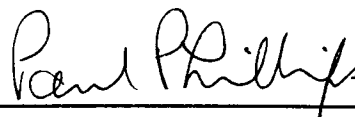


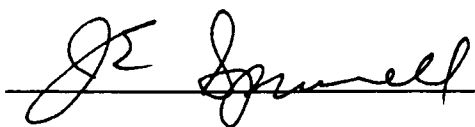
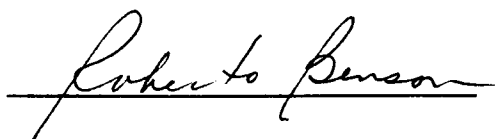
graduate Council:

I am submitting herewith a thesis written by Robert Breiner Allen entitled "Influence of Crystallinity on Mechanical Properties of Poly (ethylene terephthalate), PET, and PET/AS4 Composite." I have examined the final copy of this thesis for form and content and recommend it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Polymer Engineering.



Paul J. Phillips, Major Professor

We have read this thesis
and recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor
and Dean of The Graduate School

***Influence of Crystallinity on Mechanical Properties
of Poly (ethylene terephthalate), PET, and PET/AS4
Composite***

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

Robert Breiner Allen

December, 1994

Dedicated to my wife

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Abstract

Thermoplastic composites show considerable promise for structural applications. Some of the advantages of these materials compared to current thermoset resin composites are the ease of formability, processing ability, damage repair, and bonding as well as better environmental resistance and reprocessing capabilities. For thermoplastic resin matrices capable of some degree of crystallization there is promise of increased toughness, elastic modulus, reduced moisture degradation, and chemical resistance required for use in many aerospace and automotive applications. These properties are thought to vary with the crystallinity of the semi-crystalline resin.

The degree of crystallinity and size of the crystallites in a semi-crystalline polymer have profound effects on the mechanical properties of the polymer and polymer based composites. Therefore, the major objective of this investigation is to evaluate the relationships between mechanical properties and the crystallinity for a nonreinforced polymer of polyethylene terephthalate (PET) and for carbon PAN based fiber reinforced PET composite, PET\AS4. Although PET\AS4 composites are not commonly used in structural applications, insight into the effects of bulk crystalline content on thermoplastic-carbon composites will be provided. This investigation of the mechanical properties, crystallization kinetics, and morphological attributes of PET and its composite with PAN-based carbon AS4 fiber, PET\AS4, has identified several interesting phenomena.

Basic bulk crystallization studies using DSC analysis and mechanical performance testing concluded that, as expected, the tensile modulus increased. The significance lies in the magnitude of that increase. There is a greater increase in the percent change in tensile modulus for the PET\AS4 composite than for the neat polymer. This increase in the percent change in tensile modulus of the composite over the neat polymer suggests improved interface strengths as crystalline content is increased. The improved interface strength will increase the overall strength of the composite until the point that brittle matrix transverse fracture occurs.

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1. Introduction

Thermoplastic composites show considerable promise for structural applications. Some of the advantages of these materials compared to current thermoset resin composites are the ease of formability, processing ability, damage repair, and bonding as well as better environmental resistance and reprocessing capabilities. For thermoplastic resin matrices capable of some degree of crystallization there is promise of increased toughness, elastic modulus, reduced moisture degradation, and chemical resistance required for use in many aerospace and automotive applications. These properties are thought to vary with the crystallinity of the semi-crystalline resin.

It is recognized that the mechanical properties of semi-crystalline thermoplastics depend strongly on the crystalline structure of the polymer. The degree of crystallinity and size of the crystallites in a semi-crystalline polymer have profound effects on the mechanical properties of the polymer, and in order to explain these properties one must have an understanding of the nature of these crystalline regions. Therefore, the major objective of this investigation is to evaluate the relationships between mechanical properties and the crystallinity for a nonreinforced polymer of polyethylene terephthalate (PET) and for graphite fiber reinforced PET composite, PET\AS4.

Although PET\AS4 composites are not commonly used in structural applications, they will provide insight into the effects of bulk crystalline content on thermoplastic-carbon composites. PET is an excellent candidate for this study because of its possible range of crystallinity (0 to 80 percent). The crystalline range is produced using normal crystallization temperatures and elevated pressures as developed by Phillips [1]. Additionally, PET, a semi-crystalline polyester, is one of the best characterized polymers; many crystallinity studies have been performed which can be utilized. This investigation of the mechanical properties, crystallization kinetics, and morphological attributes of polyethylene terephthalate, PET and its composite with PAN-based carbon AS4 fiber, PET\AS4, has identified several interesting phenomena.

Basic bulk characterization studies on the crystallization of PET conclude that under normal processing conditions adequate cooling systems are required to control the quantity of bulk crystallization--cooling rates in excess of 75°C/min are desirable. This is not unusual for thermoplastic materials and is one disadvantage in their application in polymer-carbon composites.

From the tensile test results of both the neat polymer and the composite, the tensile modulus increased as expected. The significance lies in the magnitude of that increase. There is a greater increase in the percent change in tensile modulus for that of the PETAS4 composite than that of the neat polymer. This increase in the percent change in tensile modulus of the composite over the neat polymer suggests improved interface strengths as crystalline content is increased. The improved interface strength will increase the overall strength of the composite until the point that brittle matrix transverse fracture occurs. This is supported by the presence of a maximum in the tensile strength curve as a function of bulk crystalline content and the SEM analysis showing the rise and decline of the presence of hackles. It is hypothesized that the increased moduli above the predicted values are the result of an oriented matrix crystal structure.

It is postulated that annealing of the composite at elevated temperatures in this case 220°C with the applied pressure polymer crystals may align. There are two possible hypotheses for polymer crystal alignment. The first is epitaxial growth between the graphite crystal structure of the fiber and the PET crystal stems. The second hypothesis is that as discussed for the 45% crystalline composite the fiber acts as a simple nucleating agent. Upon annealing and subsequent melting of less than perfect crystals the nuclei are retained on the fiber or are newly generated on the fiber and chain stems align within the microsurfaces of the fiber. Upon chain folding the crystal would be perfectly aligned with the fiber thus allowing the alignment of the tie molecules.

2. Theoretical Background

Techniques have been developed to study the effects of crystallization on the physical properties of both neat polymers and composites. Interpreting the results from these techniques without a basic understanding of the general principles involved could lead to poor analysis and predictions. Therefore, this theoretical and literature review will present the relevant theories of polymer crystallization and polymer based composites, their make-up, modes and mechanisms of failure.

2.1 Composites

The discovery of materials with ever-improving physical properties has been an important aspect in the advancement of engineering. Composites are one of the most recent materials which have added to this advancement. The term composite is a general term and may include natural as well as man made materials. A composite is commonly defined as the combination of a reinforcement material (such as a particle or fiber) in a matrix or binder material. Matrices may include materials such as polymers, ceramics, and metals, while the reinforcements are generally fibers, particles, and whiskers. The reinforcements may be comprised of many of the same materials as the matrices.

The uses of composites have grown steadily since the first glass-reinforced phenolic-nylon fishing pole was developed in 1945. Typical industries using composites include but are not limited to; aerospace, aircraft, automotive, electrical, medical, sporting equipment, and textiles. The attraction of composites stems primarily from their ability to replace standard lightweight, high strength metals or wood with an even lighter-weight higher-strength alternative. Composites may offer additional design flexibilities as well as improving corrosion and wear resistance, low thermal conductivity and possibly an increased fatigue life. However, using composites may increase the costs of manufacturing [2, 3, 4, 5].

2.1.1 Matrices

The matrix of a composite functions in two ways. First, it transfers loads to the reinforcement. Secondly, it protects the reinforcement from adverse environmental effects.

The polymer matrices, also known as resins, are the most common and are divided into two classifications, thermosets and thermoplastics.

Thermosets and thermoplastics differ in their respective intermolecular structures with the thermoset materials being crosslinked in their final state, and the thermoplastic materials generally not crosslinked. Thermosets are generally liquid resins (epoxies) which are heat-activated (cured) to achieve crosslinking of their molecular structure. Basically, a thermoplastic is any polymer which passes through a definite sequence of property changes as temperature is increased (the material softens). Both amorphous and crystalline thermoplastics are glassy at low temperatures and change to rubbery at higher temperatures. This change occurs over a narrow temperature range which is known as the glass transition temperature. Amorphous polymers behave differently from crystalline polymers. As the temperature of the amorphous polymer is increased the elastomeric phase gradually changes to a soft, extendible elastomeric phase, then to gum, and finally to a liquid. Crystalline polymers retain their elastomeric properties until the temperature reaches the melting point. These characteristics of thermoplastics are useful in the molding and shaping of composites because they can be heated, molded into the desired shape and then cooled.

2.1.2 Reinforcements

Reinforcements for composites can be fibers, particles, or whiskers. Each has its own application; however, fibers are the most common in composites because they have the greatest influence on mechanical properties. Fibers have one very long axis and are generally circular in cross-section, although many studies have developed square, star and other configurations. The strength of these fibers lies in the longitudinal direction, and is generated by drawing the fibers. Particles have no preferred orientation; therefore, their shape has far less impact on strength properties than that of fibers. Particles are small compared to fibers, have increased handling ability. Whiskers are single crystals which can be thought of as elongated particles with significantly improved properties. Whiskers are the preferred reinforcement because they are smaller in both length and diameter than fibers, and they provide adequate improvement in mechanical properties, with ease of

handling and manufacturing.

Many types of glass fibers are manufactured today but only four are extensively used in composites: E-glass, S-glass, C-glass, and quartz. E-glass fibers are used when strength and high electrical resistivity are required. S-glass fibers have greater strength properties than E-glass and perform well at elevated temperatures. C-glass is used in corrosive environments because of its chemical stability. Quartz is used in electrical applications where a low dielectric material is required.

The demand for reinforcement fibers with greater strength and moduli than those of glass fibers led to the development of carbon and/or graphite fibers. The preferred methods for making carbon fibers use polyacrylonitrile (PAN), rayon and pitch as starting materials. Each process offers distinct advantages and disadvantages in terms of costs and material properties. PAN-based fibers have good properties with relatively low costs for the standard modulus products. Higher modulus fibers tend to have greater manufacturing costs because of elevated processing temperatures. Pitch-based fibers are lower in cost than PAN-based but can not reach the property levels of PAN fibers. Rayon-based fibers are much more expensive because of higher costs of starting materials, but typically have greater and more uniform properties.

2.2 Polymer Crystallization

Since the onset of polymer science it has been understood that polymer molecules may crystallize. Crystallization is dependent upon the polymer and its molecular structure. The effects of crystallization lead to many concerns in the processing of polymeric materials since they may crystallize during processing. Many factors influence the rate and extent of crystallization for a particular polymer. These factors include processing variables such as cooling rates, orientation in the melt, and fluctuation in the processing temperature around the polymer's melt temperature. Other factors include the tacticity, molar mass of the polymer, extent of branching and additives which have been added to enhance properties.

Crystallization is the process by which an ordered structure is produced from a disordered phase (melt or dilute solution). When the temperature of a polymer melt is reduced to its

melting temperature there is a tendency for the random tangled molecules in the melt to become aligned and form small ordered regions. The ordered regions are called nuclei, and are stable only below the melting temperature. Nuclei are disrupted by thermal motion above the melting temperature. The second step in the crystallization process is growth where the crystal nuclei enlarge due to the attachment of additional chains. Therefore, crystallization is a two step process of nucleation and growth, these steps should be considered separately [6].

2.2.1 Polymer Morphologies

As discussed, many polymers can crystallize to some extent; this is remarkable because of the considerable length of the molecule. Several polymeric factors effect the ability of a polymer to crystallize. These factors include but are not limited to tacticity (structural regularity) of the molecule, absence of large or bulky side chains, the presence of vibrational and rotational motion within the polymer chain, and the mobility of the main chain constituents. Polymers which crystallize either from the melt (and/or annealing such as the ridged polymer of PET) or solution form structures in which the molecules fold upon themselves in a ribbon like fashion. The polymer crystal can take many shapes.

2.2.1.1 Single Crystals

Lamellar single crystals are formed upon the cooling of dilute polymer solutions. A single crystal is one lamella on which the polymer molecules nucleate and crystallize from the solution. Kellar [7] demonstrated the technique by growing polyethylene single crystals from dilute solution. Single crystals are small, and are in the form of small platelets on the order of 100 Å in thickness with the molecular fold composing the top and bottom surfaces, see Figure 1. Growth occurs predominantly along the lateral faces of the single crystal and consists of the folding of molecules along the lateral faces. They generally appear as rhomboids or in the form of hollow pyramids which often collapse upon collection or drying.

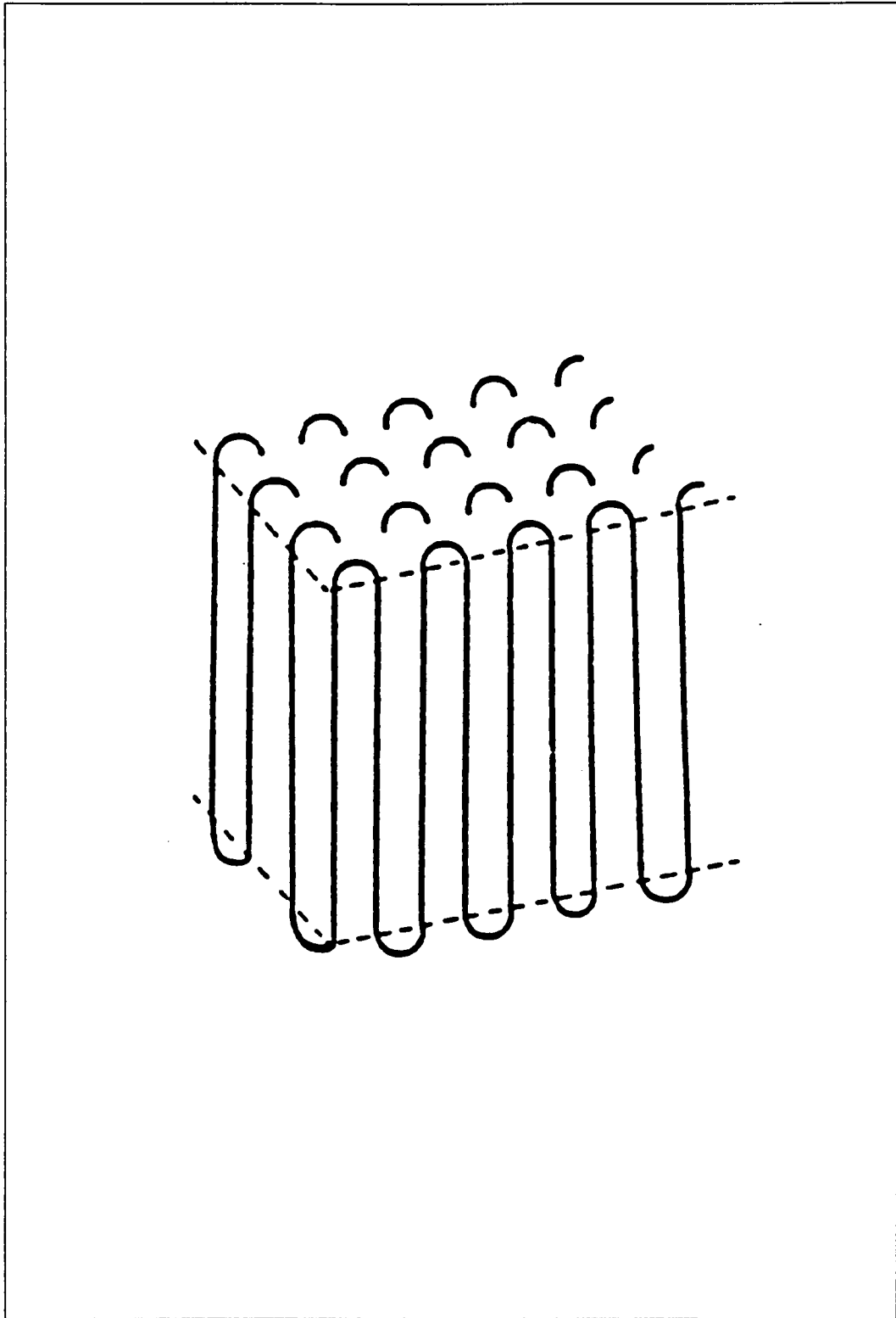


Figure 1: Typical Lamellar Single Crystal.

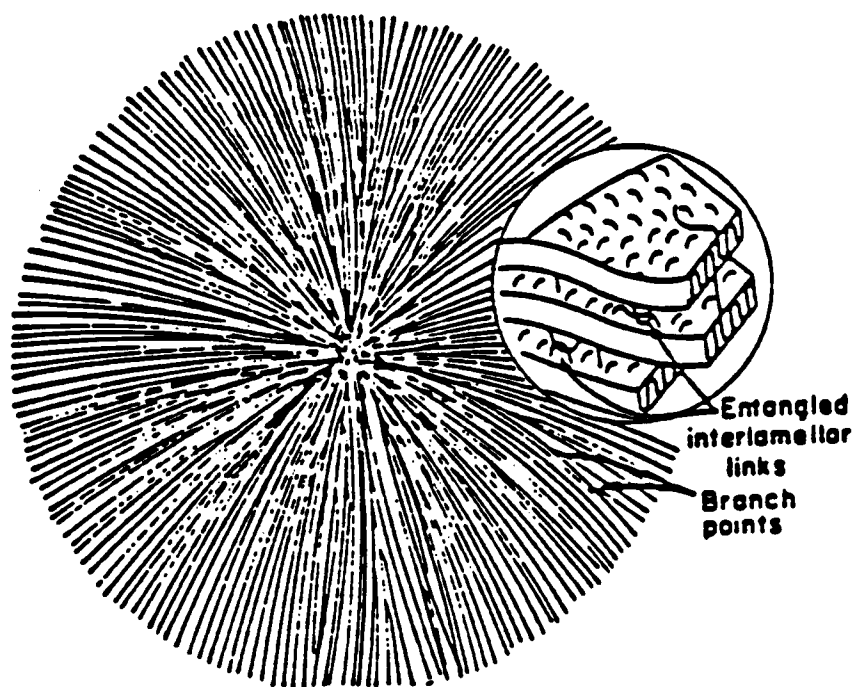


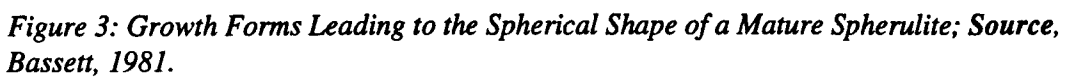
Figure 2: Chain Folded Lamellae of a Polymer Spherulite; Source, Hoffman, et. al., 1976.

2.2.1.2 Spherulites

Polymers crystallized from the melt often exhibit a spherulitic morphology. A spherulite consist of lamellae radiating from a nucleus to form a sphere, until which time it impinges with another spherulite, see Figure 2. The development of a spherulite depends upon its nucleation process. Primary crystallization begins with a single crystal, a stack of single crystals, or an inhomogenous entity, upon which it evolves through sheaf-like morphologies until reaching spherical form. A typical growth pattern was developed by Bassett [8] and is shown in Figure 3. The spherical shape is maintained until impingement resulting in a polyhedral shape. Secondary crystallization can take place within the spherulite, thus transforming portions of the amorphous regions between lamellae into crystalline material. Spherulites from polymers usually exhibit a “maltese cross” when viewed through cross-polars as a result of reorientation of the polarization by the symmetry and orientation of the crystal. Spherulites vary in size according to the polymer system and the crystallization temperature, and pressure, with larger spherulites being formed at higher crystallization temperatures.

2.2.1.3 Axialites

Axialites include intermediate morphologies between single crystals and spherulites. Axialites are collections of crystal lamellae and exhibit characteristics of single crystals and spherulites dependent upon the perspective. Axialites feature a splayed lamellae which yields a less compact structure than that of a sphere, resembling two slightly open books placed back to back. Optically, axialites show little birefringence when viewed normal to their basal plane. Niegisch [9] while working with hedrites revealed that radially oriented fibrous lamellae can form known as ovoids. These lamellae may crystallize in a spirally oriented fashion creating what are termed spiral ovoids, as discovered by Rabek [10]. Later it was suggested by Hearle [11] that the tie molecules may limit the extent of splaying in the axialite.



2.2.2 Crystallization Models

Since polymer crystallization was discovered, there has been a great deal of controversy over the methods by which polymers crystallize. Initially through the process of X-Ray line broadening it was revealed that the polymer crystals were small, but the method by which the molecules arranged themselves was a mystery. Today several theories of polymer crystallization exist.

One of the first models was provided by Herman et al [12] in 1930. This model, known as the Fringed-Micelle, suggested that polymer molecules contain regions of ordered and disordered molecules, see Figure 4a. This model accounted for small crystal size and described why the crystal dimensions are smaller than the molecular length. However, upon the identification of spherulitic morphologies in the 1940's the Fringed-Micelle model was shown to be inaccurate. Spherulitic morphologies were not completely understood until the late 1950's when Jaccodine [13] obtained rhombic shaped crystals of relatively low molecular weight polyethylene from dilute solutions of benzene and xylene. The Jaccodine model was further elaborated by Keller [14], Fischer [15], and Till [16] by working with linear polyethylene. Using electron microscopy and electron diffraction it was concluded that the polyethylene molecules lay with the long chain axis perpendicular to the crystal surface. With this evidence they were able to postulate that the polymer molecules fold back onto themselves after exiting the crystal. These ideas prompted the adjacent reentry model proposed by Keller which postulates that once the polymer molecule exits the crystal folds back upon itself adjacent to the last crystallized segment, see Figure 4b. Keller's model explained the small lamellar thickness, molecular orientation and the surface packing density.

The switchboard reentry model proposed by Flory [17] was introduced in the early 1960's. Flory's model suggested longer folds of polymer molecules which reenter the crystal but are not necessarily adjacent, see Figure 4c. Flory based his model on differences found in the crystalline densities obtained experimentally and those obtained from unit cell dimensions. According to Flory, the lower experimental densities are the result of an amorphous zone and transpire from non-adjacent reentry.

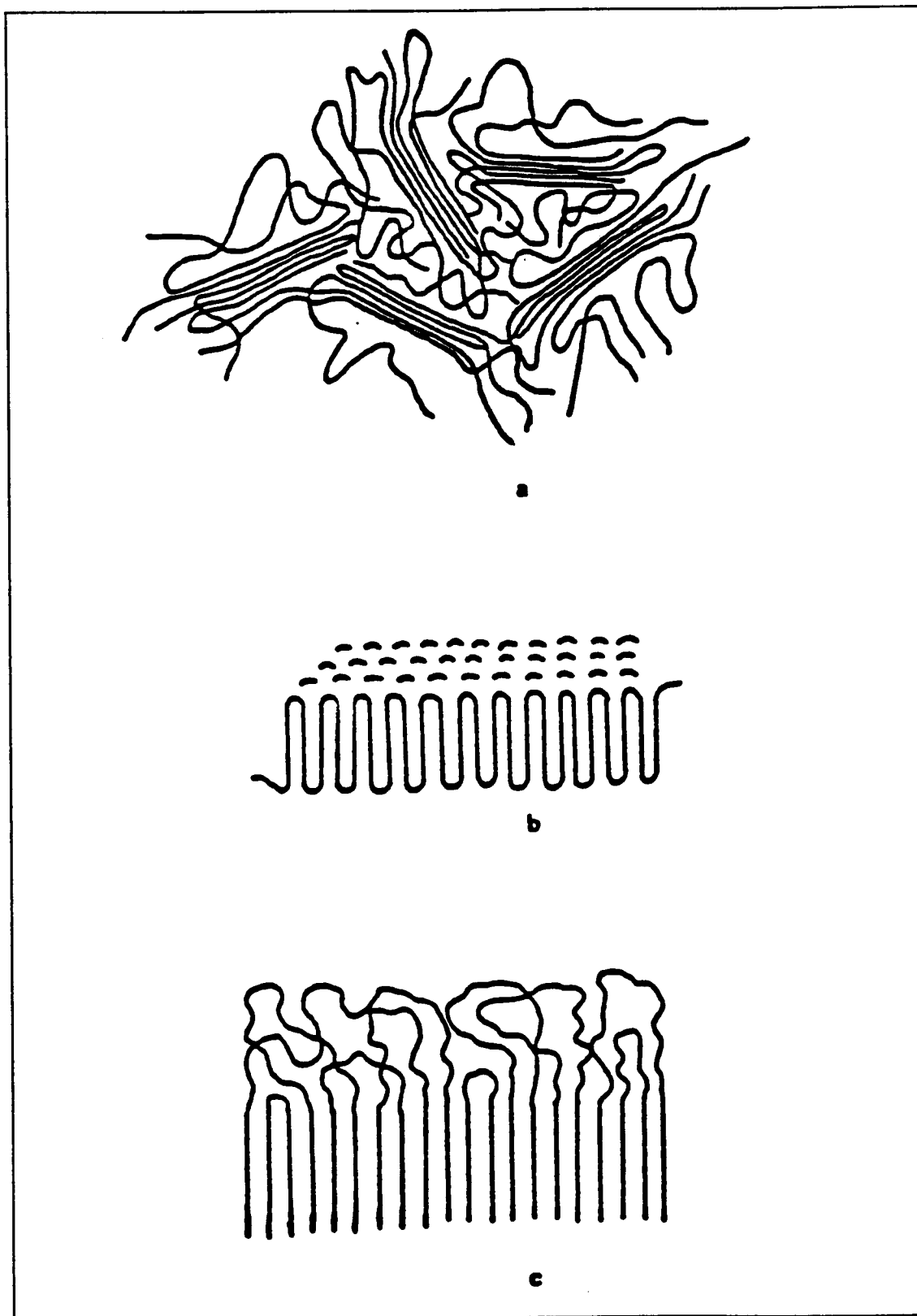


Figure 4: Polymer Crystallization Models: a) Fringed-Micelle, b) Adjacent Reentry, c) Switchboard Reentry

An additional model similar to Flory's Switchboard model was developed by Mandelkern in the 1970's. Mandelkern [18] proposed an interzonal model which implies that the polymer molecules form an ordered amorphous region as they leave the crystal thus resulting in a true disordered state some distance from the crystal's surface.

2.2.3 Nature of Polymer Folding

Many arguments have been made and continue to occur over the nature of the fold surface. These arguments arise from experimental results in areas such as density, neutron scattering, as well as developments concerning the mobility of the crystalline melt. While the physics developed for crystallization are the same for polymers crystallized from either the melt or dilute solutions, these two environments could be no further apart. Single crystals formed in dilute solution have their polymer molecules surrounded by solvent molecules and, therefore, are free from entanglement with other polymer molecules in the uncrystalline state. In the melt, polymer molecules are entangled with each other inhibiting their mobility; therefore, restricting the ability of the molecules to diffuse to the crystal growth front. Additionally, polymers crystallized from the melt do not crystallize in the form of single crystals but rather in the form of spherulites or axialites, these aggregates are composed of many lamellae. Lamellae formed from melt are much harder to study than those developed in dilute solution.

Polymer single crystals have densities which are below those determined from unit cell dimensions using X-Ray diffraction techniques. This discrepancy in the densities is attributed to the amorphous zones resulting from non-adjacent reentry as developed in the switchboard model. In the adjacent reentry model the density discrepancy is attributed to the surface roughening arising from loose loops.

With the advancement of neutron scattering techniques, much information has been gained about the behavior of molecules crystallized from the melt. Neutron scattering enables researchers to study systems other than those of dilute solutions. Neutron scattering is used to investigate the size, shape and trajectory of a deuteriated "tagged" polymer molecule. Results for melt grown crystals have indicated that the radius of gyration, the

root mean square distance from the molecule's center of gravity, is slightly shorter than in the melt. Flory and Yoon [19] claimed that this is a result of the fact that adjacent reentry is absent from the stems in the crystal, and in turn supports the switchboard theory. However, Hoffman [20] explains the deviations in radius of gyration in semi-crystalline polymers as the result of tie molecules and multiple nucleation at distant points within the same lamellae, therefore, supporting adjacent reentry as the primary mode of chain folding.

Additional arguments have been made concerning the mobility of the polymer molecules. Yoon and Flory [21] stated that the polymer molecules' rate of disentanglement is not fast enough to allow adjacent reentry. DiMarzio [22] and proponents of adjacent reentry contend that reptation, the ability of a polymer molecule to move along its length as postulated by DeGennes [23, 24], increases the expected rate of rearrangement such that a short sequence of adjacent reentry is possible. Hoffman [25] included effects of reptation in the crystallization process, in effect concluding that growth rate and molecular weight have an inverse relation to one another, such as is known from experiment.

2.2.4 Crystallization Theories

Crystallization is a process consisting of the following steps; primary nucleation, growth and secondary crystallization. Primary nucleation is the formation of crystalline or ordered cells in which molecules initiate crystalline growth. Two types of primary crystallization exist, homogeneous and heterogeneous. Homogeneous nucleation is the random formation of nuclei throughout the melt, while heterogeneous nucleation is the formation of a nucleus at or upon impurities within the melt. Heterogeneous nucleation is instantaneous and is the predominant form of nucleation of processed polymers and thermoplastic composites.

Thermodynamically, the formation of a nuclei is a lowering of enthalpy as the polymer molecules crystallize. The governing thermodynamic equation is the Gibb's free energy equation.

$$G = H - TS \quad (1)$$

As the polymer seeks its lowest energy state, the free energy, G , is related to the enthalpy, H , and the entropy, S , by the Gibb's equation where, T , is the absolute temperature. When the free energy is at a minimum the system is in equilibrium. A polymer melt consists of randomly coiled and entangled chains¹, and has a much higher entropy than if the molecules are in the form of extended chains because there are many more conformations available to a coil than to a fully extended chain. This greater entropy leads to a lower free energy. If the melt is cooled to a temperature below the melting point of the polymer, T_m , crystallization may occur. There is a high degree of order in polymer crystals which leads to a considerable reduction in entropy upon crystallization. This entropy is generally offset by the large reduction of enthalpy that occurs during crystallization. If the enthalpy change, ΔH_m , (latent heat) is greater than that of the product of the melting temperature and entropy change ($T_m \Delta S_m$), crystallization will be favored thermodynamically since a lower value of free energy will result as initially indicated by Flory [26].

Once the primary nucleus is formed an additional segment of the molecule may nucleate upon the growth face. This process is known as secondary nucleation. Crystal growth continues this cyclic pattern of secondary nucleation followed by the laying down of the polymer molecule which nucleated upon the crystal face. Adjacent reentry is considered to be the preferred crystallization model for this segment of growth. The speed at which growth occurs is dependent upon temperature, molecular weight, pressure and chain mobility.

Lauritzen and Hoffman [27] developed a crystallization theory assuming adjacent reentry which furthered the understanding of polymer crystallization and the prediction of crystallization kinetics. This theory is modeled in Figure 5. Surface nuclei grow in the "g" direction with the measured growth in the "G" direction. The change of free energy as a result of ν molecular strands with $(\nu-1)$ folds and length, l , ignoring chain end effects is:

$$\Phi_s = 2bl\sigma_s + 2(\nu - 1)ab\sigma_e \quad (2)$$

¹ Much like a can of worms where the polymer strands would be much longer than those of the individual worm (length to diameter ratio of 10,000 to 1 rather than 25 to 1).

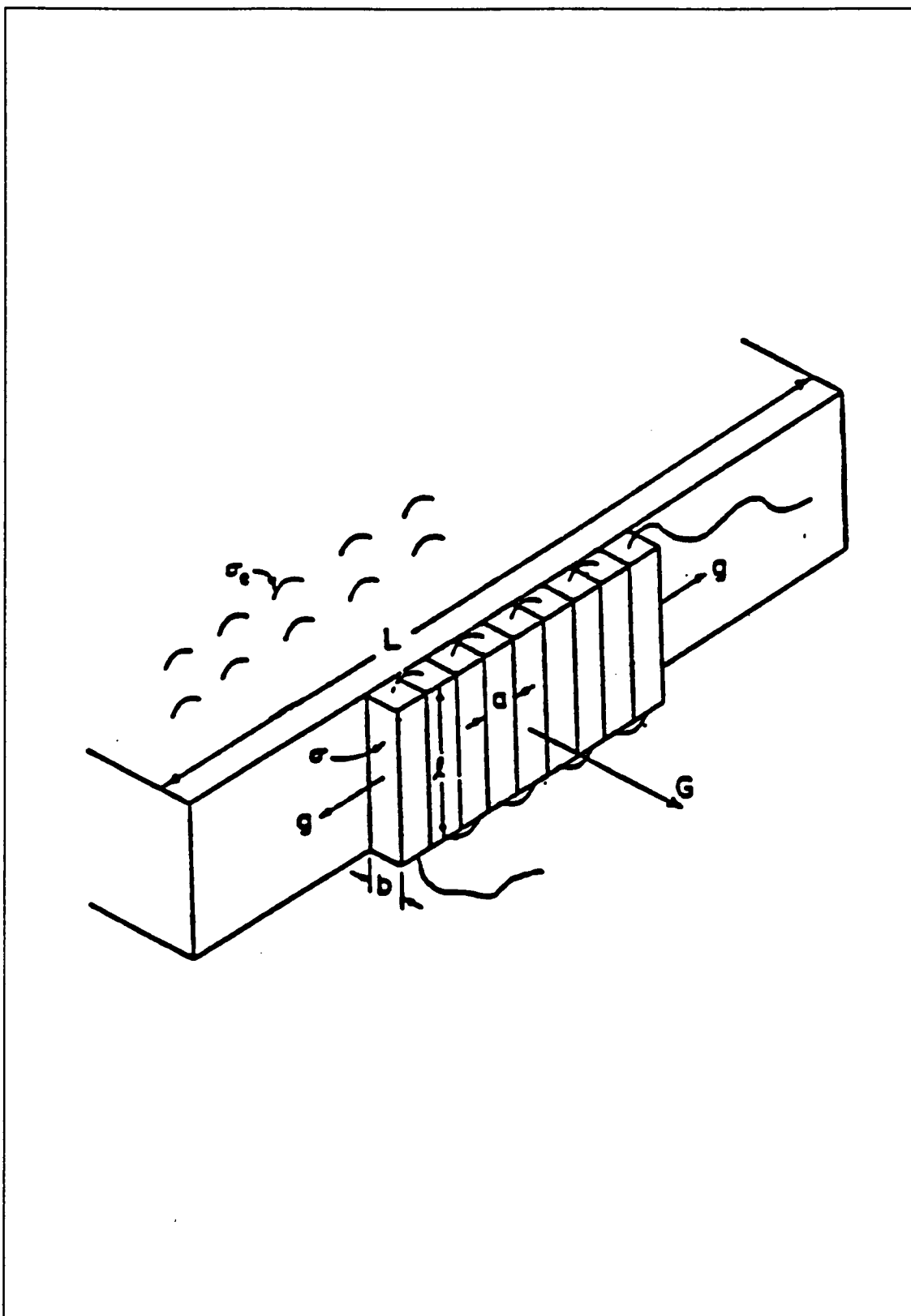


Figure 5: Idealized Schematic Model for Lamellar Crystal Growth; Source, Hoffman et. al., 1976.

This is due to the creation of three new surfaces for each new stem which lays down as well as the replacement of one surface by an identical one. For the generation of each new stem there is the creation or formation of a new surface in the "g" direction, $(2bl\sigma_s)$, resulting in two identical new surfaces at the fold, $(2ab\sigma_e)$. If, for example, the next stem rests upon the crystal surface in a non-adjacent reentry manner, the increase in free energy would be, $3bl\sigma_s + 2ab\sigma_e$. This increase in free energy is the result of the creation of five new surfaces as opposed to three with the adjacent reentry theory. Therefore, adjacent reentry is the favored thermodynamic model.

The reduction in the free energy due to the incorporation of strands is given by:

$$\Phi_c = -vabl\Delta f \quad (3)$$

By combining equations 2 and 3, the expression results in the total change of free energy.

$$\Delta G_v = 2bl\sigma_s + 2(v-1)ab\sigma_e - vabl\Delta f \quad (4)$$

By assuming a large number of stems, the $-2ab\sigma_e$ term is negligible. Rearranging the total change in free energy equation gives the following results.

$$\Delta G_v = 2bl\sigma_s + vab(2\sigma_e - l\Delta f) \quad (5)$$

The creation of a secondary nucleus initially leads to an increase in the free energy, and the nucleus may detach from the surface or grow by the addition of new stems. As the nucleus grows it reaches a region of stability at which there is no longer a chance of molecules detaching.

The complete theory of Lauritzen and Hoffman involves several other considerations which allow for accurate modeling of kinetic isothermal crystallization behavior. The theory predicts the existence of three regimes of growth. The first regime occurs when the rate of lateral spreading is much greater than the nucleation rate. When the two rates are equal it is said to be in the second regime. In the third regime, Phillips [28] suggests the rate of surface nucleation greatly exceeds that of lateral spreading.

2.2.5 Polymeric Annealing

Heat treatment of a polymer system which does not result in large scale melting is referred to as annealing. Similar to annealing in a metal system, annealing a polymer system results in morphological changes, however, on a much smaller scale than that of a metal system. Annealing of a semi-crystalline polymer at low temperature in relation to crystallization temperature results in crystal perfection. Lamellae can thicken in the solid state, crystal, by absorbing molecular chains from other regions of imperfect crystals or from the amorphous regions. At higher annealing temperatures, imperfect crystals have the tendency to melt while the bulk crystalline material remains in the solid state. As a function of increasing time the melt will recrystallize in the form of thicker lamellae and form a generally more perfect crystal, thus increasing its melting point. Annealed recrystallization can be identified via differential scanning calorimetry (DSC) as a shoulder or small peak at a temperature slightly above that of the annealing temperature.

2.2.5.1 Observation of Annealing

The mechanisms of annealing were first described by Keller and O'Conner [29] revealing that the small angle long period of single crystal mats increased from 120 Å to 200 - 300 Å. The long period is the height of the lamellae plus the amorphous zone. By further developing the work of Keller, Stanton and Geil [30] using techniques of electron microscopy of single crystals with annealing temperatures near the melt confirmed the increase in long period. Additionally, Stanton found lamellae with holes in them which were termed "Swiss cheese" or "amoebae-like" morphologies. Stanton concluded that regions of lamellae were thickening at the expense of imperfect regions and thus produced holes. Through annealing single crystals of polyethylene, Holland [31] was able to produce "picture frame" morphologies. Holland deduced that this resulted from the inner material migrating and recrystallizing at the edges. The long period increase upon annealing was found to be time and temperature dependent by Fisher and Schmidt [32]. Using defocus imaging techniques with transmission electron microscopy and bulk polyethylene, Petermann & Gleiter [33] observed the migration of amorphous regions resulting in solid state crystal growth. Transmission electron microscopy studies on isotactic polystyrene

crystals identified that slow heating favored solid state thickening, while greater heating rates yielded melting and recrystallization. Petermann and Gohil [34] also observed the growth of thicker lamellae at the expense of both thinner and bent lamella--imperfect crystals.

An applied study of Kapur and Rogers [35] evaluated the effects of room temperature annealing on quenched polypropylene. Kapur found no changes in the bulk crystallinity, structure or size of crystals, but identified a 16 percent increase in yield stress, 150 percent increase in draw stress, and a 185 percent increase in modulus. Kapur concluded that these results were due to relaxation of residual stress resulting from quenching.

2.2.5.2 Mechanisms of Annealing

There are several mechanism which attempt to explain the experimental observations of annealing. One of these mechanisms is the idea that molecules pull themselves through the lattice in an effort to generate a thicker lamella at the expense of lamellar width. Reneker [36] proposed point dislocations or molecular kinks which result in extra $\text{-CH}_2\text{-}$ units within the crystal and could be the source of thickening. Dreyfuss and Keller suggest thickening could occur by mutual rearrangement within a folded molecule without coordinated displacement of the molecule, see Figure 6.

Peterlin developed an extensive theory based upon thermodynamic, molecular weight and diffusion characteristics. In an effort to explain the temperature dependence of the extension of the long period Peterlin postulated that the source of the extension was from the free ends of the molecule. The most extensive mathematical theory to explain this phenomenon was developed by Sanchez et. al [37, 38]. At the core of this theory is the consideration that the fold surface free energy is roughly ten times greater than that of the lateral surface energy; therefore, the reduction of surface free energy serves as the driving force for crystal thickening. Assuming the process is irreversible the rate of crystal thickening is said to be proportional to the surface free energy;

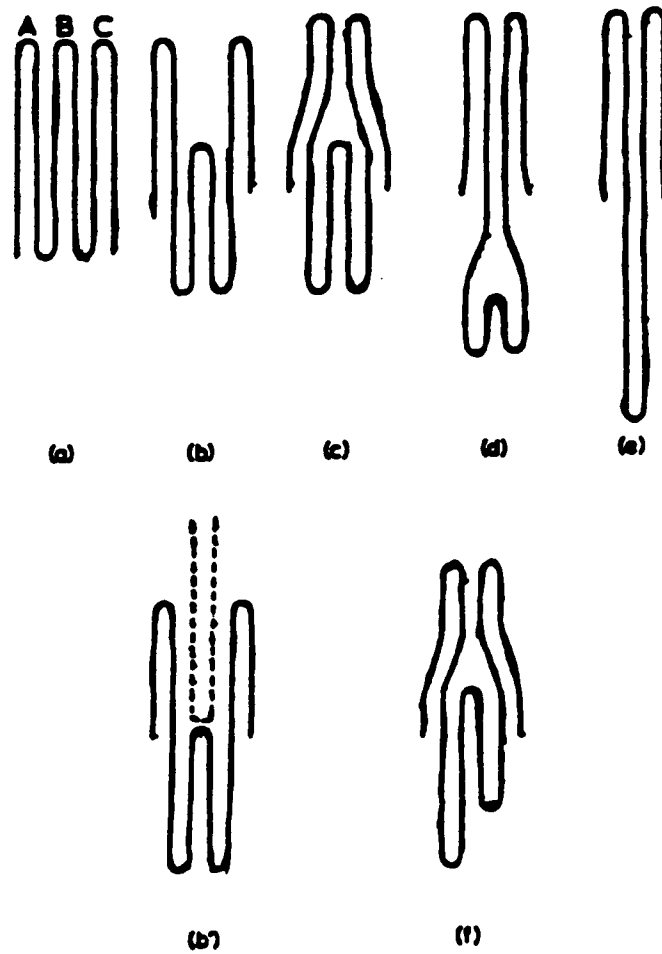


Figure 6: Representation of Thickening Mechanism; Source, Dreyfuss & Keller, 1970.

$$x^2 \frac{dl}{dt} = -k \frac{d\sigma_e}{dl} \quad (6)$$

where x is the lateral dimension of the crystal and l is the thickness. With a few assumptions this equation can be integrated producing an equation for lamellae thickness as a function of time.

Using the Sanchez theory of thickening, Phillips and Rensch [39] analyzed lamellae thickening behavior of poly(ϵ -caprolactone). Phillips developed an isothermal thickening curve for different molecular weights and calculated an activation energy from the shift factors which were obtained. Phillips concluded that an active unit involved in thickening was one stem and further suggested that thickening could occur through an “omega defect”, first developed by Hoffman, to explain the physical origin of substrate length in regime theory; refer to Figure 7a. An illustration of the “omega defect” is shown in Figure 7b, and according to Phillips could result in a one stem thickening unit.

2.2.6 Transcrystallinity

This morphology originally termed row structure by Keller [40] is crystal growth from closely spaced nuclei which are situated at the surface or in the case of composites, fibers. Each nucleus is the origin of radiating crystal growth which normally leads to spherulitic structures. However, in this case where the nuclei are so closely spaced, growth only occurs normal to the surface--perpendicular to the fiber.

Many thermoplastic polymer composites are capable of exhibiting a transcrystalline interphase, examples are PAN-based AS4 carbon\PEEK, AS4 carbon\PEK and AS4 carbon\PPS [41 42]. The mechanical properties of the transcrystalline phase are known to be different from that of the neat resin. The change in properties is attributed to the transcrystalline morphology. The effects of transcrystallinity on mechanical properties of composite materials are currently being debated. Porter et al. [41] suggested that transcrystallization improved the transverse properties in low fiber content AS4/PEEK composite. Hagenson et al. [43] showed that the transcrystalline interphase did not change

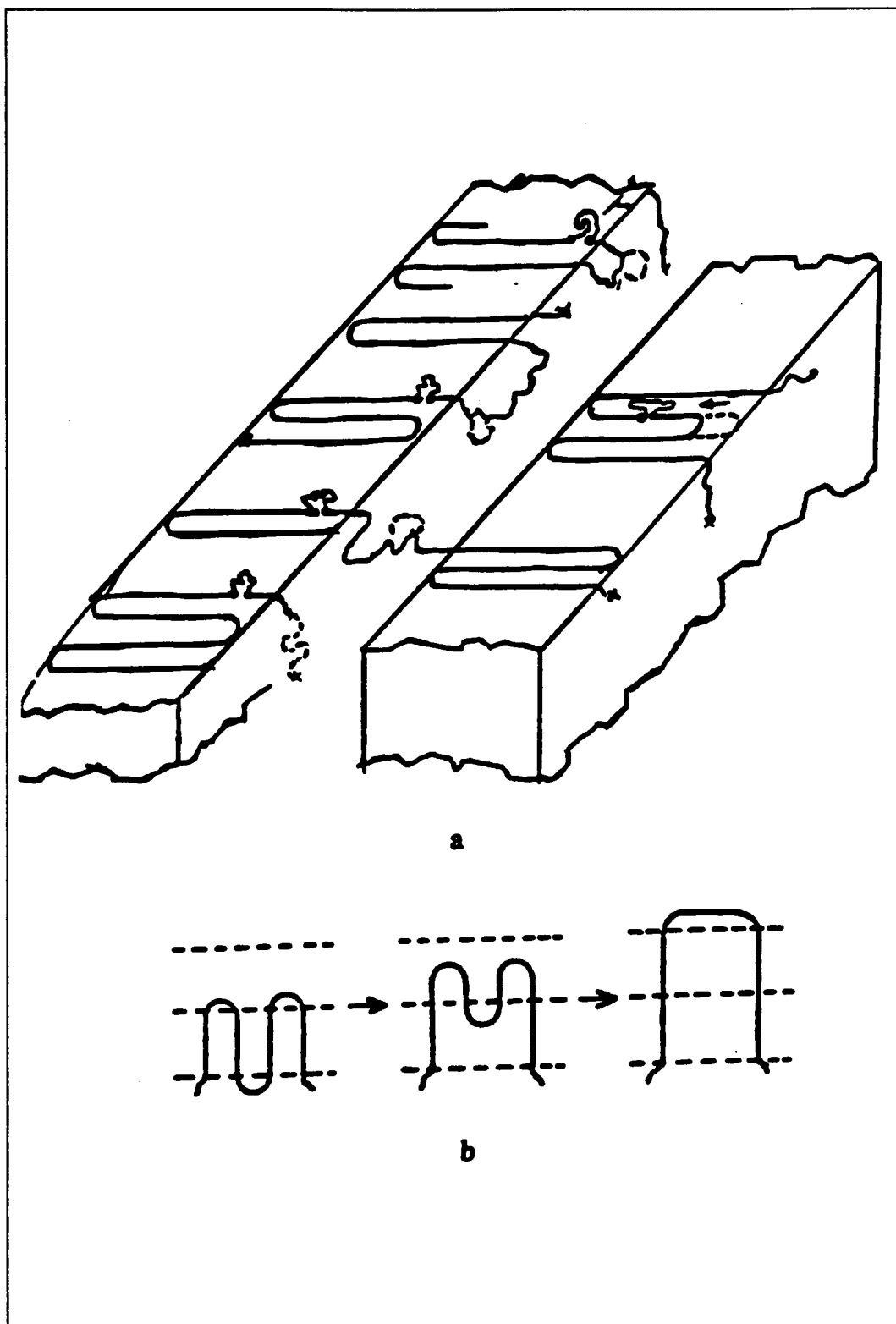


Figure 7: Omega Defect; a) Structures Allowing Formation of Omega Defects in Chain Folded Systems; Source, Hoffman, 1985, b) Omega Defect Mechanism; Source, Phillips & Rensch, 1989.

mechanical properties in PPS composites. Bessell et al. [44] reported that transcrystalline morphology led to poor interfacial bonding. There are many ongoing studies as to the effects and control of the transcrystalline interphase within thermoplastic composites, Hsiao [45] provides an excellent review of the mechanisms of transcrystallinity.

2.2.7 Determining Degree of Crystallization

Maintaining consistency in the degree of isothermal crystallinity is a key component in any study. Several methods may be used to determine the degree of crystallization in polymers. However not all of these methods will be applicable to composite materials or may require slight changes to their normal operating procedures.

2.2.7.1 Density Gradient Column

Density gradient columns (DGC) have been used for several years to determine the density of polymer samples. This method is strongly dependent on the homogeneity of the samples, that is, free of voids or impurities. The presence of discontinuities will provide false results of the molecular density of the polymer. Additionally, a suitable density gradient column must be determined for the polymer which is being tested, i.e. polyurethane foam would not be a viable sample polymer for water gradients. Once a column is made this is the easiest but most time consuming method of determining the crystallinity. A column is simultaneously filled with dense and less dense solutions, and a linear gradient is established. Small samples cut from films are identified by their shape and placed in the column. Their density is determined from the linear gradient established directly from the DGC. The degree of crystallinity is directly determined from the following relationship.

$$X_c = \frac{\rho_c}{\rho} \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (7)$$

For a composite material the theoretical density may be calculated from the rule of mixtures and thus, the density may be determined using the DGC. However, there are some potential problems with this method. The void volume in the composite will decrease the measured density from the DGC. For the purpose of determining crystalline

content in a thermoplastic composite it is essential to keep the void volume to a minimum, ideally less than one percent, resulting in negligible changes in the degree of crystallinity.

2.2.7.2 X-Ray Diffraction

X-Ray diffraction is an important method for investigating the structure of crystalline polymers. X-Ray diffraction occurs in polymeric materials because of the electron density surrounding atoms along the polymeric chain. If the chains are randomly orientated the resultant scattering is an amorphous broad peak. However, other conditions cumulatively add to this amorphous zone such as scattering by air, depolarization effects, background radiation, etc. The scattering which gives rise to the amorphous background may include scattering from voids, imperfections in crystallites and unit cell lattice defects. If the chains are arranged in an ordered lattice or unit cell, sharp diffraction peaks of intense scattering occur along certain reflective planes. These reflection planes are a function of the Bravais lattice of the material being studied. For polyethylene which is orthorhombic the principal diffraction planes are 110 and 200. These planes will be represented by sharp diffraction peaks at Bragg angles of $2\Theta = 21.3^\circ$ and $2\Theta = 23.5^\circ$. The broad amorphous peak is generally centered and symmetric about $2\Theta = 20^\circ$. Diffraction occurs from these planes according to Bragg's law.

$$n\lambda = 2d_{hk} \sin\theta \quad (8)$$

All methods of determining crystallinity by X-Ray diffraction are based on the ability to separate the amorphous and crystalline regions. Several methods have been developed to analyze the raw data, yet all involve some guess work. Hermans and Weidinger [46] have presented a method for determining the crystalline fraction in polymers such as polyethylene which have a limited number of highly intense diffraction peaks.

The method consists of the following steps indicated in Figure 8:

1. A 2Θ scan is made over a limited angular range.
2. Background scattering is subtracted from the scan.
3. A reasonable distinction is made between the crystalline and amorphous regions.

4. The integral intensities proportional to the crystalline and amorphous fraction are measured (estimate the area).
5. The crystallinity index is calculated from the resolved peak areas:

$$X_c = \frac{A_c}{A_c + K A_a} = \frac{I}{I + KR} \quad (9)$$

Using thermoplastic composites with carbon type fibers creates a problem. The diffraction peak of the fibers interferes with or covers the dominant peaks of the matrix. This is the case for AS4/PET, where the broad diffraction peak of the carbon fibers, centered at 26° (2θ) interval, obscures the dominant PET reflections [47]. The carbon diffraction is not as great in the region of the (010) and (011) reflections of PET; however, these reflections are not as prominent.

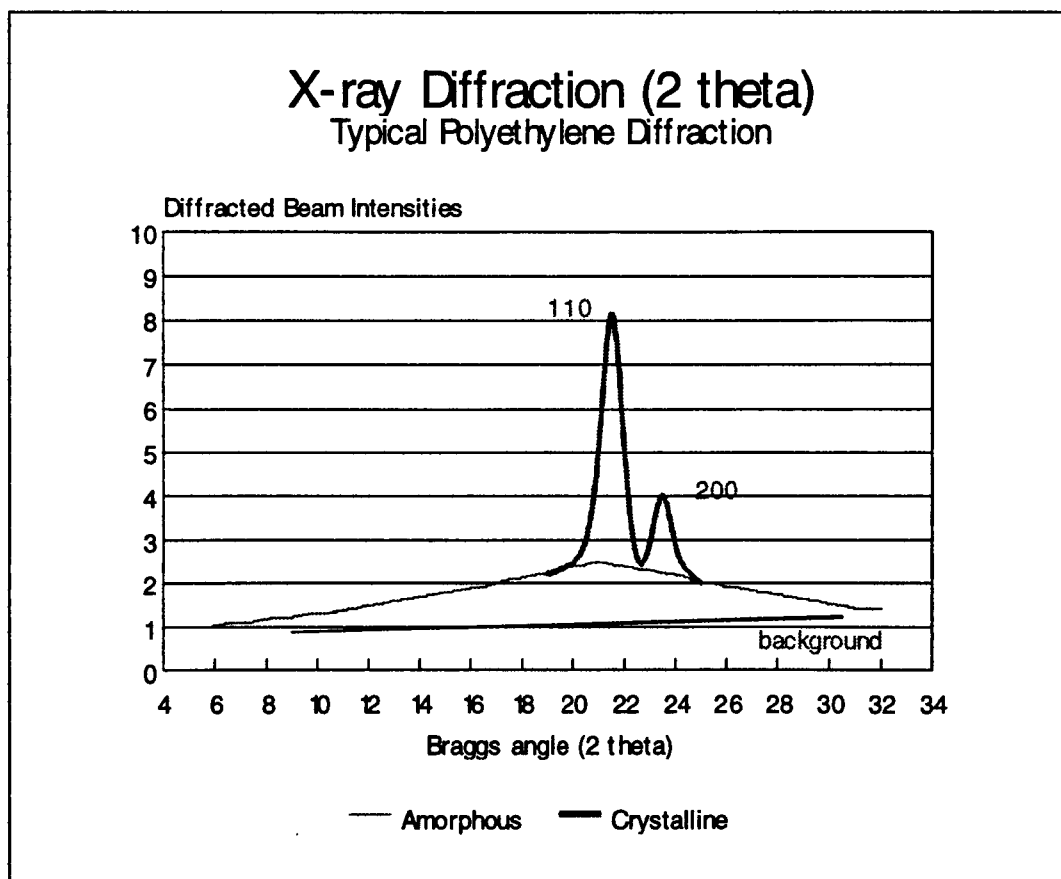


Figure 8: X-Ray Diffraction (2θ) Showing Distinction of Amorphous and Crystalline Regions.

2.2.7.3 Differential Scanning Calorimetry

The differential scanning calorimeter (DSC) works on the principle of differential heat absorption. In the DSC, two sample holders which are thermally isolated from each other and which contain a sample and a reference material are heated in parallel using a linear temperature program. For each measurable temperature difference between the reference, R, and sample, S, the corresponding amount of energy is immediately compensated for by a variable filament power. The filament power is recorded, and the DSC provides continuous recording of the specific heat, c_p . Direct integration of the measured peak area gives the measured heat energy. A typical DSC diagram for a semi-crystalline polymer such as polyethylene is displayed in Figure 9. As shown in the figure, by scanning through the melting zone a “melting peak” is obtained whose area is proportional to the melting enthalpy, $\Delta H_{m,x}$.

$$\Delta H_{m,x} \approx \int_{T_1}^{T_2} c_p \Delta dT \quad (10)$$

Where T_1 and T_2 are the temperatures at the beginning and end of the melt peak, respectively [48]. These calculations are performed by the DSC; however, it is necessary to join the background on both sides of the peak by a “base line”. The determination of the base line determines the area of peak and ΔH values. When the width of the peak is small determining the base line is simple. However, as in LDPE when the melting process occurs over a wide range of temperatures and the width of the peak is large, the base line is difficult to establish.

The crystallinity can be determined using Equation 11 when the melt heat, ΔH_m , of a completely crystalline sample is known.

$$X_c = \frac{\Delta H_{m,x}}{\Delta H_m} \quad (11)$$

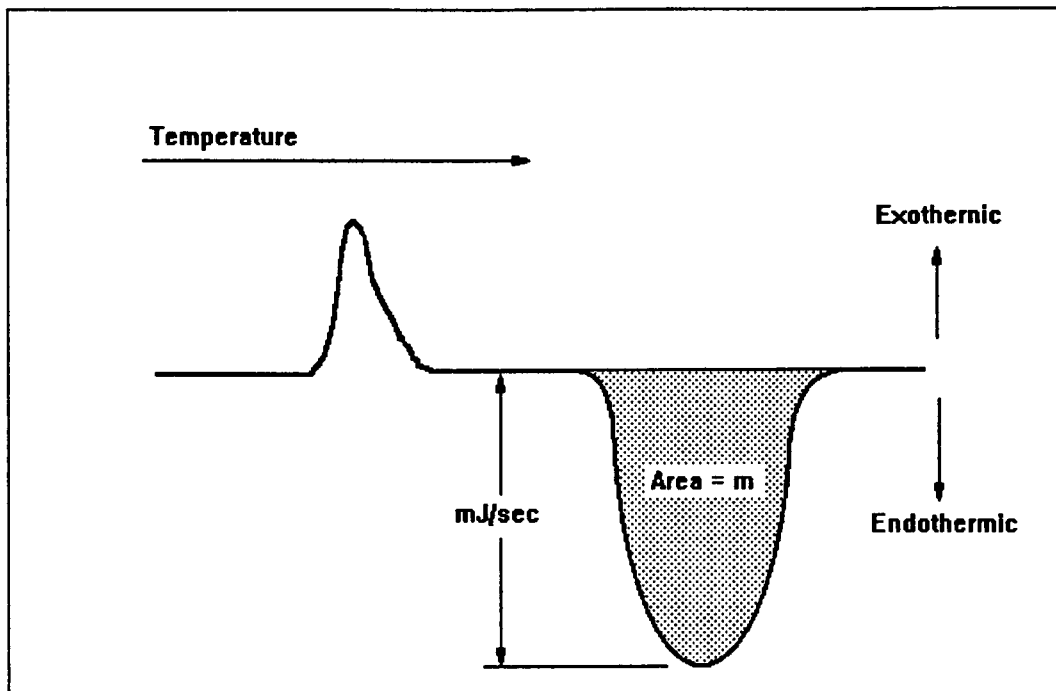


Figure 9: Typical DSC Diagram.

In evaluating the crystallinity of a composite, adjustments are made to Equation 12 to allow for the carbon content

$$X_c = [(X_c)_{measured}] / (WP) \quad (12)$$

where WP is the weight percent of the polymer in the composite [49]. A potential problem exists with using the DSC for the evaluation of crystalline content of thermoplastic composites. Composites that are crystallized at low crystallization temperatures can generate more crystals while the DSC scan is running at temperatures greater than T_c . These new crystals will melt as the scan temperature is increased. It is possible to subtract or ignore endotherms significantly greater than T_c .

2.3 Characterization of Poly (ethylene terephthalate) PET

Poly (ethylene terephthalate), PET, is a condensation polymer that has experienced rapid growth in popularity within the commercial industry. PET is a well characterized polymer, of which the affects of molecular weight distributions and crystallization kinetics have been studied by many authors. PET has a number average molecular weight range of 19,000 to 39,000. Van Antwerpen & Van Krevelen [50] in the early 1970's studied the

influence of crystallization temperature, molecular weight and additives on PET. Growth rate studies indicated that at a given crystallization temperature there is no significant difference in growth rate between isothermal crystallization from melt and from glassy state.

Not until the late 1970's when Mehta et.al., [51] provided consistent values of basic parameters, such as, equilibrium melting point and heat of fusion. Although, Mehta provided conflicting results in regards to growth rates from melt and glassy states compared to those reported by Van Antwerpen. Palys and Phillips [52] studied lamellar growth kinetics and lamellar thickness crystallized from the glassy state in which they determined the side and end surface free energies and residual lamellar thickness.

Thermal studies of PET crystallized isothermally often exhibits double melting endotherms depending on the crystallization temperature and the heating rate during melting. This double melting behavior observed during DSC of PET has been attributed by many authors [53, 54, 55, 56, 57, 58] to melting and recrystallization during scanning. Earlier authors [59, 60] contended that this melting behavior was a result of different morphologies (extended chain and folded chain crystals).

In the early 1980's Groeninckx et. al., [61] provided a detailed description of morphology and the complex melting behavior of PET crystallized isothermally within the range of 100-245°C. Using differential scanning calorimetry, double or single melting endotherms can be obtained simply by varying the heating rate of the calorimeter. Groeninckx postulated that the first melting endotherm corresponded to the melting of the crystalline material generated at the crystallization temperature, and the second melting endotherm was the melting of a fraction of the original crystalline material reorganized during heating. The appearance of a single melting endotherm indicated the melting of the original structure or the melting of a completely transformed structure.

Groeninckx described the melting behavior of isothermally crystallized PET as studied by DSC as complex and dependent on both crystallization temperatures and DSC heating rates. Using heating rates greater than 32°C/min. only one melting endotherm was

observed, while at slower heating rates two melting endotherms were present as a consequence of transformation of part of the original crystallites formed at the crystallization temperature. The sum of the areas under the melting endotherms, either single or double, remained constant during the transformation. Groeninckx detailed a morphological study using electron microscopy, small angle and wide angle X-ray scattering which questioned the concepts of two phase morphology (extended chain and folded chain crystals).

Groeninckx & Reynaers [62] discussed the morphology and melting behavior of annealed PET. Groeninckx stated that annealing under isothermal conditions above the crystallization temperature has a marked influence on the morphology resulting in increased thermal stability of the crystalline structure as indicated by an increase in the melting point. The morphological changes caused by annealing were dependent on the thermal history, i.e., crystallization temperature and heating cycles. Depending on the annealing process, various parameters characterizing the semicrystalline state can be affected such as the degree of crystallinity, long period, thickness of amorphous and crystalline layers, crystal perfection, and the fold surface structure. Groeninckx stated that annealing of PET involves a solid-state transformation of the original crystalline structure including crystal perfection without thickening or a melting followed by recrystallization with crystal perfection and crystal thickening.

Groeninckx concluded that annealing of PET crystallized at low crystallization temperatures is strongly dependent on the initial crystallization temperature and apparently does not depend on the annealing conditions. Using small-angle X-ray scattering, (SAXS) the long spacing with increased annealing temperature is increased up to 60% for samples that were quickly heated to 245°C. However, the slowly heated samples revealed less change, in fact the long spacing remained constant up to annealing temperatures of 230°C. Since the crystallinity increases, from DSC studies, Groeninckx postulated that during slow heating the new crystalline material developed at the fold surface of the existing crystals at the expense of neighboring amorphous layers, resulting in crystal thickening and fold surface smoothing without increasing the long period.

In more recent studies Santa Cruz et. al., [63] determined that by comparing the linear degree of crystallinity using SAXS with the degree of crystallinity as determined from wide-angle X-ray or from density, that the material is not homogeneously filled with lamellar stacks. The broad distributions of crystal thickness, amorphous thickness and long period can be determined with greater accuracy using the interface distribution function rather than the correlation function. Santa Cruz reasoned that the distribution function was less affected by the superposition of the maxima or minima of the broad distribution than the relevant shape of the correlation function. The long period obtained by simply applying Bragg's law is considerably larger than the true values as determined by Santa Cruz.

Santa Cruz postulated that the coherently scattering lamellar stack consists of only 3-6 lamellae. Additionally, amorphous regions exist outside of the lamellar stacks which are larger than those within but still small enough to contribute to the detected diffuse small-angle X-ray scattering, refer to Figure 10. The fraction of these regions decrease with increasing crystallization temperature. Santa Cruz found supporting information from electron microscope investigations that larger amorphous regions of irregular size exist between the lamellar stacks.

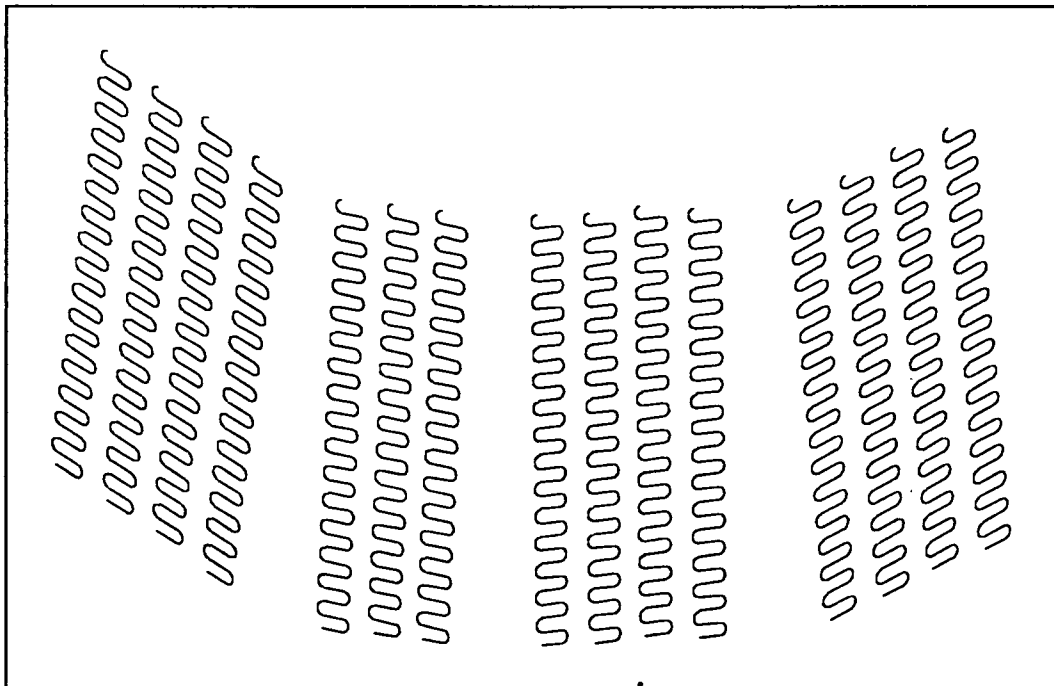


Figure 10: Schematic Representation of Random Lamellar Stacking Sequence

2.4 Macromechanics of a Lamina

Lamina are the basic building blocks of laminated fiber-reinforced composites. Knowledge of a single lamina will provide the aperture for the understanding of the laminated composite. Macromechanics of a lamina are the behavior of the lamina when only the average apparent mechanical properties are considered, not the interactions of the constituents of the composite. The basic restriction is that of linear elastic behavior of a lamina.

2.4.1 Generalized Hooke's Law

Elementary strength of materials instructs us that Hooke's law is the fundamental relationship between stress and strain. A laminated composite can exhibit Hookian relationships classified anywhere from homogenous isotropic to heterogeneous anisotropic. Following is a brief discussion of the elastic constants which characterize the behavior of isotropic, orthotropic, and anisotropic materials [64, 65].

For an isotropic material the stress strain relationship is:

$$\sigma = E\varepsilon \quad (13)$$

However, a composite may not be an isotropic material. Depending on the materials and fabrication of the composite, more elastic constants may be required to write the constitutive relationships between stress and strain. For a three dimensional stress state, the generalized Hooke's law for an anisotropic material is:

$$\sigma_{pq} = C_{pqrs} \varepsilon_{rs}, p, q, r, s = 1, 2, 3, 4 \quad (14)$$

In its expanded form,

$$\begin{Bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{32} \\ \sigma_{31} \\ \sigma_{13} \\ \sigma_{12} \\ \sigma_{21} \end{Bmatrix} = \begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1132} & C_{1131} & C_{1113} & C_{1112} & C_{1121} \\ C_{2211} & C_{2222} & C_{2233} & C_{2223} & C_{2232} & C_{2231} & C_{2213} & C_{2212} & C_{2221} \\ C_{3311} & C_{3322} & C_{3333} & C_{3323} & C_{3332} & C_{3331} & C_{3313} & C_{3312} & C_{3321} \\ C_{2311} & C_{2322} & C_{2333} & C_{2323} & C_{2332} & C_{2331} & C_{2313} & C_{2312} & C_{2321} \\ C_{3211} & C_{3222} & C_{3233} & C_{3223} & C_{3232} & C_{3231} & C_{3213} & C_{3212} & C_{3221} \\ C_{3111} & C_{3122} & C_{3133} & C_{3123} & C_{3132} & C_{3131} & C_{3113} & C_{3112} & C_{3121} \\ C_{1311} & C_{1322} & C_{1333} & C_{1323} & C_{1332} & C_{1331} & C_{1313} & C_{1312} & C_{1321} \\ C_{1211} & C_{1222} & C_{1233} & C_{1223} & C_{1232} & C_{1231} & C_{1213} & C_{1212} & C_{1221} \\ C_{2111} & C_{2122} & C_{2133} & C_{2123} & C_{2132} & C_{2131} & C_{2113} & C_{2112} & C_{2121} \end{bmatrix} \begin{Bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ \epsilon_{23} \\ \epsilon_{32} \\ \epsilon_{31} \\ \epsilon_{13} \\ \epsilon_{12} \\ \epsilon_{21} \end{Bmatrix} \quad (15)$$

There are 81 constants. Fortunately, not all are independent; in fact, there are only 21 independent elastic constants for an anisotropic material. This reduction in the number of constants is obtained from the symmetry of the strain tensor,

$$\epsilon_{rs} = \epsilon_{sr} \quad \vee \quad C_{pqrs} = C_{rspq} \quad (16)$$

thereby reducing the number of constants to 54. Also, the symmetry of the stress tensor,

$$\sigma_{pq} = \sigma_{qp} \quad \vee \quad C_{pqrs} = C_{rspq} \quad (17)$$

reduces the number of constants to 36. Further reductions occur through the energy density function and because the order of partial differentiation should not affect the result, this means:

$$C_{ijkl} = C_{klij} \quad (18)$$

The physical significance of the symmetry of C_{ijkl} is that, for example in the case of C_{3323} , the symmetry of C_{3323} would imply that if a given σ_{33} causes ϵ_{23} at a point, then a given ϵ_{23} will cause σ_{33} . Equation 15 is now reduced in contracted notation to:

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{Bmatrix} \quad (19)$$

where the strains are now engineering strains, $\epsilon_4 = \gamma_{23}$, $\epsilon_5 = \gamma_{31}$, $\epsilon_6 = \gamma_{12}$, and $\sigma_4 = \tau_{23}$, $\sigma_5 = \tau_{31}$, $\sigma_6 = \tau_{12}$. Therefore, the above equation may be written in terms of compliance as:

$$\sigma_i = C_{ij} \epsilon_j, \quad i, j = 1, 2, 3, 4, 5, 6 \quad (20)$$

or in terms of stiffness as:

$$\epsilon_i = S_{ij} \sigma_j, \quad i, j = 1, 2, 3, 4, 5, 6 \quad (21)$$

This contracted notation reduces the constitutive equation of 81 constants to 21 constants [66].

2.4.1.1 Reduction of Elastic Constants

Consider a material composed of atoms connected by springs. The spring constants are different in all three directions, and the springs do not make right angles with each other. In this case the response of the material will be different in each direction. If a load is applied in one direction along an axis, the result will be a change in length and angles along and between all the axes. Therefore, a strain applied in any direction will yield all six stress components or an applied stress in any direction will result in a change in all six strain components. All 21 elastic constants will be needed to write the constitutive equations.

A monoclinic material exhibits symmetry of its elastic constants with respect to one plane and the spring constants are different in all three directions, for example, X_1 - X_2 plane. Note, X_1 - X_2 - X_3 are the regular orthogonal axes and Y_1 - Y_2 - Y_3 are material axis, X_2 coincides with Y_2 , and X_3 coincides with Y_3 . However, X_1 does not coincide with Y_1 . Also, Y_1 is perpendicular to Y_3 , and Y_2 is perpendicular to Y_3 , but Y_1 is not perpendicular to Y_2 . Also, the spring constants are different in three directions. The symmetry along the orthogonal X_1 - X_2 plane is expressed by the requirement that the elastic constants do not change under transformation. Through the use of directional cosines this condition will only be satisfied when $C_{1123} = 0$. Similarly, it can be shown that $C_{1123} = C_{2223} = C_{3323} = C_{1131} = C_{2231} = C_{3331} = C_{1223} = C_{1231} = 0$ (note that all the constants in the C_{ijkl} matrix where the subscript 3 appears an odd number of times will be zero for

the material having symmetry with respect to X_1 - X_2 plane). The physical significance of certain elastic constants being zero is that an applied stress σ_{33} does not cause any shear stress τ_{13} , whereas a non-zero C_{1112} means that an applied stress σ_{11} will cause shearing strain, γ_{12} . Thus the contractive notation for the constitutive relationship contains 13 independent constants:

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{21} & C_{22} & C_{23} & 0 & 0 & C_{26} \\ C_{31} & C_{32} & C_{33} & 0 & 0 & C_{36} \\ 0 & 0 & 0 & C_{44} & C_{45} & 0 \\ 0 & 0 & 0 & C_{54} & C_{55} & 0 \\ C_{61} & C_{62} & C_{63} & 0 & 0 & C_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{Bmatrix} \quad (22)$$

An orthotropic material exhibits symmetry of its properties with respect to two orthogonal planes. One of these symmetry requirements was explained with the monoclinic structure by following a similar process and imposing an additional symmetry requirement with respect to an additional X_2 - X_3 plane. Through the use of directional cosines this implies that $C_{1112} = 0$. Similarly it is shown that $C_{1112} = C_{2212} = C_{3312} = C_{1323} = 0$.

Because the material axes are orthogonal, the applied normal stress along the material axes does not cause shear strains, and applied shearing strains along material axes do not cause normal strains. There is no interaction between normal stress and shear strains. Thus the constitutive equation for an orthotropic material will have 9 independent constants.

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{Bmatrix} \quad (23)$$

In addition to symmetry along two orthogonal planes as in an orthotropic material, the tetragonal material has the same elastic constants along two axis. Assuming the elastic constants are the same along the X_1 and X_2 axes, this implies that if the reference is

rotated by 90° along the X_3 axis, the elastic constants should remain unchanged. From directional cosines and retaining only the non-zero terms it is found that the indices 1 and 2 are interchangeable. The constitutive equation for a tetragonal material contains 6 independent constants.

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{Bmatrix} \quad (24)$$

If at every point of a material there is one plane in which the elastic constants remain unchanged in all directions, the material is said to be transversely isotropic. Assuming that plane is X_1 - X_2 , this means that not only are the indices 1 and 2 interchangeable (as in tetragonal material) but the elastic constants remain unchanged after rotation of the axis by any angle in the X_1 - X_2 plane. By eliminating the zero terms as previously explained, and since indices 1 and 2 are interchangeable as well as the stress tensor, strain tensor and C_{ijkl} being symmetric, this yields the following constitutive equation in which there are 5 independent constants.

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(C_{11} - C_{12}) \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{Bmatrix} \quad (25)$$

A unidirectional composite specimen may be treated as a transversely isotropic material.

A cubic material has the same properties along all three orthogonal axes. Thus for a cubic material additional constraints have to be imposed on tetragonal material such that the invariance is preserved after rotation about the X_1 or X_2 axes. Consequently, it can be said

that all three indices in the C_{ijkl} matrix are interchangeable. Thus the constitutive equation for a cubic material contains three independent constants.

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{Bmatrix} \quad (26)$$

The elastic constants in an isotropic material are independent of axes orientation. Thus for an isotropic material an additional constraint must be placed on the cubic material such that the rotation of the reference frame with respect to any axis will not change the elastic constants. With this in mind the constitutive equation for an isotropic material contains two independent constants.

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(C_{11} - C_{12}) & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}(C_{11} - C_{12}) & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(C_{11} - C_{12}) \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{Bmatrix} \quad (27)$$

A mechanics of composite materials approach from tensor analysis is given in an excellent presentation by Tsai [67].

2.4.2 Plane Stress

In the theory of beams and plates, certain assumptions are made regarding the stress and strain distribution. Certain stresses and strains are assumed to be much smaller, comparatively, and are thus neglected. These assumptions greatly simplify the stress strain relationships. As plane-strain implies, they are simplifications in which certain engineering problems may be modeled and analyzed as two dimensional problems, thus simplifying the constitutive relationships.

If the 1-2 plane is the plane of interest, a state of plane-stress would exist if σ_1 , σ_2 , and σ_6 are functions of components only in the 1 and 2 directions; and any components in the 3 direction are zero. These parameters are also true for plane-strain.

For anisotropic materials the compliance constitutive equations are:

$$\begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{Bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{12} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{13} & S_{23} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{14} & S_{24} & S_{34} & S_{44} & S_{45} & S_{46} \\ S_{15} & S_{25} & S_{35} & S_{45} & S_{55} & S_{56} \\ S_{16} & S_{26} & S_{36} & S_{46} & S_{56} & S_{66} \end{bmatrix} \begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{Bmatrix} \quad (28)$$

For an orthotropic material the compliance constitutive equations are:

$$\begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \gamma_{23} \\ \gamma_{31} \\ \gamma_{12} \end{Bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & 0 & 0 & 0 \\ S_{12} & S_{22} & S_{23} & 0 & 0 & 0 \\ S_{13} & S_{23} & S_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{66} \end{bmatrix} \begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \tau_{23} \\ \tau_{31} \\ \tau_{12} \end{Bmatrix} \quad (29)$$

If interests are in the stresses and strains only in the 1-2 plane-stress plane, a solution is required for the following three equations in which there are 4 independent constants; E_1 , E_2 , ν_{12} , and G_{12} .

$$\epsilon_1 = S_{11}\sigma_1 + S_{12}\sigma_2 = \frac{1}{E_1}\sigma_1 - \frac{\nu_{21}}{E_2}\sigma_2 \quad (30)$$

$$\epsilon_2 = S_{12}\sigma_1 + S_{22}\sigma_2 = -\frac{\nu_{12}}{E_1}\sigma_1 + \frac{1}{E_2}\sigma_2 \quad (31)$$

$$\gamma_{12} = S_{66}\tau_{12} = \frac{1}{G_{12}}\tau_{12} \quad (32)$$

For a lamina in the 1-2 plane see Figure 11, a plane stress condition occurs when σ_3 , σ_4 (or τ_{23}) and σ_5 (or τ_{13}) are zero resulting in the following compliance constitutive equation.

$$\begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \gamma_{12} \end{Bmatrix} = \begin{bmatrix} S_{11} & S_{12} & 0 \\ S_{21} & S_{22} & 0 \\ 0 & 0 & S_{66} \end{bmatrix} \begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \tau_{12} \end{Bmatrix} \quad (33)$$

The compliance matrix (or S_{ij}) can be inverted to provide the reduced stiffness constitutive equations. For an orthotropic lamina the Q_{ij} matrix takes the following form:

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} Q_{11} & Q_{12} & 0 \\ Q_{21} & Q_{22} & 0 \\ 0 & 0 & Q_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \gamma_{12} \end{Bmatrix} \quad (34)$$

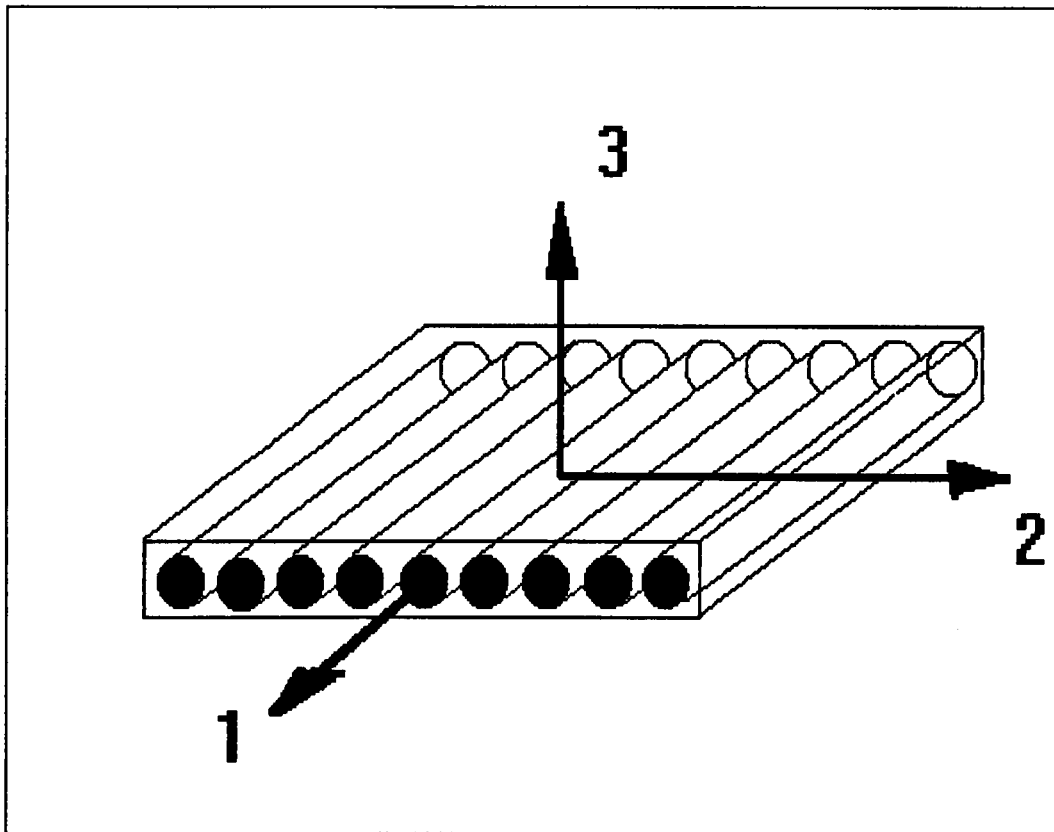


Figure 11: Unidirectional Composite Lamina in the 1-2 Plane.

In terms of engineering constants:

$$Q_{11} = \frac{E_1}{1 - \nu_{12}\nu_{21}} \quad (35)$$

$$Q_{12} = \frac{\nu_{12}E_2}{1 - \nu_{12}\nu_{21}} = \frac{\nu_{21}E_1}{1 - \nu_{12}\nu_{21}} \quad (36)$$

$$Q_{22} = \frac{E_2}{1 - \nu_{12}\nu_{21}} \quad (37)$$

$$Q_{66} = G_{12} \quad (38)$$

2.4.3 Strength of an Orthotropic Lamina

In the determination of the strength of any material the element of interest is at the instant and location where failure occurs. The engineering strengths for most common materials can be found in materials handbooks and have been determined experimentally by tensile tests, compressive tests, or shear tests. In conventional isotropic materials under simple or axial loading, failure will occur when the applied stress reaches the corresponding strength of the material. Therefore, under these simple conditions failure can be predicted with ease. Consider a situation where there are an infinite number of combinations of different stresses which may cause the material to fail. It becomes impractical to obtain laboratory data for each combination of applied stress fields in order to determine when failure will occur. In these situations it becomes necessary for a “failure criterion” or “failure theory” to predict the strength of a material. For isotropic materials the failure criteria are expressed in terms of principle stresses, and ultimate tensile, compressive and shear strengths.

2.4.3.1 Failure Theories for Isotropic Materials

The selection of one or several failure theories often depends on the materials being tested and the confidence required in determining failure strength. The maximum distortion energy theory has been found to agree best with available data for ductile materials. The maximum normal strain theory is unsafe for ductile materials. The maximum normal stress theory is also unsafe for ductile materials when the principle stresses are of opposite sign.

For brittle materials, the maximum normal stress theory is generally found to be most suitable.

The maximum normal stress theory predicts failure of a specimen subjected to any combination of loads when the maximum normal stress at any point reaches the uniaxial failure stress as determined by an axial tensile or compressive test of the same material. For the maximum normal stress theory analyses are done to determine the principle stresses which are compared with the axial tensile or compressive strength. The limiting stress, σ_f , is the failure stress for any given material when loaded axially. Any combination of biaxial principle stresses σ_x and σ_y greater than σ_f will cause failure.

The maximum shearing stress theory predicts failure of a specimen subjected to any combination of loads when the maximum shearing stress at any point reaches the failure stress, $\tau_f = \frac{1}{2}\sigma_f$, as determined by an axial tensile or compressive test. Therefore, failure will occur when $\tau_{\max} = \frac{1}{2}\sigma_{\max} = \frac{1}{2}\sigma_f$, where $\sigma_{\max}$ is the larger of σ_x or σ_y , or when the greater of σ_x or $\sigma_y = \sigma_f$. Additionally, failure will occur if $\sigma_x - \sigma_y = \pm\sigma_f$.

The maximum normal strain theory predicts the failure of a specimen subjected to any combination of loads when the maximum normal strain at any point reaches the failure strain, σ_f/E , at the proportional limit as determined by an axial tensile or compressive test. The limiting strain in the positive x direction is:

$$\epsilon_x = \frac{\sigma_f}{E} = \frac{\sigma_x - \nu \sigma_y}{E} \quad (39)$$

which is a line passing through the point $(\sigma_f, 0)$ with a slope of $1/\nu$. The limiting strain in the positive y direction is:

$$\epsilon_y = \frac{\sigma_f}{E} = \frac{\sigma_y - \nu \sigma_x}{E} \quad (40)$$

which is a line passing through the point $(0, \sigma_f)$ with a slope of ν .

The maximum strain energy theory predicts the failure of a specimen subjected to any combination of loads when strain energy per unit volume of any portion of the stressed

member reaches the failure value of the strain energy per unit volume as determined by an axial tensile or compressive test. Once the principle stresses σ_x , σ_y , and σ_z have been determined the strain energy per unit volume is:

$$u = \frac{1}{2E} [\sigma_x^2 + \sigma_y^2 + \sigma_z^2 - 2\nu(\sigma_x\sigma_y + \sigma_y\sigma_z + \sigma_z\sigma_x)] \quad (41)$$

The maximum strain energy theory has been largely replaced by the maximum distortion energy theory. This theory differs from the maximum strain energy theory in that the portion of the strain energy producing a volume change is considered ineffective in causing failure by yielding. The portion of strain energy producing a shape change of the element is assumed to be completely responsible for the failure of the material by inelastic action. To calculate the distortional part of the energy, the portion of energy which is responsible for volume change is subtracted from the maximum strain energy theory equation. There are only two sources that contribute to the strain energy, the energy required for volume change and that required for shape change. Thus the strain energy can be resolved into two parts, energy due to volume change, u_v , and energy due to distortion, u_d . Therefore, the strain energy resulting from volume change is:

$$u_v = \frac{1-2\nu}{6E} (\sigma_x + \sigma_y + \sigma_z)^2 \quad (42)$$

The energy resulting from distortion is:

$$u_d = \frac{1+\nu}{6E} [(\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2] \quad (43)$$

According to this theory, failure will occur when the energy from distortion exceeds the limiting value obtained from a tensile test. For a tensile test, only one principle stress will be non-zero. If this stress is σ_f , the limiting value of u_d becomes (substitute $\sigma_x = \sigma_f$ and $\sigma_y = \sigma_z = 0$):

$$(u_d)_f = \frac{1+\nu}{3E} \sigma_f^2 \quad (44)$$

Therefore, for a limiting case the failure criterion from the maximum distortion energy theory is:

$$2\sigma_f^2 = [(\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2] \quad (45)$$

For a plane-stress situation the maximum distortion energy theory reduces to:

$$\sigma_f^2 = \sigma_x^2 - \sigma_x \sigma_y + \sigma_y^2 \quad (46)$$

2.4.3.2 Failure Theories for Orthotropic Lamina

In the case of composite or orthotropic materials, failure criteria are much more complex than for an isotropic material where all the failure criteria can be based on an uniaxial test. Major complexities arise from the fact that the strength of an orthotropic material is directionally dependent. Therefore, the concept of principal stresses as they apply to isotropic materials is of no value for composite lamina. The strengths are direction dependent in the composites, and the criteria can not be based on the largest stress component. In addition the tensile and compressive strengths are not the same. For the formulation of failure criteria for composite materials, at least five strength values in the principle material direction are needed. These are:

X_t = Longitudinal strength in tension

X_c = Longitudinal strength in compression

Y_t = Transverse strength in tension

Y_c = Transverse strength in compression

S = Shear strength

The failure criteria for orthotropic materials are written in terms of stresses along the principle material direction rather than the principle stresses. Furthermore, the first step in all calculations is to transform the stresses along the principle material directions so that comparisons can be made with the appropriate strengths.

In the maximum stress theory, failure occurs when the stresses in the principle material directions exceed their respective strengths, i.e.

$$\sigma_1 < X_t ; \sigma_2 < Y_t ; |\tau_{12}| < S ; \sigma_1 < X_c ; \sigma_2 < Y_c$$

Note that the sign of the shear stress does not matter. If any one of these five inequalities is violated, the specimen is assumed to have failed by a failure mode associated with the allowable stress. Also, there are no interactions between the modes of failure in this failure criterion. In fact, there are five subcriteria.

Consider an orthotropic lamina subjected to a uniaxial stress, σ_x , making an angle, Θ , with the fiber direction. For the application of the maximum stress criterion, the stresses in the body must be transformed to stresses in the principle material direction.

$$\begin{aligned}\sigma_1 &= \sigma_x \cos^2(\Theta) \\ \sigma_2 &= \sigma_x \sin^2(\Theta) \\ \tau_{12} &= -\sigma_x \sin(\Theta)\cos(\Theta)\end{aligned}\tag{47}$$

Failure will occur when σ_x exceeds the smallest of:

$$\begin{aligned}\sigma_x &< \frac{X}{\cos^2 \Theta} \\ \sigma_x &< \frac{Y}{\sin^2 \Theta} \\ \sigma_x &< \frac{S}{\sin \Theta \cos \Theta}\end{aligned}\tag{48}$$

The maximum strain theory is similar to the maximum stress theory; however, strains are limited rather than stresses. Therefore, according to this theory failure occurs when any of the following inequalities are violated;

$$\epsilon_1 < X_{et} ; \epsilon_2 < Y_{et} ; |\gamma_{12}| < S_e ; \epsilon_1 < X_{ec} ; \epsilon_2 < Y_{ec}$$

When considering a composite lamina subjected to a uniaxial stress, σ_x , and making an angle, Θ , with the fiber direction, the maximum strain criterion becomes:

$$\begin{aligned}
 \sigma_x &< \frac{X}{\cos^2 \Theta - \nu_{12} \sin^2 \Theta} \\
 \sigma_x &< \frac{Y}{\sin^2 \Theta - \nu_{21} \cos^2 \Theta} \\
 \sigma_x &< \frac{S}{\sin \Theta \cos \Theta}
 \end{aligned} \tag{49}$$

The maximum work energy theory is also known as the Tsai-Hill theory. Similar to the maximum distortion energy theory for isotropic materials, Hill proposed a yield criterion for anisotropic materials. In the case of isotropic materials, only distortional energy was included in the failure criterion. However, for orthotropic materials, distortion is always dilational energy and, therefore, these two parts of energy can not be separated. For plane stress in the 1-2 plane of a unidirectional lamina, with fibers in the 1-direction, the following conditions exist: $\sigma_3 = \tau_{13} = \tau_{23} = 0$. Also, from the cross section of the lamina $Y = Z$ (the strength in the Y and Z directions are equal), this failure criterion states that failure will occur when:

$$\frac{\sigma_1^2}{X^2} - \frac{\sigma_1 \sigma_2}{X^2} + \frac{\sigma_2^2}{Y^2} + \frac{\tau_{12}^2}{S^2} \geq 1 \tag{50}$$

This theory provides a single equation to predict strength while accounting for the interaction between strengths. As an example of this criterion, assume that if a stress, σ_x , is applied at an angle, Θ , from the fiber axis, then the stress in the principal material direction will be given as:

$$\frac{\cos^4 \Theta}{X^2} + \left(\frac{1}{S^2} - \frac{1}{X^2} \right) \cos^2 \Theta \sin^2 \Theta + \frac{\sin^4 \Theta}{Y^2} = \frac{1}{\sigma_x^2} \tag{51}$$

2.4.4 Strength of Orthotropic Lamina

For orthotropic materials basic tests can be performed to obtain the properties in the principal material directions. These experiments can provide both strength and stiffness characteristics if conducted properly. The stiffness characteristics are:

$$E_1 = \text{longitudinal tensile modulus (1-direction)}$$

E_2 = transverse tensile modulus (2-direction)

$\nu_{12} = -\epsilon_2/\epsilon_1$ for $\sigma_1 = \sigma$ (all other $\sigma = 0$)

$\nu_{21} = -\epsilon_1/\epsilon_2$ for $\sigma_2 = \sigma$ (all other $\sigma = 0$)

G_{12} = shear modulus in the 1-2 Plane

and the strength characteristics are:

X_t = longitudinal tensile strength

Y_t = transverse tensile strength

X_c = longitudinal compressive strength

Y_c = transverse compressive strength

S = shear strength in the 1-2 plane

Several experiments can be performed to obtain the basic stiffness and strength properties.

The primary assumption in these experiments is that the stress-strain behavior of the materials is linear from zero load to fracture. This behavior is typical of brittle polymers and glass/epoxy composites. The characteristic of linear elastic behavior to fracture is similar to the analysis of bodies that exhibit elastic behavior until the onset of plasticity.

The major assumption in the experimental determination of the strength and stiffness properties in a lamina is the imposition of a uniform stress state throughout the specimen. This loading is easily obtained in isotropic materials. However, in composite materials, when loaded in nonprincipal material directions, orthotropy often introduces coupling between:

- 1) normal stresses and shear strains
- 2) shear stresses and normal strains
- 3) normal stresses and bending curvatures
- 4) bending stresses and normal strains

2.4.4.1 Uniaxial Longitudinal Tension Test

This test is performed on a flat specimen of unidirectionally reinforced lamina, see Figure 12. The strains ϵ_1 and ϵ_2 are measured in the test where, A , is the cross-sectional area of the specimen end perpendicular to the applied load;

$$\sigma_1 = \frac{P}{A} \quad (52)$$

$$E_1 = \frac{\sigma_1}{\epsilon_1} \quad (53)$$

$$\nu_{12} = -\frac{\epsilon_2}{\epsilon_1} \quad (54)$$

$$X = \frac{P_{ult}}{A} \quad (55)$$

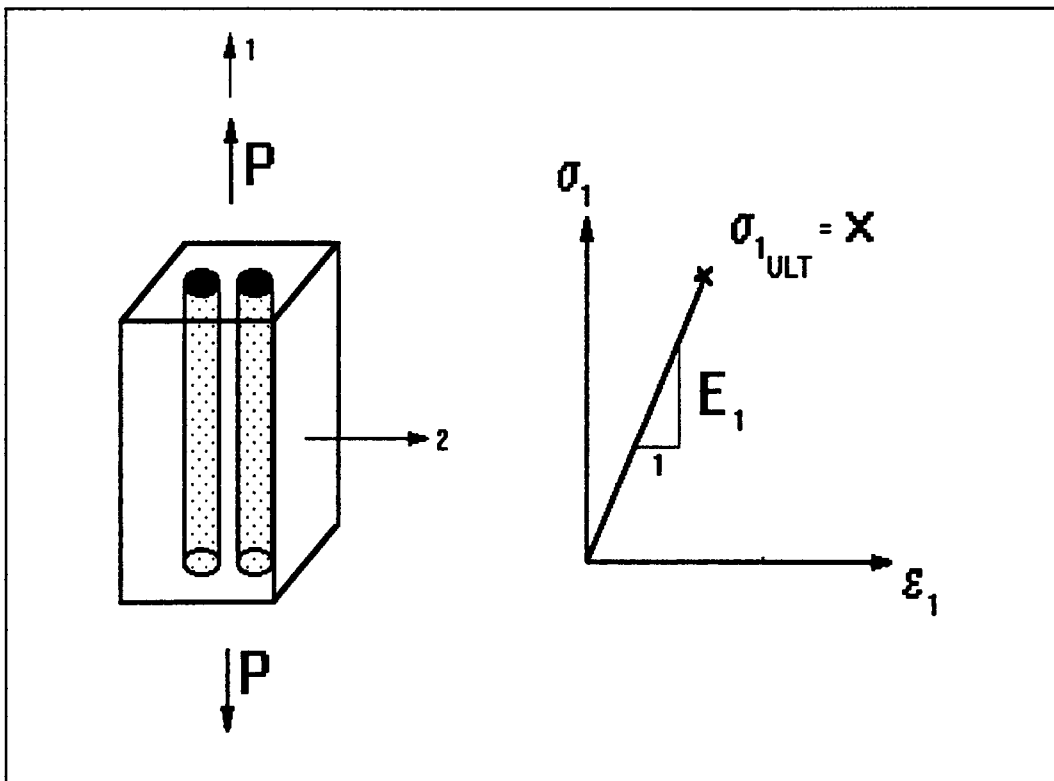


Figure 12: Uniaxial Longitudinal Loading.

2.4.4.2 Uniaxial Transverse Tensile Test

Similar to the longitudinal test the specimen is a flat piece of unidirectionally reinforced lamina. Again the strains ϵ_1 and ϵ_2 are measured where, A , is the cross-sectional area of the specimen end perpendicular to the applied load, refer to Figure 13;

$$\sigma_2 = \frac{P}{A} \quad (56)$$

$$E_2 = \frac{\sigma_2}{\epsilon_2} \quad (57)$$

$$\nu_{21} = -\frac{\epsilon_1}{\epsilon_2} \quad (58)$$

$$Y = \frac{P_{ult}}{A} \quad (59)$$

The stiffness and strength properties in both the longitudinal and transverse directions should satisfy the reciprocal relationship;

$$\frac{\nu_{12}}{E_1} = \frac{\nu_{21}}{E_2} \quad (60)$$

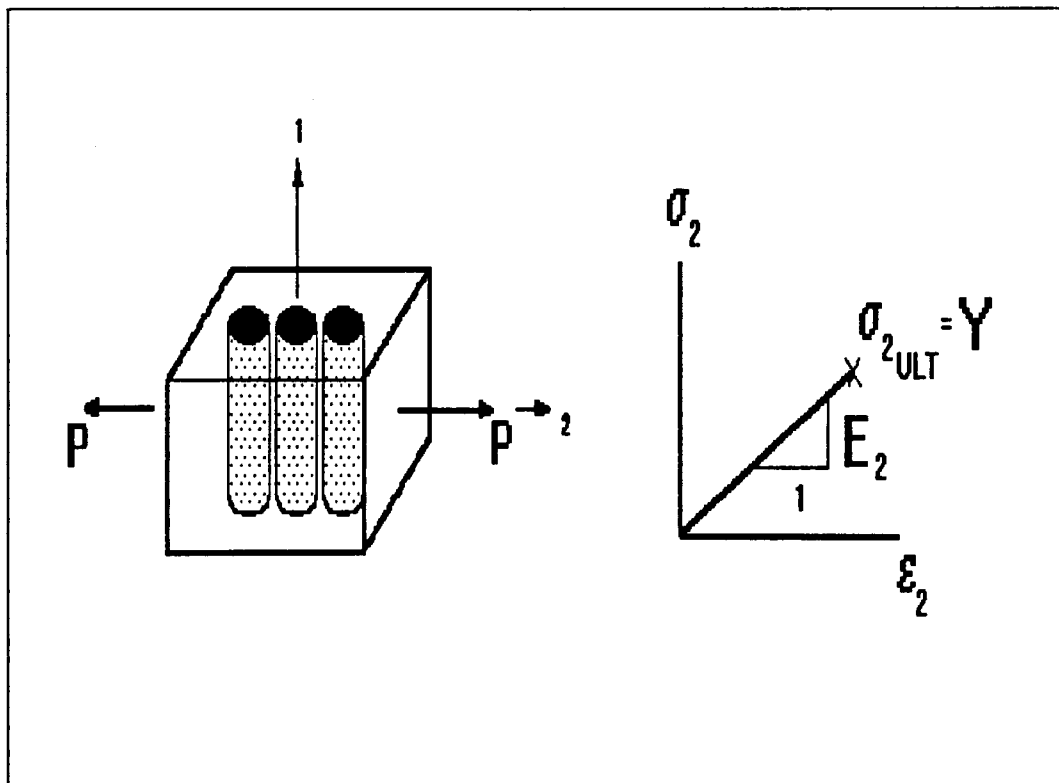


Figure 13: Uniaxial Transverse Loading.

2.4.4.3 Uniaxial Shear Loading

For uniaxial shear loading, a tension test at 45° to the principal material axis (1-direction) is performed on a flat piece of lamina. By measuring ϵ_x , the stiffness in the x-direction may be determined, see Figure 14.

$$E_x = \frac{P\epsilon_x}{A} \quad (61)$$

Transformation relationships of the orthotropic materials are given as:

$$G_{12} = \frac{1}{\left(\frac{4}{E_x} - \frac{1}{E_1} - \frac{1}{E_2} + \frac{2\nu_{12}}{E_1}\right)} \quad (62)$$

Strength unlike stiffness does not transform, thus this experiment cannot be relied upon to determine S, the ultimate shear stress.

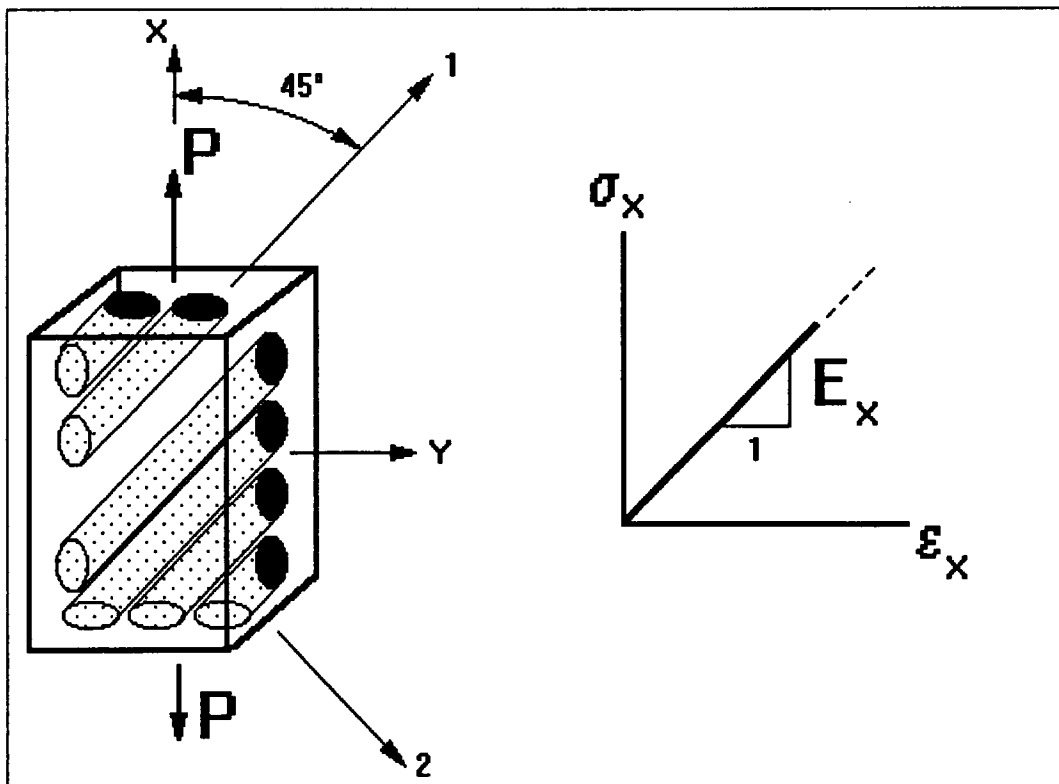


Figure 14: Uniaxial Shear Loading.

2.5 Micromechanical Behavior of a Lamina

So far the discussion has been directed at the “apparent” properties of a lamina. However, we have not answered the question of “How can the stiffness and strength be varied in the composite?” or “How can the relative amounts of constituent materials be varied to arrive at the desired stiffness and strength?”. To answer these questions the lamina behavior must be understood. There are two divisions of the behavior of composite materials, micromechanics and macromechanics, which are defined as follows:

Micromechanics - The study of composite material behavior wherein the interaction of the constituent materials is examined in detail as part of the definition of the behavior of the heterogeneous composite material.

Macromechanics - The study of composite material behavior wherein the material is presumed homogenous and the effects of the constituent materials are detected only as averaged properties of the composite.

It is possible to predict the lamina properties by the procedures of micromechanics and to measure lamina properties by physical means from a macromechanical analysis of the structure. Knowledge of how to predict properties is essential to constructing composites that must have certain apparent or macroscopic properties.

There are two basic approaches to the micromechanics of composite materials, mechanics of materials and elasticity. The mechanics of materials approach employs the usual concept of simplifying assumptions regarding the hypothesized behavior of the mechanical system. The elasticity approach is actually three approaches: (1) bounding principles, (2) exact solutions, and (3) approximate solutions.

Regardless of the micromechanical approach used, the basic restrictions on the composite material are: (1) the lamina is macroscopically homogenous, linearly elastic, macroscopically orthotropic, and initially stress free, (2) the fibers are homogeneous, linearly elastic, isotropic, regularly spaced, and perfectly aligned, and (3) the matrix is

homogeneous, linearly elastic, and isotropic. In addition, the bonds between the fiber and matrix are perfect.

2.5.1 Mechanics of Material Approach to Stiffness

The basic element of the mechanics of materials approach to stiffness is simplifying assumptions regarding the mechanical behavior of a composite material. The dominant assumption is that strains in the fiber direction of a unidirectional fibrous composite are the same in the fiber as in the matrix. Therefore, sections of the composite which were plane prior to being stressed remain plane during and after a stress is applied. On this assumption the mechanics of materials expressions for the apparent orthotropic moduli of a unidirectionally reinforced fibrous composite can be derived. The stiffness characteristics are:

E_1 = longitudinal tensile modulus (1-direction)

E_2 = transverse tensile modulus (2-direction)

ν_{12} = $-\epsilon_2/\epsilon_1$ for $\sigma_1 = \sigma$ (all other $\sigma = 0$)

ν_{21} = $-\epsilon_1/\epsilon_2$ for $\sigma_2 = \sigma$ (all other $\sigma = 0$)

G_{12} = shear modulus in the 1-2 plane

2.5.1.1 Longitudinal Tensile Modulus

The first modulus to be determined is that of the composite in the 1-direction or fiber direction.

$$\epsilon_1 = \frac{\Delta L}{L} \quad (63)$$

The strain in the 1-direction applies to both the fiber and matrix. If both constituent materials behave elastically the stresses are:

$$\sigma_f = E_f \epsilon_f \quad (64)$$

$$\sigma_m = E_m \epsilon_m \quad (65)$$

The average stress, σ_1 , acts on the cross sectional area, A ; σ_f acts on the cross sectional area of the fibers, A_f ; and σ_m acts on the cross-sectional area of the matrix, A_m . The resultant force on the element of the composite is:

$$P = \sigma_1 A = \sigma_f A_f + \sigma_m A_m \quad (66)$$

By substitutions of stresses and volume fractions the modulus in the 1-direction simplifies to what is known as the rule of mixtures for the apparent tensile modulus in the direction of the fibers.

$$E_1 = E_f V_f + E_m V_m \quad (67)$$

2.5.1.2 Transverse Tensile Modulus

The transverse tensile modulus, E_2 , is determined using the same assumptions as for the longitudinal modulus. The stress, σ_2 , is assumed to be applied to both the fiber and the matrix. Therefore, the strains in the fiber and matrix are:

$$\begin{aligned} \epsilon_f &= \frac{\sigma_2}{E_f} \\ \epsilon_m &= \frac{\sigma_2}{E_m} \end{aligned} \quad (68)$$

The transverse dimension over which the average strain in the fiber acts is approximately $V_f W$, whereas the strain in the matrix acts on $V_m W$ where, W , is a unit of symmetric width about the fiber. The total transverse deformation is;

$$\epsilon_2 W = V_f W \epsilon_f + V_m W \epsilon_m \quad (69)$$

with substitution of equivalent strains and simplifications, becomes:

$$E_2 = \frac{E_f E_m}{V_m E_f + V_f E_m} \quad (70)$$

2.5.1.3 Poisson's Ratio

The major Poisson's ratio is obtained using the same approaches as for both tensile moduli. The Poisson's ratio is defined as

$$\nu_{12} = -\frac{\epsilon_2}{\epsilon_1} \quad (71)$$

For the stress state $\sigma_1 = \sigma$ and all other stresses equal to zero, the transverse deformation is:

$$\Delta_w = -W\epsilon_2 = W\nu_{12}\epsilon_1 \quad (72)$$

or

$$\Delta_w = \Delta_{mw} + \Delta_{fw} \quad (73)$$

For this analysis the deformations with respect to the fiber and matrix are as follows

$$\begin{aligned} \Delta_{mw} &= WV_m\nu_m\epsilon_1 \\ \Delta_{fw} &= WV_f\nu_f\epsilon_1 \end{aligned} \quad (74)$$

With substitutions and simplifications the result is a rule of mixtures for the major Poisson's ratio,

$$\nu_{12} = V_m\nu_m + V_f\nu_f \quad (75)$$

2.5.1.4 Shear Modulus

The in-plane shear modulus of a lamina, G_{12} , is determined by assuming that the shearing stresses on the fiber and the matrix are in fact the same, therefore;

$$\begin{aligned} \gamma_m &= \frac{\tau}{G_m} \\ \gamma_f &= \frac{\tau}{G_f} \end{aligned} \quad (76)$$

At this point the non-linear shear strain behavior typical in fiber-reinforced composites is considered to be linear. On a microscopic scale the shearing deformations are defined as

$$\begin{aligned}\Delta_m &= V_m W \gamma_m \\ \Delta_f &= V_f W \gamma_f\end{aligned}\tag{77}$$

Since the total shearing deformation is the sum of the deformation of both the fiber and matrix, the shear stress is a rule of mixtures.

$$\gamma = V_m \gamma_m + V_f \gamma_f\tag{78}$$

Upon substitutions the shear modulus may be written as

$$G_{12} = \frac{G_m G_f}{V_m G_f + V_f G_m}\tag{79}$$

2.5.2 Elasticity Approach to Stiffness

Elasticity approaches to stiffness may be further divided into many different subgroups. Bounding techniques of linear elasticity employed by Paul [68] were used to examine the moduli of alloyed materials. Energy principles of classical elasticity theory are used to determine the upper and lower bounds on lamina moduli. Paul's approach generally leads to bounds that may not be sufficiently close for practical use. Yet, another approach using the principles of elasticity theory is used in determining exact solutions. Due to the resulting complexity of the many problems, advanced analytical and numerical solution procedures are necessary. However, assumptions made in such analyses, such as interactions between fiber and matrix, are not entirely realistic. Another approach with a more realistic fiber-matrix interaction is the continuity approach. This method is referred to as a semiempirical method by Chamis and Sendeckyi [69]. The continuity method involves linear combinations of moduli with fibers in contact with each other and fibers isolated from one another. The continuity is expressed as greater than zero yet less than one and has a linear effect on the moduli. The most commonly used elasticity approach to predicting stiffness is equations provided by Halpin and Tsai [70].

2.5.2.1 Halpin-Tsai Equations

Halpin-Tsai developed an interpolation process that is an approximation of more complicated micromechanics results. The advantage to these equations is that they can be

used in design processes and are accurate if the fiber volume fraction does not approach one. Halpin-Tsai procedures showed that Herman's solution [71] generalizing Hill's self-consistent model [72] can be reduced to the approximate form:

$$E_1 \equiv E_f V_f + E_m V_m \quad (80)$$

$$\nu_{12} = \nu_f V_f + \nu_m V_m \quad (81)$$

and

$$\frac{M}{M_m} = \frac{1 + \xi \eta V_f}{1 - \eta V_f} \quad (82)$$

where

$$\eta = \frac{(M_f / M_m) - 1}{(M_f / M_m) + \xi} \quad (83)$$

in which

M = composite modulus E_2 , G_{12} , or ν_{23}

M_f = corresponding fiber modulus E_f , G_f , or ν_f

M_m = corresponding matrix modulus E_m , G_m , or ν_m

and ξ , is a measure of fiber reinforcement of the composite that depends on the fiber geometry, packing geometry, and loading conditions. The variable ξ is determined through the comparison of Equations 82 and 83 with exact elasticity solutions and assessing a value of or function for ξ by curve fitting techniques.

The expressions for E_1 are the accepted rule of mixtures. Halpin-Tsai equations are also applicable to fiber, ribbon, or particle composites. Halpin and Thomas [73] applied Halpin-equations to stiffness of glass ribbon-reinforced composites rather successfully.

The difficulty in using Halpin-Tsai equations is in determining an appropriate value for ξ . Halpin and Tsai were in agreement with Adams' and Doner's [74, 75] results for circular fibers in a square motif when $\xi = 2$ for calculations of E_2 , and $\xi = 1$ for calculations of G_{12}

with a fiber volume fraction of 0.55. Using the same values for ξ similar agreements were obtained with Foye's [76, 77] results for square fibers in a diamond motif when the fiber volume fraction ranged up to 0.9.

2.6 Macromechanical Behavior of a Laminate

A laminate consists of two or more laminae bonded together which act as an integral structural element. Laminae principal material directions are oriented such as to produce a structural element capable of resisting load in several directions. The stiffness of such a composite is obtained from the properties of the laminae. Laminate static strength is also influenced by the presence of residual stress, elastic stress concentrations, and interlaminar stress.

2.6.1 Classical Lamination Theory

This theory predicts the properties of a laminate from the properties, orientation and geometrical arrangement of individual laminae by modeling a unidirectional lamina as orthotropic material in plane stress.

The stress-strain relations in the principal material coordinate system for a lamina of an orthotropic material in plane stress are:

$$\begin{Bmatrix} \sigma_1 \\ \sigma_2 \\ \tau_{12} \end{Bmatrix} = \begin{bmatrix} Q_{11} & Q_{12} & 0 \\ Q_{21} & Q_{22} & 0 \\ 0 & 0 & Q_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_1 \\ \epsilon_2 \\ \gamma_{12} \end{Bmatrix} \quad (84)$$

where the components of the reduced stiffness are defined as:

$$Q_{11} = \frac{E_1}{1 - \nu_{12}\nu_{21}} \quad (85)$$

In any other direction in the plane of the lamina the stress-strain relations are defined using the transformation matrix and are thus:

$$\begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{Bmatrix} = \begin{bmatrix} Q'_{11} & Q'_{12} & Q'_{16} \\ Q'_{12} & Q'_{22} & Q'_{26} \\ Q'_{16} & Q'_{26} & Q'_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_x \\ \epsilon_y \\ \gamma_{xy} \end{Bmatrix} \quad (86)$$

Equations 84 and 86 are thought of as the stress-strain relations for the k^{th} layer of a multidirectional laminate. The stress-strain relation of the k^{th} layer is written as:

$$(\sigma)_k = [Q']_k (\epsilon)_k \quad (87)$$

Considering the deformation of a section of a laminate, see Figure 15. Assume that segment ABCD is originally straight and perpendicular to the midplane of the laminate and it remains straight and perpendicular to the midplane in the deformed state. This assumption is equivalent to neglecting shearing deformations, and also equivalent to assuming that the laminae that make up the laminate cross-section do not slip over each other. In addition, the normals, i.e. AD, are presumed to have constant length so that strain perpendicular to the middle surface is ignored as well.

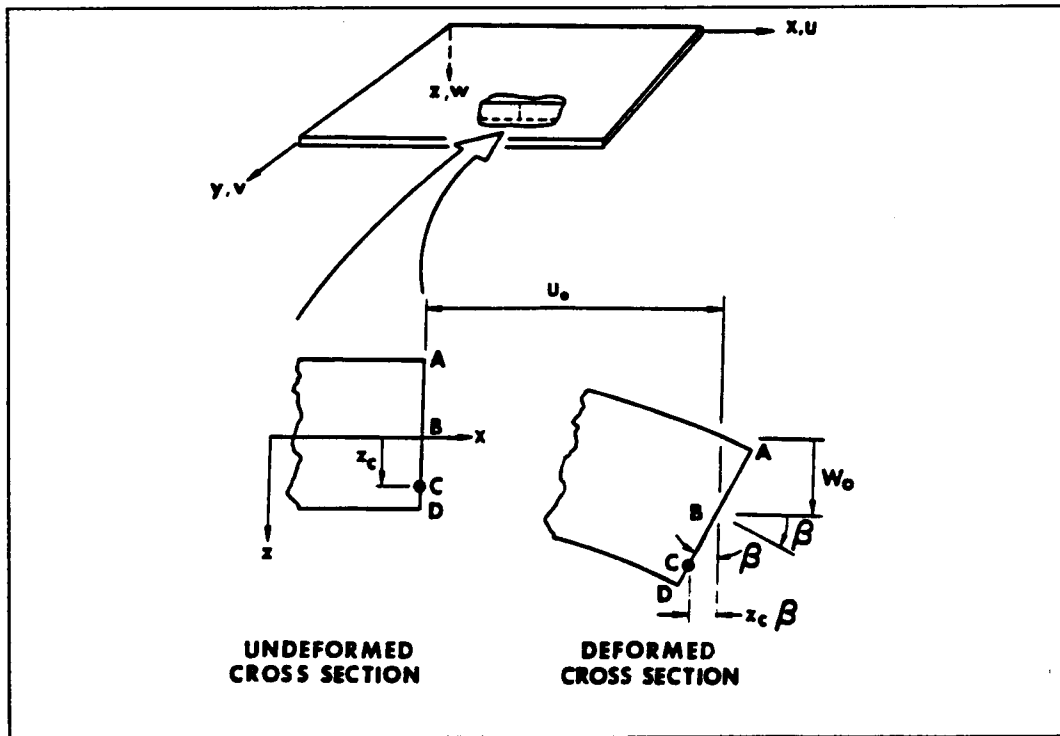


Figure 15: Deformation in the XZ Plane.

The strains are:

$$\epsilon_x = \frac{\partial u}{\partial x} = \frac{\partial u_o}{\partial x} - z \frac{\partial^2 w_o}{\partial x^2} \quad (88)$$

$$\epsilon_y = \frac{\partial v}{\partial y} = \frac{\partial v_o}{\partial y} - z \frac{\partial^2 w_o}{\partial y^2} \quad (89)$$

$$\gamma_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} = \frac{\partial u_o}{\partial y} + \frac{\partial v_o}{\partial x} - 2z \frac{\partial^2 w_o}{\partial x \partial y} \quad (90)$$

or

$$\begin{Bmatrix} \epsilon_x \\ \epsilon_y \\ \gamma_{xy} \end{Bmatrix} = \begin{Bmatrix} \epsilon_x^o \\ \epsilon_y^o \\ \gamma_{xy}^o \end{Bmatrix} + z \begin{Bmatrix} \kappa_x^o \\ \kappa_y^o \\ \kappa_{xy}^o \end{Bmatrix} \quad (91)$$

Where ϵ^o are the middle surface strains,

$$\begin{Bmatrix} \epsilon_x^o \\ \epsilon_y^o \\ \gamma_{xy}^o \end{Bmatrix} = \begin{Bmatrix} \frac{\partial u_o}{\partial x} \\ \frac{\partial v_o}{\partial y} \\ \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \end{Bmatrix} \quad (92)$$

and K are the middle surface curvatures,

$$\begin{Bmatrix} \kappa_x \\ \kappa_y \\ \kappa_{xy} \end{Bmatrix} = - \begin{Bmatrix} \frac{\partial^2 w_o}{\partial x^2} \\ \frac{\partial^2 w_o}{\partial y^2} \\ 2 \frac{\partial^2 w_o}{\partial x \partial y} \end{Bmatrix} \quad (93)$$

Therefore, the strains in the laminate vary linearly across the thickness. Knowing the mid-plane strains and curvatures, the stress in the k^{th} lamina can be determined using Equation 86, resulting in the following:

$$\begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{Bmatrix}_k = \begin{bmatrix} Q'_{11} & Q'_{12} & Q'_{16} \\ Q'_{12} & Q'_{22} & Q'_{26} \\ Q'_{16} & Q'_{26} & Q'_{66} \end{bmatrix}_k \begin{Bmatrix} \epsilon_x^o \\ \epsilon_y^o \\ \gamma_{xy}^o \end{Bmatrix} + z \begin{bmatrix} Q'_{11} & Q'_{12} & Q'_{16} \\ Q'_{12} & Q'_{22} & Q'_{26} \\ Q'_{16} & Q'_{26} & Q'_{66} \end{bmatrix}_k \begin{Bmatrix} \kappa_x \\ \kappa_y \\ \kappa_{xy} \end{Bmatrix} \quad (94)$$

The strain in the k^{th} layer is a linear relationship with respect to laminate thickness coordinate z . Since the stiffness matrix of each lamina may be different, the stress across the thickness may not be a linear function of z , see Figure 16. However, the stresses will be linear across the thickness within each lamina. The stresses are discontinuous at the interface of two laminates.

2.6.2 Resultant Laminate Forces and Moments

Since the stresses within a laminate vary from layer to layer equations are developed in terms of equivalent forces and moments acting on the laminate. The equivalent forces are defined as:

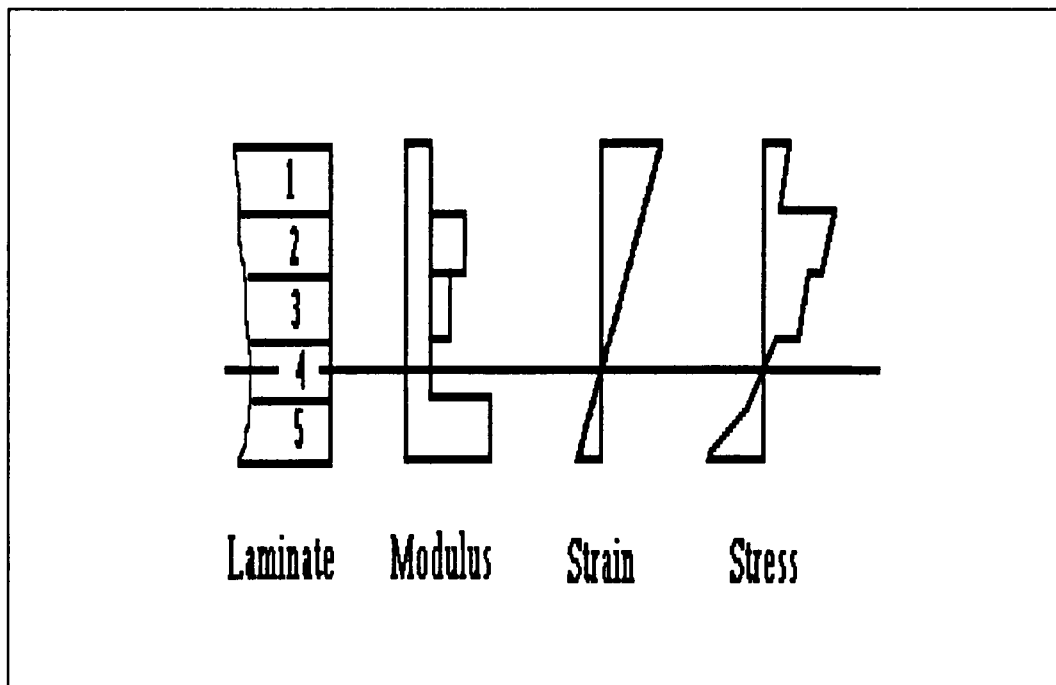


Figure 16: Stress Discontinuity Throughout Laminate.

$$N_i = \int_{-\frac{t}{2}}^{\frac{t}{2}} \sigma_i dz \quad (95)$$

The equivalent moments are defined as:

$$M_i = \int_{-\frac{t}{2}}^{\frac{t}{2}} \sigma_i z dz \quad (96)$$

For laminates consisting of N laminae, the force-moment system acting at the midplane is obtained by replacing the continuous integral of equations 95 and 96 with a summation of integrals representing the contribution of each layer:

$$\begin{Bmatrix} N_x \\ N_y \\ N_{xy} \end{Bmatrix} = \int_{-\frac{t}{2}}^{\frac{t}{2}} \begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{Bmatrix} dz = \sum_{k=1}^N \int_{z_{k-1}}^{z_k} \begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{Bmatrix}_k dz \quad (97)$$

and

$$\begin{Bmatrix} M_x \\ M_y \\ M_{xy} \end{Bmatrix} = \int_{-\frac{t}{2}}^{\frac{t}{2}} \begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{Bmatrix} z dz = \sum_{k=1}^N \int_{z_{k-1}}^{z_k} \begin{Bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{Bmatrix}_k z dz \quad (98)$$

By combining with the midplane equation and numerous simplifications, the following set of equations is derived.

$$\begin{Bmatrix} N_x \\ N_y \\ N_{xy} \end{Bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{16} \\ A_{12} & A_{22} & A_{26} \\ A_{16} & A_{26} & A_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_x^o \\ \epsilon_y^o \\ \gamma_{xy}^o \end{Bmatrix} + \begin{bmatrix} B_{11} & B_{12} & B_{16} \\ B_{12} & B_{22} & B_{26} \\ B_{16} & B_{26} & B_{66} \end{bmatrix} \begin{Bmatrix} \kappa_x \\ \kappa_y \\ \kappa_{xy} \end{Bmatrix} \quad (99)$$

$$\begin{Bmatrix} M_x \\ M_y \\ M_{xy} \end{Bmatrix} = \begin{bmatrix} B_{11} & B_{12} & B_{16} \\ B_{12} & B_{22} & B_{26} \\ B_{16} & B_{26} & B_{66} \end{bmatrix} \begin{Bmatrix} \epsilon_x^o \\ \epsilon_y^o \\ \gamma_{xy}^o \end{Bmatrix} + \begin{bmatrix} D_{11} & D_{12} & D_{16} \\ D_{12} & D_{22} & D_{26} \\ D_{16} & D_{26} & D_{66} \end{bmatrix} \begin{Bmatrix} \kappa_x \\ \kappa_y \\ \kappa_{xy} \end{Bmatrix} \quad (100)$$

Where

$$\begin{aligned}
 A_{ij} &= \text{Extensional Stiffness} = \sum_{k=1}^N (Q'_{ij})_k (z_k - z_{k-1}) \\
 B_{ij} &= \text{Coupling Stiffness} = \frac{1}{2} \sum_{k=1}^N (Q'_{ij})_k (z_k^2 - z_{k-1}^2) \\
 D_{ij} &= \text{Bending Stiffness} = \frac{1}{3} \sum_{k=1}^N (Q'_{ij})_k (z_k^3 - z_{k-1}^3)
 \end{aligned} \tag{101}$$

The total laminate constitutive equation is written thusly:

$$\begin{Bmatrix} N \\ M \end{Bmatrix} = \begin{bmatrix} A & B \\ B & D \end{bmatrix} \begin{Bmatrix} \epsilon^o \\ \kappa \end{Bmatrix} \tag{102}$$

The extensional stiffness relates the resultant forces to the midplane strains. Bending stiffness relates the resultant moments to the plate curvatures. The presence of the coupling matrix in the plate constitutive equations implies coupling between bending and extension of a laminated plate.

2.6.3 Longitudinal Tensile Failure Mode

In the broadest sense, failure of a structural element is stated as having taken place when it ceases to perform its designed function. The definition of failure will continue to change from one application to another. In composite materials, the internal material failure generally initiates prior to any change in its macroscopic appearance. Internal material failure may be in many forms such as a) breaking of the fibers, b) microcracking of the matrix, c) separation of the fibers and matrix (debonding) and d) separation of the laminae from each other (delimitation),

In a unidirectional composite consisting of brittle fibers subjected to longitudinal tensile load the failure initiates by fiber breakage at their weakest point. The crack at the broken end of the fiber can interact with the matrix material in one of the three following manners: The first possibility is that the crack propagates in the matrix as a brittle crack producing a transverse failure. The second possibility is that the matrix in the vicinity of the broken fiber yields and blunts the crack relieving the stress concentration. These matrix yield

zones then spread along the fiber resulting in a stepped transverse and longitudinal failure. The final possibility is that the interface or the matrix adjacent to the fiber fails, unloading of the fiber and allowing it to relax. Matrix failures are generally longitudinal failures.

2.7 Fiber Matrix Interface

The interface of matrix and fiber influences the mechanical and physical properties of composites. Stresses acting on the matrix are transmitted to the fiber across the interface. In the absence of chemical, physical, or mechanical bonding between the layers, the composite would have no tensile strength in the transverse direction. It follows that if the high stiffness and strength of the fibers are to be utilized they must be strongly bonded with the matrix. Interfaces may arise in polymer systems for two reasons, 1) surfaces exist between two mutually insoluble and chemically distinct phases which are at equilibrium with respect to each other, and 2) surfaces may exist between two essentially miscible components which have not reached equilibrium. Also of great importance is the relatively high viscosity of polymers.

2.7.1 Mechanisms of Adhesion

Adhesion can be attributed to five main mechanisms at the interface which may occur individually or in combination to yield the bond between fiber and matrix. These are wetting, interdiffusion, elastomeric attraction, chemical bonding and mechanical bonding. Wetting is the term usually reserved for the interaction of liquids with solid surfaces. On a microscopic scale the fiber surface is rough. Therefore, for effective wetting the liquid resin must cover every crevice of the fiber surface, displacing all air. The idea of wetting was first explored by Young in 1805. Young's equation states the following relationship:

$$\cos \Theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (103)$$

where Θ is the contact angle of the degree of wetting; γ is the surface energy or surface tension and the subscripts 'sv', 'sl', and 'lv' are for solid/vapor, solid/liquid, and liquid/vapor interfaces, respectively. Three classes of wetting behavior can be distinguished. The degree of wetting where Θ lies between 0 and 180 is referred to as

partial wetting. As Θ tends to zero, the liquid drop spreads over the solid forming a thin layer; the solid is completely wet. As Θ tends to 180, the liquid drop forms a perfect sphere tangent to the solid surface, refer to Figure 17.

A useful parameter in considering the wetting of fibers by resin is based on critical surface tensions, τ_c . By using a series of liquids which have slightly different surface tensions and determining the contact angle of each on a particular surface, a plot of $\cos\Theta$ as a function of surface tension produces a linear relationship. Extrapolation of the curve to the point where the contact angle becomes zero ($\cos\Theta = 1$) gives the critical surface tension for the solid. If the surface energy of a solid is τ_c , only liquids with $\tau_{lv} < \tau_c$ will spontaneously spread on the solid, provided the viscosity of the resin is not too high.

The diffusion theory describes the penetration of the substrate by the adhesive prior to the solidification of the adhesive. It is possible to form a bond between two polymer surfaces by diffusion of the polymer molecules on one surface into the molecular network of the

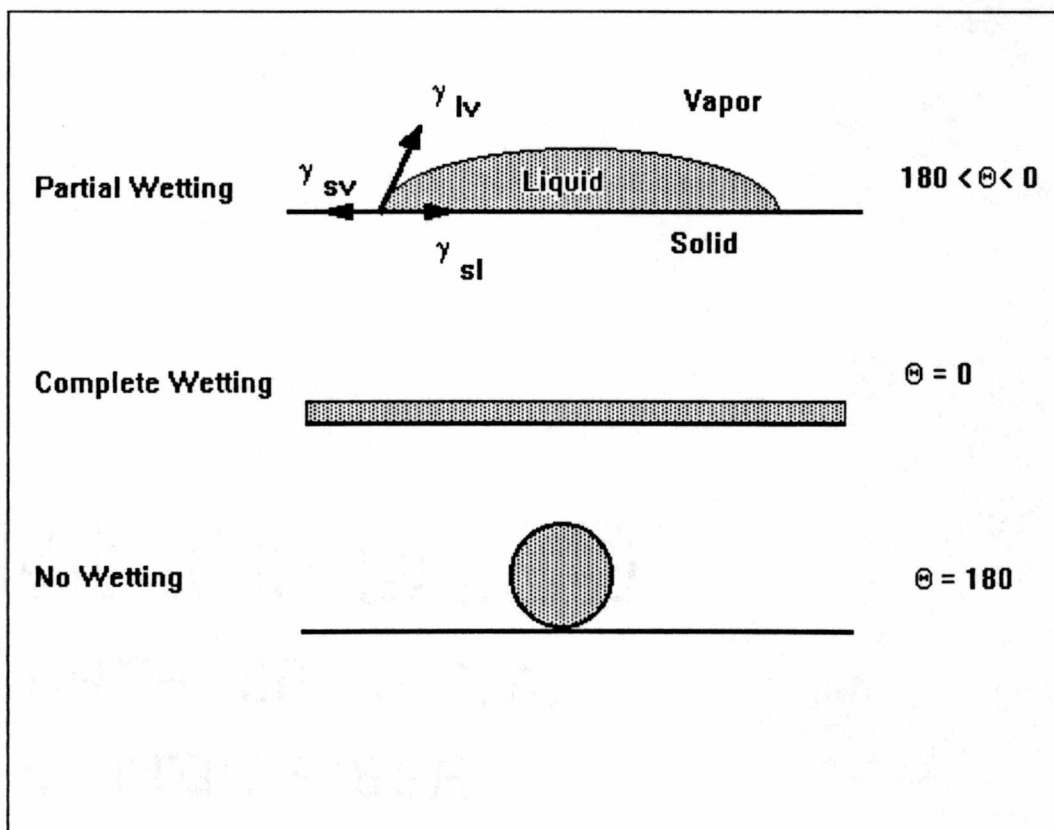


Figure 17: Wetting of Solids by a Drop of Liquid in Contact With its Vapor.

other surface. The bond strength will depend on the amount of entanglement and the number of molecules involved.

Another mechanism of adhesion is electrostatic attraction which occurs between two oppositely charged surfaces as in the case of acid-base interaction and ionic bonding. The strength of interface will depend on the charge density; however, electrostatic attraction is not likely to make major contributions to the interfacial bond strength of fiber-matrix composites.

Chemical bonding is of particular interest because it provides an explanation for the use of coupling agents on glass fibers and the strength of the bond between carbon fibers and polymer matrices. A chemical bond is formed between a chemical grouping on the fiber surface and a compatible chemical group in the matrix. The strength of the interface depends on the number and type of chemical bonds. Interfacial failure involves the breaking of chemical bonds.

Some bonding may occur only by the mechanical interlocking of two surfaces. Resin may flow into the crevices of the fiber surface and thus establish a mechanical bond. The shear strength of the interface is attributable to the mechanical bond between fiber and matrix.

The interface between fibers and polymers has become an area of great interest. Research has not yet identified what is needed for the ideal fiber composite. In general, composite materials with relatively weak interfaces have relatively low strength and stiffness but high resistance to fracture, displaying high fracture toughness. Conversely, composite materials with strong interfaces display high strength and stiffness but are quite brittle, displaying low fracture toughness.

2.7.2 Interfacial Bond Strength

Fiber-matrix bond strength is usually characterized by the fiber-matrix interfacial shear strength and is characterized by the fiber critical length. Fiber critical length is that length when the total shear force carried by the embedded length of the fiber equals the tensile force necessary to cause the fiber to fracture.

Measuring the interface and interphase properties of composite materials is quite difficult because of the small diameter of the fibers, usually less than 10 microns. Four methods are currently used to measure the properties of interfaces, see Figure 18. Each test has its attributes; however, the methods provide conflicting results. Further difficulty lies in the uncertain nature of the failure modes of the interfaces [78].

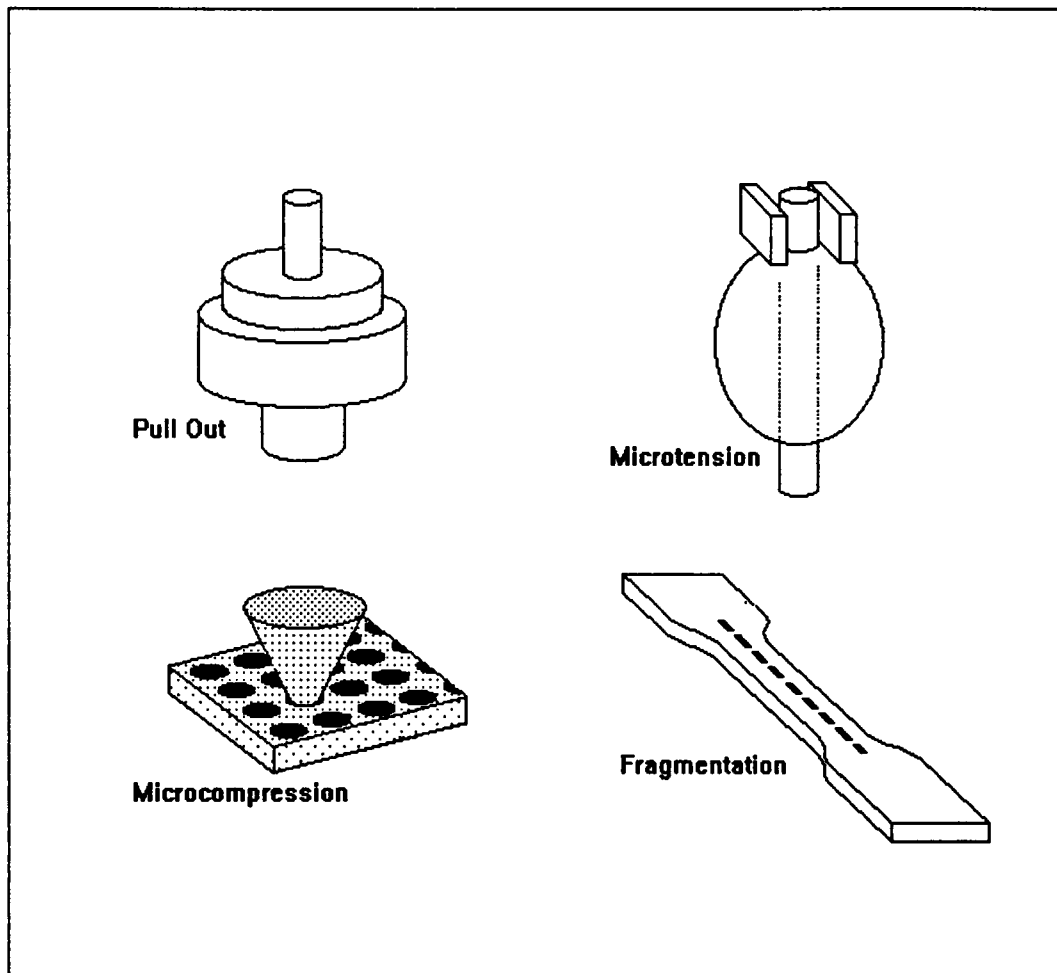


Figure 18: Methods Used to Determine Interface Properties

3. Experimental

3.1 Materials

Films of 1, 10 and 20 mil PETG and PET were provided by Eastman Chemical. Kodar PETG copolyester 6763 is an amorphous polymer based on poly(ethylene terephthalate) and has a number average molecular weight of about 26,000. Kodar PET 7352, poly(ethylene terephthalate) has a number average molecular weight of 28,000. AS4-12K graphite fiber is produced by Hercules and donated by DuPont.

3.1.1 Polymer Sample Preparation

To obtain the desired differentials of crystallinity in the polymer coupons, amorphous plates were quenched and then allowed to isothermally crystallize at the desired crystallization temperature. A special picture frame mold in the desired shape of the coupons was designed. Amorphous PET and PETG coupons were cut from plate materials and placed into the mold and press. The press was then heated to a temperature of 300°C, 15° above the melting temperature, and held for a dwell time of 5 minutes. Water was then flushed through the platens of the press allowing the mold to cool at a maximum rate of 35°C/min. The temperature of the PET coupons was then elevated to the crystallization or annealing temperature and held for time, t . The annealing times were varied to allow differentials in bulk crystallization between coupon sets. To obtain the highest bulk crystallization, pressure 0.2 Kbar (≈ 2000 psi) was applied during the annealing period. Coupons were identified as to the processes applied to them and stored in a dry box for later testing.

3.1.2 Composite Sample Preparation

Prepregs of PET/AS4 and PETG/AS4 were produced using a card winder. Fiber tows of Hercules graphite 12k, and one and five mil films of PET and PETG were used to produce the composite prepregs. Thick prepregs (0.025 in) were made by placing films between each of three layers of fiber rows. These mats ($\approx 6'' \times 6''$) were then placed into the press and heated to 300°C, held for five minutes and quenched under a compressive load of

20,000 lb. force. Upon retrieval from the press the prepregs were identified and placed into dry storage. Density measurements through water displacement ASTM D-792 were conducted on random prepregs. On average the fiber volume fraction, V_f , of both the PET/AS4 and PETG/AS4 composites were 0.60, or 60 percent.

Prepregs were trimmed to 6" x 6" to be placed into the mold for consolidation. The consolidation process mimics that of the polymer sample preparation. Upon retrieval from the press, composite plates were cut into 0.5" x 6" coupons. A diamond wheel cutting tool was adapted to a three axis adjustable table with a water circulation system. This cutting system produced excellent results in regard to parallel cuts. Coupon width variations were limited to 0.001". Two coupons were selected at random for DSC analysis and the remaining samples were tabbed. Shell EPON® resin 828 and curing agent MPDA were used to adhere aluminum T6 tabs 0.050" thick onto all composite coupons. Coupons were then identified and returned to dry storage until testing could be performed.

3.2 Testing Procedures

The testing methodologies and procedures are described herein, if applicable standards exist they are listed with the key points of the procedure.

3.2.1 Tensile Testing

Tensile testing was performed on a PC controlled Interlaken hydraulic testing apparatus in accordance with polymer and composite tensile testing procedures ASTM D-876 and B-314, respectively. This testing apparatus contains a 22,000 lb. load cell with gain adjustments to employ fractions of the cell; typically 10 and 20 percent were used for the polymer and composite samples. The sensitivity at 2,200 lb. is 5.4 lb. and at 20 percent (4,400 lb.) a sensitivity of 10.8 lb. All polymer and composite samples were tested in displacement control at a rate of 2mm/sec. Data acquisition was performed within the Interlaken PC system and data points were sampled at a rate of 120 data points per second. A Micromeasurements extensometer with a gage length of one inch was used to

measure actual displacement and load. Raw data was then later transferred into spreadsheet format for calculations and presentation.

3.2.2 Transcrystallinity

To determine if the PET/AS4 composite exhibits a transcrystalline phase several AS4 fibers were placed between two 0.5 mil (~13 microns) PET films and placed between slides. The slides were then placed into a Mettler hot stage. The hot stage was installed on an optical microscope and heated to 290°C for a dwell time of 5 minutes. The sample was viewed through the microscope as it cooled and observed for the transcrystalline phase. The Mettler hot stage was programmed to cool at a rate of 2°C/min.

3.2.3 Determining the Bulk Crystallinity

The bulk crystallization of PET is used as a control for the composite PET/AS4. Five PET samples of each crystalline range were tested in a density gradient column, small sections from the corner of each sample being removed prior to mechanical testing. This density gradient column was made of sodium-bromide and water in accordance with ASTM standard 1505. The spheres of known density are placed into the column of solution and allowed to settle. A good density gradient will exhibit a linear correlation between density and depth. Polymer samples are then placed into the column after the samples have reached a stable depth that depth was measured. The densities of the polymer samples were linearly extrapolated from the densities of the known spheres.

A suitable density gradient column for the required density range of the PET/AS4 composite is not available at the University. Additionally, the void volume content of crystalline composite is uncertain. Air bubbles or voids in a composite have dramatic consequences in the determination of density using a gradient column. Additional methods of determining the bulk crystallinity were explored. Wide angle X-ray scattering, WAXS, was discredited because the diffraction of the fibers interferes with the dominant peaks of the PET matrix, reported by Wakelyn [47].

Differential scanning calorimetry can be used for the determination of bulk crystallinity of thermoplastic composites. However, PET is known to recrystallize during the DSC

evaluation and thus melt additional crystalline PET during the DSC scan creating double melting endotherms and leading to possible erroneous results. These double melting peaks can be eliminated by using scanning rates greater than $32^{\circ}\text{C}/\text{min}$. as reported by Groeninckx [62]. Groeninckx goes on to state the sum of the melting endotherms either single or double remains constant for annealed PET. Therefore, DSC can provide a reference between the neat polymer and PET/AS4 composite.

Using a Perkin Elmer DSC-7 the crystalline content of both the polymer and composite coupons were determined. For both the polymer and composite coupons small sections from the corner were removed to be scanned in the DSC prior to mechanical testing. All scanning rates were at a constant $10^{\circ}\text{C}/\text{min}$. In an effort to maintain consistency in the method of determining crystalline content, the beginning and ending points for the calculation of the change in enthalpy, ΔH , were constant throughout each series. The effect of the fiber in the composite simply adds to the slope—specific heat, of the composite. The fiber content does not effect the method to determine the bulk crystallinity. The sum of the melting endotherms either single or double was used to determine ΔH . From this point the bulk crystallinity was determined by the fraction of measured and theoretical heats of fusion.

Since the fibers did not produce a discernible transcrystalline region (determined using an optical microscope) or act as a catalyst for additional crystallization in the composite, a relationship between the two methods, density gradient column, DGC, and DSC was established using the results of the neat polymer. Using this relationship an accurate estimate of the PET/AS4 crystallinity was determined. The density of these composites can also be determined if necessary.

4. Results

4.1 Transcrystallinity

To determine if the PET\AS4 composite would exhibit a transcrystalline phase two 0.5 mil films were sandwiched above and below single AS4 fibers and placed in a Mettler hot stage. The hot stage installed on an optical microscope was heated to 290°C for a dwell time of 5 minutes. The sample was viewed through the microscope as cooling occurred at a rate of 2°C/min. No transcrystalline interphase was observed and no additional tests were performed.

4.2 Bulk Crystallinity

Differential scanning calorimetry (DSC) is known to be an effective method for determining the bulk crystallinity of semi-crystalline polymers. The graphite fibers in the composites do not effect the results or methods of determining bulk crystallinity using DSC. Because of the ability to use DSC for both the polymer and composite samples it was used in this investigation.

4.2.1 Cooling Rate Effects

Initially the bulk crystallization of PET as a function of cooling rate was studied. This was essential because it provided insight into the cooling rates required to maintain some control of the bulk crystallization of both polymer and composite samples. Although this test was performed in a controlled environment within the DSC, the results gave an indication of the ability to control crystalline content throughout the processing of samples, both polymer and composite. The results of this study are provided in Table 1 and Figure 19. To determine the apparent crystallinity a theoretical heat of fusion of $\Delta H_f = 129 \text{ J/g}$ was used [79].

From this data it is evident that the cooling rates must exceed 100°C/min. if little or any control of the bulk crystallization of PET is to be obtained. Because of the effects of cooling rate, control of the processing from polymer melt will be difficult to obtain. Large

bulk presses with water jackets or water cooled platens generally cannot exceed cooling rates greater than 35°C/min.

Table 1: Bulk Crystallinity as a Function of Cooling Rate.

Sample Identification	Cooling Rate °C/min.	ΔH Change in Enthalpy J/g	Apparent Crystallinity X_c %
PET-15-500	500 °C/min.	0.55 J/g	1 %
PET-16-300	300 °C/min.	4.20 J/g	2 %
PET-19-200	200 °C/min.	13.10 J/g	10 %
PET-17-100	100 °C/min.	26.33 J/g	20 %
PET-20-75	75 °C/min.	33.00 J/g	25 %
PET-21-50	50 °C/min.	38.12 J/g	30 %
PET-18-30	30 °C/min.	53.24 J/g	41 %
PET-22-10	10 °C/min.	47.92 J/g	39 %

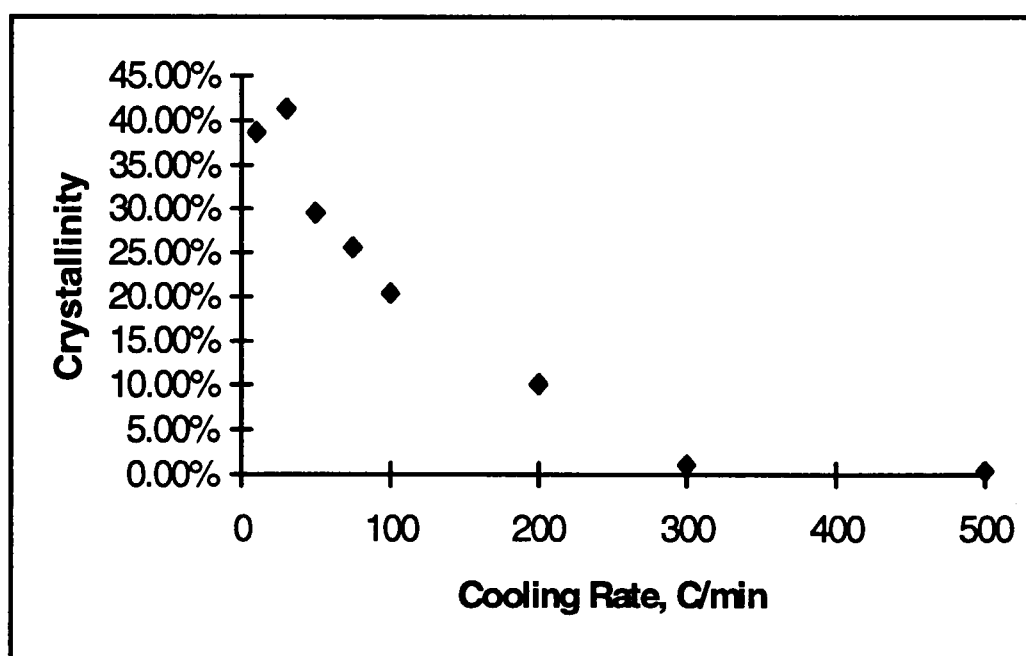


Figure 19: Bulk Crystallization as a Function of Cooling Rate.

The cooling rate of the Wabash press was determined using a thermocouple and a stopwatch. The thermocouple was mounted onto the process mold and placed into the Wabash press. The platen temperature was raised to 300 °C for 30 min. thus ensuring the

mold had reached equilibrium. Water was then flushed through the platens and the cooling rate was measured. Surprisingly, the cooling rate was constant at 47°C/min.

This test provided the necessary evidence to support the inability of the existing press to obtain the lower range of bulk crystalline content from melt conditions. At a cooling rate of 50°C/min. the minimum obtainable bulk crystallinity would be approximately 40%. Injection molded amorphous PET plates were supplied by Eastman. These plates were machined and annealed to the desired crystalline levels.

4.2.2 Neat Polymer Crystallization

As described previously in the Experimental section, amorphous PET plates were acquired from Eastman Co. These plates are injection molded with the necessary cooling media to attain an amorphous morphology. Coupons were machined into the specified dogbone configuration in accordance with ASTM-D-882. Three test coupons were then press fit into the mold and annealed at the required time, temperature and pressure to obtain the desired bulk crystalline content. Sections of each coupon were removed and placed into the density gradient column described previously in the experimental section. One coupon was selected at random for DSC analysis. A small section (approximately 8 mg) was removed from the extreme corner of the selected coupon. The results from density gradient and DSC analyses are provided in Table 2,

Table 3, Figure 20 and Figure 21. The linear equation and the correlation coefficient presented in Figure 20 represents only the consistency and linearity of the gradient column and was not used to determine the densities of each sample. The densities of each sample were determined by linear extrapolation between each known density. The DSC scans represented in Figure 21 have been normalized (the heat flow was divided by the sample mass) to provide for a visual comparison.

The results of bulk crystalline content for both density gradient and DSC are plotted in Figure 22. The results of this comparison are similar to those of Groeninckx who determined crystallinity of fast annealed PET. Groeninckx's results are also provided in

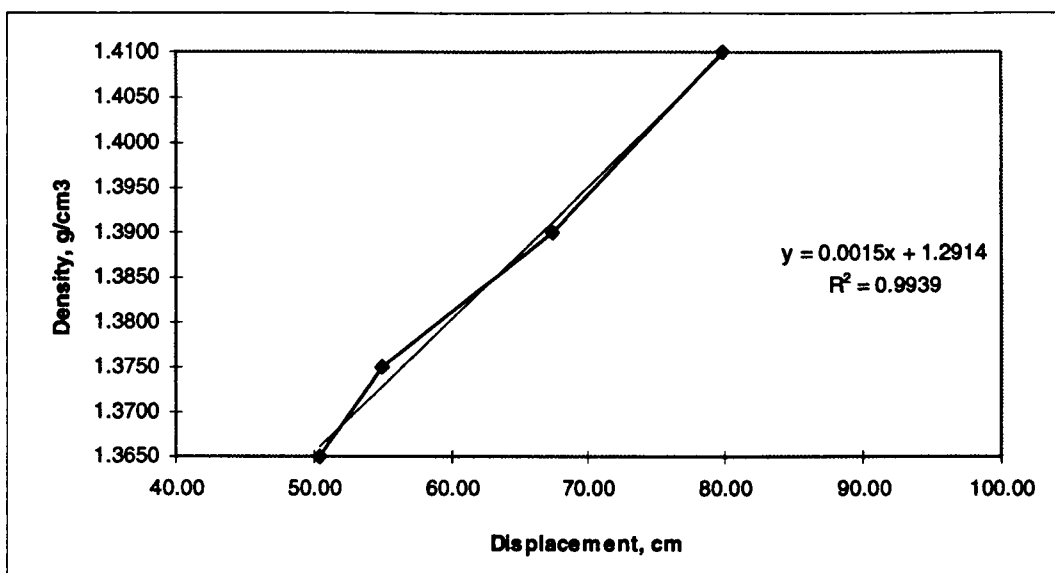


Figure 20: Density Gradient Plot

Table 2: Density gradient

Crystalline Group	Depth cm	Density g/cm ³	Apparent Crystallinity, X _c
120-a	51.40	1.367	31%
120-b	50.85	1.365	30%
120-c	52.10	1.368	32%
120-d	51.70	1.367	31%
120-e	50.85	1.365	30%
mean	51.38	1.367	31%
Standard dev.	0.5438	0.0012	1.12%
220-a	62.85	1.384	47%
220-b	63.00	1.384	47%
220-c	63.30	1.385	48%
220-d	65.20	1.387	50%
220-e	64.75	1.386	49%
mean	63.82	1.385	48%
Standard dev.	1.0785	0.0013	1.21%
220+P-a	71.60	1.397	58%
220+P-b	72.30	1.398	59%
220+P-c	71.80	1.397	59%
220+P-d	71.60	1.397	58%
220+P-e	72.10	1.397	59%
mean	71.88	1.40	59%
Standard dev.	0.3114	0.0005	0.45%

Table 3: Bulk Crystalline Content of Grouped PET

Crystalline Group	Annealing Temperature - Time Pressure	ΔH Change in Enthalpy J/g	Apparent Crystallinity X_c %
PET-30	120° C -- 30 min.	32.592 J/g	25 %
PET-45	200° C -- 30 min.	44.843 J/g	35 %
PET-60	220° C -- 30 min. --2 ksi	54.630 J/g	42 %

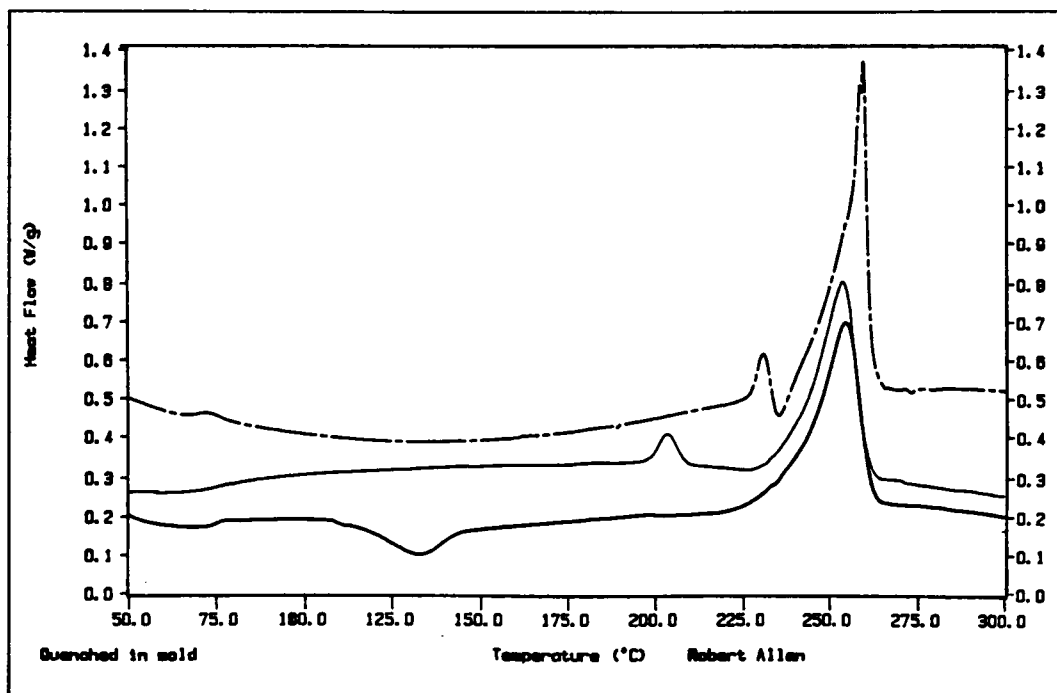


Figure 21: Family of annealed PET Bulk Crystallization.

Figure 22. A strong linear correlation exists between the two methodologies, a correlation coefficient, r^2 , of 0.9978. The experimental crystallization results for different crystalline groups (annealing cycles) from the two methodologies, DSC and DGC are provided in Table 4.

Table 4: Conversion From DSC to DGC.

Crystalline Group	Annealing Temperature - Time Pressure	X_c %, DSC	X_c %, DGC
CPET-30	120° C -- 30 min.	25 %	32 %
CPET-45	200° C -- 30 min.	33 %	45 %
CPET-60	220° C -- 30 min. --2 ksi	44 %	62 %

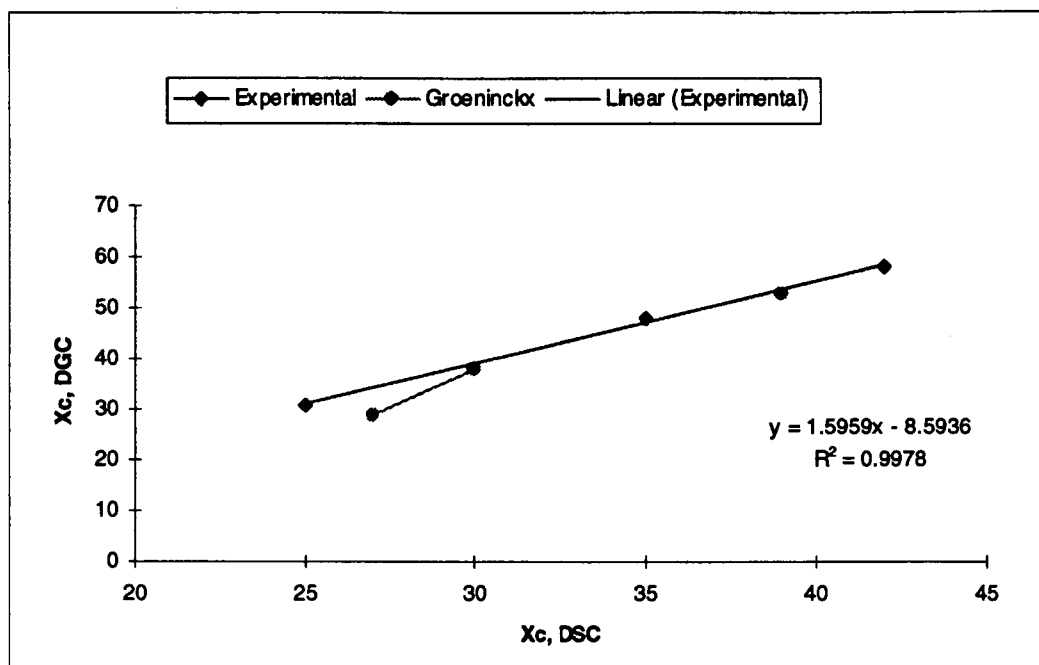


Figure 22: Comparison of DSC to DGC Methodologies

4.2.3 PET/AS4 Crystallinity

As described previously in the Experimental section for composite manufacturing, prepreg plates were stacked in the appropriate sequence-unidirectional and consolidated. This required the quenching of the composite and subsequent annealing at the described temperature to obtain the desired bulk crystalline content. Upon removal from the mold the composite plates were machined into the coupon configuration in accordance with ASTM-D-3039. After machining the plate into the specified coupon dimensions two coupons were selected at random for DSC analysis (strained samples should not be analyzed). The results from this analysis are provided in Table 5 and Figure 23. To determine the crystalline content of the composite the mass of the sample was adjusted based on the designed 60% fiber volume fraction of the composite. The mass matrix fraction is theoretically 32.11%. Additionally, the DSC scans have been normalized to provide for a visual comparison.

These composite DSC results are in agreement with the DSC results of the neat polymer, that is there are no significant increases in the bulk crystallinity as a result of graphite

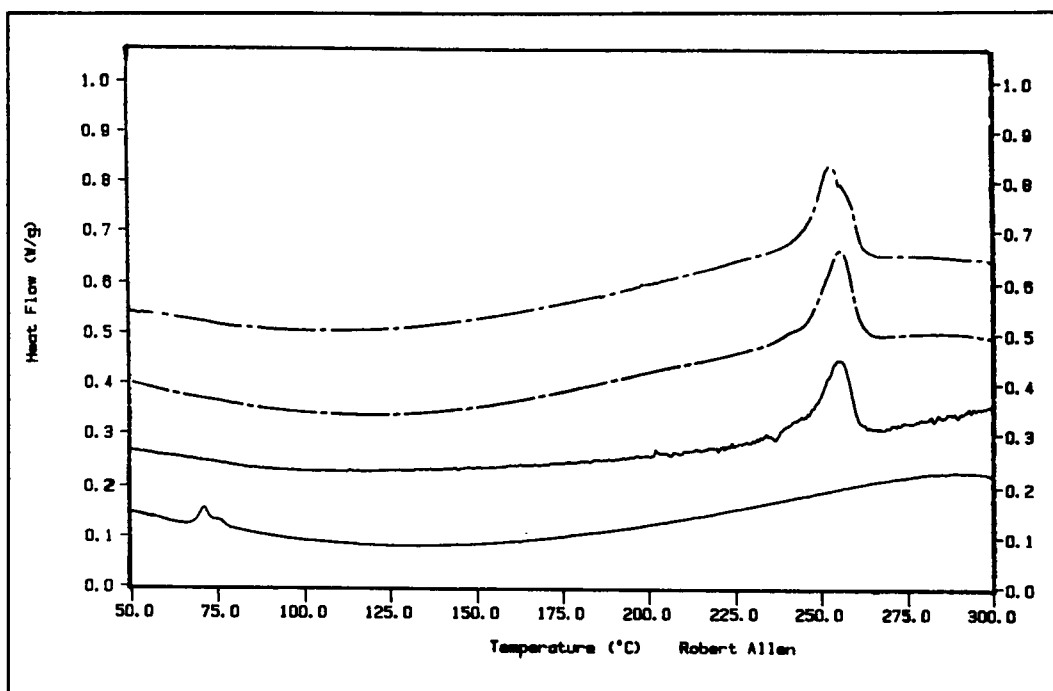


Figure 23: Family of annealed PET/AS4 Bulk Crystallization.

fibers in the composite. This evidence provides the support of the acceptance of using the bulk crystallization data obtained from density gradient column.

Table 5: Bulk Crystalline Content of Grouped PET/AS4 Composite.

Crystalline Group	Annealing Temperature - Time - Pressure	ΔH Change in Enthalpy J/g	Apparent Crystallinity X_c %
CPET-30-1	120° C -- 30 min.	31.93 J/g	25 %
CPET-30-2	120° C -- 30 min.	33.28 J/g	26 %
CPET-30 mean (a)			25.5 %
CPET-45-1	220° C -- 30 min.	43.06 J/g	33 %
CPET-45-2	220° C -- 30 min.	42.81 J/g	33 %
CPET-45 mean (a)			33 %
CPET-60-1	220° C -- 30 min. --2 ksi	54.56 J/g	42 %
CPET-60-2	220° C -- 30 min. --2 ksi	58.96 J/g	46 %
CPET-60 mean (a)			44 %

These composite DSC results are in close agreement with the DSC results of the neat polymer. For annealing temperature of 120°C the crystalline values are in agreement at 25% for both the composite and neat polymer. The crystalline values for the 220°C annealing temperature are 33% and 35% for the composite and neat polymer respectively.

For the 220°C annealing temperature the crystalline values are 44% and 42% for the composite and neat polymer respectively. This evidence supports the optical microscopy results that no discernible transcrystalline phase exists. Additionally the fiber does not appear to be acting as a nucleating agent, the presence of fibers having no adverse affect on the bulk polymer crystallinity.

4.3 Tensile Test

Tensile tests were performed in accordance with ASTM-D-882 and D-3039 for polymer and composite coupons.

4.3.1 Polymer

The polymer tensile tests were conducted on a hydraulic Interlaken 22 kip testing apparatus using 10 percent load capacity of 2,200 lb. These tensile tests were conducted in compliance with ASTM standard D-882. The testing controls were set using the computer interface (software developed by Interlaken). All tests were done in the displacement control, that is displacement was used as the feedback control. The rate of displacement (crosshead speed) was 0.001 in. /sec. for all tests. A Micromeasurement extensometer with a 1" gage length was used to measure displacement/strain. Testing coupons were of 3" dogbone configuration with an average cross-section of 0.125" x 0.250". These testing results are grouped by their apparent bulk crystallinity and presented in the following tables and graphs.

4.3.1.1 Amorphous PETG

Results from the amorphous PETG tensile tests are provided in Table 6 and Figure 24. The tensile modulus was determined from linear regression using the first 20 data points. The tensile strength is the maximum stress supported by the coupon. Strain at yield is the strain at the maximum tensile strength.

Table 6: Tensile Test Results of Amorphous PETG

File Name	Modulus, psi	Tensile strength	Strain @ Yield
PETG-1	2.17 E5	10,331 psi	0.0601 in/in
PETG-2	2.21 E5	9,620 psi	0.0579 in/in
PETG-3	2.27 E5	10,518 psi	0.0571 in/in
Mean (a)	2.22 E5	10,156 psi	0.0584 in/in
Standard, σ	5.03 E3	474 psi	0.0016 in/in

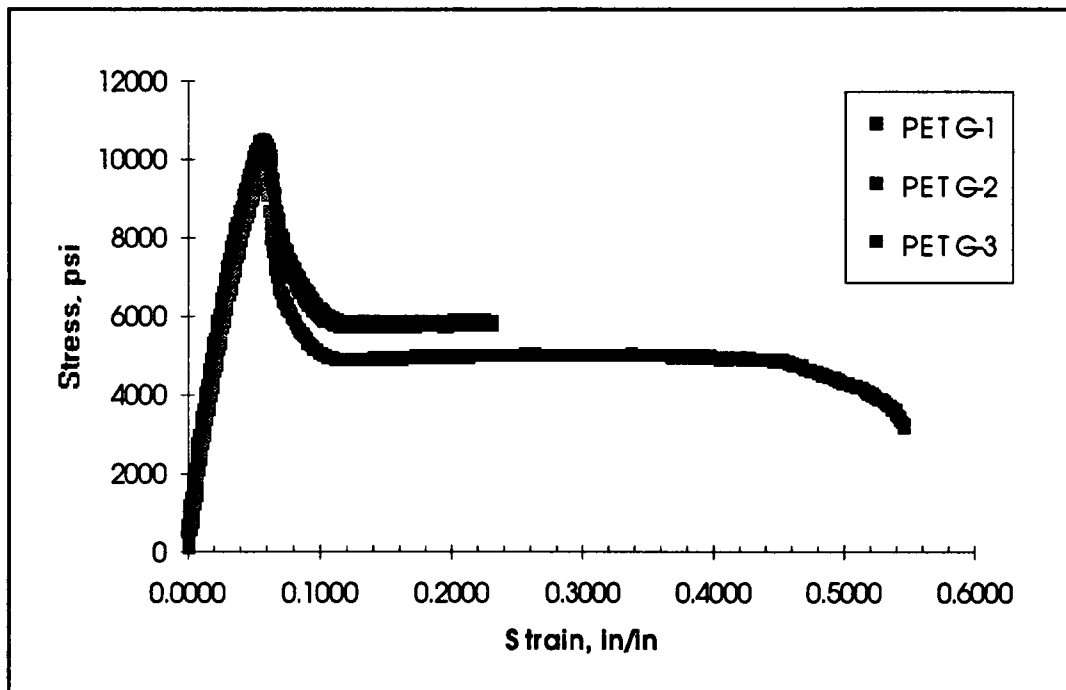


Figure 24: Tensile Test Results of Amorphous PETG

4.3.1.2 30% Crystalline PET

Results from the amorphous PETG tensile tests are provided in Table 7 and Figure 25.

The tensile modulus was determined from linear regression using the first 20 data points.

The tensile strength is the maximum stress supported by the coupon at yield. Strain at yield is the strain at the maximum tensile strength.

Table 7: Tensile Test Results of 30% Crystalline PET.

File Name	Modulus, psi	Tensile strength	Strain @ Yield
PET30-1	2.31 E5	9,208 psi	0.0557 in/in
PET30-2	2.36 E5	10,181 psi	0.0601 in/in
PET30-3	2.31 E5	9,395 psi	0.0608 in/in
Mean (a)	2.33 E5	9,595 psi	0.0589 in/in
Standard, σ	2.87 E3	516 psi	0.0028 in/in

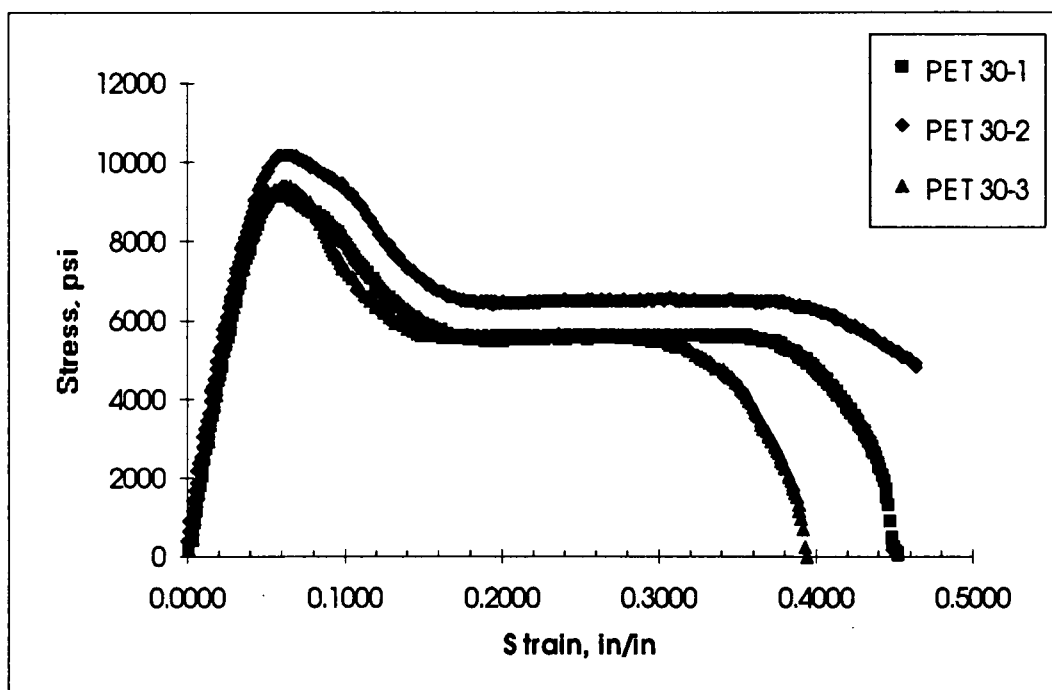


Figure 25: Tensile Test Results of 30% crystalline PET

4.3.1.3 45% Crystalline PET

Results from the amorphous PETG tensile tests are provided in Table 8 and Figure 26.

The tensile modulus was determined from linear regression using the first 20 data points.

The tensile strength is the maximum stress supported by the coupon. Strain at yield is the strain at the maximum tensile strength.

Table 8: Tensile Test Results of 45% Crystalline PET

File Name	Modulus, psi	Tensile strength	Strain @ Yield
PET45-1	2.42 E5	10,293 psi	0.0557 in/in
PET45-2	2.58 E5	11,565 psi	0.0601 in/in
PET45-3	2.58 E5	10,892 psi	0.0608 in/in
Mean (a)	2.53 E5	10,916 psi	0.0630 in/in
Standard, σ	9.24 E3	636 psi	0.0072 in/in

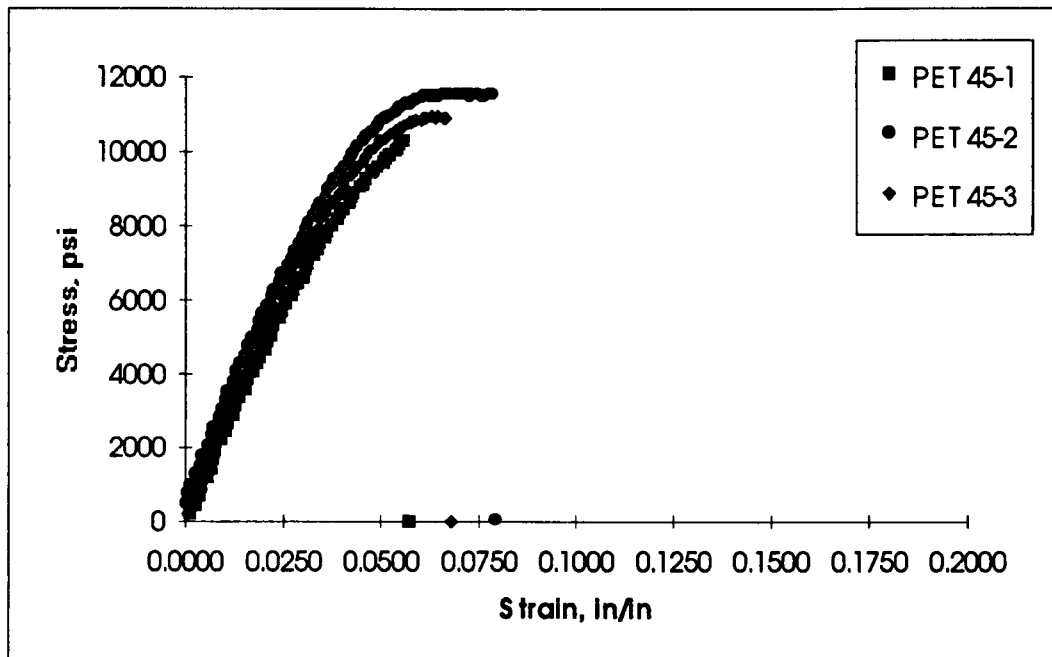


Figure 26: Tensile Test Results of 45% Crystalline PET.

4.3.1.4 60% Crystalline PET

Results from the amorphous PETG tensile tests are provided in Table 9 and Figure 27.

The tensile modulus was determined from linear regression using the first 10 data points due to the limited number of data points. The tensile strength is the maximum strength at yield, supported by the coupon. Strain at yield is the strain at the maximum tensile strength. Attempts to test several test coupons generally resulted in brittle fracture caused by grip pressure. It is for this reason there are limited test results. Although sample PET45-1 fractured prematurely through the shoulder of the dogbone the data is provided and used in the mean average of tensile modulus.

Table 9: Tensile Test Results of 60% Crystalline PET

File Name	Modulus, psi	Tensile strength	Strain @ Yield
PET60-1	2.70 E5	3,394 psi	0.0139 in/in
PET60-2	2.87 E5	7,162 psi	0.0286 in/in
Mean (a)	2.79 E5	7,162 psi	0.0286 in/in
Standard, σ	1.20 E4		

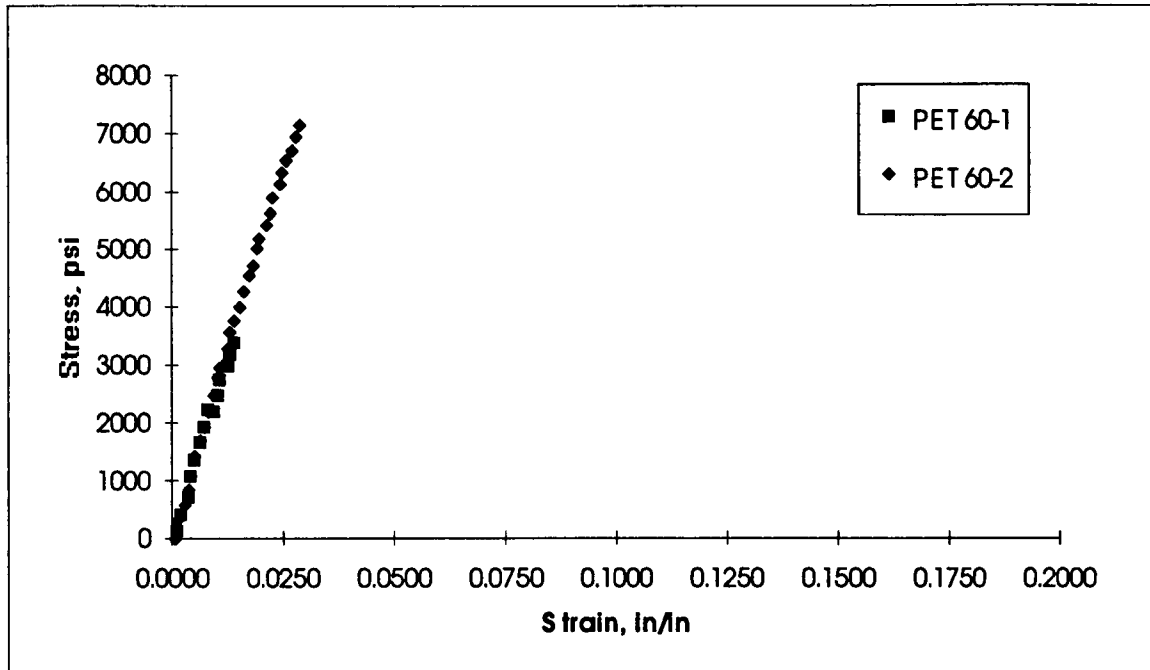


Figure 27: Tensile Test Results of 60% Crystalline PET

4.3.2 Composite

The composite tensile tests were conducted on a hydraulic Interlaken 22 kip testing apparatus using 20 percent load capacity of 4,400 lb. These tensile tests were conducted in compliance with ASTM standard D-3039. The testing controls were set using the computer interface (software developed by Interlaken). All tests were done in the displacement control, that is displacement was used as the feedback control. The rate of displacement (crosshead speed) was 0.001 in./sec. for all tests. Shell EPON® resin 828 and curing agent MPDA were used to adhere aluminum T6 tabs 0.050" thick onto all composite coupons. These testing results are grouped by their apparent bulk crystallization and presented in the following tables and graphs.

4.3.2.1 Amorphous PETG\AS4 Composite

Results for the amorphous composite testing are provided in Table 10 and Figure 28.

Using statistical analysis, specifically Chauvenet's criterion, it was identified that the results of the tensile strength obtained from sample Cpetg-1 exceeded the ratio of maximum acceptable deviation to standard deviation, $d_{\max} / \sigma$, and therefore are identified as dubious data. The calculation of arithmetic mean and standard deviation do not include dubious data. Thus it was not used in the determination of these values.

Table 10: Tensile Test Results of Amorphous PETG\AS4 Composite.

File Name	Modulus, psi	Tensile strength	Strain @ Yield
CPETG-1	16.62 E6	139254 psi	
CPETG-2	16.97 E6	208931 psi	0.0115 in/in
CPETG-3	18.42 E6	199381 psi	0.0107 in/in
CPETG-7	15.92 E6	161980 psi	0.0123 in/in
CPETG-9	18.40 E6	166285 psi	0.0093 in/in
CPETG-10	15.64 E6	204754 psi	0.0115 in/in
Mean (a)	17.00 E6	188,265 psi	0.0111 in/in
Standard, σ	1.19 E6	22,341 psi	0.0011 in/in

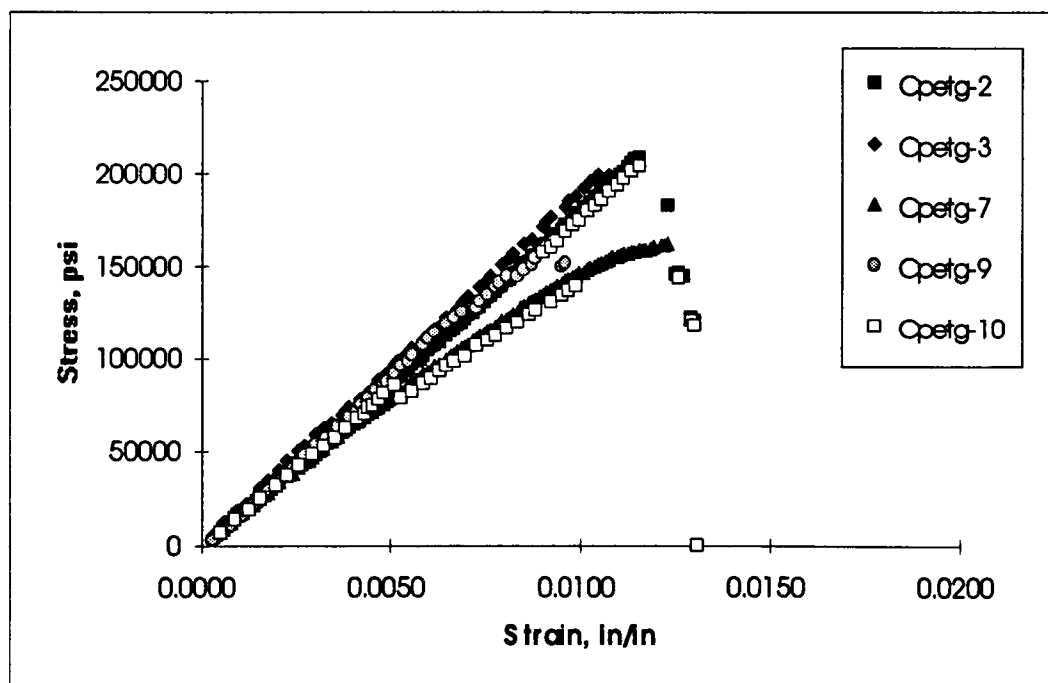


Figure 28: Tensile Test Results of Amorphous PETG\AS4 Composite.

4.3.2.2 30% Crystalline PETAS4 Composite

Results for the tensile test of the 30% crystalline PETAS4 composite testing are provided in Table 11 and Figure 29. The calculations of standard deviation and arithmetic means are provided in Table 9.

Table 11: Tensile Test Results of 30% Crystalline PETAS4 Composite.

File Name	Modulus, psi	Tensile Strength	Strain @ Yield
CPET30-2	19.31 E6	193,708 psi	0.0090 in/in
CPET30-3	18.97 E6	189,936 psi	0.0090 in/in
Mean (a)	19.14 E6	191,822 psi	0.0090 in/in
Standard, σ	2.40 E5	2667 psi	0.0000

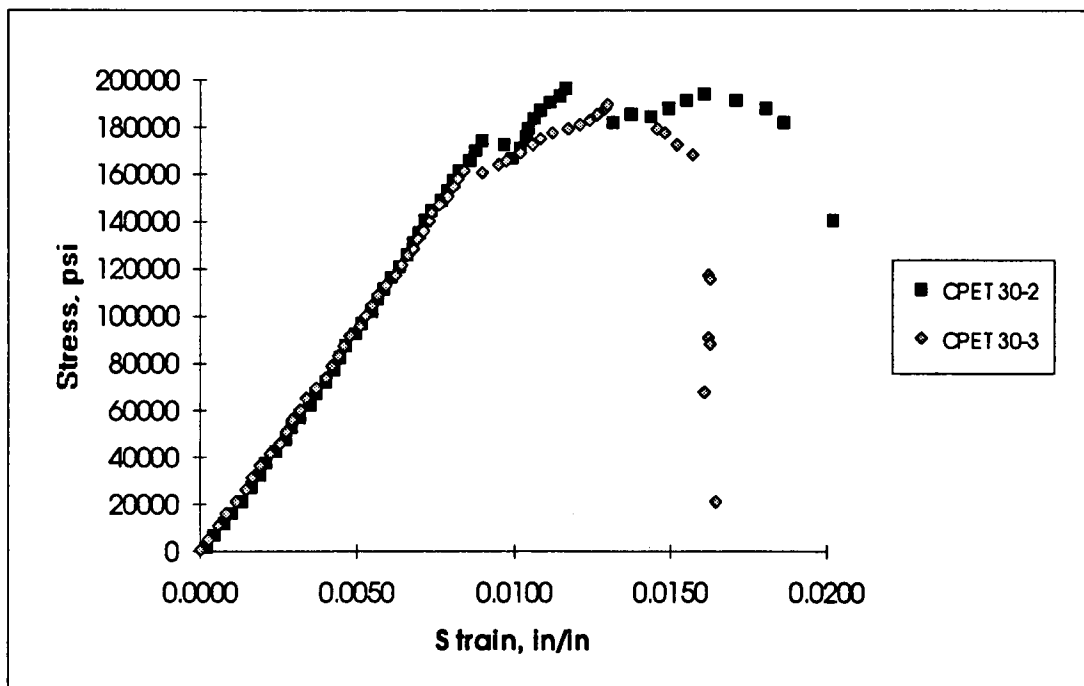


Figure 29: Tensile Test Results of 30% Crystalline PETAS4 Composite.

4.3.2.3 45% Crystalline PETAS4 Composite

Results from the tensile test of the 45% crystalline PETAS4 composite are provided in Table 12 and Figure 30. Using statistical analysis, specifically Chauvenet's criterion, it was identified that the results for the modulus obtained from sample CPET45-8 exceeded the ratio of maximum acceptable deviation to standard deviation, $d_{\max} / \sigma$, and therefore are

identified as dubious data. The calculation of arithmetic mean and standard deviation do not include dubious data, thus it was not used in the determination of these values.

Table 12: Tensile Test Results of 45% Crystalline PETAS4 Composite.

File Name	Modulus, psi	Tensile Strength	Strain @ Yield
CPET45-1	20.74 E6	241,271 psi	0.0095 in/in
CPET45-2	18.45 E6	191,345 psi	0.0079 in/in
CPET45-3	20.36 E6	222,663 psi	0.0105 in/in
CPET45-4	19.42 E6	200,526 psi	0.0074 in/in
CPET45-5	20.79 E6	193,889 psi	0.0108 in/in
CPET45-6	20.14 E6	198,884 psi	0.0085 in/in
CPET45-7	21.09 E6	164,879 psi	0.0079 in/in
CPET45-8	15.74 E6	182,184 psi	
CPET45-9	23.25 E6	224,961 psi	0.0098 in/in
Mean (a)	20.53 E6	202,289 psi	0.0090 in/in
Standard	1.39 E6	23,604 psi	0.0013 in/in

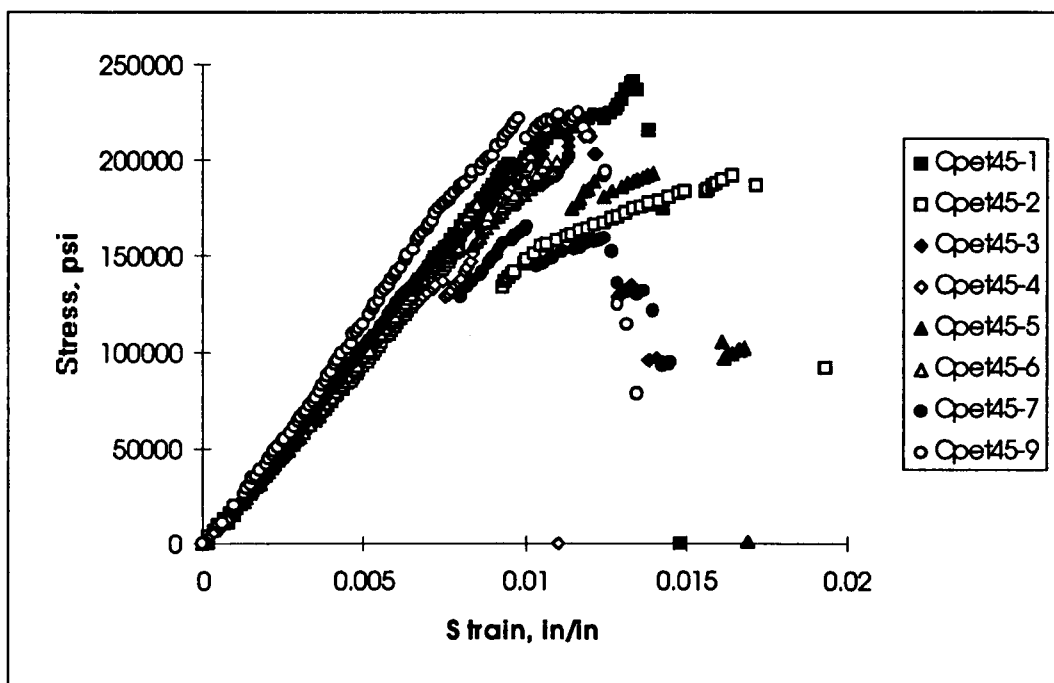


Figure 30: Tensile Test Results of 45% Crystalline PETAS4 Composite.

4.3.2.4 60% Crystalline PETAS4 Composite

Results for the tensile test of the 60% crystalline PETAS4 composite testing are provided in Table 13 and Figure 31.

Table 13: Tensile Test Results of 60% Crystalline PETAS4 Composite.

File Name	Modulus, psi	Tensile Strength	Strain @ Yield
CPET60-3	25.44 E6	176,964 psi	0.0069 in/in
CPET60-5	24.48 E6	179,508 psi	0.0072 in/in
CPET60-6	26.01 E6	168,633 psi	0.0065 in/in
CPET60-7	25.61 E6	188,095 psi	0.0072 in/in
Mean (a)	25.39 E6	178,300 psi	0.0070 in/in
Standard	0.65 E6	8,013 psi	0.0003 in/in

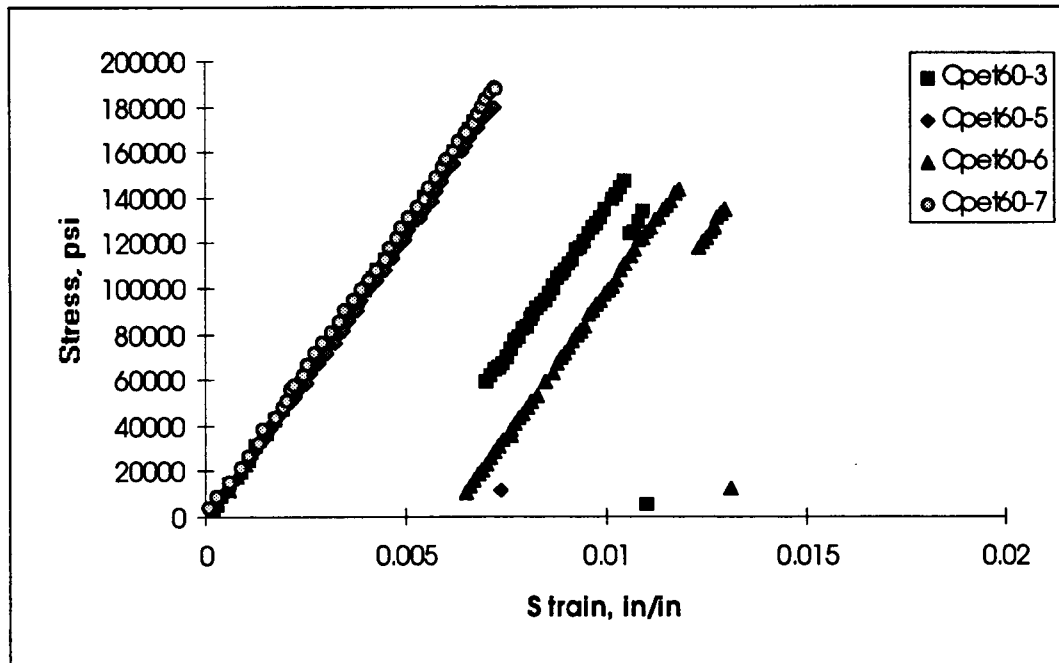


Figure 31: Tensile Test Results of 60% Crystalline PETAS4 Composite.

4.4 Scanning Electron Microscope (SEM)

Using the SEM to identify wettability and adhesion in composite materials provides a visual presentation of the fiber/matrix surface. Small fragments of each crystalline group were collected after failure from tensile testing. These fragments were coated with gold and photomicrographs were taken. There are no analytical approaches to determining the fiber

matrix interface strengths using SEM. These micrographs can provide an indication of the fiber matrix interface strength by the size of "hackle" on the fragmented fiber. No hackle indicates poor fiber matrix interface strength or fiber pull-out. Micrographs of each composite crystalline group are shown in Figure 32 through Figure 34.

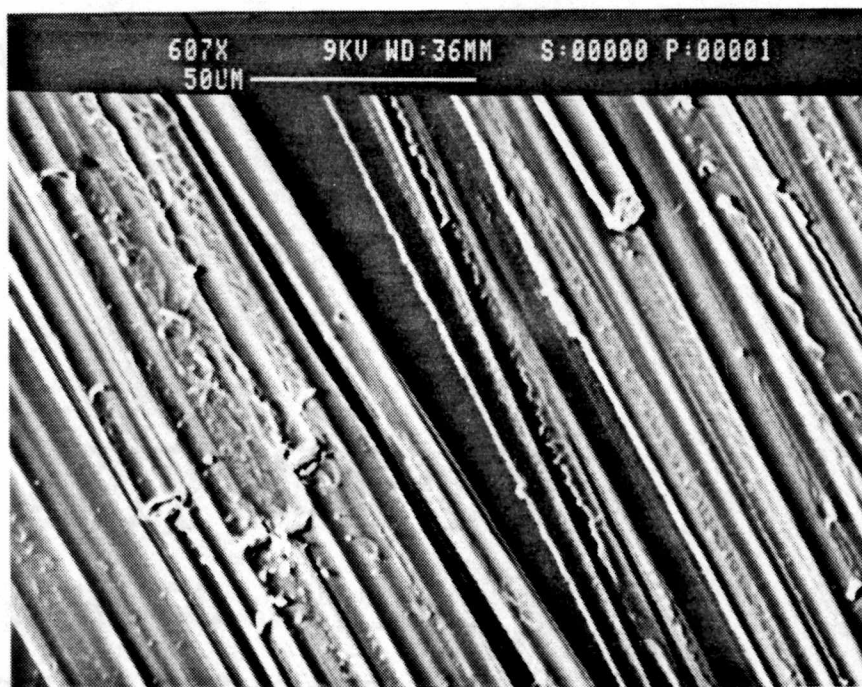
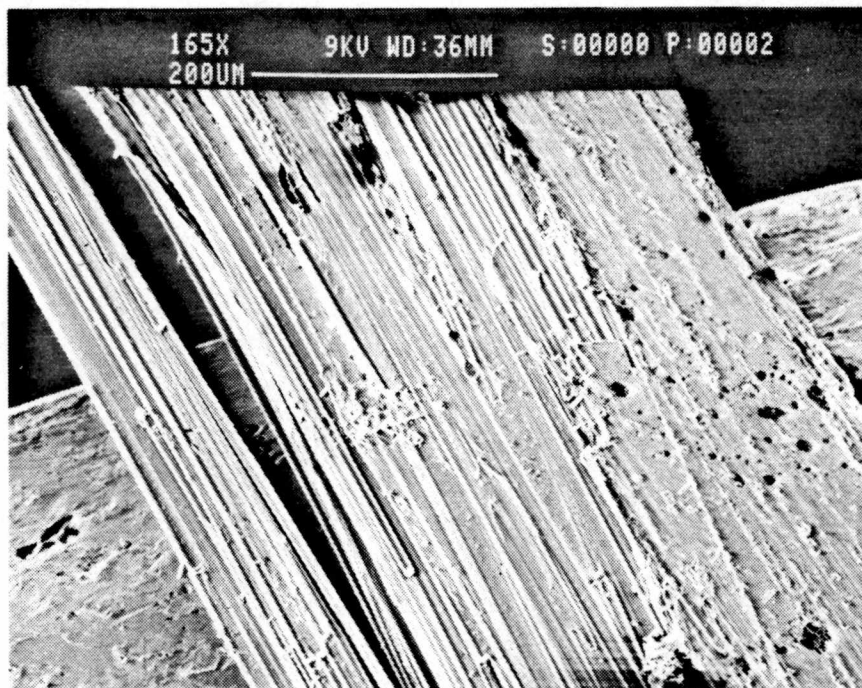


Figure 32: SEM Photomicrograph of Amorphous PETGAS4 Composite.

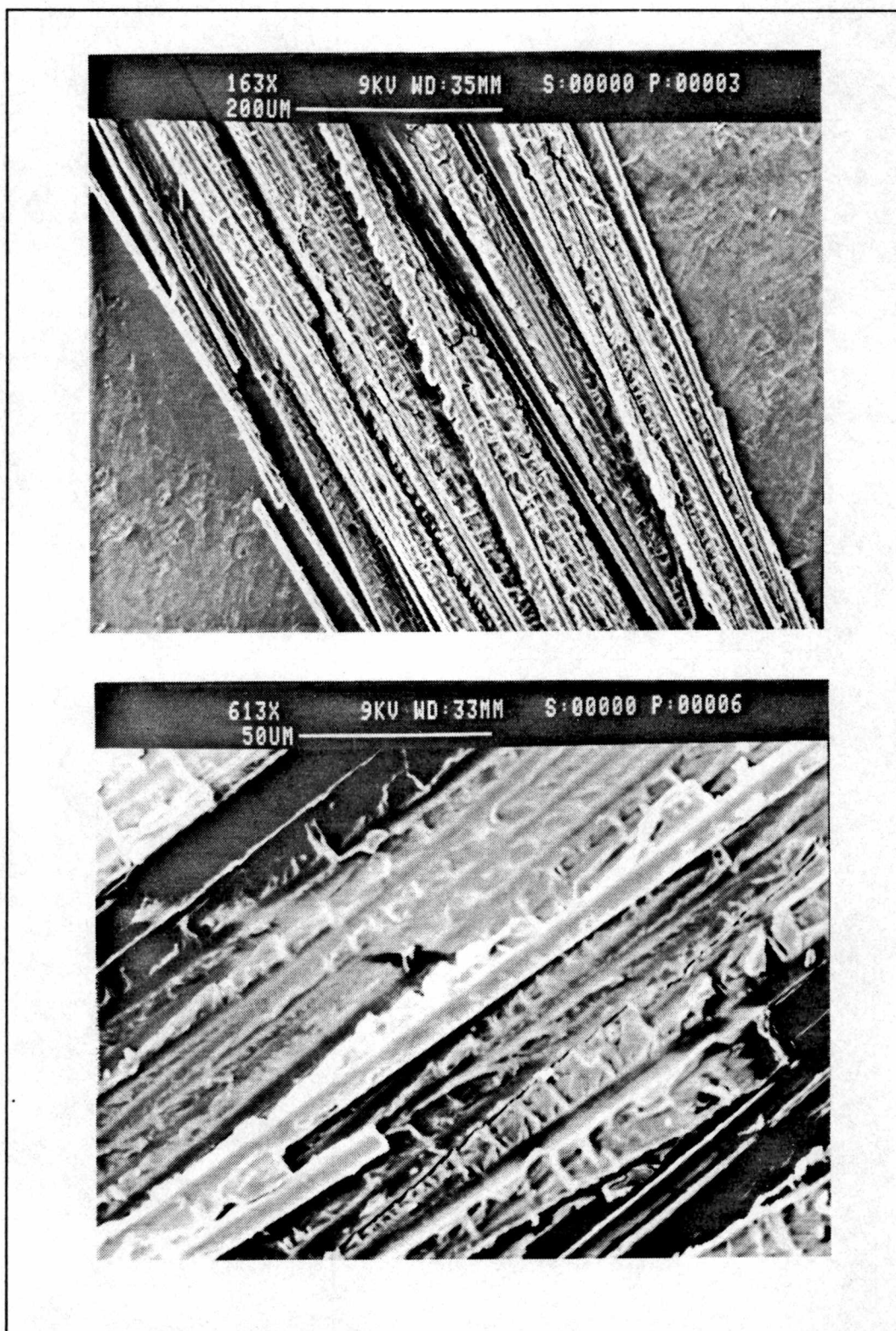


Figure 33: SEM Photomicrograph of 45% Crystalline PETAS4 Composite.

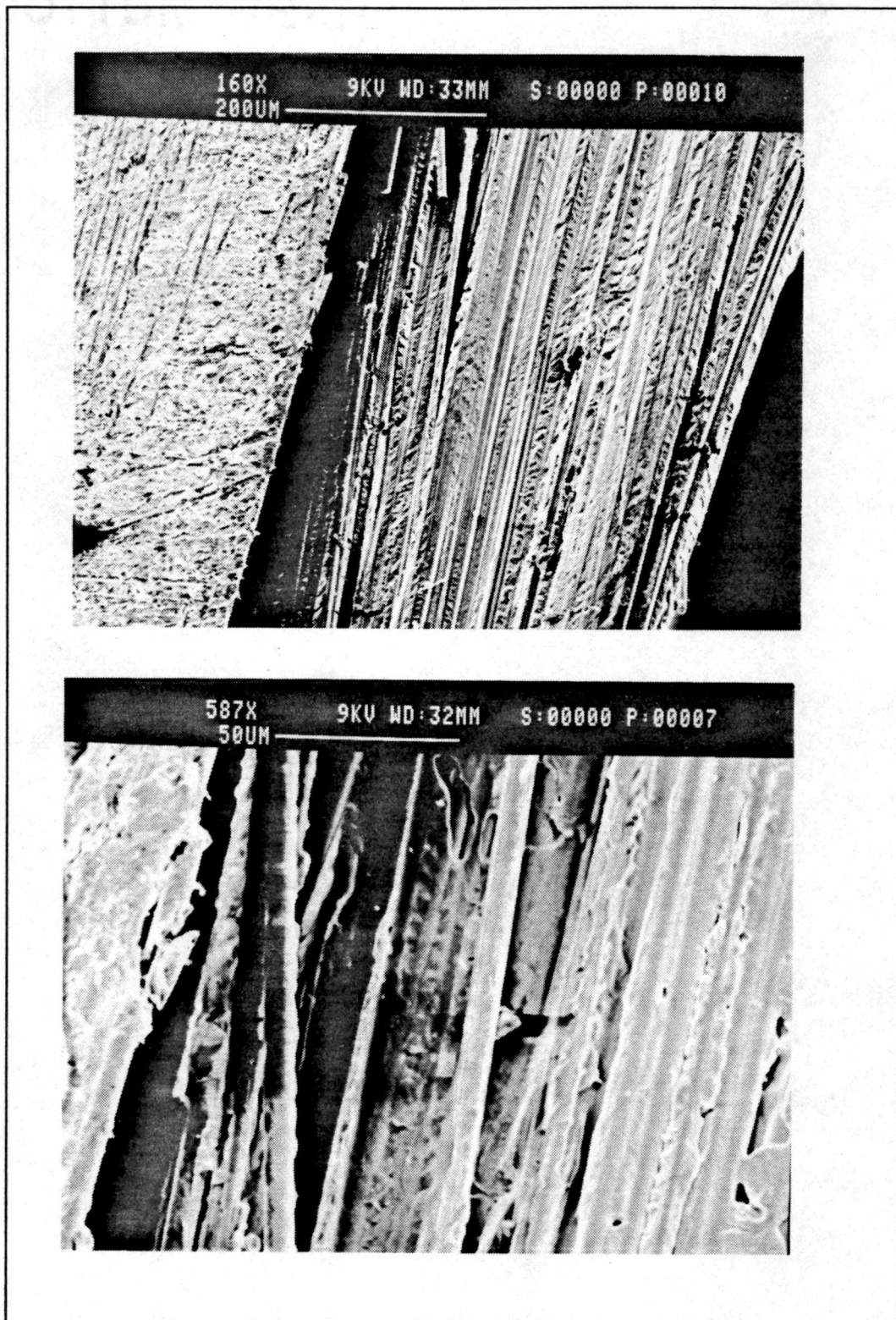


Figure 34: SEM Photomicrograph of 60% Crystalline PETAS4 Composite.

5. Discussion

5.1 Bulk Crystalline Effects on Neat Polymer, PET

The effects of bulk crystallization on PET are most evident in Table 14 and Figure 35. The values of tensile modulus are slightly lower than the estimated values of 2.9E5 provided by Eastman; however, they are well within acceptable tolerances. The tensile strengths at yield values identified in this study are greater than the estimated tensile strength at yield of 7,100 psi. provided by Eastman.

Table 14: Effects of Bulk Crystalline Content on PET.

	Young's Modulus, psi	Standard Deviation, σ	Tensile Strength, psi	Standard Deviation, σ	Strain @ Yield, in/in	Standard Deviation, σ
PETG	2.22 E5	5.03 E3	10,156	474	0.0584	0.0016
PET-30	2.33 E5	2.87 E3	9,595	516	0.0589	0.0028
PET-45	2.53 E5	9.24 E3	10,916	636	0.0630	0.0072
PET-60	2.79 E5	1.12 E4	7,162		0.0286	

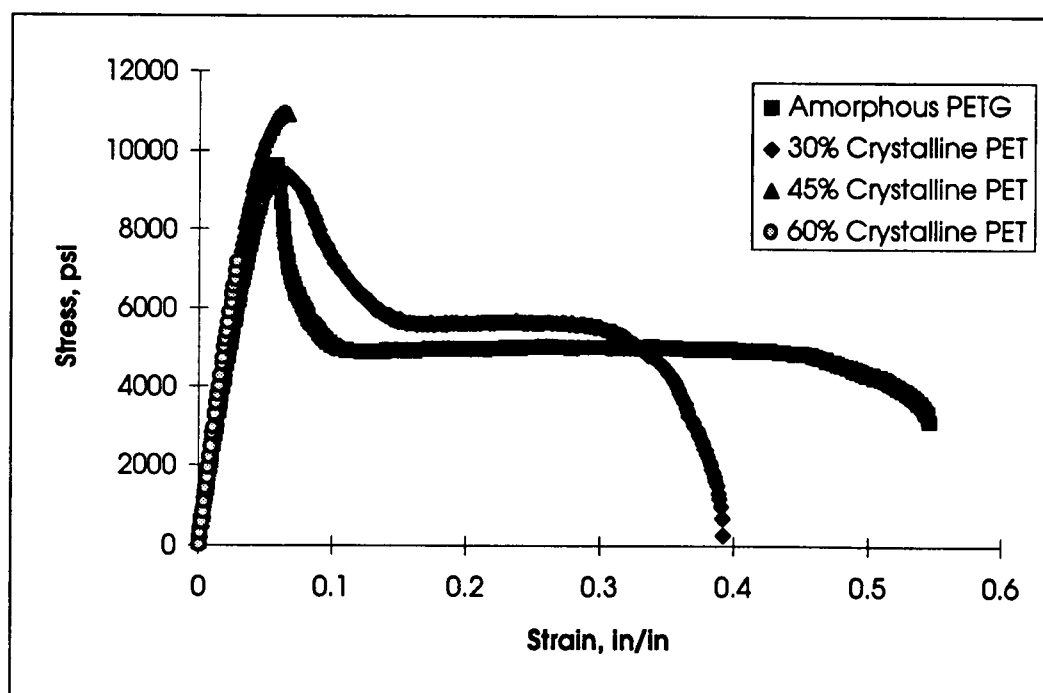


Figure 35: Effects of Bulk Crystalline Content on PET.

From Figure 35 it is evident that both the amorphous and 30 % crystalline samples form stable necks and undergo cold drawing. The 45% crystalline sample demonstrates ductile failure, while the 60% crystalline sample is observed to be brittle fracture.

There exists a modest 26% increase in the mean tensile moduli for amorphous PETG and the 60% crystalline PET samples. Similarly, small changes occurred in the tensile strengths at yield and the strains at yield. These changes as a result of bulk crystalline content are illustrated for the tensile modulus and tensile strength at yield in Figure 36 and Figure 37, respectively.

5.2 Bulk Crystalline Effects on PET\AS4 Composite

The effects of bulk crystalline content on the PET\AS4 composite are illustrated in table 15 and Figure 38. Unlike the neat PET there are no comparative figures for tensile modulus and strength at yield. However, from the basic rule of mixtures and the material properties provided by Eastman and Hercules the stiffness in the 1-direction is estimated as 19.32E6. This is a reasonable approximation for “industry standard” processing;

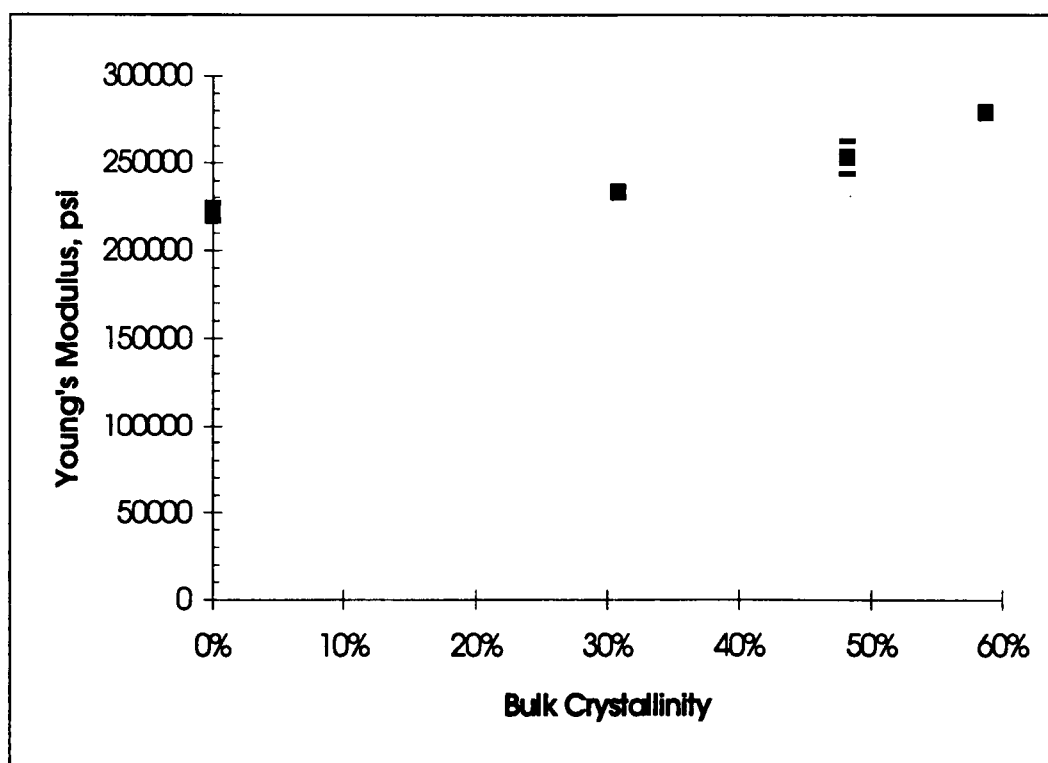


Figure 36: Bulk Crystalline Effects on the Tensile Modulus of PET.

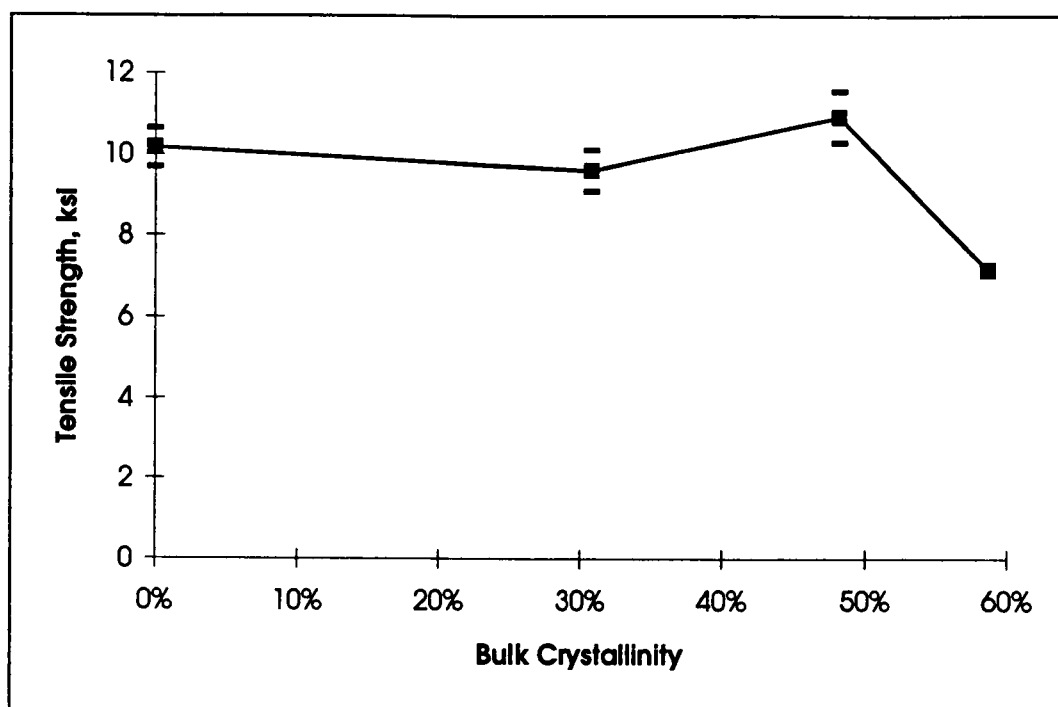


Figure 37: Bulk Crystalline Effects on the Tensile Strength of PET.

cooling rates of approximately 50°C/min. would yield for PET a bulk crystalline content of 30%-35%.

Table 15: Effects of Bulk Crystalline Content on PET\AS4 Composite.

	Young's Modulus, psi	Standard Deviation, σ	Tensile Strength, psi	Standard Deviation, σ	Strain @ Yield in/in	Standard Deviation, σ
CPETG\AS4	17.00 E6	1.19 E6	188,265	22,341	0.0111	0.0011
CPET-30\AS4	19.14 E6	2.40 E5	191,822	2,667	0.0090	0.0000
CPET-45\AS4	20.53 E6	1.39 E6	202,289	23,604	0.0090	0.0013
CPET-60\AS4	25.39 E6	6.5 E5	178,300	8,013	0.0070	0.0003

There exists a substantial 49.35% increase in the mean tensile modulus from the amorphous PETG\AS4 to the 60% crystalline PET-45\AS4 samples. Similarly, there appears to be a gradual increase in the mean tensile strength at yield, with a maximum at roughly 40% crystallinity. These changes as a result of bulk crystalline content are illustrated for the tensile modulus and tensile strength at yield in Figure 39 and Figure 40, respectively. The maximum in the tensile strength properties has additional support from the scanning electron microscopy data presented earlier in Figure 32-34 on pages 86-88.

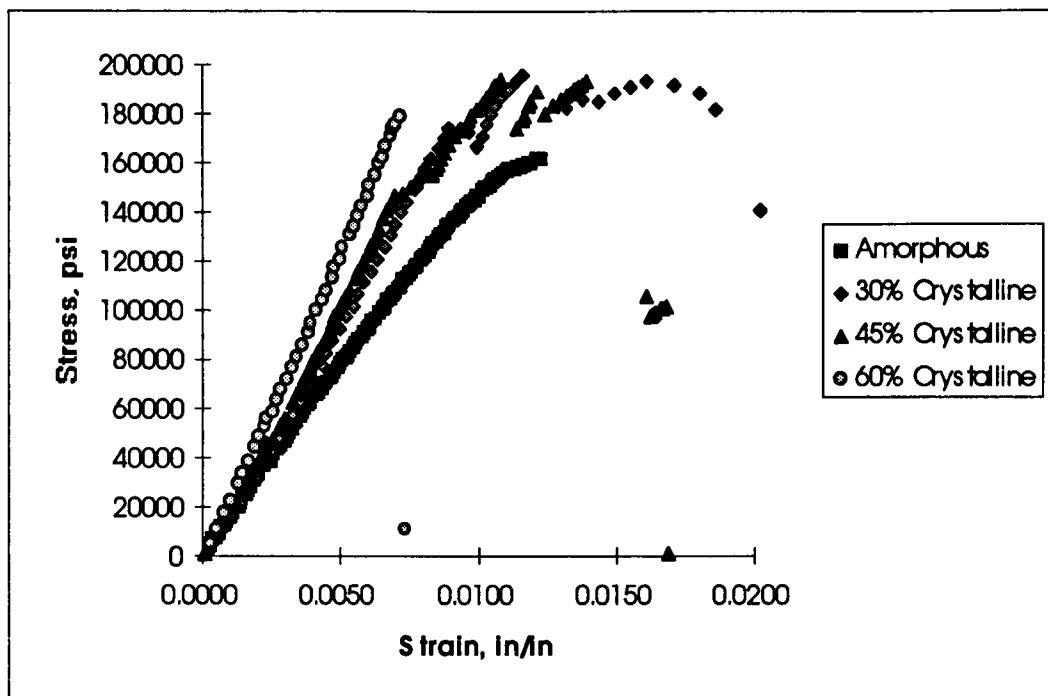


Figure 38: Effects of Bulk Crystalline Content on PETAS4 Composite.

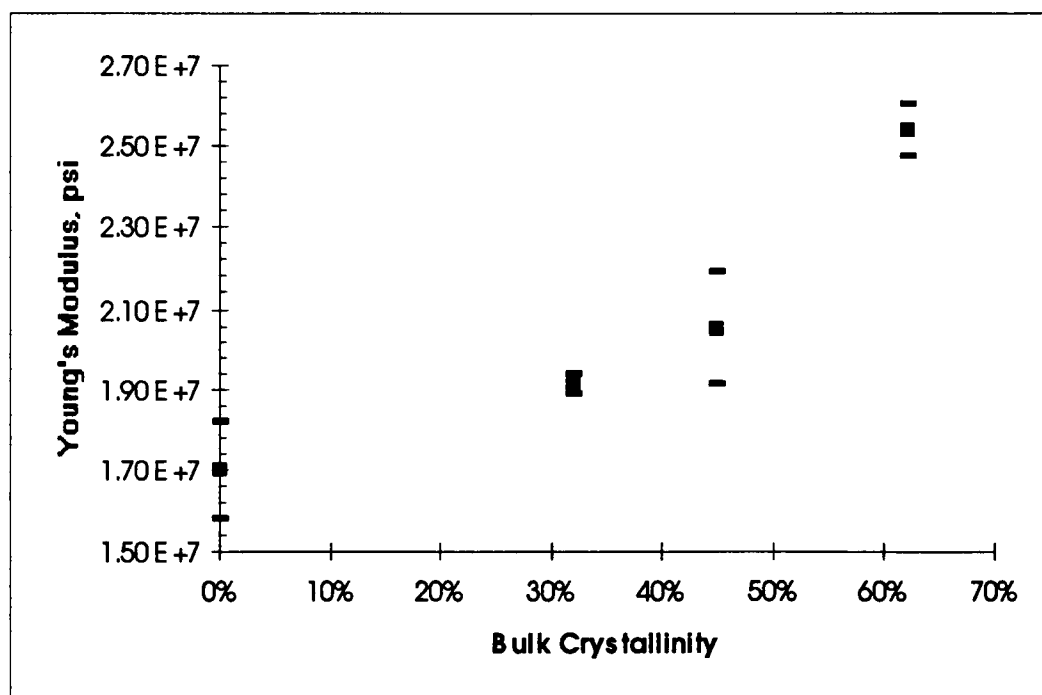


Figure 39: Bulk Crystalline Effects on the Tensile Modulus of PETAS4 Composite.

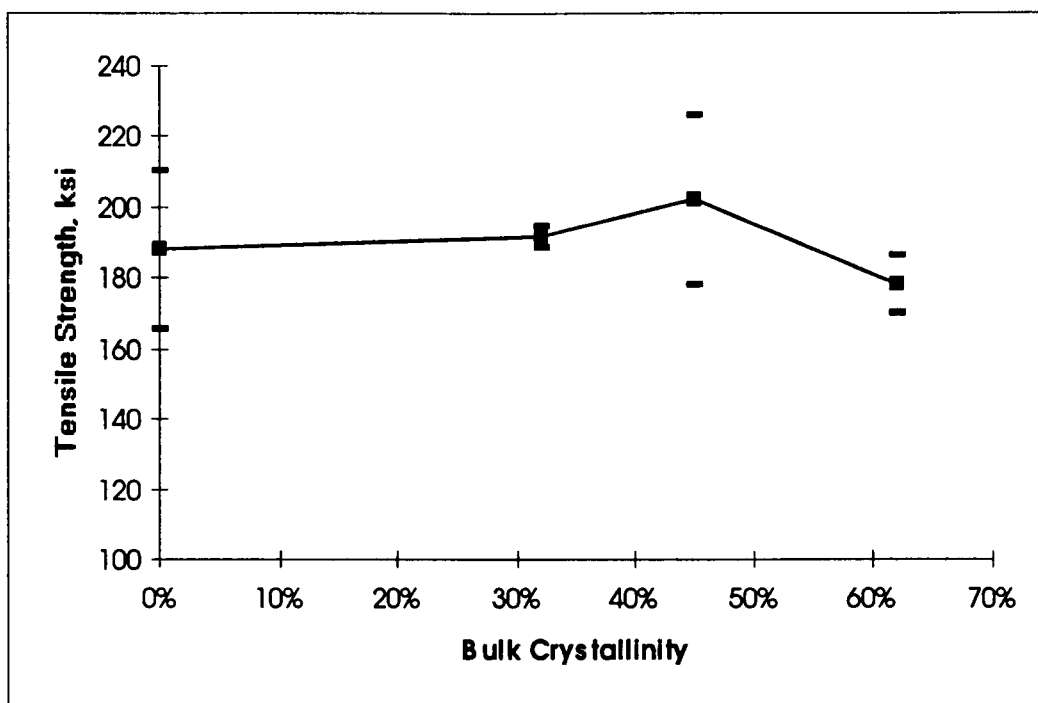


Figure 40: Bulk Crystalline Effects on the Tensile Strength of PET/AS4 Composite.

The photomicrographs presented evidence of the increase and subsequent decrease of the presence of hackles on the fibers as the bulk crystalline content increased, thus indicating a maximum for the presence of hackles and the properties they effect.

An increase in both tensile modulus and strength have been noted by several authors, and is illustrated in work by Springer [80, 81]. The majority of studies performed on crystallization effects have controlled the crystallization by varying the cooling rates, which is the primary control within the realm of manufacturing.

The tensile test results of both the neat polymer and the composite, the tensile modulus increased as expected. The significance of these results lies in the magnitude of that increase. For the neat polymer tensile modulus increased by 26%, from the amorphous to 60% crystalline state. The composite PET/AS4 demonstrated a larger increase of 50%, from the amorphous to 60% crystalline state. There is a greater increase in the tensile modulus for that of the PET/AS4 composite than that of the neat polymer. This is presented in Figure 41. From linear regression the comparative slope values are 0.74 and

0.40 with R^2 values of .0.8562 and 0.8431 for the composite and neat polymer, respectively.

If as hypothesized by Young [82], and demonstrated with experimental results the polymer tensile modulus increases linearly with increasing crystallinity, based on the rule of mixtures and a 60% fiber volume fraction the increase in composite moduli should not exceed 40% of the increased matrix moduli as a function of crystallinity. It is evident that this is not the case and that the modulus increases dramatically above 35% crystalline content.

The greater increase in the percent change in tensile modulus of the composite over the neat polymer suggests improved interface strengths as crystalline content is increased. The improved interface strength will increase the overall strength of the composite until which point that brittle matrix transverse fracture occurs. This is supported by the maximum in the tensile strength curve of Figure 40, and the SEM analysis showing the rise and decline of the presence of hackles.

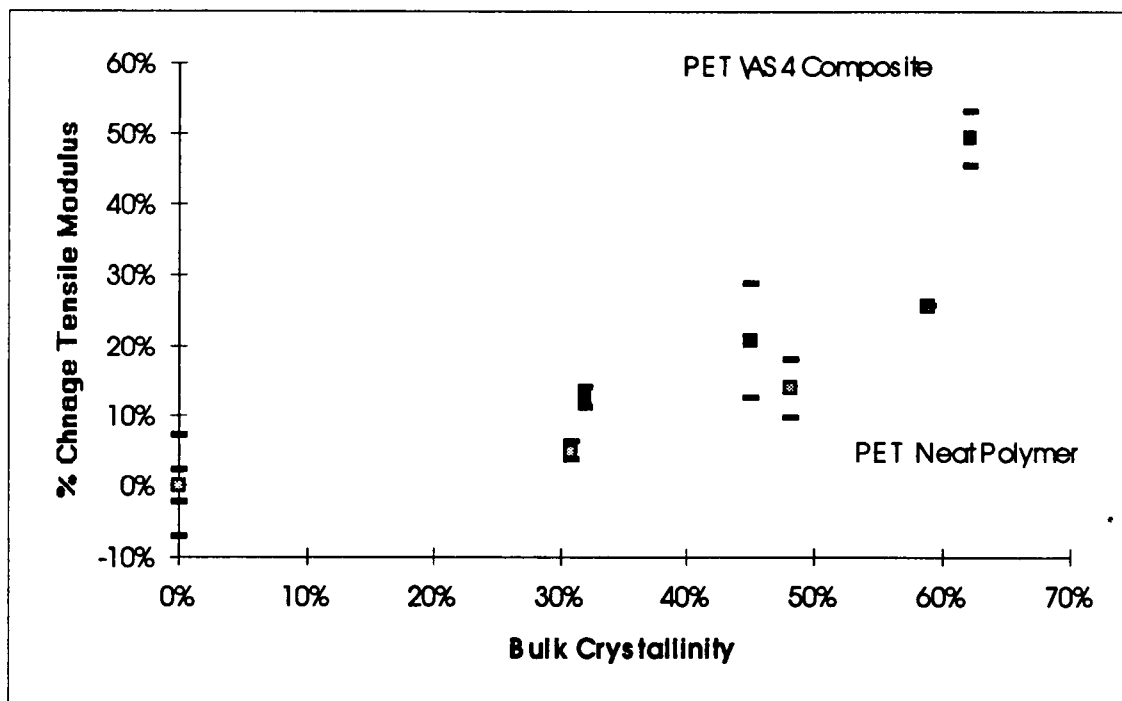


Figure 41: Effects of Bulk Crystalline Content on Tensile Modulus.

The experimental tensile moduli of the neat PET is applied to the general rule of mixtures for tensile modulus and is plotted with the experimental results of the PET/AS4 composite, refer to Figure 42. It is clear that the rule of mixtures is appropriate only for a small crystalline range, approximately 25% to 35%. It should be noted that under normal processing conditions, quenching from the melt the crystalline content is within this range. However, for the amorphous and highly crystalline content the rule of mixtures fails. To understand or postulate as to the reasons for these deviations from the rule of mixtures it must be understood that the rule of mixtures is an "ideal" means of estimating composite properties. The rule of mixtures assumes ideal wetting and adhesion between particle-fiber and matrix.

The observation of the composite test coupons after testing provided indications to the mechanisms of failure. With a weak interface upon breakage of fibers at scattered locations the amorphous composite failed with longitudinal debonding. If the interface was stronger, the stress concentration at the broken fiber may not yield the interface resulting in increased stress concentrations on the neighboring fiber, in which case they may break resulting in brittle fracture, as was the case for the 60% crystalline PET/AS4 composite. The best strength is obtained under mixed failure modes, as was the case for both the 30 and 45 percent crystalline composites.

It is observed that these failure modes are suggested based on the relative strengths of the matrix material. With small increases in the matrix strengths as shown in Figure 37 these changes in suggested failure modes may be additionally influenced by the increase in bulk crystallinity, rather than matrix strength alone.

It is clear from the SEM photomicrographs that there is a lack of adhesion in the amorphous PET/AS4 composite. This composite demonstrated longitudinal debonding as a failure mode which is generally associated with a weak matrix and an obvious lack of adequate adhesion between fiber and matrix.

The photomicrographs of the fractured 45% crystalline PET/AS4 composite show the presence of large hackles. The maximum height of these hackles is 5 microns, the same

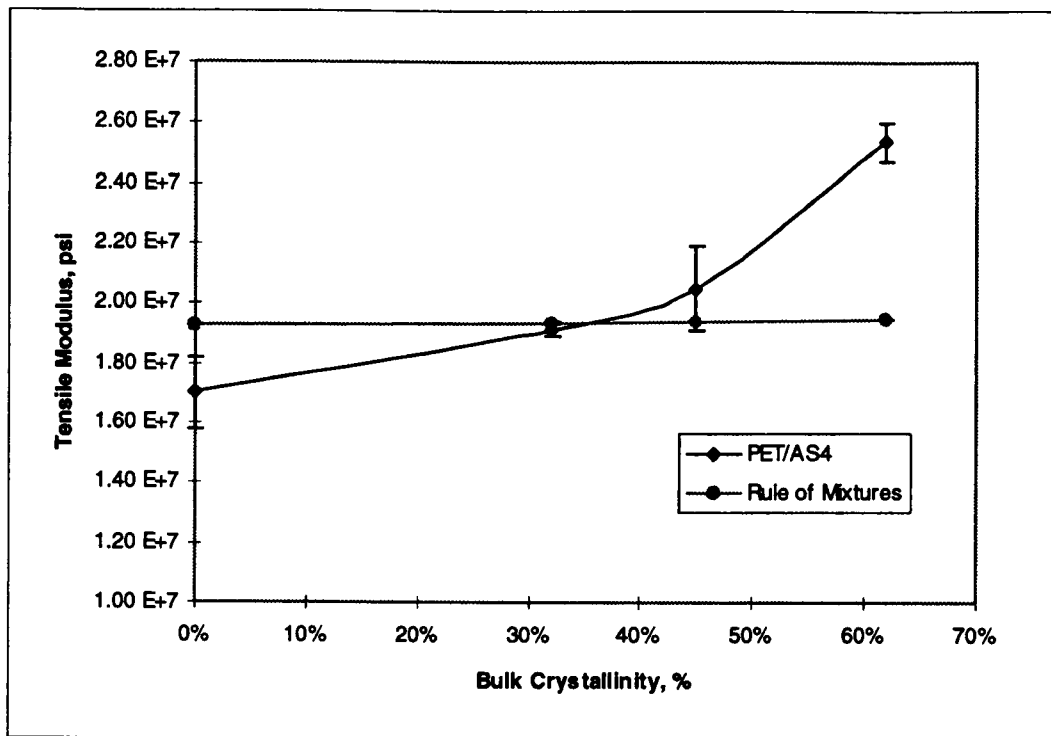


Figure 42: Rule of Mixtures to predict Tensile Moduli

magnitude as the fiber diameter (8 microns). The presence of these hackles indicates secure adherence between matrix and fiber. This region of bulk crystallization is also in agreement with the estimated modulus from the rule of mixtures.

At this time it is appropriate to discuss the fiber packing to explain the size of the hackles present in the mid-crystalline range. In unidirectional composites the fibers are spaced randomly throughout the composite thickness. For the purpose of this discussion the fibers are assumed to be in hexagonal packing, with a fiber volume fraction, V_f , of 0.60 and a fiber diameter of 8 microns. The center to center distance of fibers is 10 microns; therefore, the smallest spacing between fibers is 2 microns.

The maximum spherulite radii of PET crystallized from melt and glassy states of various molecular weight was fully explored by Van Antwerpen [50]. The maximum spherulite radii are approximately 3.75 microns crystallized at 120°C from either melt or glassy states. Since annealing of polymers thickens the lamella and does not increase the size of spherulites these dimensions are assumed to be reasonable for this discussion. A pattern of

hexagonal packing is overlaid on a group of impinged spherulites in Figure 43. At bulk crystallinity of 30% the PET spherulites should be impinged.

It is suggested that to obtain hackles with the heights shown in the photomicrograph of 45% PET/AS4 composite the fiber may be acting as a nucleation site. These samples were quenched and then annealed quickly at 220°C. To reach this annealing temperature some melting, nucleation and recrystallization will occur, additionally, at 220°C the chains should have considerable mobility.

The dramatic increase in modulus of 60% crystalline PET/AS4 over the predicted modulus from the rule of mixtures is an astounding increase. Using the rule of mixtures the modulus of the matrix material is backed out and would be 15E6 psi. This magnitude of modulus from a thermoplastic polymer is obtainable only in highly oriented crystal structures.

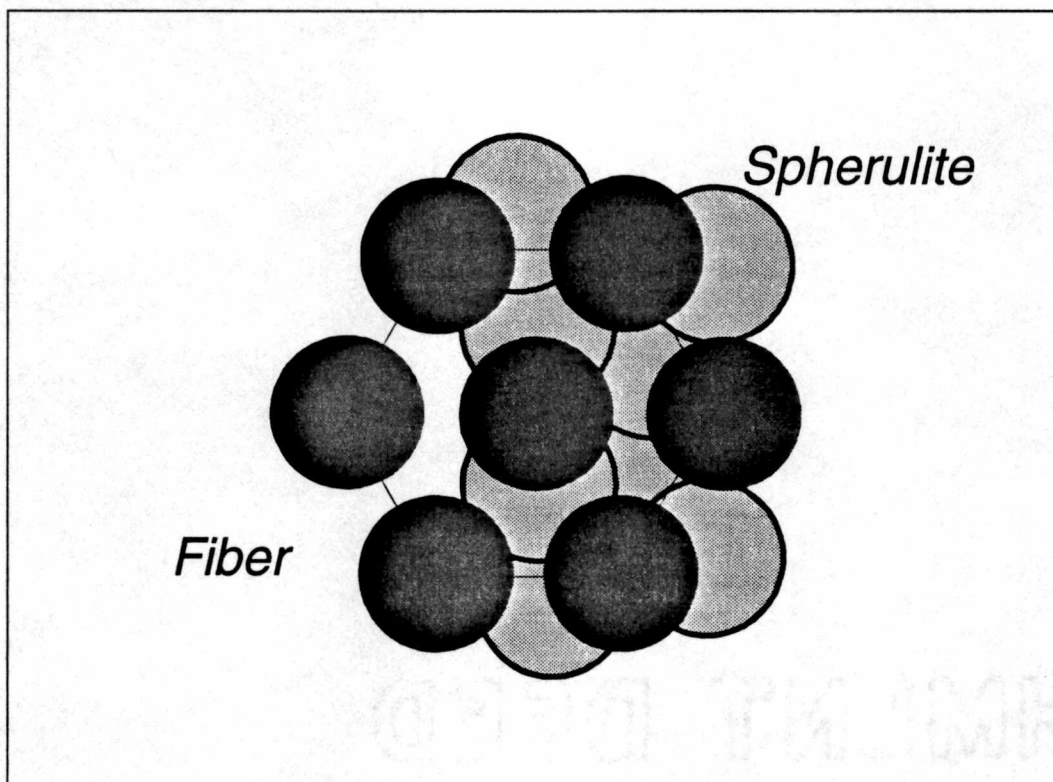


Figure 43: Fiber Packing Schematic.

The 60% crystalline PET/AS4 samples are produced identically to the 40% composite samples with the exception of the applied pressure. The dramatic increases in modulus are only evident in the composite samples, thus eliminating general crystal reorganizations induced by pressure as demonstrated by inducing high annealing to polymer crystallization as demonstrated by Phillips [1].

Viewing the photomicrographs of the 60% crystalline PET/AS4 composite it can be seen that the fibers are completely wetted and short uniform hackles are present which completely cover the fiber. Carbon fibers have a surface roughness generated by the basal planes or their edges which are predominantly longitudinal to the fiber. Based on the processing technique and base materials these basal planes are the primary source of surface microroughness. Although PAN based fibers are relatively smooth, Greso [83], longitudinal surface microroughness is present in PAN based AS4 fibers.

It is postulated that annealing of the composite at elevated temperatures in this case 220°C with the applied pressure polymer crystals may align. There are two possible hypotheses for polymer crystal alignment. The first is epitaxial growth between the graphite crystal structure of the fiber and the PET crystal stems. The second hypothesis is that as discussed for the 45% crystalline composite the fiber acts as a simple nucleating agent. Upon annealing and subsequent melting of less than perfect crystals the nuclei are retained on the fiber or are newly generated on the fiber and chain stems align within the microsurfaces of the fiber. Upon chain folding the crystal would be perfectly aligned with the fiber thus allowing the alignment of the tie molecules.

6. Conclusion

Although PET\AS4 composites are not commonly used in structural applications, they provided insight into the effects of bulk crystalline content on thermoplastic-carbon composites. An investigation of the mechanical properties, crystallization kinetics, and morphological attributes of polyethylene terephthalate, PET and its composite with PAN-based carbon AS4 fiber, PET\AS4 has been accomplished. Several interesting phenomena have been uncovered in the course of these analyses.

Basic bulk characterization studies on the crystallization of PET conclude that under normal processing conditions adequate cooling systems are required to control the quantity of bulk crystallization. Cooling rates in excess of 75°C are desirable. This is not unusual for thermoplastic materials and is one disadvantage in their application in polymer-carbon composites.

From the tensile test results of both the neat polymer and the composite, the tensile modulus increased as expected. The significance lies in the magnitude of that increase. For the neat polymer tensile modulus increased by 26%, from the amorphous to 60% crystalline state. The composite PET\AS4 demonstrated a larger increase of 50%, from the amorphous to 60% crystalline state. There is a greater increase in the tensile modulus for that of the PET\AS4 composite than that of the neat polymer. Linear regression analysis of the resolved tensile modulus (percent increase in tensile modulus) provides comparative slope values of .74 and .0040 with R^2 values of 0.8562 and 0.8431 for the composite and neat polymer, respectively.

The greater increase in the resolved tensile modulus of the composite over the neat polymer suggests improved interface strengths as crystalline content is increased. The improved interface strength will increase the overall strength of the composite until which point that brittle matrix transverse fracture occurs. This is supported by the presence of a maximum in the tensile strength curve as a function of bulk crystalline content and the SEM analysis showing the rise and decline of the presence of hackles. It is hypothesized

that the increased moduli above the predicted values are the result of an oriented matrix crystal structure.

It is postulated that annealing of the composite at elevated temperatures in this case 220°C with the applied pressure polymer crystals may align. There are two possible hypotheses for polymer crystal alignment. The first is epitaxial growth between the graphite crystal structure of the fiber and the PET crystal stems. The second hypothesis is that as discussed for the 45% crystalline composite the fiber acts as a simple nucleating agent. Upon annealing and subsequent melting of less than perfect crystals the nuclei are retained on the fiber or are newly generated on the fiber and chain stems align within the microsurfaces of the fiber. Upon chain folding the crystal would be perfectly aligned with the fiber thus allowing the alignment of the tie molecules.

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Vita

Robert Breiner Allen was born in Altadena, California, on October 27, 1961. He graduated from Highland Senior High in Pocatello, Idaho, in 1979. He entered Idaho State University later that year and dropped out the following year because of lack of interest due to the sudden loss of his father. Returning to Idaho State Vocational Technical school in 1982, Robert completed training and received an Associate of Arts degree in drafting in May of 1984. Employed by EG&G Idaho from 1984 through 1987, he regained the drive and incentive to complete his education. In August of 1987 Robert enrolled in the college of engineering at the University of Tennessee, Knoxville where he was counselled to consider other objectives because he would most likely never achieve his educational goals. In three years he received his Bachelor of Science degree in mechanical engineering. In the fall of 1990, after marriage to his lovely wife Heidi, Robert began his studies again at the University of Tennessee, Knoxville and received his Master of Science degree in polymer engineering in December of 1994.

Robert is happily married and now has two wonderful daughters, Kiah and Jeffrey – dreams do come true, mine have.