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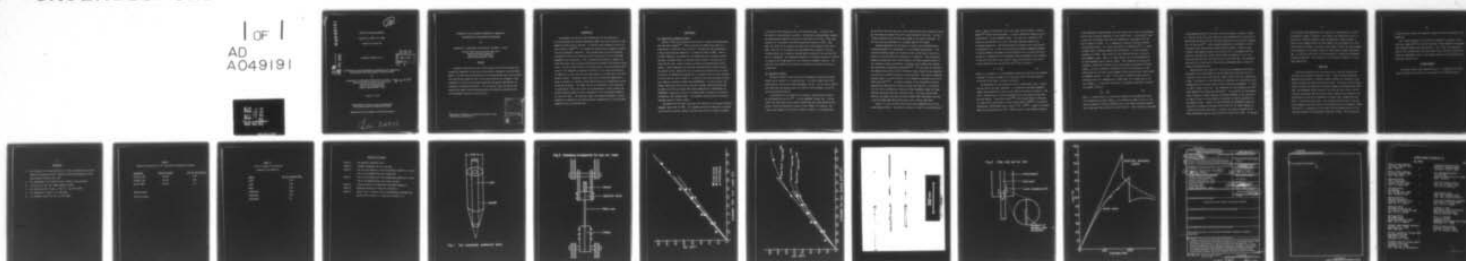
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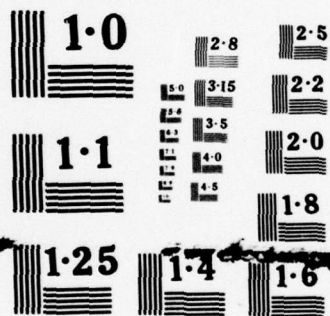
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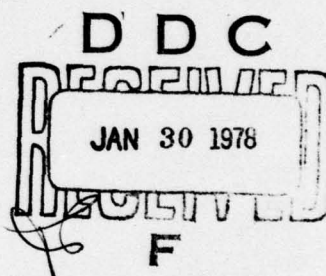
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"EXTRUSION OF SELF REINFORCED THERMOPLASTIC COMPOSITES:
ILLUSTRATED WITH HIGH DENSITY POLYETHYLENE"

by

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EXTRUSION OF SELF REINFORCED THERMOPLASTIC COMPOSITES:
ILLUSTRATED WITH HIGH DENSITY POLYETHYLENE

By

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ABSTRACT

A method is described for solid state coextrusion of self-reinforced and transparent composites of high density polyethylene composed of core and sheath phases. The high density polyethylenes are coextruded below their melting points. The cocylindrical composites have a high tensile modulus and strength, a high orientation for both core and sheath components and possess considerable resistance to core/sheath separation. This resistance to pull out due to compressive and radial stresses developed during the composite coextrusion and not to bonding by epitaxial crystallization.

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INTRODUCTION

A new method, called solid state coextrusion, for the coextrusion of ultra-oriented high density polyethylene (HDPE) films and filaments of high modulus has been recently reported. It involves using preformed, split or tubular billets of HDPE^(1,2). This method has herewith been extended to coextrusion of cocylindrical composites. This has been done by drilling preformed cylindrical billets into a tube form and filling the core with a second HDPE component prior to extrusion. Such a coextrusion can produce a composite in which both sheath and core phases have enhanced orientation and mechanical properties. To gain insight into this coextrusion process and the mechanical properties of the composites so produced, we chose first to study the production of composites in which both core and sheath phases are of HDPE and of the same molecular weight. Subsequent studies were made on coextruded composites in which a difference in molecular weight and/or density for polyethylene distinguished the two phases. This paper details the production of such composites in cocylindrical fiber form as well as the measurements of their modulus and tensile strength properties and an assessment of their core/sheath integrity by "pull out" tests. The techniques appear also generally amenable to insitu production of composites from semicrystalline thermoplastics in this and other geometries such as laminated films.

EXPERIMENTAL

(a) Coextrusion of Composite Fibers.

Billets of HDPE were prepared free of voids in a specially-designed apparatus described elsewhere⁽²⁾. Briefly, pellets of polymer were packed in a press having a cylindrical bore of 0.95 cm. The press was then evacuated by a rotary vacuum pump and immersed in a silicone oil bath at 165°C. After a 15 minute immersion, the pressure on the polymer melt was increased by screwing down a threaded plunger, so inducing crystallization. The press was removed from the bath, cooled to ambient and defect-free polyethylene billets removed. Sheath components were prepared from these billets by drilling out the central section, whereas the core was produced by turning down on a lathe a billet of the appropriate polyethylene to a diameter equal the inner diameter of the drilled out billet (Figure 1). Initially, both core and sheath sections were prepared from DuPont Alathon 7050 (A7050/A7050). In later studies, the polymer combinations were varied to include an Alathon 7026 and Phillips Marlex 6003 core within an Alathon 7050 sheath (abbreviated as A7050/A7026 and A7050/M6003 respectively), and also on Alathon 7050 core within a low density polyethylene sheath (Alathon 2821). The molecular characteristics of the polyethylenes used are listed in Table I.

The composite billets were inserted in the reservoir of an Instron Capillary Rheometer (model TTM) at 110°C. The rheometer outlet was fitted with a polished conical brass die having a nominal extrusion draw ratio of 12 which is defined

as the ratio of die entrance to exit cross sectional areas. Initially, the die outlet is restricted by an arrestor. The Instron crosshead/plunger assembly was then lowered to maintain a pressure of 1000 Atm on the billet. After equilibration for ~15 minutes at the desired extrusion conditions (110°C. , 1000 Atm), the restrictor was removed and coextrusion of the composite fiber initiated. The first ~15 cm length of the coextruded fiber composite is of ever increasing draw ratio, reaching a maximum when the volume of the cone (see Figure 1) is exhausted. The subsequent extrudate is of constant draw and is limited in length by the volume capacity of the cylindrical rheometer reservoir. The outer and inner diameter of the composite extrudates were 0.278 and 0.115 cm respectively.

(b) Mechanical Testing.

The break strength of the cocylindrical polyethylene composite was determined using an Instron in its extension mode. The tensile modulus was determined using an Instron strain gage extensometer (10 mm). For all tests, samples were taken from the constant draw ratio region of the extrudates, see the Results and Discussion Section.

The resistance of the composite to interfacial separation was assessed by core/sheath pull out tests⁽³⁾. The core embedment lengths (0.5 - 5.0 cm) within the sheath layer was varied by trimming away the sheath peripheral component, leaving the appropriate length of core filament for clamping. The samples were clamped in the Instron as shown in Figure 2. An aluminum block

was drilled so that the fiber core of the composite would pass through the block, but the sheath was mounted flush on the upper surface of the block. The core filament extending below the block was clamped to the Instron crosshead. All pull out tests were performed at a crosshead speed of 0.02 cm/min.

Strength enhancement and resistance to fracture can be obtained when a reinforcing material is incorporated in a low strength polymer matrix. The interfacial bonding between the reinforcing fiber and the matrix plays an important role on the mechanical performance of a composite. Self-reinforcing composites (composites from a single polymer), have been prepared recently in this laboratory using the difference in melting points between high strength and conventional polyethylene morphologies^(4,5). Pull out tests on these polymer composites have shown that the interfacial shear strength of the composites is due mainly to bonding by epitaxial crystallization. The origin of composite bonding, however, is quite different for the composites produced here by solid state coextrusion^(1,2). The adhesive bonding of the coextruded cylindrical components was measured here by pull out tests (see Figure 3). The maximum pull out force is plotted as a function of fiber embedment length for three different coextruded concentric composite fibers: one had an Alathon HDPE 7050 core and sheath; the other two had an Alathon HDPE 7050 sheath; one with a core of Alathon HDPE 7026 and the other a core of Marlex HDPE 6003.

Figure 4 is a plot of the pull out force versus embedment area for the three composite fibers. The slope of such plots is equal to the uniform shear

stress τ , which resists the pull out of the fiber from the sheath. Previous workers^(4,5) have used the parameter τ to assess fiber/matrix bonding (τ_0) by extrapolating τ to zero embedment length. The values of τ obtained in this study (maximum 0.85 MPa), are 6-12% the values previously reported for one polymer composites. The difference may be principally due in the method of evaluation of τ_0 . In pull out experiments performed on embedded filaments of varying diameter and length, the load required to pull out the fiber from the matrix is proportional to the embedded length and diameter of the diameter. If the end of the fiber is not sealed or fused into the matrix, the tensile is then required to pull out the fiber core⁽³⁾ and is given by

$$G = K \frac{L}{d} \quad (1)$$

where K is a constant, L is the embedment length and d the fiber core diameter. A constant (τ_0) must be added on the right hand side of the above equation if the end of the fiber is sealed in the matrix.

An explanation for this relation is that a uniform shear stress τ resists the pull out of the fiber, therefore, τ is constant for the whole embedment length range studied and is given by the slope of the curves in Figure 4. However, a uniform stress is clearly impossible unless the sheath and core have the same modulus. In previous studies^(4,5), the oriented fibers of HDPE were in contact with a melted matrix, either Alathon 7050 at 139^o⁽⁴⁾ or low density polyethylene (Alathon 2820) over a range of 110^o - 139^o⁽⁵⁾. Contact of oriented HDPE with a melted matrix at 132^o - 139^o may result in some epitaxial bonding

at the interface of the two phases, but such process occurs with the simultaneous partial loss of tensile properties of the oriented fiber. In the present study no such loss is possible, since the core component was coextruded within the matrix (sheath) at 110°C. i.e., a temperature substantially below the annealing and melting range. For a fiber core melted in a HDPE matrix⁽⁴⁾, a τ value of about 5 MPa is reported, whereas the corresponding τ for the coextruded composite is 0.8 MPa. These values are less disparate than the τ_0 values at zero embedment length. There is a higher percent error in the determination of actual embedded area at shorter lengths. Since damage due to cutting can influence a significant fraction of very short samples, we believe the extrapolated τ_0 is not as reliable an indication of pull out resistance as is the slope of the pull out force versus embedded surface area plot over a wider range of embedment lengths (1 - 5 cm). A fiber core of diameter d breaks prior to pulling out when it is embedded over a length equal to or greater than a critical length L_c . If the end of the fiber is not bonded to the matrix, the critical length is given by

$$\frac{L_c}{d} = \frac{\sigma_f}{4\tau} \quad (2)$$

where τ is constant and σ_f is the tensile strength of the polyethylene fiber. In our studies the critical length, L_c , was found to be equal to ~8.5 cm. Despite the absence of epitaxial bonding, most of the sheaths developed longitudinal cracks upon fiber core pull out (see Figure 5). These cracks were developed

in the debonding process of the fiber core from the matrix as shown in Figure 6. They are likely due to the inability of the oriented matrix to plastically deform under the pull out stress and which therefore fails as would be expected for a brittle matrix⁽³⁾. Such a debonding mechanism is followed by a purely functional stress which develops between fiber and matrix. Figure 7 shows a typical load extension curve for our results and is in accordance with the curve for a brittle matrix which indicates that the region 0- to -X is not linear and that the fiber core pulls out by a stick-slip mode. Alternatively, the curve for a plastic matrix (low density polyethylene) shows a linear 0X region and different profile.

Some deviation from linearity in the load versus embedment area plots is associated with the development of the aforementioned cracks that result in a periodic stress release and therefore require pull out forces of reduced magnitude. This behavior is not exhibited by a composite with a low density polyethylene matrix and likewise does not suffer from crack development. A τ value -2.5 MPa is found in this case. The coextrusion of a two component concentric fiber composite has interesting implications. In our studies, we used combinations of A7050 as a sheath component with A7030 and M6003 as core components. As shown in Table II we have been able to enhance the tensile properties of the composite fiber. Indeed, for the A7050/A7026 and A7000/A6003 composites the tensile strength was increased from 0.25 GPa for the A7050 component to 0.45 GPa and 0.5 GPa respectively. Similarly, the tensile strength of the A2821 (LDPE)/A7050 composite was estimated to be equal to 0.2 GPa. The results

of the present study demonstrate that coextrusion of polyethylenes of different molecular weights is feasible. This leads to the interesting idea of coextrusion of different molecular weight polyethylenes or other polymers in which the two component phases are fused together and coextruded by the solid state coextrusion method. Extrusion of such composite fibers has been extended to the production of continuous lengths of high molecular weight polyethylene ($M_w = 2 \times 10^5$) at a draw ratio of 25X and resulted in significant enhancement of tensile properties. This subject will be discussed in details in a subsequent publication.

CONCLUSION

Solid state coextrusion has been found to be a versatile technique for the extrusion of concentric composite fibers. These have been prepared by combining polyethylenes of different molecular weights and extruding at temperatures substantially below their melting ranges. Extrusion at this low temperature precludes the formation of epitaxial bonding at the matrix/fiber interface, the "debonding" forces required in the pull out tests reflect the magnitude of the compressional and radial stresses induced in the composites during extrusion as well as the subsequent frictional stress between fiber and matrix. The uniform shear stress τ was evaluated from the slope of the load versus embedment area plots and not from extrapolation to zero embedment length. The value of τ so obtained is of the order 1 MPa and becomes smaller as the molecular weights of the polyethylene components diverge. The incorporation

of high molecular weight core components improves the tensile strength of the composites.

The τ values obtained in this study are comparable to polyester resin-soft glass composites⁽⁶⁾ but are lower than the τ values obtained for polyethylene composites formed from a melted matrix. This is due to the decreased ability of an oriented matrix to deform under stress, with the resultant formation of longitudinal cracks in the sheaths, parallel to the extrusion axis, upon fiber core pull out.

ACKNOWLEDGEMENTS

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TABLE I

Molecular Characteristics for High Density Polyethylenes Studied

<u>Designation</u>	<u>Molecular Weight</u>	<u>Mol. Wt. Distribution</u>
Alathon ⁺ 7050	59.000	2.96
Alathon ⁺ 7026	147.000	4.40
Marlex [*] 6003	195.000	7-13

⁺DuPont Product

^{*}Phillips Product

TABLE II

Tensile Strength of Polyethylene
Components and Composites

<u>Sample</u>	<u>Tensile Strength (GPa)</u>
A7050	0.25
A7026	0.35
M6003	0.40
A7030/A7030	0.25
A7030/A7026	0.45
A7030/M6003	0.5

CAPTIONS FOR FIGURES

- Figure 1: Two component preformed billet
- Figure 2: Clamping arrangement for pull out tests
- Figure 3: Pull out load (Newtons) of the polyethylene composite as a function of the embedded fiber core length (cm)
- Figure 4: Pull out load (Newtons) of the polyethylene composite as a function of the embedded fiber core lateral surface
- Figure 5: Fracture behavior of polyethylene coextruded composites
- Figure 6: Debonding mechanism of fiber core from matrix
- Figure 7: Typical load - extrusion curve of polyethylene coextruded composites with a brittle (—) and plastic matrix (---)

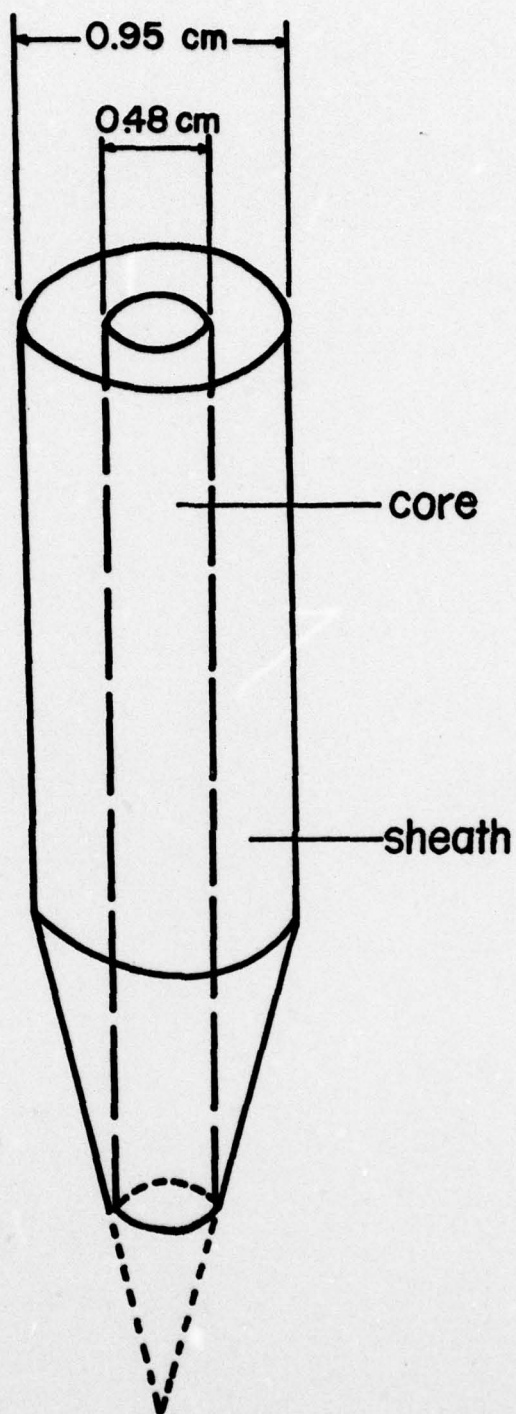
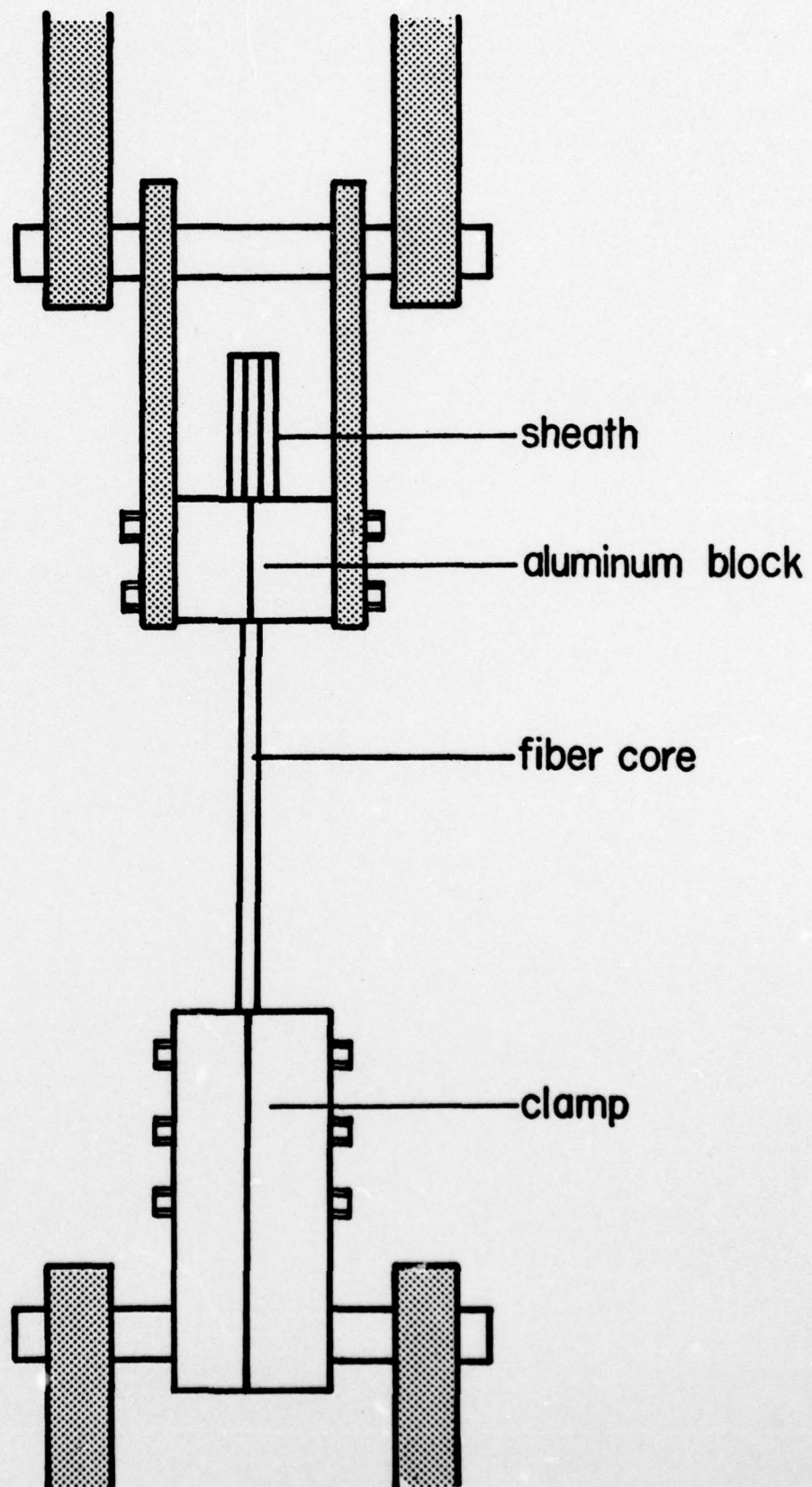
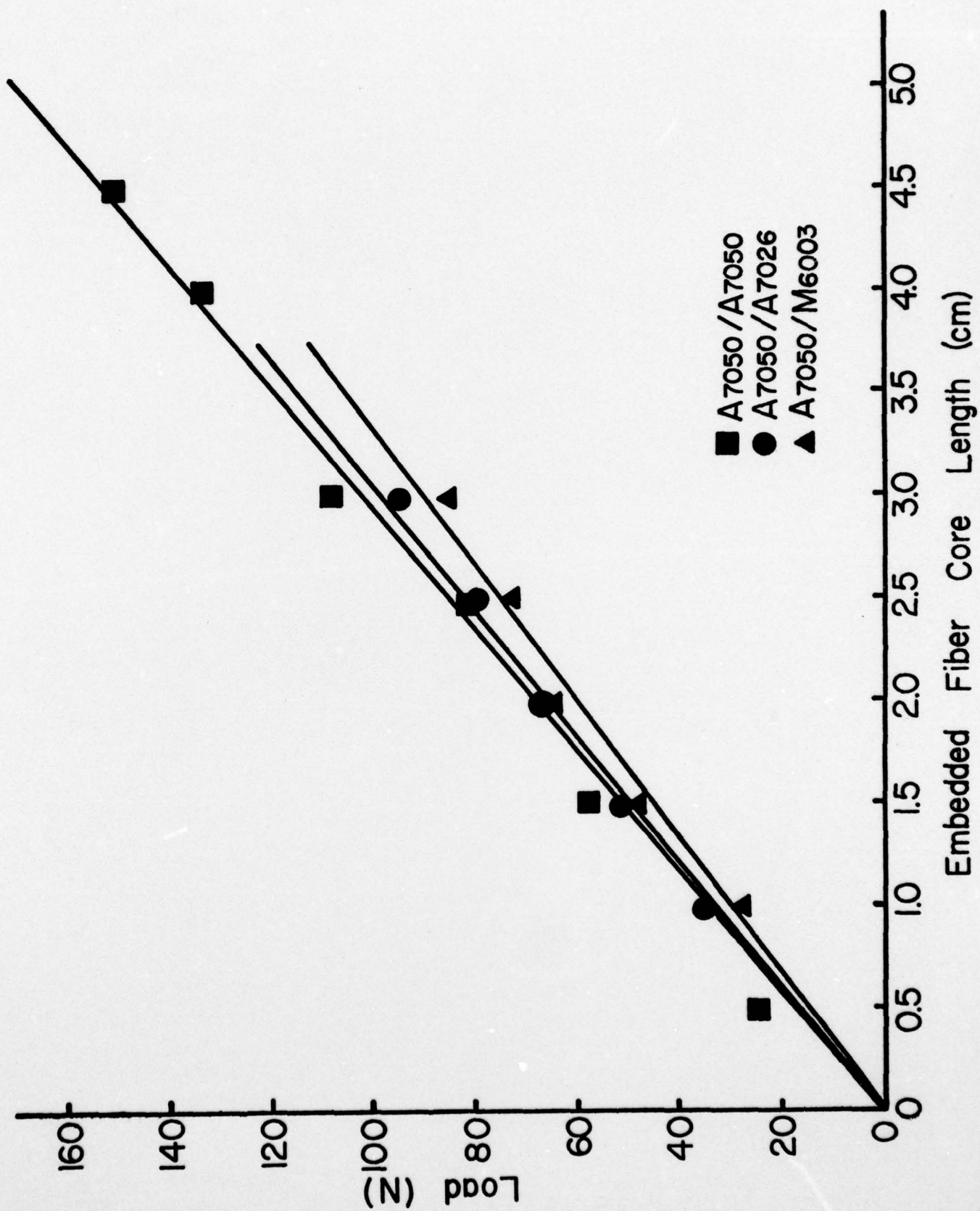
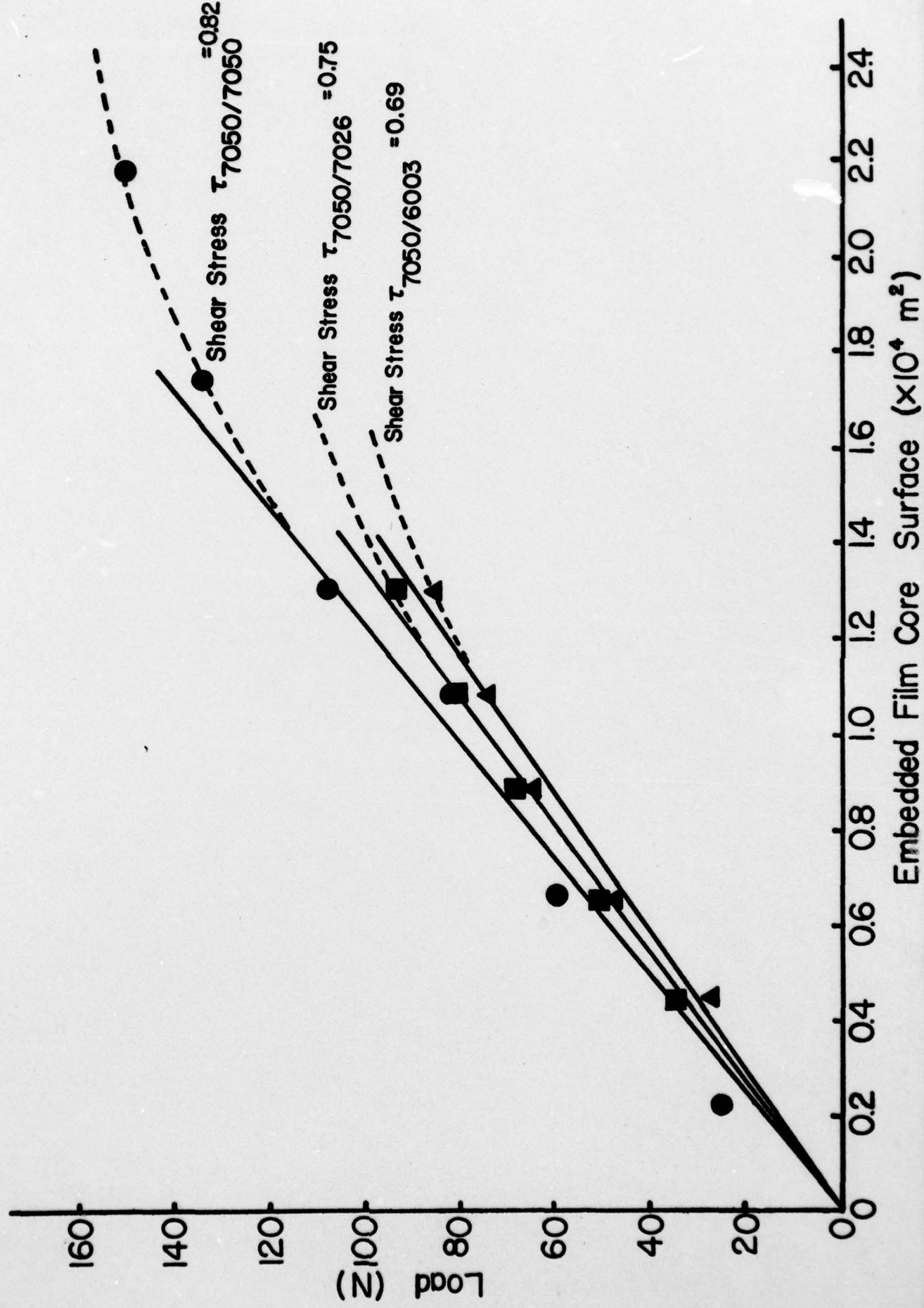


Fig. 1 Two component preformed billet

Fig. 2 Clamping arrangement for pull out tests



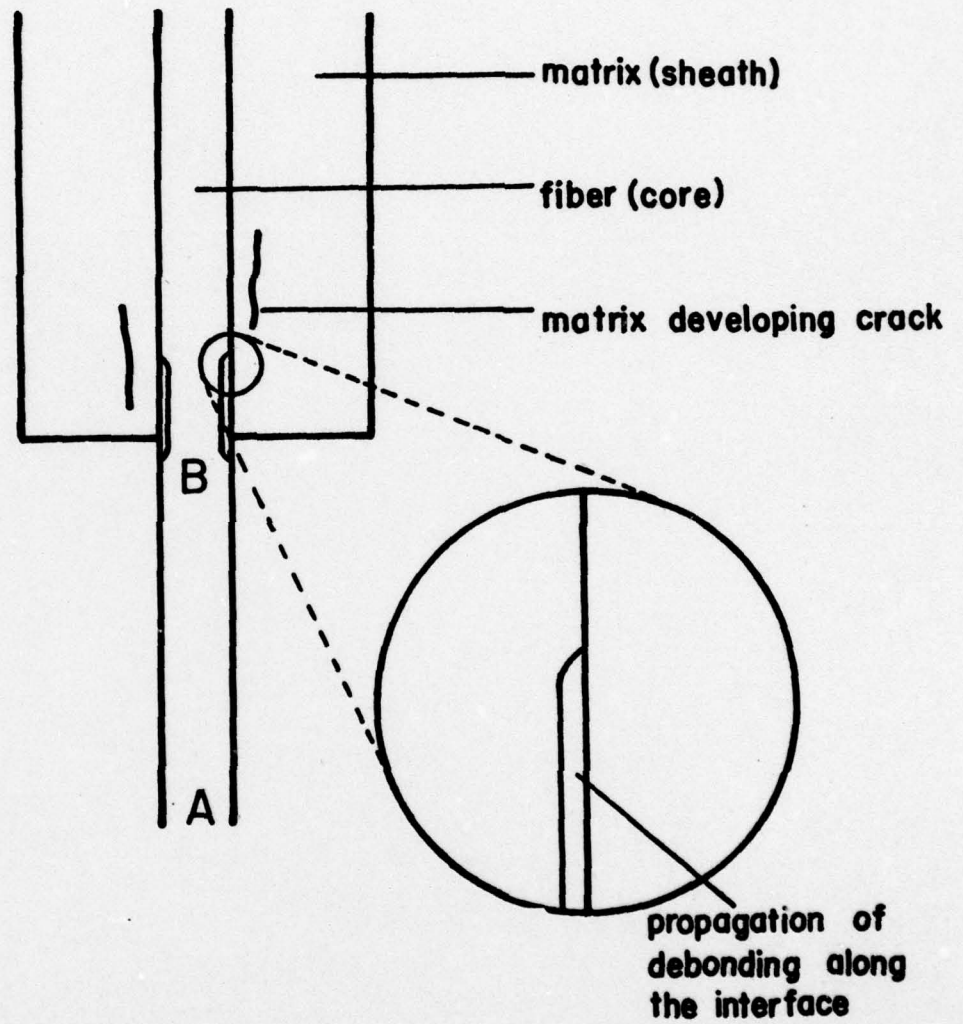


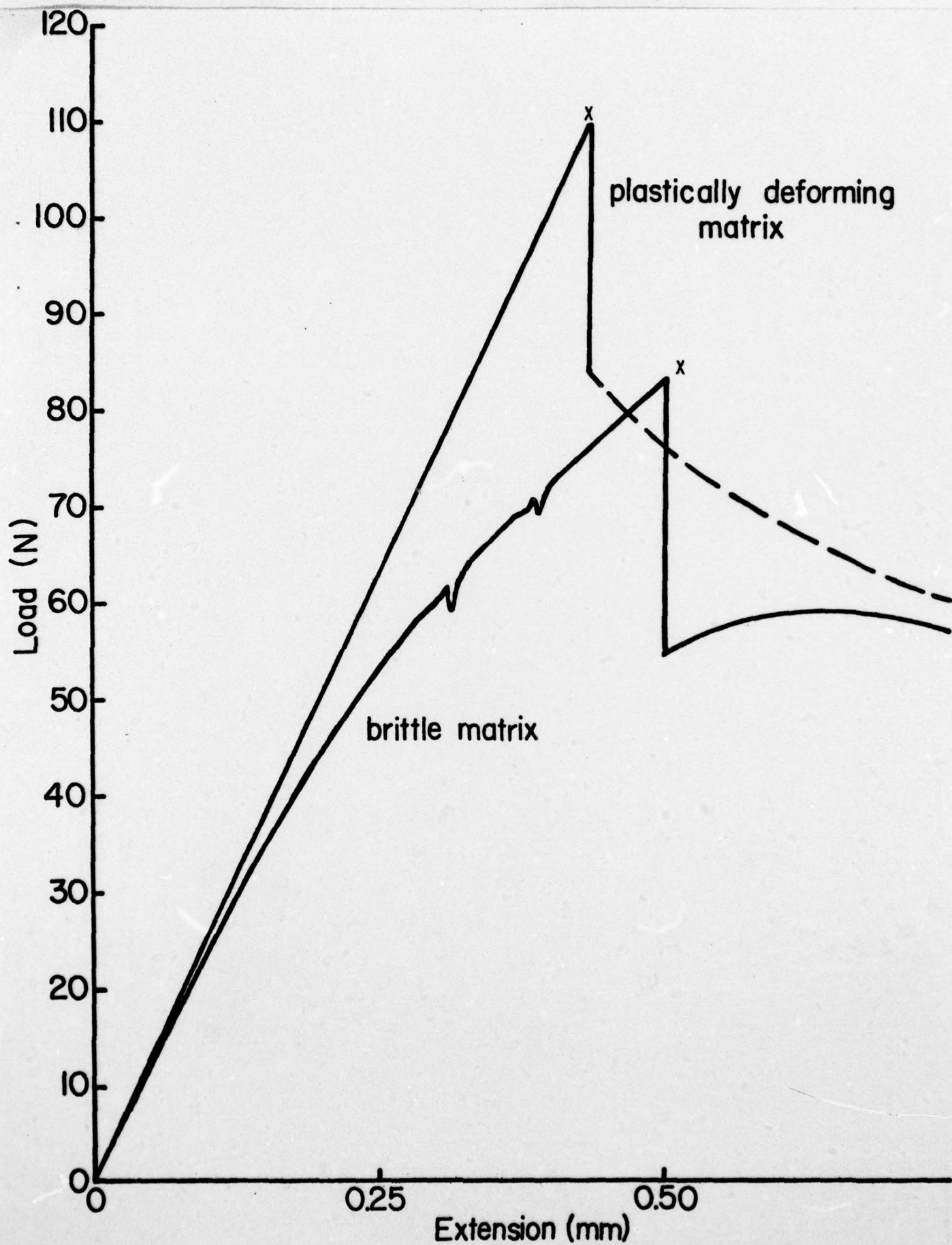


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Fig. 6 Fiber core pull out test





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