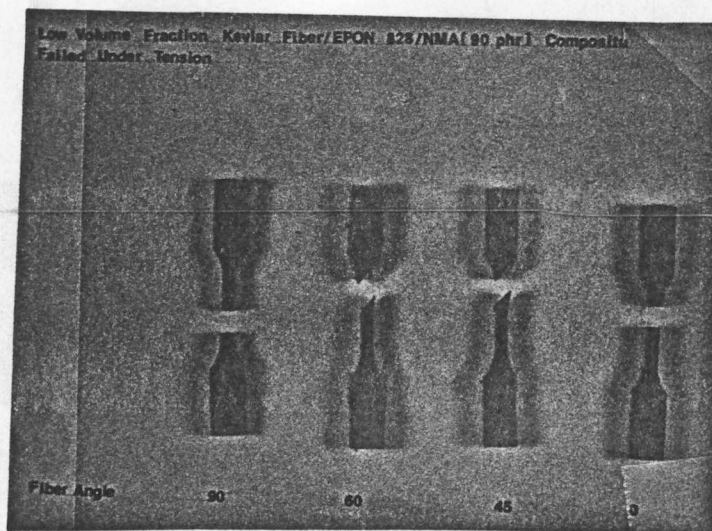


Figure 66. Angular dependence of composite failure for 2.88% volume fraction fiber reinforced EPON 828/NMA (90 phr)/BDMA failed under tension.

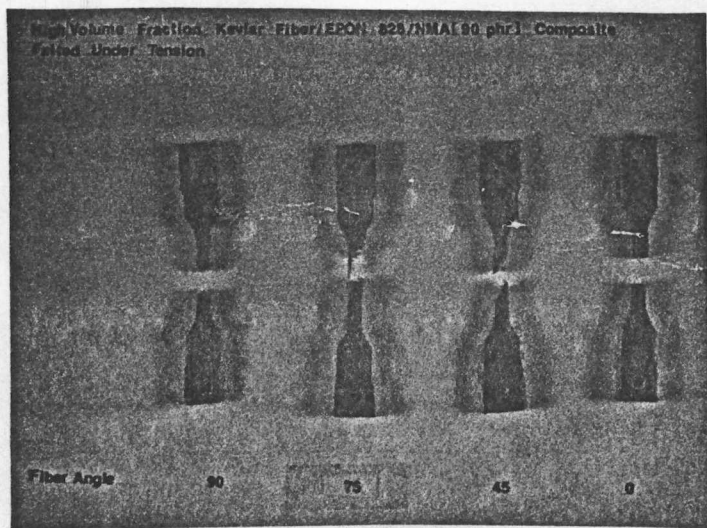


Figure 67. Angular dependence of composite failure for 8.60% volume fraction fiber reinforced EPON 828/NMA (90 phr)/BDMA failed under tension.

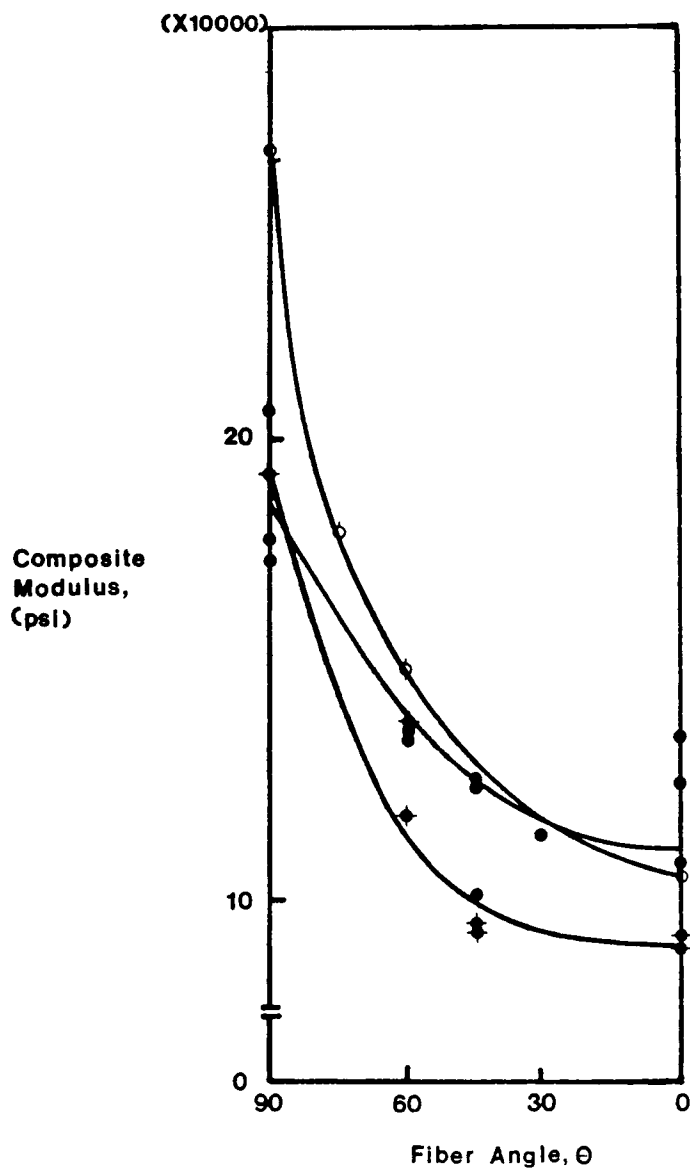


Figure 68. The angular dependence of composite modulus.

EPON 828/NMA (90 phr), 2.88 vol. % •
 EPON 828/NMA (90 phr), 8.60 vol. % ◊
 DER 332/DETA (12 phr), 6.57 vol. % ◆

$$E_{11} = E_f V_f + E_m V_m$$

$$E_{22}/E_m = \frac{1 + \xi \eta V_f}{1 - \eta V_f}$$

$$\eta = \frac{E_f/E_m - 1}{E_f/E_m + 2} .$$

By using the experimentally determined value $\xi = 2$, $E_m = 130000$ for EPON 828/NMA (90 phr)/BDMA and 105000 for DER 332/DETA (12 phr), $E_f = 190000000$, $V_f = 0.0288$, 0.0860 and 0.0657, one obtains $E_{11} = 67000$ psi, $E_{22} = 140000$ psi for 2.88 volume percent Kevlar^R fiber reinforced EPON 828/NMA (90 phr)/BDMA and $E_{11} = 1800000$ psi, $E_{22} = 170000$ psi for 8.60 volume percent EPON 828/NMA (90 phr)/BDMA and $E_{11} = 1300000$ psi and $E_{22} = 130000$ psi for 6.57 volume percent DER 332/DETA (12 phr). These E_{11} values are higher than the experimental values by more than a factor of four. E_{22} values are higher than the experimental values by a factor of about 1.3. The interfacial conditions may have caused a substantial decrease in tensile modulus of the composites. Relative slip due to poor bonding may also result in a lower modulus. Since the transverse properties of the composites are matrix controlled, the agreement in the calculated E_{22} values with the experimental values are reasonable.

The ultimate tensile strength of the specimens was calculated from the maximum load carried by the specimens. The tensile strength of the EPON 828/NMA (90 phr)/BDMA, DER 332/DETA (12 phr) and DER 332/MPDA (14 phr) was found to be 13000 psi (90 MPa), 10500 psi (72 MPa), 7000 psi (48 MPa), respectively. The strength of the 8.60 volume

percent and 2.88 volume percent Kevlar^R fiber reinforced EPON 828/NMA (90 phr)/BDMA composites has been plotted as a function of the fiber angle in Figure 69. It may be noted that the strength of the composites drops very sharply as the angle between the fibers and the loading axis increases or θ decreases. The drop in strength is reduced as the angle between the two exceeds 45 degrees. It may also be noted that the composite strength of fiber angles less than 60 degrees is lower than the tensile strength of the matrix. The strength of 8.60 volume percent composite is higher than 2.88 volume percent composite up to the fiber angle of 60 degrees but is lower in the 45 degree and 0 degree composites. The experimental results can be compared with the predictions of various failure theories for the composites. Two of these theories, the maximum work theory of Tsai and Hill (Section II.5.B) and the maximum stress theory of Liu and Stowell (Section II.5.B) have been plotted in Figure 69. In the present study composite strength along, and perpendicular to the unidirectional fibers, X and Y respectively have been directly measured, and an estimate of the in plane shear strength, T, has been made from the knowledge of strength σ_θ for a fiber angle of 60 degrees (2). The experimental values closely follow the maximum work theory. The maximum stress theory on the other hand overestimates the strength of the composites. The strength of 2.88 volume percent EPON/NMA (90 phr)/BDMA and 2.62 volume percent DER 332/MPDA (14 phr) composites are compared in Figure 70. From Figure 70 it can be deduced that although the strength of the matrices differ by approximately 20 percent, if the difference is not large, the same volume fraction Kevlar^R

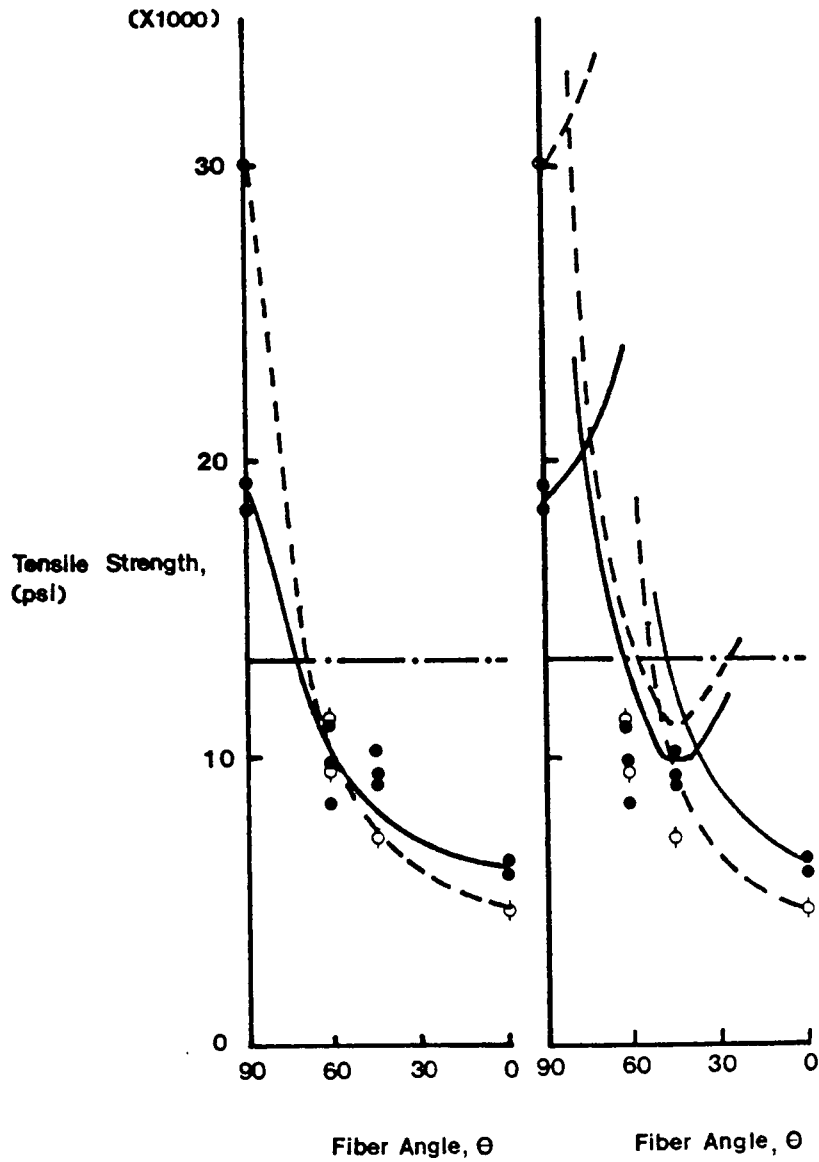


Figure 69. The angular dependence of tensile strengths. --- EPON 828/NMA (90 phr), — Tsai-Hill Theory, ---- Stowell-Liu Theory, ● 2.88 vol. % EPON 828, ○ 8.60 vol. % EPON 828.

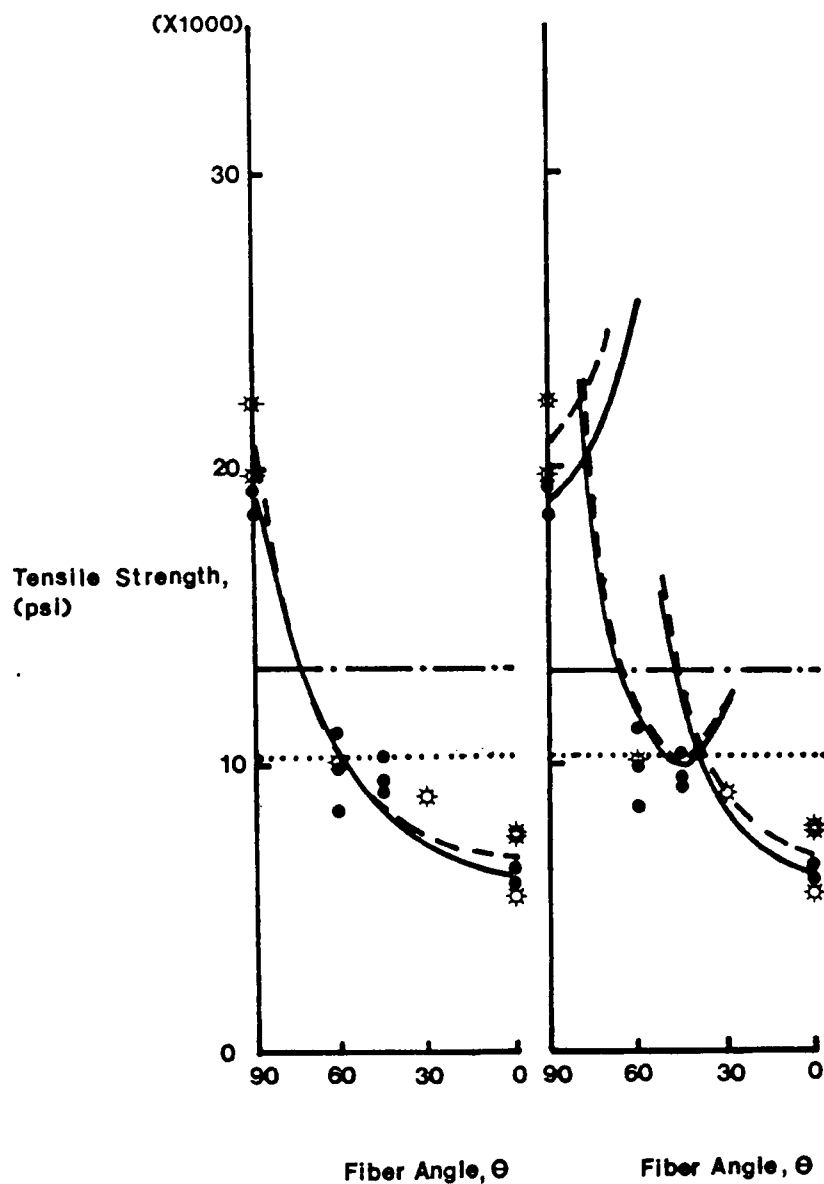


Figure 70. The angular dependence of tensile strengths for low volume fraction composites. —•— EPON 828/NMA (90 phr), ... DER 332/MPDA (16 phr), ● 2.88 vol. % EPON 828, ○ 2.62 vol. % DER 332, — Tsai-Hill Theory, --- Stowell-Liu Theory.

fiber composites result in similar tensile behavior. The strength of 8.60 volume percent EPON 828/MNA (90 phr)/BDMA and 6.57 volume percent DER 332/DETA (12 phr) composites are compared in Figure 71.

The angular dependence of the elongation at break for 2.88 volume percent EPON 828/NMA (90 phr)/BDMA composites is shown in Figure 72. The elongation at break continuously decreases as θ decreases. The elongation at break of EPON 828/NMA (90 phr)/BDMA is shown on the left side of the figure with an open circle, and it may be noted that the elongation at break of composites with fiber angles of 60 degrees or smaller is less than the elongation at break of the epoxy matrix.

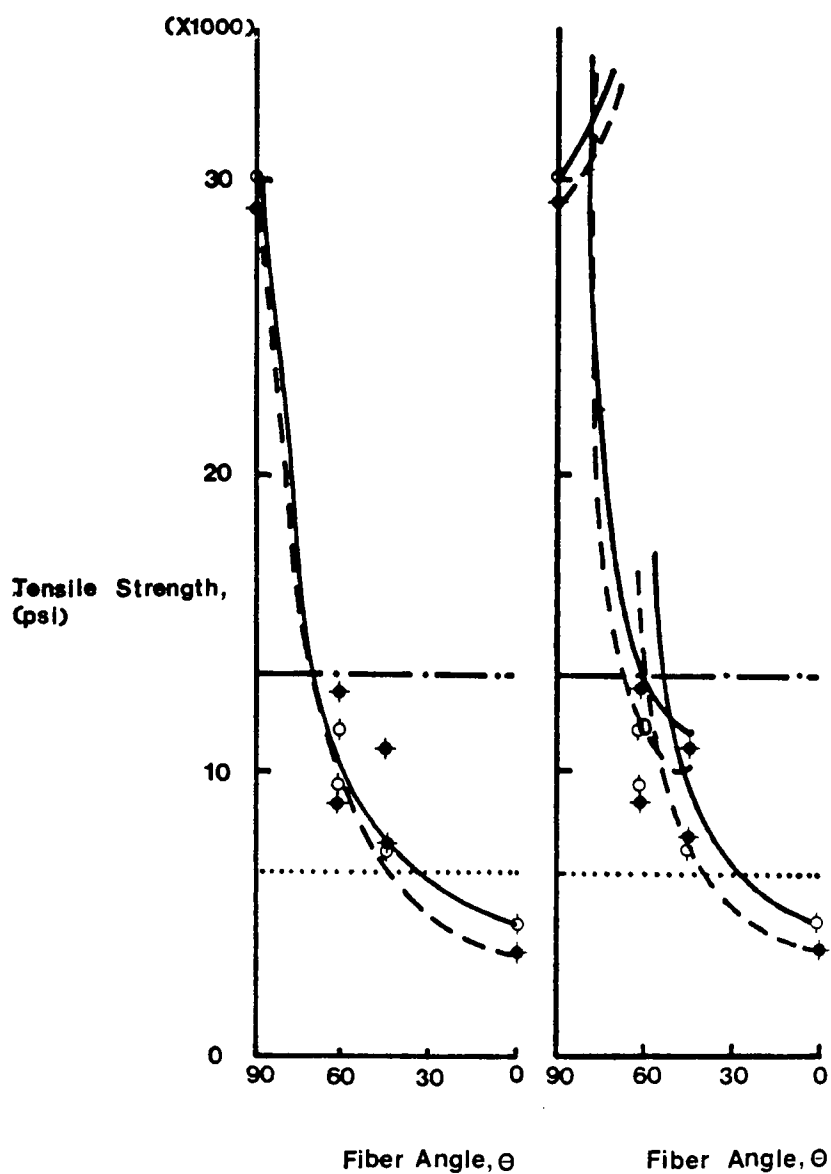


Figure 71. The angular dependence of tensile strengths for high volume fraction composites. —•— EPON 828/NMA (90 phr), ... DER 332/DETA (14 phr), $\circ$ 8.60 vol. % EPON 828, $\blacklozenge$ 6.57 vol. % DER 332, — Tsai-Hill Theory, ---- Stowell-Liu Theory.

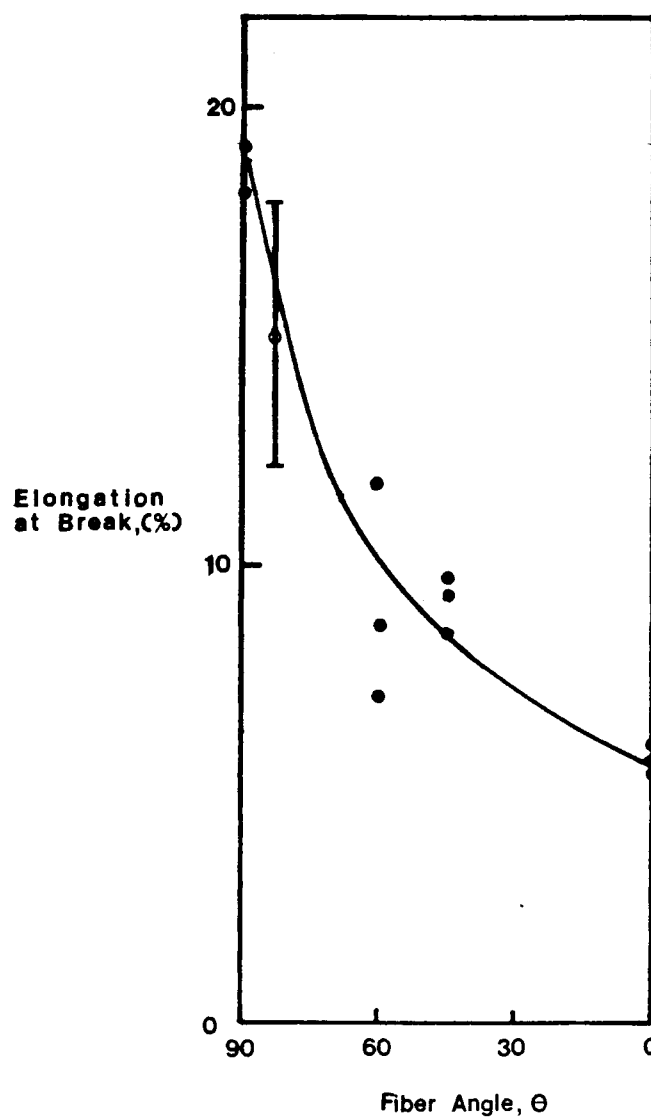


Figure 72. The angular dependence of the elongation at break for 2.88 vol. % EPON 828/NMA (90 phr) composite. ○ EPON 828, ● EPON 828 composite.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

In this chapter the major conclusions resulting from the present experimental study are summarized, and the recommendations for further studies are given.

VII.1 CONCLUSIONS

The highly crosslinked epoxy resins gave rise to the isotropic scattering patterns and applying tensile stresses resulted in very little scattering changes. The epoxy resins are believed to be microporous based on the experiments on liquid epoxy resins which resulted in the similar scattering patterns. The dynamic scattering studies on the epoxy resins indicate the failure process as a catastrophic dynamic process with fractures initiating from surface or internal flaws. The crack propagates very fast across the whole sample in a very short time to complete failure.

The Kevlar^R fibers are microporous giving rise to equatorially elongated anisotropic scattering patterns. These microvoids can be partially filled by liquid epoxy. Based on comparisons of the volume fraction of the microvoids obtained by SAXS absolute intensity measurements and by the density measurements, two sizes of microvoids are present in the Kevlar^R 49 fibers--one in the range of a few hundred angstroms and the other much larger. Degradation of Kevlar^R 49 fibers is accompanied by an increase in the volume fraction of voids and an increase in

the average radius of gyration of the smaller microvoids. Applying tensile stresses results in an increase in the scattering intensities and in the volume fraction of smaller microvoids. The average radius of gyration of these microvoids remained constant, and hence the number of these smaller microvoids must have increased in order to account for increased scattering intensities. It is thus concluded that the failure of Kevlar^R 49 fibers is accompanied by the increase in number of smaller microvoids and the enlargement of the larger microvoids along the fiber axis direction. When the Kevlar^R 49 fibers were examined under a scanning electron microscope, the fibers split readily, and some structural defects were observed. The degraded Kevlar^R 49 fibers showed roughening of the surfaces.

Low volume fraction unidirectional Kevlar^R 49 fiber reinforced epoxy composites gave rise to the anisotropic scattering patterns perpendicular to the fiber axis direction, and it is believed these scatterings are due to voids within the fibers and voids entrapped along the fiber matrix interface during processing. The dynamic scattering studies on the composites indicate the failure as a catastrophic dynamic process, fracture initiating in the epoxy matrix and the fibers not being able to carry the load, thus failing catastrophically as well. The failure is thus instantaneous once incipient failure occurs. When the fractured surfaces of composites were examined using an SEM, fiber splits and fiber pullouts were observed. When the fiber reinforcement angles were 0 degree, 30 degrees and 45 degrees, the fiber skin had pulled apart giving rise to the wedge-shaped fiber splits.

The mechanical investigation results showed the composite moduli, the composite strengths and the elongations at break decreasing as the angle between the fibers and the loading axis increase. The composite modulus was approximately equal to the modulus of the epoxy resins below fiber angles of about 50 degrees. The tensile strength of the composites with fiber angles less than 60 degrees was lower than the tensile strength of the epoxy resin matrices. The strength of high volume percent composites was lower than the low volume fraction composites when the fiber angles were 45 degrees and 0 degree. The explanation of the reason why there is an angular dependence of the ultimate strengths of composites, when it was shown by small angle X-ray scattering experiments that the incipient failures occur within the matrix regardless of the angle of fiber reinforcements, can be inferred from the results of scanning electron microscopie observations where it was shown the fibers fail by extensive splitting when the composite is loaded along the fiber axis direction. On the other hand, when the composite is loaded in the directions other than along the fiber axis direction, the splitting of fibers are less extensive. Thus the fibers carry some of the applied load before they fracture by splitting and debonding mechanisms. These mechanisms are most effective along the fiber axis direction.

VII.2 RECOMMENDATIONS

The following recommendations for further study of the problem of the failure mechanisms in the Kevlar^R fiber reinforced epoxy composites are made:

1. Continued analysis of the quantitative small angle X-ray diffraction data to determine both the volume fraction of microvoids and the microvoids size distribution in degraded Kevlar^R fibers, epoxies and the composites are recommended for further study.
2. Dynamic scattering experiments as a function of time are recommended for epoxies and the composites not only at room temperature but at varying temperature.
3. Dynamic scattering experiments on Kevlar^R fiber reinforced matrices other than the epoxy resins are recommended so that one can study the failure mechanisms in softer and tougher matrices where it is known that the incipient failures occur in the fibers, the matrices being able to deform plastically.

REFERENCES

REFERENCES

1. Adams, D. F. and D. R. Doner, J. Comp. Mat. 1, 152 (1967).
2. Agarwal, B. D. and J. N. Narang, Fibre Sci. and Tech. 10, 37 (1977).
3. Alexander, L. E., X-ray Diffraction Methods in Polymer Science, Wiley-Interscience, New York (1969).
4. Allen, F. J. and W. M. Hunter, J. App. Chem., London, 7, 86 (1957).
5. Anderson, H. C., SPE J. 16, 1241 (1960).
6. Ashton, J. E., J. C. Halpin and P. H. Petit, Primer on Composite Materials: Analysis, Technomic Publishing Co., Stamford, Conn. (1969).
7. Aveston, J. and A. Kelly, J. Mat. Sci. 8, 352 (1973).
8. Azzi, V. D. and S. W. Tsai, Exp. Mech. 5, 283 (1965).
9. Ballou, J. W., Polym. Preprint 17, 75 (1976).
10. Bascom, W. D. and J. B. Romans, Ind. Eng. Chem. Prod. Res. Develop. 7, 172 (1968).
11. Beahan, P., M. Bevis and D. Hull, Phil. Mag. 24, 1267 (1971).
12. Blades, H., U.S. Patent 3,767,756 (1973).
13. Bobalek, E. G., E. R. Moore, S. S. Levy and C. C. Lee, J. Appl. Poly. Sci. 8, 625 (1964).
14. Bodaghi, H., M.S. Thesis, The University of Tennessee, Knoxville (1982).
15. de Boer, J. H., Trans. Faraday Soc. 32, 10 (1936).
16. Bohn, C. R., J. R. Schaefgen and W. O. Statton, J. Poly. Sci. 55, 531 (1961).
17. van den Boogart, A., Physical Basis of Yield and Fracture Conference Proceedings, Oxford (1966), p. 167.
18. Broutman, L. J. and F. J. McGarry, J. Appl. Poly. Sci. 9, 609 (1965).

19. Brown, H. and E. Kramer, J. Macromol. Sci., Phy. Ed. B19, 487 (1981).
20. Brown, J. R. and D. K. C. Hodgeman, Polymer 23, 365 (1982).
21. Bueche, F., J. Appl. Phys. 26, 1133 (1955).
22. Bueche, F., J. Appl. Phys. 28, 784 (1957).
23. Bueche, F., J. Appl. Phys. 29, 1231 (1958).
24. Burchill, P. J., J. Mat. Sci. 13, 2275 (1978).
25. Carothers, W. H., Chem. Rev. 8, 402 (1931).
26. Cartz, L., Nature 178, 1115 (1957).
27. Castan, P., Brit. Patent 518,057.
28. Cherepanov, G. P., Mechanics of Brittle Fracture, McGraw-Hill Inc., New York (1979).
29. Christensen, R. M., J. of Rheology 25, 517 (1981).
30. Christiansen, A. and J. B. Shortall, J. Mat. Sci. 11, 1113 (1976).
31. Cook, J. and J. E. Gordon, Proc. Roy. Soc. A282, 508 (1964).
32. Cooper, G. A., J. Mech. Phys. Solids 14, 103 (1966).
33. Cooper, G. A. and M. R. Piggott, Fracture, Vol. 1, Waterloo, Canada (1977), p. 557.
34. Corten, H. T., Fundamental Aspects of Fiber Reinforced Plastic Composites, Interscience, New York (1968), p. 89.
35. Cuthrell, R. E., J. Appl. Poly. Sci. 11, 949 (1967).
36. Cuthrell, R. E., J. Appl. Poly. Sci. 12, 955 (1968).
37. Cuthrell, R. E., J. Appl. Poly. Sci. 12, 1263 (1968).
38. Dearborn, E. C., R. M. Fuoss and A. F. White, J. Poly. Sci. 16, 20 (1955).
39. Dobb, M. G., D. J. Johnson, A. Majeed and B. P. Saville, Polymer 20, 1284 (1979).
40. Dobb, M. G., D. J. Johnson and B. P. Saville, Trans. Roy. Soc. Lon. A294, 483 (1979).

41. Dobb, M. G., D. J. Johnson and B. P. Saville, J. Poly. Sci. Poly. Phys. Ed. 15, 2201 (1977).
42. Dobb, M. G., D. J. Johnson and B. P. Saville, J. Poly. Sci. Poly. Symposium 58, 237 (1977).
43. Doyle, M. J., A. Maranci, E. Orowan and S. T. Stork, Proc. Roy. Soc. Lon. A329, 137 (1972).
44. Dusek, K., M. Bleha and S. Lunak, J. Poly. Sci. Poly. Chemistry Ed. 15, 2393 (1977).
45. Dusek, K., J. Plestil, F. Lednický and S. Lunak, Polymer 19, 393 (1978).
46. Eagles, D. B., B. F. Blumentritt and S. L. Cooper, J. Appl. Poly. Sci. 20, 435 (1976).
47. Erath, E. H. and M. Robinson, J. Poly. Sci. C(3), 65 (1960).
48. Erath, E. H. and R. A. Spurr, J. Poly. Sci. 35, 390 (1958).
49. Fellers, J. and A. Golovoy, J. Appl. Poly. Sci. 15, 731 (1971).
50. Flory, P. J., J. Am. Chem. Soc. 63, 3083 (1941).
51. Flory, P. J., Principles of Polymer Chemistry, Cornell University Press, Ithaca (1953).
52. Flory, P. J., Proc. Roy. Soc. Lon. A234, 60 (1956).
53. Fisch, W. and W. Hofmann, J. Poly. Sci. 12, 497 (1954).
54. Fischer, R. F., J. Poly. Sci. 44, 155 (1960).
55. Gent, A. N., J. Mat. Sci. 5, 925 (1970).
56. Gillham, J. K., Poly. Eng. Sci. 19, 676 (1979).
57. Griffiths, R. and D. G. Holloway, J. Mat. Sci. 5, 302 (1970).
58. Grimes, G. C. and J. M. Whitney, SAMPE Quarterly, July 1 (1974).
59. Guinier, A., X-ray Diffraction, W. H. Freeman and Co., San Francisco (1963).
60. Guinier, A. and G. Fournet, Small Angle Scattering of X-rays, John Wiley, New York (1955).

61. Halpin, J. C. and N. J. Pagano, J. Comp. Mat. 3, 720 (1969).
62. Hale, D. K. and A. Kelly, Ann. Rev. Mat. Sci. 2, 405 (1972).
63. Hancock, T. A., J. E. Spruiell and J. L. White, J. Appl. Poly. Sci. 21, 1227 (1977).
64. Hancox, N. L., J. Mat. Sci. 12, 884 (1977).
65. Hancox, N. L., Rev. Def. Beh. of Mat. 2, 53 (1977).
66. Hashin, Z. and B. W. Rosen, J. Appl. Mech. 86, 223 (1964).
67. Hendricks, R. W., J. Appl. Cryst. 11, 15 (1978).
68. Hendricks, R. W., S. Suehiro and J. S. Lin, Bull. Am. Phys. Soc. 27, 357 (1982).
69. Hermans, P. H., D. Heikens and A. Weidinger, J. Poly. Sci. 35, 145 (1959).
70. Hill, R., Proc. Roy. Soc., Series A 193, 281 (1948).
71. Hill, R., The Mathematical Theory of Plasticity, Oxford University Press, London (1950), p. 317.
72. Hosemann, R., A. Schonfeld and W. Wilke, Advances in Structure Research by Diffraction Methods, Vol. 3, R. Brill and R. Mason editors, Pergamon Press, Oxford (1970), pp. 101-172.
73. Houwink, R., Trans. Faraday Soc. 32, 122 (1936).
74. Jackson, P. W. and D. Cratchley, J. Mech. Phys. Solids 14, 49 (1966).
75. Jaffe, M., Am. Chem. Soc. Poly. Preprint 19, 355 (1978).
76. Kaelble, D. H., Epoxy Resin: Chemistry and Technology, C. A. May and Y. Tanaka editors, Marcel Dekker, New York (1973), Chapter 5.
77. Kambour, R. P., Appl. Poly. Sci. Symposia 7, 215 (1968).
78. Kambour, R. P., J. Poly. Sci. D-7, 1 (1973).
79. Kambour, R. P. and R. R. Russell, Polymer 12, 237 (1971).
80. Kausch, H. H., Polymer Fracture, Springer-Verlag, Berlin (1978).
81. Kelly, A. and G. J. Davies, Metall. Reviews 10, 1 (1965).

82. Kelly, A. and G. J. Davies, *Metall. Reviews* 10, 37 (1965).
83. Kelly, A. and W. R. Tyson, *J. Mech. Phys. Solids* 13, 329 (1965).
84. Kelly, A. and W. R. Tyson, High Strength Materials, Wiley, New York (1965), p. 578.
85. Kenyon, A. S. and L. E. Nielsen, *J. Macromol. Sci. Chem. Edition A-3*, 275 (1969).
86. Kline, R. A. and F. H. Chang, *J. Comp. Mat.* 14, 315 (1980).
87. Kohn, E. J., A. G. Sands and R. C. Clark, *Ind. Eng. Chem. Prod. Res. Dev.* 7, 179 (1968).
88. Konopasek, L. and J. W. S. Hearle, *J. Appl. Poly. Sci.* 21, 2791 (1977).
89. Kratky, O. and G. Miholic, *J. Poly. Sci. Part C-2*, 449 (1963).
90. Kreibich, V. T. and R. Schmid, *J. Poly. Sci. Symposium* 53, 177 (1975).
91. Kulkarni, H. T., Ph.D. Dissertation in Mechanical Engineering, The University of Tennessee, Knoxville (1976).
92. Kwei, T. K., *J. Poly. Sci. A-1*, 2985 (1963).
93. Kwolek, S. L., U.S. Patent 3,600,350 (1971).
94. Kwolek, S. L., U.S. Patent 3,671,542 (1972).
95. Kwolek, S. L., P. W. Morgan and W. R. Sorensen, U.S. Patent 3,063,966 (1962).
96. Labana, S. S., S. Newman and A. J. Chomppff, Polymer Networks, A. J. Chomppff and S. Newman editors, Plenum Press, New York (1971), o. 453.
97. Lauterwasser, B. D. and E. J. Kramer, *Phil. Mag.* A39, 469 (1979).
98. Lee, H. and K. Neville, Handbook of Epoxy Resins, McGraw-Hill, New York (1967).
99. Legrand, D. G., R. P. Kambour and W. R. Haaf, *J. Poly. Sci. A2* 10, 1565 (1972).
100. Lewis, A. F., M. J. Doyle and J. K. Gillham, *Poly. Eng. Sci.* 19, 683 (1979).
101. Lilley, J. and D. G. Holloway, *Phil. Mag.* 28, 215 (1973).

102. Lin, J. S., R. W. Hendricks, L. A. Harris and C. S. Yust, J. Appl. Cryst. 11, 621 (1978).
103. Luzzati, V., X-ray Optics and X-ray Microanalysis, H. H. Pattee, V. E. Cosslett and A. Engstrom editors, Academic Press (1963).
104. Marom, G. and E. F. T. White, J. Mat. Sci. 7, 1299 (1972).
105. Matyi, R. J. and B. Crist, Jr., J. Poly. Sci. Poly. Phys. Ed. 16 (1978).
106. Matyi, R. J., D. R. Uhlmann and J. A. Koutsky, J. Poly. Sci. Poly. Phys. Ed. 18, 1053 (1980).
107. May, C. A. and Y. Tanaka, Editors Epoxy Resins: Chemistry and Technology, Marcel Dekker, Inc., New York (1973).
108. Misra, S. C., J. A. Mason and L. H. Sperling, Epoxy Resin Chemistry, R. S. Bauer, Editor ACS Symposium Series 114, Washington, D.C. (1979), p. 157.
109. Morgan, R. J., J. Appl. Poly. Sci. 23, 2711 (1979).
110. Morgan, R. J. and E. T. Mones, UCRL-84016 Preprint, Lawrence Livermore Laboratory (1980).
111. Morgan, R. J., E. T. Mones and W. J. Steele, UCRL-84949 Preprint, Lawrence Livermore Laboratory (1980).
112. Morgan, R. J., E. T. Mones, W. J. Steele and S. B. Deutscher, UCRL-83875 Preprint, Lawrence Livermore Laboratory (1980).
113. Morgan, R. J., E. T. Mones, W. J. Steele and S. B. Deutscher, UCRL-84208 Preprint, Lawrence Livermore Laboratory (1980).
114. Morgan, R. J. and J. E. O'Neal, J. Mat. Sci. 12, 1966 (1977).
115. Morgan, R. J. and J. E. O'Neal, J. Macromol. Sci. B-15, 139 (1978).
116. Morgan, R. J. and J. E. O'Neal, Poly. Plast. Tech. and Eng. 10(1), 49 (1978).
117. Morgan, R. J., J. E. O'Neal and D. L. Fanther, J. Mat. Sci. 15, 751 (1980).
118. Morgan, R. J., J. E. O'Neal and D. B. Miller, J. Mat. Sci. 14, 109 (1979).
119. Mullin, J. V., J. M. Berry and A. Gatti, J. Comp. Mat. 2, 82 (1968).

120. Mullin, J. V. and V. F. Mazzio, J. Mech. Phys. Solids 20, 391 (1972).
121. Murayama, T. and J. P. Bell, J. Poly. Sci. A-2, 8, 437 (1970).
122. Nelson, B. E. and D. T. Turner, J. Poly. Sci. A-2, 10, 2461 (1972).
123. Nielsen, L. E., J. Macromol. Sci.- Rev. Macromol. Chem. C-3, 69 (1969).
124. Nielsen, L. E., J. Appl. Phys. 41, 4626 (1970).
125. Northolt, M. G., Eur. Poly. Jour. 10, 799 (1974).
126. Northolt, M. G. and V. Aartsen, J. Poly. Sci. Symposia 58, 283 (1977).
127. Parrat, N. J., Rubber Plastics Age 263 (1960).
128. Patrick, R. L., W. G. Gehman, L. Punbar and J. A. Brown, J. Adhesion 165 (1971).
129. Penn, L. and F. Larson, J. Appl. Poly. Sci. 23, 59 (1979).
130. Penn, L., H. A. Newey and T. T. Chiao, J. Mat. Sci. 11, 190 (1976).
131. Pilz, I., J. Colloid and Interface Sci. 30, 140 (1969).
132. Pilz, I. and O. Kratky, J. Colloid and Interface Sci. 24, 211 (1967).
133. Potter, W. G., Epoxide Resins, Plastics Institute, London (1970).
134. Proctor, B. A., Physical Basis of Yield and Fracture Conference Proceedings, Oxford (1966), p. 218.
135. Pruneda, C. O., W. J. Steele, R. P. Kershaw and R. J. Morgan, UCRL-85744 Preprint, Lawrence Livermore Laboratory (1981).
136. Racich, J. L. and J. A. Koutsky, J. Appl. Poly. Sci. 20, 2111 (1976).
137. Regel, V. R., Fracture, Vol. 4, Waterloo, Canada (1977), p. 155.
138. Rosen, B. W., AIAA Jour. 2, 1985 (1964).
139. Rosen, B. W., Fiber Composite Materials, American Society for Metals, Cleveland (1965), p. 37.
140. Sarkar, K., Ph.D. Dissertation in Engineering Science, The University of Tennessee, Knoxville (1980).
141. Schechter, L., J. Wynstra and R. P. Kurkijy, Ind. Eng. Chem. 48, 94 (1956).

142. Schneider, N. S., J. F. Sprouse, G. L. Hagnauer and J. K. Gillham, Poly. Eng. Sci. 19, 304 (1979).
143. Selby, K. and L. E. Miller, J. Mat. Sci. 10, 12 (1975).
144. Shaffer, B. W., AIAA Jour. 2, 348 (1964).
145. Shen, Y., M.S. Thesis in Polymer Engineering, The University of Tennessee, Knoxville (1981).
146. Sih, G. C. and E. P. Chen, Mechanics of Fracture Vol. 6: Cracks in Composite Materials, Martinus Nijhoff Publishers, Hague (1981), p. XXII.
147. Simmens, S. C. and J. W. S. Hearle, J. Poly. Sci. Poly. Phys. Ed. 18, 871 (1980).
148. Slutsker, L. I., L. E. Utevskii, Z. Chereiskii and K. E. Perepelkin, J. Poly. Sci. Poly. Symposium 58, 339 (1977).
149. Statton, W. O., J. Poly. Sci. 22, 385 (1956).
150. Statton, W. O., J. Poly. Sci. 58, 205 (1962).
151. Statton, W. O., Newer Methods of Polymer Characterization, K. Bacon Editor, Interscience Publishers, New York (1964), p. 231.
152. Statton, W. O. and G. M. Goddard, J. Appl. Phys. 28, 1111 (1957).
153. Statton, W. O. and L. C. Hoffman, J. Appl. Phys. Series 2 31, 404 (1960).
154. Stowell, E. Z. and T. S. Liu, J. Mech. Phys. Solids 9, 242 (1961).
155. Tanaka, Y. and T. F. Mika, Epoxy Resins: Chemistry and Technology, C. A. May and Y. Tanaka Editors, Marcel Dekker, Inc., New York (1973), Chapter 3.
156. Tetelman, A. S., Composite Materials: Testing and Design ASTM STP 460 American Society for Testing and Materials (1969), p. 473.
157. Theocaris, P. S. and C. A. Stassinakis, J. Comp. Mat. 15, 133 (1981).
158. Tsai, S. W., Fundamental Aspects of Fibre Reinforced Plastic Composites, R. T. Schwartz and H. S. Schwartz Editors, Interscience, New York (1968), Chapter 1.
159. Tsai, S. W. and E. M. Wu, J. Comp. Mat. 5, 58 (1971).

160. Tsai, S. W. and N. J. Pagano, Composite Materials Workshop, S. W. Tsai, J. C. Halpin and N. J. Pagano Editors, Technomic Publishing Co., Stamford, Conn. (1969), p. 233.
161. Uhlmann, D. R., A. L. Renninger, G. Kitchevsky and J. Van der Sande, J. Macromol. Sci. B-12, 153 (1976).
162. Walker, B. E., Jr., C. T. Ewing and R. R. Miller, Ind. Eng. Chem. Prod. Res. Dev. 8, 112 (1969).
163. Ward, I. M., Mechanical Properties of Solid Polymers, Wiley-Interscience, London (1971).
164. Watts, A. A., Editor, Commercial Opportunities for Advanced Composites, ASTM STP 704 American Society for Testing and Materials (1980).
165. Wendorff, J. H. and E. W. Fischer, Kolloid Z. Z. Poly. 251, 884 (1973).
166. Westbrook, P., M.S. Thesis in Polymer Engineering, The University of Tennessee, Knoxville (1982).
167. Whiting, D. A. and D. E. Kline, J. Appl. Poly. Sci. 18, 1043 (1974).
168. Zhurkov, S. N. and V. E. Korsukov, Sov. Phys.- Solid State 15, 2071 (1973).
169. Zhurkov, S. N. and V. S. Kuksenko, Int. J. of Fracture 11, 629 (1975).
170. Zhurkov, S. N., V. S. Kuksenko and D. I. Frolov, Sov. Phys.- Solid State 16, 2201 (1974).
171. Zhurkov, S. N., V. S. Kuksenko and A. I. Slutsker, Sov. Phys.- Solid State 20, 296 (1969).
172. Zhurkov, S. N., V. A. Marikhin and A. I. Slutsker, Sov. Phys.- Solid State 10, 1159 (1959).
173. Zhurkov, S. N., V. A. Marikhin and A. I. Slutsker, Sov. Phys.- Solid State 11, 1060 (1960).
174. Zhurkov, S. N., V. I. Vettegren', V. E. Korsukov and I. I. Novak, Sov. Phys.- Solid State 20, 290 (1969).
175. Zhurkov, S. N., V. A. Zakrevskii, V. E. Korsukov and V. S. Kuksenko, Sov. Phys.- Solid State 22, 2004 (1971).
176. Zhurkov, S. N., V. A. Zakrevskii, V. E. Korsukov and V. S. Kuksenko, J. Poly. Sci. A-2, 10, 1509 (1972).

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