

CRAZE DEVELOPMENT IN HIGH-IMPACT POLYSTYRENE (HIPS)

A Dissertation

Presented to

the Faculty of the Department of Mechanical Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

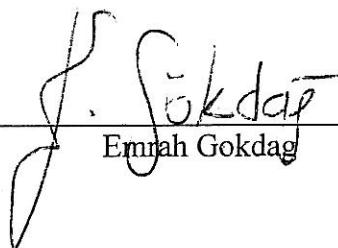
in Mechanical Engineering

By

Emrah Gokdag

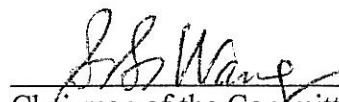
December 2007

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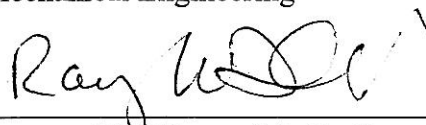
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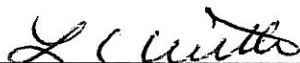
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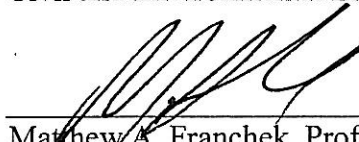
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ACKNOWLEDGMENT

First and foremost, I would like to express my sincere thanks to my advisor, Professor Su Su Wang, for his continuous and invaluable assistance throughout my study at University of Houston. I also would like to express my deepest gratitude to the members of thesis committee for their effort in evaluating this work.

Sincere thanks is extended to people at Composite Engineering and Applications Center including my fellow lab-workers for their help and assistance.

Special acknowledgment is made to TOTAL Petrochemicals, Inc. for the financial support they gave for this research.

Finally, here is my family. I would like to dedicate this work to my mom and to my sister, Ebru. God knows, I wouldn't able to make it without them. We have started this journey together, and thanks god we are finishing happily and together. Thank you both for instilling in me the strength to continue doesn't matter what. I love you so much.

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ABSTRACT

Craze damage development in high-impact polystyrene (HIPS) has been studied experimentally, theoretically and numerically. In the experimental program, six different grades of compression-molded HIPS were investigated. The results were analyzed and compared to understand the significance of morphological features of the blends, such as the particle volume fraction, size and its distribution in achieving the desired effects.

Toughening glassy polystyrene (PS) into the HIPS depends on characteristics of crazing. The statistical nature of craze formation has been studied in terms of craze density, craze orientation and craze size. Craze density in the HIPS was determined first and corresponding density and cumulative functions of craze orientation and craze size were obtained at different strain levels. The results reveal that cumulative and density distributions of craze length follow the form of a three-parameter Weibull's function. Cumulative and density distributions of craze orientation can be described with a normal distribution function.

Additional experiments were conducted to examine the characteristics of craze damage and its evolution. Craze damage development, thermodynamic driving force, and damage evolution under uniaxial loading were addressed. Results show that craze damage increases initially with strain but eventually approaches to a saturation state. Further loading does not cause an appreciable amount of damage increase. An orthotropic craze damage theory has been developed, based on a continuum damage mechanics approach. A damage tensor is introduced, and constitutive equations for the damaged

polymer are derived. Theoretical predictions of damage mechanics variables are compared with experimental results.

Micromechanics modeling based on a finite element method has been conducted to obtain occluded particle volume fraction and size effects on craze formation in a HIPS polymer. Numerical results show that stress concentrations at the equator of a particle is amplified with increasing occluded particle volume fraction. Crazes are most probably initiated from the large particle's equator in a HIPS with a bimodal particle distribution. Craze interactions are also modeled with an observed HIPS microstructure to address their potential growth under stress.

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1. INTRODUCTION

Rubber modification of a brittle polymer has long been recognized as a means to improve toughness of the material. For example, incorporation of a small amount of polybutadiene into brittle polystyrene, known as HIPS, increases the toughness of the modified polystyrene at least by a factor of two [1].

Macroscopic toughening of many glassy polymers has been achieved by a mechanism of inelastic deformation, called crazing, including the one in HIPS. Crazing, caused by a negative, local hydrostatic pressure, consists of an array of microscopic cavities, equivalent to a crack with surfaces tied by load-bearing fibrils, in the polymer. The craze-induced inelastic deformation dissipates energy and increases material's crack resistance. A craze could be a precursor of a crack, leading to fracture at the end unless in a well-controlled condition [2]. These dual roles are governed by the microstructure of the polymer blend, such as the particle volume fraction, size and its distribution to attain the desired effect.

This research addresses several important issues of craze damage development in high-impact polystyrene. It includes experimental, theoretical and numerical descriptions of craze-induced inelastic deformation. These subjects are investigated both microscopically and macroscopically.

Some of the important features of microscopic craze damage may be described by density and cumulative distribution functions, owing to the inherent microstructure of craze formation and growth, with exhibit statistical characteristics in length and orientation. Proper experimental methods are developed to quantify the craze damage

development in HIPS. Craze density may also be defined with corresponding cumulative concept. The density functions of craze orientation and craze size in HIPS are constructed at different strain levels.

Continuum damage mechanics (CDM), based on irreversible thermodynamics, has been used for evaluation of the damage state and macroscopic property degradation of a polymer. In this study, deformation, damage and failure of six different grades of HIPS polymers are evaluated and compared. A craze damage tensor is introduced, and constitutive equations of a polymer with distributed crazes are derived using effective stress concept and associated strain equivalence principle. Theoretical predictions of damage mechanics variables are compared with experimental data.

Micromechanics modeling, based on a finite element method, has been conducted to study the effects of occluded particle volume fractions and size distribution on crazing in a HIPS polymer.

The research is presented in the next nine chapters. A brief literature review is given in Chapter 2. The objectives of the research are presented in Chapter 3. An experimental program is described in Chapter 4, including compositions and mechanical properties of the polymers used, types of the experiments conducted, and data acquisition and analyses. The statistical nature of craze damage is discussed in Chapter 5. Chapter 6 is devoted to micromechanics of HIPS. Mechanical properties of the polymers are estimated using proper micromechanics models with rubber-phase incompressibility. Continuum damage mechanics for craze damage is developed in Chapter 7. Basic continuum damage mechanics variables are introduced first. Formulation of an orthotropic craze damage theory is made and constitutive equations of a damaged

polymer are derived. Computational micromechanics for HIPS crazing is conducted in Chapter 8. Finite element models are used to investigate the influence of polymer properties and microstructure on craze formation and growth. In Chapter 9, experimental, theoretical and numerical results are presented and compared. Craze damage formation, accumulation and evolution are addressed. Correlations between microscopic and macroscopic damage are also discussed. In Chapter 10, the conclusions obtained from the study are presented and a list of recommendations for future studies is given in Chapter 11.

2. LITERATURE REVIEW

2.1 Inelastic Deformation in Amorphous Polymers and HIPS

Damage and fracture of amorphous polymers are related to plastic deformation, crazing, and crack growth. Their mechanical responses to applied load vary differently. For example, polystyrene and polymethymethacrylate are brittle under tension whereas polycarbonate is intrinsically tough [3]. Toughening brittle amorphous polymers has been done successfully by addition, most often blending, of a second-phase elastomer.

Under tension, the following molecular mechanisms, typical for polycarbonate, are likely involved in polymer deformation. Usually, for strains less than 1% or 2%, stress is proportional to strain. Thus, deformation is homogeneous and linear elastic. At this point, polymer chains are displaced from their equilibrium positions. The material returns to its original shape when the load is released. When a polymer is subject to a monotonically increasing load beyond the elastic limit, plastic deformation starts. At this stage, segment chain motions and permanent slips between the chains occur. In fact, mechanical properties of amorphous polymers depend on how easy the chains can move relative to one another. As the material is further extended, the load passes a maximum ("yield strength") with localized deformation. The plastic flow may follow with a strain softening or hardening. The non-uniform plastic softening with large scale chain movement continues as the tension proceeds until the onset of strain hardening. Orientation of drawn chains stabilizes the strain localization process and results in the strain hardening response of the material. Eventually, with separation of the chains, fracture occurs [4, 5].

Glassy, high molecular weight amorphous polymers exhibit two distinct modes of plastic deformation: shear yielding and crazing. Depending on the loading rate, temperature, stress state and other factors, polymers may deform with either one or both mechanisms [6].

The shear yielding is a localized, irreversible shear deformation [7, 8] of a polymer. It takes place at a constant volume and often emerges as shear bands, which form at about 45° to the normal stress direction.

Crazing is generally considered to be a primary source of plastic strain response in rubber-modified polymers. Sauer et al. (1949), for the first time, have proved that the crazes are not true cracks. They investigate polystyrene (PS) and obtain little or no change on its mechanical characteristics with the presence of crazes.

Crazing is a major source of toughening for brittle polymers. Thus, it has been the subject of many studies. Particularly, characteristics of crazing in PS at room temperature have been extensively studied [9] and well documented in the literature over the last few decades.

2.1.1 Craze Initiation

Craze initiation in glassy polymers has been studied extensively but not fully understood because of complex interactions among various microscopic factors.

In 1968, Sternstein, Silverman and Ongchin [2, 6] have studied formation and growth of polymer crazes in bi-axial stress fields. They propose a criterion for craze formation, which requires the first stress invariant satisfy a specified relationship. They also show that a craze propagates normal to the major principal stress direction. They test

polymethylmethacrylate (PMMA) in biaxial (plane stress) conditions and propose the stress invariant criterion for initiation of crazes in PMMA as

$$\sigma_b = |\sigma_1 - \sigma_2| \geq A(T) + \frac{B(T)}{I_1},$$

where σ_1 , and σ_2 are the principal stresses; σ_b , the stress bias; $I_1 = \sigma_1 + \sigma_2 + \sigma_3$, the first stress invariant; $A(T)$ and $B(T)$ are temperature dependent material parameters. Later, Sternstein and Myers [10] extend the 2-D criterion to general three-dimensional problems by interpreting σ_1 , and σ_2 as the maximum and minimum principal stresses. The lack of time dependency in the nucleation and the absence of specific correlations between the parameters and physical mechanisms of craze initiation are the major drawbacks, which limit its applicability to other particular conditions (e.g., in the presence of a crazing agent). Surface-active liquid environment promotes crazing by lowering the polymer surface tension/energy at phase boundary. Particularly in organic media, environmental stress crazing and cracking have been one of the main practical problem for glassy polymers.

Argon and Hannoosh [11] generalize the Sternstein and Ongchin's criterion to three-dimensional states of stress. They perform experiments on unoriented polystyrene, free of plasticizers, under different combinations of deviatoric stresses and negative pressure (in tension-torsion experiments) at room temperature. Under a given deviatoric stress and a negative pressure, craze density is observed to initially increase with time and then approach a saturation state. In the experiments, the delay time for craze initiation decreases and the saturated craze density increases with negative pressure. Craze nucleates as a result of localized plastic flow produced by large stress concentrations at an interface of an inclusion. Argon and Hannoosh's criterion is derived

from creep tests under a constant stress. According to their model, craze initiation time, t_i , is defined in terms of a local hydrostatic stress, σ_h , and the von Misses stress, σ_e , as

$$t_i = \tau \exp \left[\frac{C}{\sigma_e} - \frac{3\sigma_h}{2QY} \right],$$

where τ is a characteristic time constant, depending primarily on temperature; C is a temperature-dependent constant, proportional to the activation energy of micro-shear processes; Q is a measure of the interaction of the shear and the hydrostatic stress components; and Y is the tensile plastic resistance. The parameters for PS at room temperature have been reported by Piorkowska et al. [12], as: $\tau = 6.0 \times 10^{-8}$ s; $C = 1.65$ GPa; $Q = 0.0133$; $Y = 70$ MPa. Although the model is formulated for homogeneous PS, Berger and Kramer [13] have successfully predicted experimentally observed trends for other PS blends.

2.1.2 Craze Growth

Kinetics of crazing can be classified into three stages: craze initiation, propagation and thickening. Craze growth is an important stage in polymer degradation and failure. Craze propagates with two different mechanisms: craze tip advance and/or thickening as a result of drawn and stretched fibrils. Most of the craze growth studies have involved measurements of only one of these dimensional changes with time.

Klemperer [14] has investigated craze growth in the plane normal to the maximum principal stress direction. This fact is also verified later for curvilinear stress fields, such as around cavities in which craze growth is curvilinear, following the path normal to an applied principal stress [2, 6]. Direct microscopic observations appear to be

the most effective way for analysis of craze kinetics. Regel [15] uses this approach to monitor craze initiation and growth in PMMA.

Theoretical studies on craze growth have been mainly based on one-dimensional plasticity theory, such as the Dugdale model [16] or a Fourier transform solution for stress analysis [17]. In both methods, polymers outside the craze are considered to be linearly elastic with appropriate boundary conditions.

Knight [17] takes a Fourier transform solution to calculate the stress distribution along a craze. Kramer et al. [18, 19] use it for calculations of thickness profiles for PMMA and polystyrene by holography and electron microscopy, respectively. Later, Verheulpen-Heymans and Bauwens [20] state some of the shortcomings of Knight's Fourier transform solution.

Line plasticity solutions have received much attention by including craze growth kinetics. Using this approach, craze growth is quantified in terms of both length and thickness via measurements, or a critical energy release rate [21], a critical craze-tip opening angle or displacement [22].

Craze growth mechanisms have not been included in previous theoretical studies except the work conducted by Andrews and Bevan [21]. They note craze growth based on elasto-plastic expansion of cavities while excluding their initiation. Argon [23] suggests that a craze propagates by repeated formation of cavities ahead of the craze-tip following his proposed craze formation mechanism. The same homogeneous plastic flow factor that causes craze formation is also responsible for its growth. However, the work done by Salama [24] shows drawbacks of the proposed model, i.e., stress concentration ahead of a craze tip is not sufficient for cavity formation and the postulated mechanism

would give a different topology than the observed. Argon [25] subsequently postulates a new craze growth mechanism, called “meniscus instability”- craze growth with repeated convolutions that result in a yielded polymer to break up and produce new crazes each time at the polymer/air interface. As the craze tip advances, the polymer breaks up into a series of fingers, and fibrils are developed by the deformation of the polymer between fibrils, which generate a correct craze topology. Donald and Kramer [26] verify the meniscus instability model by demonstrating it on tilted, high magnification TEM micrographs of polystyrene. Michler [27] interprets his “precraze” observations, ahead of a craze tip, as an evidence of nucleation of isolated pores. Kramer and Berger [28] object this interpretation and suggest that the precrazes are previously crazed and coalesced polymer.

Argon and Salama [29, 30] also provide a theoretical model for their meniscus instability mechanism and show supporting experimental results. The Argon-Salama model is two dimensional, similar to Verheulpen-Bauwens’[20] in the sense that both consider a single craze in an infinitely large matrix with a tensile nominal stress. Verheulpen and Bauwens analyze the craze matter in two parts, i.e., craze body and craze tip, with assumed normal tractions in these regions. They use a conformal mapping method for the stress analysis. However, in Argon and Salama’s model, a single traction force normal to the craze plane is assumed. The craze matter is modeled with a yield zone ahead of the craze tip with stress, Y_c . The same mathematical procedure is used for calculation of local stress components. Even though the models are verified by a limited number of experimental data, they both do not consider any craze interaction.

2.1.3 Craze Interaction

Interaction among crazes is expected in a polymer with multiple crazes. Most craze theories concentrate on one craze only, not on its surrounding, thereby excluding the craze-craze interaction, which in turn affects their growth kinetics.

During polymer deformation, not a single, but a number of crazes initiate and grow simultaneously, causing stress redistribution adjacent to the crazing matter, which affects craze formation and growth.

Mills [31] suggests that craze interaction starts at an early stage of its growth, proposes a threshold for the interaction: interaction begins when surface crazes penetrate, normal to the free surface, more than 20% of their separation distance in the loading direction. Mills models the craze interaction by considering isolated two off-set crazes. In his two dimensional model, he adapts Argon's [23] approach and uses a single traction force across the craze matter. He predicts craze growth paths and calculates the corresponding driving force for craze growth. For PVC, he has observed overlapping surface crazes with no visible deviation in their growth paths. He shows that when the traction force in the craze matter is between 90% and 100% of the applied load, craze pairs remain parallel to each other. He also shows that modeling the craze matter with a single or two traction forces resulting in a negligible difference when the traction force in the craze matter is greater than 90% of the applied load. In addition, calculated potential energy values for craze growth reveal a decreasing trend as a result of craze interaction. In a recent study, Michler [32] mentions a phenomenon: craze growth diminishes with increasing craze interaction as interparticle distance decreases with a second-phase particles volume fraction increase for rubber-toughened PMMA samples.

2.2 Effects of Rubber Particles on Crazing

Addition of second-phase rubber particles into a glassy polymer is aimed to produce a soft but tough polymer. High-impact polystyrene (HIPS) is a toughened polymer by adding second-phase particles. Bucknall and Smith [1] provide an explanation of the rubber-toughening mechanism in HIPS. They stretch a thin film of HIPS and observe macroscopic yielding caused by the formation of multiple crazes around the rubber particles [1].

Rubber particles, which act as stress concentrators, promote a large number of craze formation and cause energy absorption. Under a tensile stress, craze initiation occurs near the equator of a particle and propagates outward. Integrity of a crazed polymer is retained as long as craze growth is controlled. The second phase particles in a polymer are characterized by their volume fraction, compliance, size and size distribution, which all affect the craze formation [32-42].

Direct electron microscope observations of rubber-particle-modified polymers reveal the microstructure of the rubber particles [43, 44]. Rubber particles in many toughened polymers are microscopic composites themselves as a result of occlusion of the continuous phase polymer inside the rubber particles. The sub-inclusions affect both compliance and volume fraction of the rubber particles, and thus, determine mechanical properties of the polymer. For a HIPS, the measured values given by Bucknall [45] show that the major constitute in an occluded particle is dispersed polystyrene. He reports that, for a HIPS with 10.5% polybutadiene by weight, the occluded-particle volume fraction is 42% of the total volume. However, the polybutadiene occupies only 28% of the occluded particle volume while the remaining 72% particle volume is polystyrene. A high

polystyrene content means a low particle compliance; hence, low craze formation efficiency of that particle. A high amount of polystyrene inclusions may also reduce craze termination ability of particles a craze can continue through an occluded particle via polystyrene sub-inclusions [46]. In addition, a high polystyrene content causes particle-break up during melt processing which resulting in loss of toughening efficiency [47]. When a polystyrene content increases inside of the occluded particle, the overall occluded-particle volume fraction in a HIPS increases resulting in more particles; thus, more stress concentration sites for craze formation.

Microstructure and mechanical properties of the particles, including volume fraction, particle size, size distribution, and compliance can be changed during polymerization process. For example, the particle compliance, size and size distribution can be controlled by the agitation rate during and after phase inversion. However, controlling the rubber particle size without affecting other microstructural parameters is not easy.

The influence of particle size on mechanical properties of a rubber-toughened polymer has been a subject of many studies [12, 48-53]. These studies conclude that there is a critical particle size, which is a microstructural property, below which no craze initiates [49, 50]. Bragaw [50] describes an "effective particle" as a particle having a diameter larger than a thickness of a craze. Keskkula [54] reports that the rubber particle size of 1-2 μ is the optimum size for HIPS. Donald and Kramer [55] also work on HIPS and provide a critical particle diameter of 0.8 μ below which no craze initiation is observed. A similar study by Gebizlioglu et al. [56, 57] reports a different critical particle size, between 0.1 to 0.4 μ , for concentric spherical shell particles. In addition to those

studies, different diameter values for optimum toughening are reported [39, 58] for various material systems in which different failure mechanisms take place. For example, Sultan and McGarry [58] test rubber-toughened epoxy samples with different average rubber particle sizes. They investigate the change of deformation mechanisms from shear yielding (shear bands) to tensile yielding (crazing) as the average rubber particle size increases.

For a polymer with a fixed occluded particle content, rubber particles with different sizes result in different toughnesses. When an average particle size is decreased, the number of particles increases. More particles means more stress concentration sites for craze formation. Studies [59, 60] have shown that, the interparticle distance is related to particle diameter and it becomes smaller as the particle size decreases. For this reason alone, shorter crazes generate when they are inhibited by neighboring particles [46] .

Argon et al. [53] have investigate the size distribution effect by comparing three HIPS grades. Using a HIPS, they harvest particles and produce two new blends with an average size of 1.03 and 3.97 microns. Their results show that the bimodal particle size distribution yields a higher toughness. In a similar study performed by Wrotecki and Charentenay [61], on the effect of the bimodal particle size distribution, four HIPS grades differing in the polybutadiene content and particle size are tested. They suggest that the microstructure of the second phase is not the main contributor in craze initiation. Moreover, synergy between small and big particles as a result of their amounts is an important factor in toughening.

Bucknall [62] proposes two possible reasons to explain high efficiency of large particles compared to small particles: either small particles are inefficient in initiating

crazes or they are inefficient in inhibiting crazes. Experiments conducted on HIPS with small rubber particles show high craze rates with increasing trends throughout the tests. On the contrary, low impact strengths with low failure strains are observed for the polymers, which support the argument that poor craze termination by small rubber particles.

With a high voltage electron microscopy, Michler [39] works on particle size effect. He stretches semi-thin (1-3 μm thick) HIPS and ABS samples while observing craze formation quantitatively. He counts particles which contribute craze formation and monitors craze thickness and craze intensity, which in turn relates to the number of crazes around a single particle. Michler suggests an efficient particle diameter in the range of about 1-2 micron, which gives the highest efficiency in terms of craze thickness and the number of crazes formed by a single particle.

Toughness increases with the particle volume fraction but decreases sharply with the particle sizes below a critical diameter, and for particle sizes significantly above the critical diameter [63, 64]. Not knowing the individual contributions of volume fraction and particle size, Wu [60] suggests using the interparticle spacing as a microstructure property for toughening. He gives an expression for the optimum interparticle spacing as a function of both volume fraction and average particle size. Later, this approach is adopted by other researchers [39, 65-67] with modified representations for a interparticle spacing formula and applied to different material systems.

2.3 Continuum Damage Mechanics for Polymer Crazing

Damage may be defined as a material microstructural change under a given mechanical loading and an environmental condition. Kachanov [68, 69] is the first to introduce the continuum damage mechanics concept. Later, Rabotnov [70] postulates an equivalent strain principle to model rupture of metals under creep. Based on the equivalent strain principle, deformation behavior of a damaged solid, as defined by its constitutive equations, may be represented by the same constitutive laws (of the virgin material), but with the usual stress replaced by an effective stress. This concept has been extended to ductile fracture and fatigue fracture by Chaboche [71], Lemaitre [72-74], Hult [75], Leckie [76] and Murakami [77, 78].

Polystyrene and high-impact polystyrene are two polymeric materials on which theoretical and experimental continuum damage mechanics studies have been conducted. Recently, a series of papers [79-85] have been published, covering various aspects of craze damage behavior of PS and HIPS. In [79], a series of tensile tests are conducted. In-plane material property degradation is reported in terms of changes in Poisson's ratio, longitudinal and transverse Young's moduli. Corresponding damage variables are proposed with a second-rank, non-symmetric damage matrix. In [80], damage driving force is determined. It has been experimentally proved that under tension, no material degradation occurs in the transverse direction. In [81, 83-86], a dissipation potential is introduced and a damage evolution law is proposed for an isotropic damage case. An orthotropic damage model is also derived assuming a second-order, symmetrical damage matrix. The damage development and evolution in the vicinity of the craze tip are studied using a modified Dugdale model and continuum damage mechanics theory. Craze

damage growth is examined experimentally and modeling of a non-linear stress-strain relation has been attempted. In the studies [79-85], material property degradation resulting from crazing is addressed via experimental methods to a certain degree. However, micromechanics and theoretical results are limited either by a single craze or isotropic damage. If not, they have suffered from lack of closed form solutions.

2.4 Micromechanics of Crazing in Rubber Toughened Polymers

Most brittle amorphous polymers, such as polystyrene (PS) and polymethylmethacrylate (PMMA), may be toughened by introducing second-phase particles. The amount of toughness achieved depends primarily on the morphology and properties of the second phase particles, such as volume fraction, compliance, size and size distribution [32-42]. Thus, prediction of the optimal morphology is useful to realize the desired mechanical properties of the polymer. Owing to inherent complexity, micromechanical models need to be established first for a better understanding of coupling between micro- and macroscopic deformation behavior.

Analytical methods may be developed for modeling polymers with simple geometry and in some limit cases [87, 88]. Numerical techniques, such as finite element methods, are generally needed to capture complex and detailed aspects of the physical material microstructure and deformation mechanisms. Modeling of the polymer microstructure and investigation of their resulting deformation mechanisms of two-phase polymers have been made by many researchers, for example, [89-96]. Huang and Kinloch [93, 94] model plastic deformation of epoxy filled with rubber particles under tension. With the development of realistic elasto-viscoplastic constitutive models [97-

100], considerable efforts have been directed towards the influence of rubber-modified polymers microstructure on its post-yield mechanical response. For instance, Steenbrink [101] models the void growth in polycarbonate, in which void interaction is included. In similar studies, Smit et al. [35, 37, 102] numerically investigate the coupling between microscopic and macroscopic stress-strain relation for toughened polycarbonate and polystyrene containing various volume fractions of rubbery particles. They conclude that in order to reach an optimal toughening, strain softening needs to be avoided by strain hardening stabilization. In a more detailed study, Boyce et al. [1] introduce a special craze element, which depicts the physical structure and properties of craze. The effects of micromechanical features, mainly the particle size, compliance and volume fraction, on craze initiation and growth are investigated on a high-impact polystyrene. Using a two-dimensional model, they simulate multiple crazing by implementing the craze elements around a particle with their normal parallel to the maximum principal stress direction. The model overestimates the stiffness of the crazed polymer, but does capture some local craze parameters correctly, such as craze thickness and fibril draw ratio. In a following study [103], a three-dimensional micromechanical model has also been developed, depicting the heterogeneous microstructure and allowing a random distribution of second phase particles. The elasto-viscoplastic deformation mechanisms of porous polycarbonate with various initial void volume fractions are investigated by replacing rubber particles with voids. Possible correlations between local mechanisms and corresponding macroscopic material responses have been sought. A constitutive model for mechanical properties of porous polymers has been proposed, based on the micromechanical model.

2.5 Craze Statistics

Craze formation and growth possess a strong directionality relative to their maximum principal stress directions [2, 6] and the crazes have a tendency to be spaced apart with somewhat regular distances [46]. Moreover, direct microscopic observations reveal that the morphology of crazing polymers exhibits well defined statistical characteristics.

The state of craze damage is governed by craze density, characteristic craze length, and distribution of craze orientation, and also inherently dependent on the local microstructure, stress state, and environment. Argon and Hannoosh [11] perform creep experiments on polystyrene and report a craze density increase with an eventual saturation. Their experiments show that the delay time for craze initiation decreases and the saturation craze density increases with negative hydrostatic pressure. In the study, the craze density observations are not explored by any quantitative theory. No data or explanation on craze length or craze orientation is reported.

Statistical descriptions of craze initiation and growth kinetics are essential for developing quantitative information on microscopic craze damage accumulation, evolution, and associated property degradation. No study or nondestructive testing method has been found in the literature to implement a rational treatment to describe the statistical nature and their distributions of microscopic crazes. However, a probabilistic model, based on statistical characteristics of microcracks, has been established to investigate microscopic fatigue damage in random short-fiber composites [104, 105]. In the study, a Weibull-form function is chosen to describe the density and cumulative distributions of evolving microcracks, and a fourth-order power form of trigonometric

function used to evaluate the statistical nature of microcrack orientation density and the cumulative distributions. Constitutive equations for the damaged polymer composite have been subsequently derived, based on the microcrack density and cumulative distribution functions, with the aid of a self-consistent micromechanics scheme.

3. RESEARCH PLAN AND OBJECTIVES

Inelastic deformation and fracture of amorphous HIPS polymers are related to craze damage growth and instability. Craze damage in HIPS is governed by local microstructure and stress state.

In this research, microscopic craze damage development and associated macroscopic property degradation of high-impact polystyrene subjected to uniaxial tensile loading have been investigated. The goal is to obtain a fundamental understanding of the basic mechanics and mechanisms of the craze damage formation and evolution in HIPS, considering the influence of microstructural features. The flow chart of overall research plan is shown in Fig.3.1.

In the experimental program, two types of tests are designed and conducted: a series of monotonic tensile experiments to acquire the data required for craze damage statistics analysis and disruptive loading-unloading-reloading tensile tests to quantify macroscopic deformation and property degradation of HIPS. The details of the experimental program are described in Chapter 4.

In the theoretical and computational program, mechanical properties of second-phase particles (with rubber-phase incompressibility) and HIPS polymers are estimated using proper micromechanics models. A quantitative, statistical description of microscopic craze evolution in HIPS is established. Continuum damage mechanics for craze damage is developed, and formulation of an orthotropic craze damage theory is made. Constitutive equations of a damaged polymer are derived. Computational

micromechanics modeling, based on a finite element method is conducted to investigate craze initiation and evolution in HIPS polymers.

This study is undertaken with the following objectives: (1) to characterize the statistical nature of craze development in HIPS polymers; (2) to quantify craze damage formation; (3) to investigate effects of second-phase particle volume fraction, size, dispersion on craze development; (4) to formulate a craze damage theory based on continuum damage mechanics in conjunction with statistical nature of craze formation in HIPS, and; (4) to compare the theoretical predictions with experimental data.

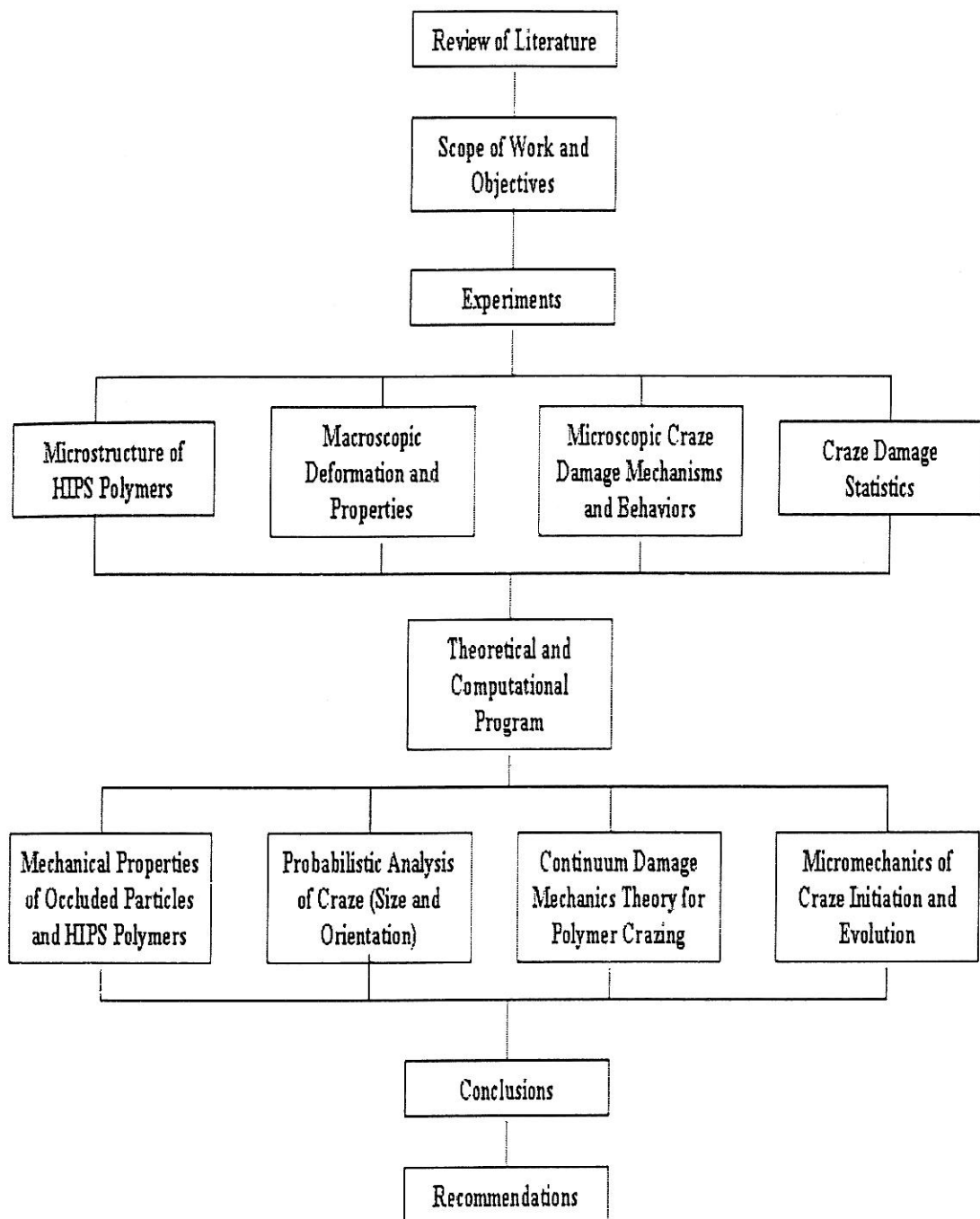


Figure 3.1.1: Flow chart of the Research Plan.

4. EXPERIMENTAL PROGRAM

A proper experimental method(s) needs to be established to characterize and quantify the statistical nature of craze damage development and associated property degradation in HIPS. In this chapter, an experimental program is described including compositions and mechanical properties of the polymers used, types of the experiments conducted, and data acquisition and analyses.

4.1 HIPS Composition and Morphology

High-impact polystyrene is a two-phase polymer system, composed of a continuous polystyrene matrix and a dispersed rubber phase, mainly polybutadiene. Polystyrene and polybutadiene have complementary mechanical properties. Polystyrene is generally very brittle with a high modulus at room temperature, and polybutadiene, an elastomer, with low T_g and rubbery at room temperature. The rubber content of the polystyrene-polybutadiene copolymer is limited to 14 % approximately by weight. During a HIPS manufacturing process, the occlusion amount with a desired particle size and shape may be controlled, using multiple agitated reactors in series [106].

4.1.1 Polystyrene

Polystyrene contains long hydrocarbon chains with a phenyl group attached to every other carbon atom. It is commonly produced by free radical polymerization from

the monomer styrene [106]. Polystyrene has a relatively simple, linear structure and its polymerization is relatively easy. It is nonpolar, chemically inert and resistant to water.

4.1.2 Polybutadiene

Polybutadiene is a homopolymer contains a monomer with four carbon atoms and six hydrogen atoms (C_4H_6). The four carbon atoms are in a straight chain containing two double bonds. It is the double bonds that are the key to polymer formation. Polybutadiene may be made by Ziegler-Natta polymerization [106].

4.1.3 High Impact Polystyrene

High-impact polystyrene (HIPS), a binary polymer system, known for its ease of processing, dimensional stability and impact strength, is produced by copolymerization or blending of a butadiene elastomer [106].

In the blending process, the PS resin is compounded with polybutadiene or styrene-butadiene-styrene rubber. The rubber phase is dispersed in the PS matrix and the mechano-chemically generated free radicals bring about grafting and cross-linking in the rubber phase [106].

A HIPS can also be made by copolymerization of styrene and butadiene elastomer. A bulk process is commonly used. In the process, rubber is dissolved in the styrene monomer along with additives and reaction takes place among the constituents. Initiation may be made thermally or by the use of initiators. During the reaction, the rubber phase is grafted to the PS matrix. The extent of grafting depends on the

copolymerization parameters, such as reaction temperature, the type and amount of initiators, grafting activators and the polybutadiene content. Phase inversion is an important stage in the polymerization and critical for achieving the desired characteristics of HIPS [106]. HIPS products can be manufactured by injection molding, injection blow molding, thermoforming and extrusion [106].

4.1.4 Specimen Materials and Manufacturing

Compression-molded HIPS specimens were used in the study. Six different kinds of HIPS were included: four from TOTAL Petrochemical, and two from other manufacturers. To explore the influence of the polymer microstructure on craze formation and evolution, TOTAL's HIPS were designed and made with controlled particle sizes and distributions: two grades containing similar average particle sizes with different size distributions and the other two with a similar particle size distribution but containing different average particle sizes. General microstructural features of the six kinds of HIPS are shown in Fig. 4.1.1. In the material with TOTAL's HIPS, low cis polybutadiene (consisting of approximately 35% cis, 55 % trans and 10% vinyl by weight) was used. Glass transition temperature, T_g , measurements (by DSC) revealed that their polybutadiene chemical compositions were similar for all the HIPS grades.

In Tables 4.1.1, 4.1.2 and 4.1.3, a summary of material and microstructure parameters is shown, including chemical compositions and mechanical properties of the HIPS samples and the properties of an unmodified polystyrene. The composition, average rubber particle sizes, and particle dispersion information were determined by AFM imaging [107] and a light-scattering [108]. Knowing the limitations (see Appendix A) of

both the AFM microscopy and the light-scattering method, the AFM data (for rubber particle size) were modified with Saltykov's [59] correction for further calculations. Details of the procedure and the corresponding particle size distributions are given in Appendix A.

4.1.5 Micromechanical Properties and Microstructure Parameters of Occluded Particles

Micromechanical properties and microstructure of occluded particles are important in the later study of craze initiation and growth. The values given in Table 4.1.3 were calculated, based on the micromechanics models in Chapter 6. [Note that the mineral oil, which was an additive to regulate the melt-flow rate in processing, was included in the calculation.] In the table, C_{oc} , ν_{oc} , μ_{oc} are the volume fraction, Poisson's ratio and shear modulus of occluded particles. Moreover, C_{PS} and C_{PB} are the volume fractions of polystyrene and polybutadiene in occluded particles, respectively. Also in Table 4.1.3, the light-scattering results were measured values obtained from a light-scattering analysis [108]. In addition, the AFM imaging results, based on the ratio of the total area of occluded particles to the overall image area, were extracted from AFM pictures taken directly from the HIPS samples.

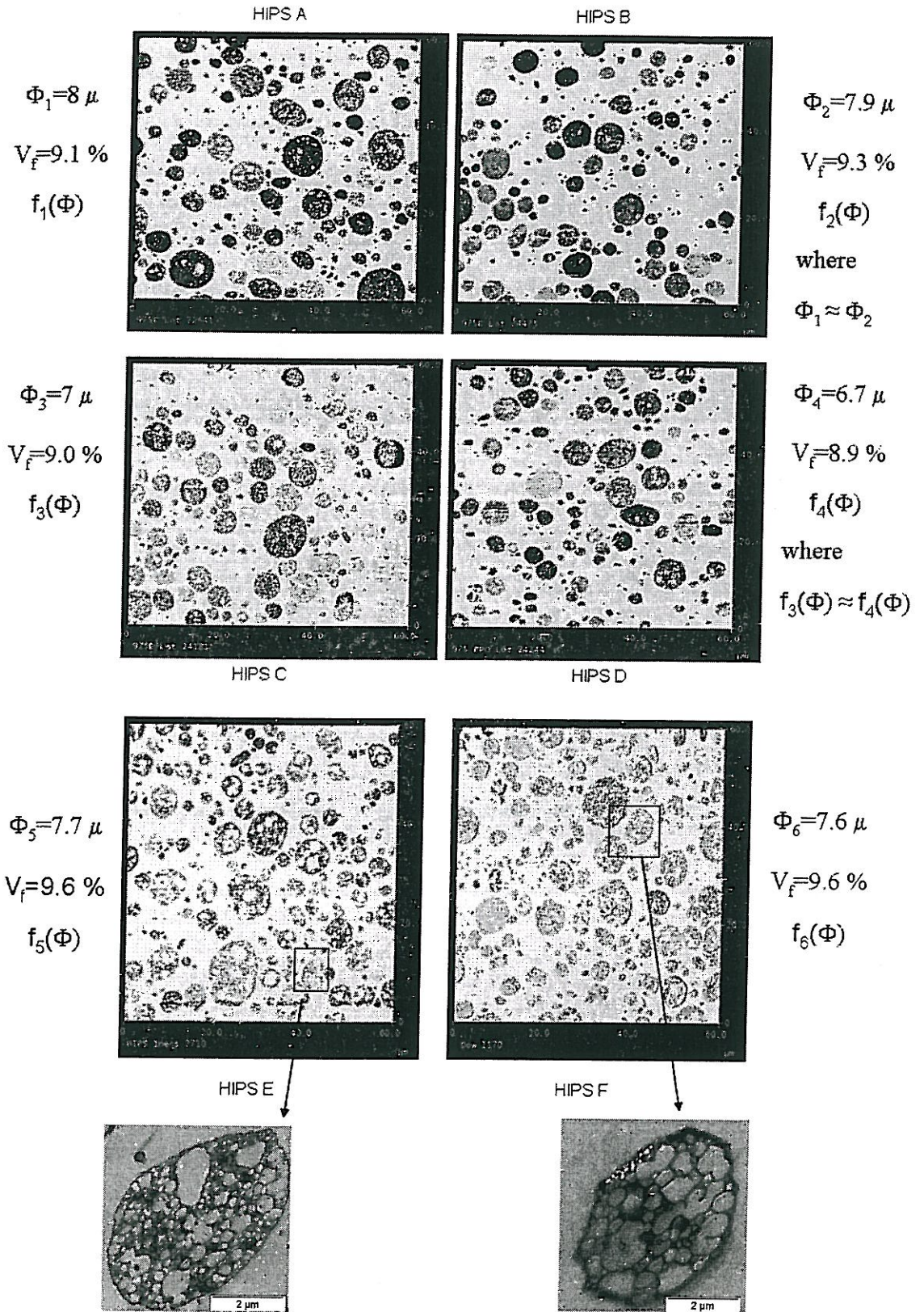


Figure 4.1.1: Microstructures of Six kinds of HIPS Used in the Study.

Table 4.1.1: HIPS Composition and Microstructure

COMPOSITION and MICROSTRUCTURE	HIPS A	HIPS B	HIPS C	HIPS D	HIPS E	HIPS F
Weight % Rubber (Polybutadiene)	8.1	8.3	8.0	7.9	8.2	8.5
Volume % Rubber (Polybutadiene), $\rho = 0.92$	9.1	9.3	9.0	8.9	9.2	9.6
Weight % Mineral Oil (Flow Modifier)	2.9	2.6	2.6	2.8	1.9	1.5
Volume % Mineral Oil (Flow Modifier), $\rho = 0.87$	3.4	3.1	3.1	3.3	2.3	1.8
Weight % Polystyrene	89.0	89.1	89.4	89.3	89.9	90.0
Volume % Polystyrene, $\rho = 1.05$	87.5	87.6	87.9	87.8	88.5	88.7
RPS* Volume Median [μm] [108]	8.0	7.9	7.0	6.7	7.7	7.6
Gel Phase volume % insolubles (in toluene)	23.3	23.9	24.8	24.7	27.2	28.8
Swell index (in toluene)	9.0	9.2	8.5	8.4	8.3	9.5
% Grafting = (% gel - % rubber) / % rubber	189	187	207	215	232	239
% Gel / % rubber (Measure of rubber utilization)	2.9	2.9	3.1	3.1	3.3	3.4
Glass Transition Temperature, T_g [°C]	102.6	102.9	102.4	102.4	104.5	106.9
Number-average Molecular Weight, M_n	81400	74760	74190	71900	82200	92870
Weight-average Molecular Weight, M_w	208850	202660	207870	200520	197870	205540
Volume Average RPS (Modified for swelling) [107]	4.88	4.82	4.27	4.09	4.70	4.63
Number Average of RPS (Measured by AFM) (after Saltykov's correction) [59]	1.16	1.34	1.16	1.35	1.74	2.30
Number Average of RPS (Measured by AFM)	1.47	1.69	1.65	1.52	1.86	1.72
Standard Deviation for # Average of RPS [Measured by AFM]	1.85	1.76	1.76	1.63	2.10	1.77
Occluded Particles' Volume Fraction (calculated)	0.251	0.256	0.244	0.249	0.351	0.433
Inter particle Distance, D_v [μm]	6.23	6.11	5.51	5.24	5.36	4.94
Number of Particles Per unit volume [#/ mm^3]	6.10E+07	4.48E+07	5.35E+07	5.18E+07	3.67E+07	2.20E+07

* RPS = Rubber particle size.

[#] = Refers to a corresponding reference.

Table 4.1.2: Mechanical Properties of PS and HIPS

MECHANICAL PROPERTIES	POLYSTYRENE	HIPS A Φ_1 $f_1(\Phi)$	HIPS B $\Phi_1 = \Phi_2$ $f_2(\Phi)$	HIPS C Φ_3 $f_3(\Phi)$	HIPS D Φ_4 $f_4(\Phi) = f_3(\Phi)$	HIPS E Φ_5 $f_5(\Phi)$	HIPS F Φ_6 $f_6(\Phi)$
E [Msi]	0.397	0.241	0.242	0.245	0.242	0.206	0.186
σ_y^u [ksi]	6.55	1.88	1.94	2.10	2.13	1.73	1.64
ϵ_y [in/in] (at σ_y^u)	0.0190	0.0095	0.0095	0.0105	0.0105	0.0105	0.0113
ϵ_f [in/in]	0.02	0.33	0.34	0.35	0.26	0.42	0.38

Table 4.1.3: Micromechanical Properties and Microstructure Parameters of Occluded Particles in HIPS Materials

HIPS Samples	C_{OC} [%]	ν_{OC}	μ_{OC} [ksi]	Inside Occluded Particle	
				C_{PS} [%]	C_{PB} [%]
HIPS A					
Mod. Matrix + Rubber*	25.14	0.392	2.38	63.80	36.20
Unmod. Matrix + Rubber**	26.39	0.389	4.18	65.50	34.50
Light Scattering	23.30	—	—	—	—
AFM Imaging	25.22-37.69	—	—	58.28-68.35	31.65-41.72
HIPS B					
Mod. Matrix + Rubber	25.60	0.392	2.47	63.70	36.30
Light Scattering	23.90	—	—	—	—
AFM Imaging	24.91-34.32	—	—	66.27-80.35	19.65-33.73
HIPS C					
Mod. Matrix + Rubber	24.38	0.399	2.32	63.10	36.90
Light Scattering	24.80	—	—	—	—
AFM Imaging	27.65-34.02	—	—	72.39-73.47	26.53-27.61
HIPS D					
Mod. Matrix + Rubber	24.88	0.391	2.48	64.20	35.80
Light Scattering	24.70	—	—	—	—
AFM Imaging	26.43-33	—	—	75.90-77.54	22.46-24.10
HIPS E					
Mod. Matrix + Rubber	35.10	0.375	7.15	73.80	26.20
Unmod. Matrix + Rubber	37.80	0.371	11.90	75.70	24.30
Light Scattering	27.20	—	—	—	—
AFM Imaging	36.94-42.61	—	—	67.59-81.59	18.41-32.4
HIPS F					
Mod. Matrix + Rubber	43.31	0.368	12.64	77.80	22.20
Unmod. Matrix + Rubber	49.20	0.363	18.70	80.50	19.50
Light Scattering	28.80	—	—	—	—
AFM Imaging	37.20-42.21	—	—	79.88-85.42	14.58-20.12

where C_{OC} , ν_{OC} , μ_{OC} are the volume fraction, Poisson's ratio and shear modulus of occluded particles. C_{PS} and C_{PB} are the volume fractions of polystyrene and rubber in occluded particles.

* Mineral oil effect included in the calculation (see Chapter 6).

** Mineral oil effect not included in the calculation (see Chapter 6).

4.2 Deformation and Craze Statistics in HIPS

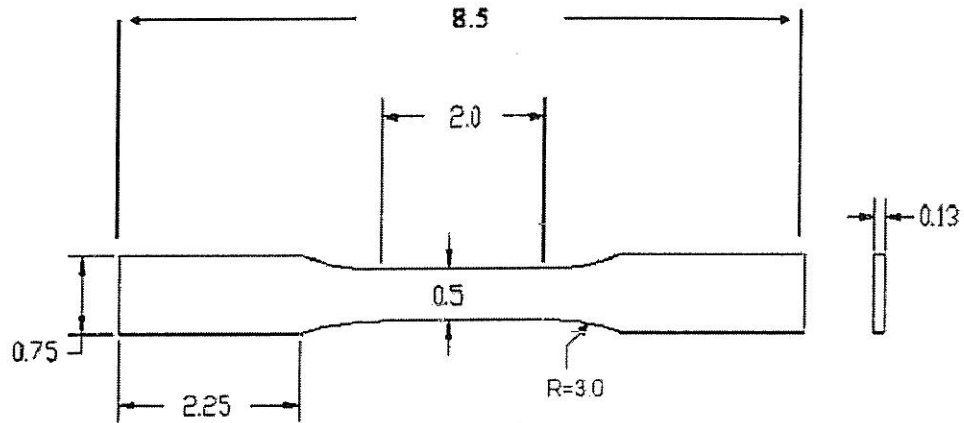
It is well recognized that crazes in a HIPS material exhibit a number of statistical features in their formation and growth. It is essential to obtain critical information on the statistical characteristics during microscopic craze damage evolution in HIPS for establishing a proper probabilistic model to quantitatively analyze and describe the craze damage development. A series of monotonic tensile experiments were designed and conducted to acquire the needed data for subsequent analyses and micromechanics modeling.

All six grades of HIPS materials used in this study were tested to determine their effective mechanical properties and to collect the craze formation and growth statistics. The monotonic tensile experiments were conducted in air at room temperature with a constant strain rate at 0.00007in/in/sec. [Repetitions with at least three samples from each grade were made to ensure the validity of the experiments.]

4.2.1 Specimen Geometry

Dumbbell-shaped test specimens (similar to the Type-I specimen defined in ASTM D638 standard [109]) were used (Fig. 4.2.1) for the experiments. In designing the test specimen, the radius of the fillet, R , was kept large while the gage length was kept short (compared to the ASTM D638 Type-I specimen.). By keeping the radius of the fillet large, stress concentration was reduced at the gripping ends; thus, undesirable heterogeneous craze initiation was avoided. The gage length was kept short for

homogeneous crazing but with adequate length to mount a standard MTS extensometer for the axial strain measurement.



(All the dimensions are in inch.)

Figure 4.2.1: Test Specimen Geometry for Statistics Study.

4.2.2 Sample Preparation

All the samples were made with the same compression-molding procedure. A summary of the compression-molding procedure is explained below:

- (1) Mold and photographic chrome plates were cleaned with a sharp razor and wiped using acetone and soft cloth to remove all polymer residues.
- (2) Backing plates and molds were laid down in an order as depicted in Fig. 4.2.2.
- (3) During the above process, polymer pellets (9.2 gram) were placed into each bar of the mold and distributed evenly.
- (4) Strips of an aluminum foil were inserted around the edges to allow for a small amount of polymer flashing on the bottom side.

(5) The entire apparatus (the sandwich of plates) was placed into a heated compression molder for curing.

(6) The following curing cycle was used:

- 1) Preheated the compression mold to 177 °C.
- 2) Applied 2 ksi pressure at 177 °C for 20 minutes.
- 3) Applied 40 ksi pressure at 177 °C for 10 minutes.
- 4) Cooled-down to room temperature at 15 °C per minute rate at 40 ksi.

(7) Cured samples were removed from the mold using an ejection plate.

For craze observations, the compression molded samples must have no surface marks or scratches. Therefore, the HIPS samples were polished to obtain a smooth surface prior to testing. A LECO VP-150 Polisher with a 150 rpm wheel speed was used for the polishing process. Three different deionized water-alumina solutions were used with 2.4% concentrations, containing 1 μ , 0.3 μ and 0.005 μ size alumina particles. Both surfaces of each sample were polished, using the solutions in a descending order, i.e., starting from the solution with the highest alumina particle size and finishing with the one with the smallest alumina size. For each solution application, both the sample and the polisher were cleaned with water. The surface quality of the sample was observed under a microscope. Polished samples were cleaned ultrasonically and dried by compressed air.

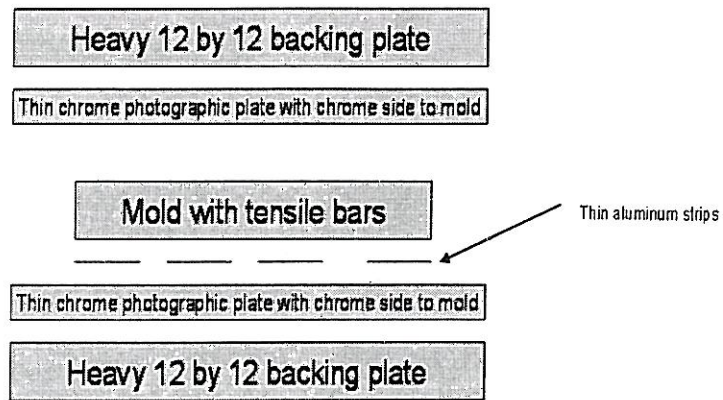


Figure 4.2.2: Sample Manufacturing by Compression Molding.

4.2.3 Test Facilities and Setup

A servo hydraulic material testing machine was used for the uniaxial mechanical tests. A standard extensometer with a 2-inch gage length was used to acquire the strain data. During the tests, specimen gage lengths were continuously recorded via a high magnification (x1300) video camera for craze observations. The experimental setup of a uniaxial tensile test for the craze analysis is shown in Fig. 4.2.3.

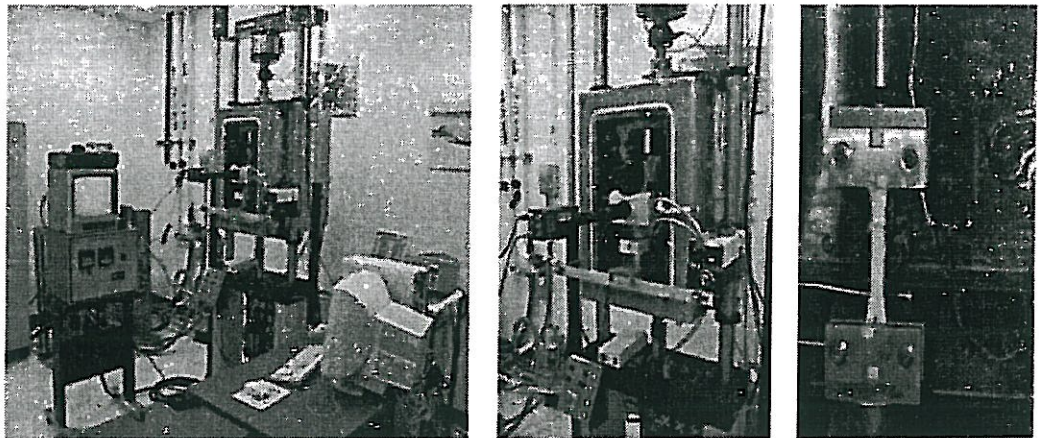


Figure 4.2.3: Experimental Facilities and Test Fixtures.

4.2.4 Experimental Procedure

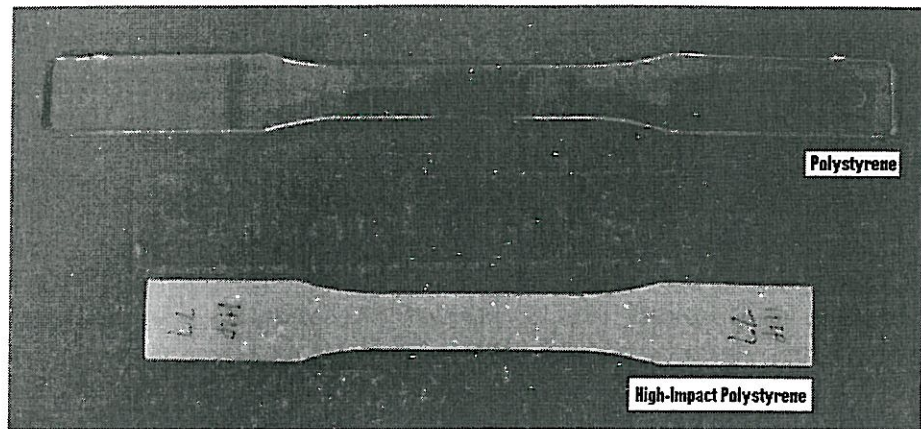
A dumbbell-shaped specimen was mounted on the test machine after a dimensional measurement. An extensometer was then attached to the specimen gage section. A uniaxial (monotonic) tensile test was conducted in a strain control mode. Specimens were loaded at the rate of 0.00007 in/in/sec. During the entire loading history the gage-section surface of the HIPS specimen was video-taped at high magnification to obtain craze initiation and growth images. The same procedure was repeated in each test and minimum three specimens were examined for each HIPS grade. Virgin PS and HIPS test specimens along with a tested HIPS specimen are shown in Fig. 4.2.4.

4.2.5 Data Acquisition and Analysis

A computer-controlled data acquisition system was used to record the applied load from a load cell mounted on the test machine, and axial deformation from an extensometer with a gage length of 2 inches.

Crazing images were continuously recorded via a high-magnification video camera (Fig. 4.2.5). Recorded images at desired strain levels were transferred to a PC for detailed analyses. Image analyses of craze length and orientation statistics were carried out using an OPTIMAS software. In Fig. 4.2.6, the selected strain levels were shown for taking pictures for the image analyses. Excel spreadsheet was used to process the digital image data extracted from the OPTIMAS and to construct the cumulative and density distribution functions of craze length and orientation.

a)



b)

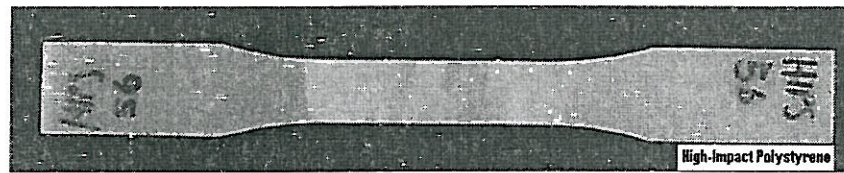


Figure 4.2.4: PS and HIPS Specimens: a) Virgin b) Tested [$\epsilon = 0.05$].

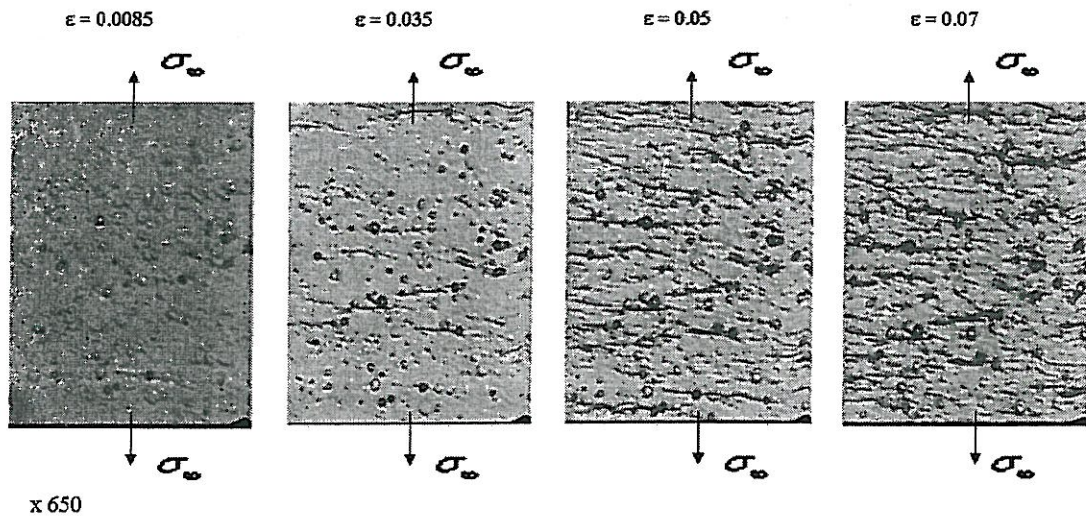


Figure 4.2.5: Craze Development in HIPS.

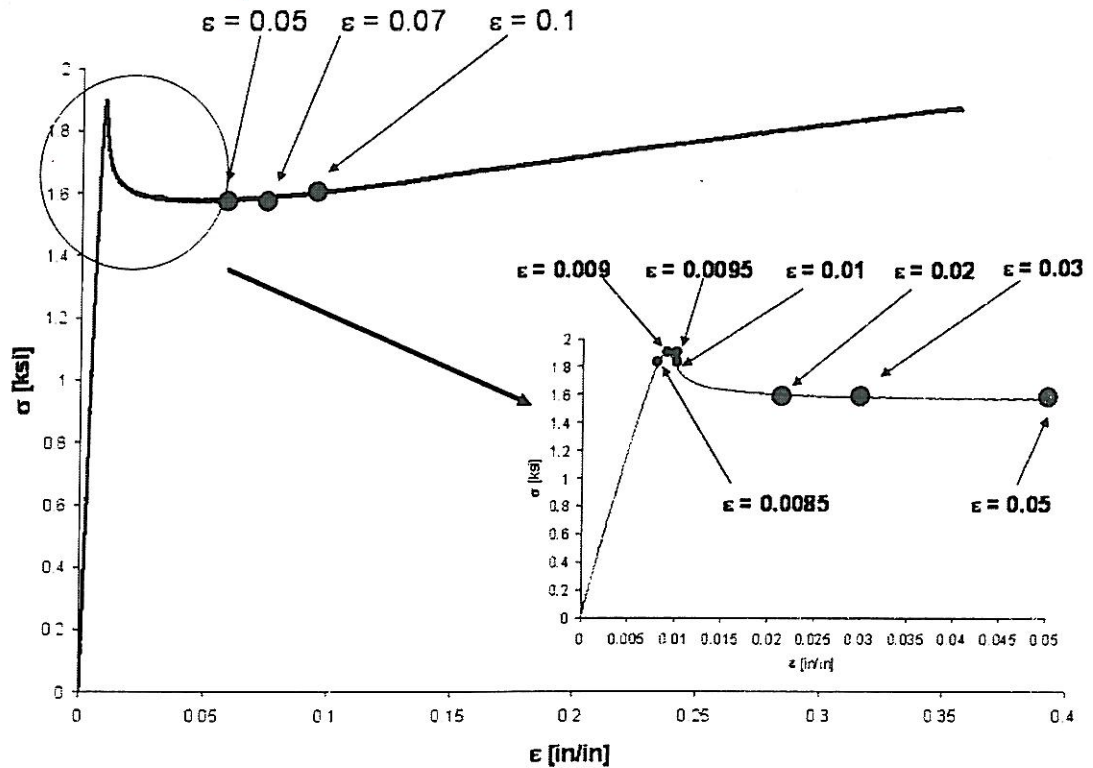


Figure 4.2.6: Strain Levels Selected for Craze Statistical Analyses.

4.3 Craze Damage Mechanics Experiments

Continuum damage mechanics (CDM) based on irreversible thermodynamics may be used to describe the damage state and property degradation of HIPS. However, proper experimental method(s) needs to be developed to quantify the craze damage development. In this section, an experimental program designed and conducted for craze damage mechanics analyses is described.

4.3.1 Specimen Geometry

HIPS specimens with the same geometry shown in Fig. 4.2.1 were used for the craze damage mechanics experiments.

4.3.2 Sample Preparation

The same compression-molded samples described in Section 4.2.2 were used for the experiments. The sample preparation was the same as described previously.

4.3.3 Test Facilities and Setup

A servo hydraulic material testing machine was used for the damage-mechanics experiments with a prescribed disruptive loading-unloading-reloading procedure. The strain data were acquired using a standard extensometer with a 2 inch gage length. The experimental setup is shown in Fig. 4.3.1.

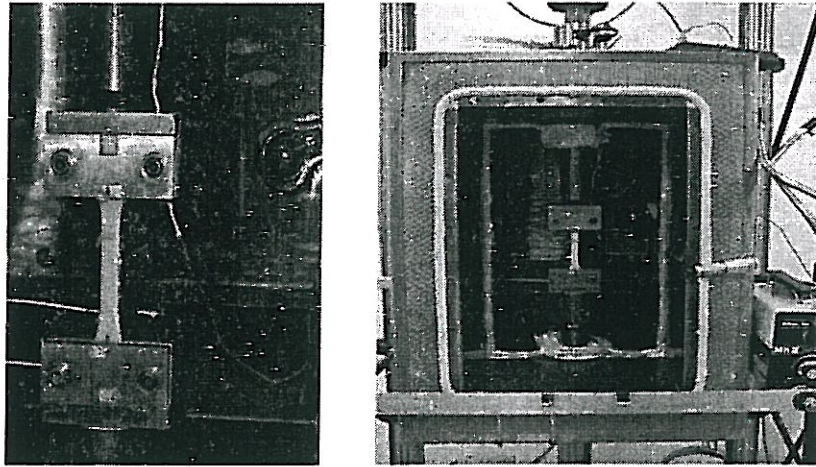


Figure 4.3.1: Test Setup for Damage-mechanics Experiments.

4.3.4 Experimental Procedure

A dumbbell-shaped specimen was mounted on a servo hydraulic machine after a measurement of the specimen dimensions. An extensometer was then attached to the

specimen gage section. A prescribed, disruptive loading-unloading-reloading tensile testing was conducted in a strain rate controlled mode. Specimens were loaded and unloaded at selected strain levels with the same loading rate of 0.00007 in/in/sec. At each unloading step, the specimen was unloaded by 10% of corresponding load level prior to its reloading (Fig. 4.3.2). The same procedure was repeated for each test and minimum three experiments were conducted for each HIPS grade material.

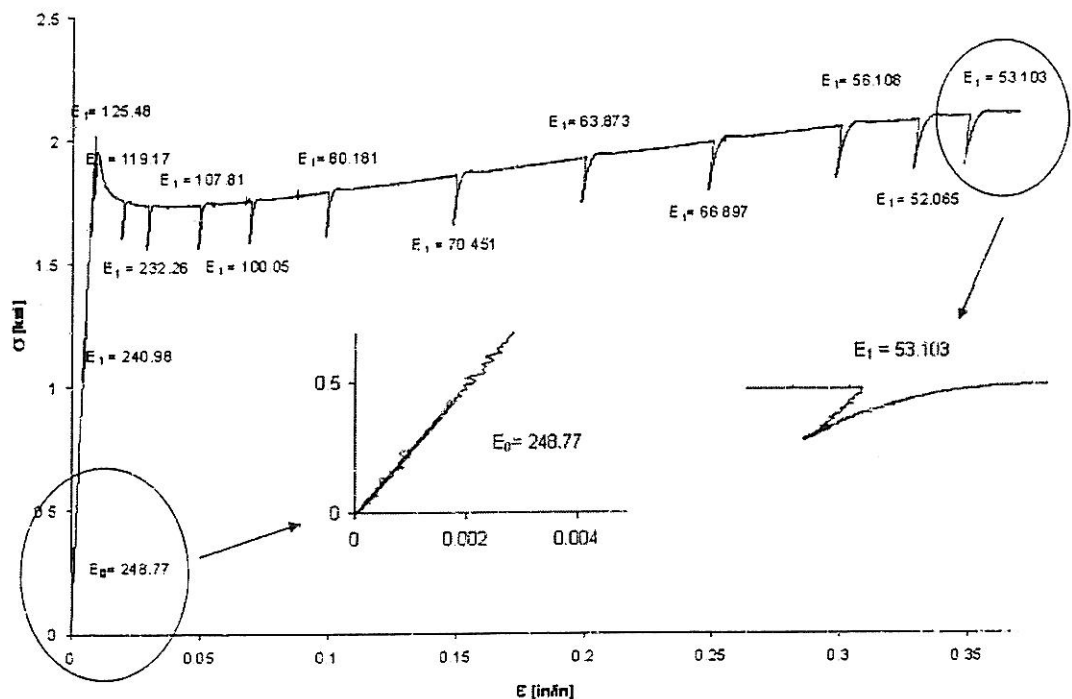


Figure 4.3.2: A Damage-mechanics Experiment Procedure to Measure Young's Modulus Degradation. [HIPS A; T= RT ; $\dot{\epsilon} = 0.00007$ in/in/sec]

4.3.5 Data Acquisition and Analysis

A computer-controlled data acquisition system was used to record the applied load from a load cell mounted on the test machine, and axial deformation from an extensometer with a gage length of 2 inches.

A direct consequence of crazing is the change of macroscopic mechanical properties. Craze damage along the loading direction may be measured in terms of modulus degradation. During testing, modulus measurements were taken in the reloading process by using the first 25 data points (Fig. 4.3.2). The modulus degradation data were used later to calculate the craze damage accumulation and evolution.

5 STATISTICAL DESCRIPTION OF CRAZE EVOLUTION IN RUBBER-TOUGHENED POLYMERS

A quantitative theory of toughening mechanics for rubber-toughened polymers such as HIPS must account for the unique characteristics of crazing in the heterogeneous solids. Thus, craze density, orientation, size and their distributions are important microstructure parameters which must be included. It is essential to describe the statistical nature of crazing with suitable mathematical expressions. In a homogeneous crazing process their distributions may be considered uniform through the thickness direction [104].

Craze density is defined as the number of crazes per unit volume. It is generally difficult to measure the craze density nondestructively and directly from the experiments. In the study, all the measurements were taken on specimen surfaces. 3-D spatial distributions of crazes in a test sample are evaluated assuming homogeneous crazing through the sample thickness direction. Denoting the craze density by λ and assuming that λ is uniform through the thickness of the material, one relates λ to the craze density function, craze per unit area, N as

$$\lambda = \frac{1}{2h} N, \quad (5.1)$$

where $2h$ is an average spacing between the occluded particles. Its formulation is given in [60] as

$$2h = \bar{\phi} \left(\frac{\pi}{6C_{oc}} \right)^{\frac{1}{3}}, \quad (5.2)$$

and $\bar{\phi}$ and C_{oc} are the average occluded particle size and the particle volume fraction, respectively. Thus, the craze density can be extracted conveniently from the images obtained from microscopic craze damage observations. Observed craze densities are in the order of several hundreds of thousands per cubic millimeter.

Microscopic craze evolution may be described by the number, size and orientation of the crazes. Owing to the statistical nature of craze formation, each craze needs to be characterized with a size, ℓ , and an angle, θ , relative to the applied loading direction. The random variables ℓ and θ may be assumed probabilistically independent, and thus density functions $f(\ell)$ and $g(\theta)$ can be determined from cumulative distribution functions $F(\ell)$ and $G(\theta)$ as

$$F(\ell) = \int_0^{\ell} f(\ell) d\ell \quad \text{with} \quad f(\ell) = \frac{dF}{d\ell} \quad (5.3)$$

and

$$G(\theta) = \int_{-\pi/2}^{\theta} g(\theta) d\theta \quad \text{with} \quad g(\theta) = \frac{dG(\theta)}{d\theta}, \quad (5.4)$$

where $F(\ell)$ and $G(\theta)$ are obtained from direct optical images (Fig. 5.1.1).

In the study, the curve fittings for the distribution functions were done using three data sets obtained from three tested samples. Parameters of the distribution functions were determined, and their effects on craze evolution are discussed.

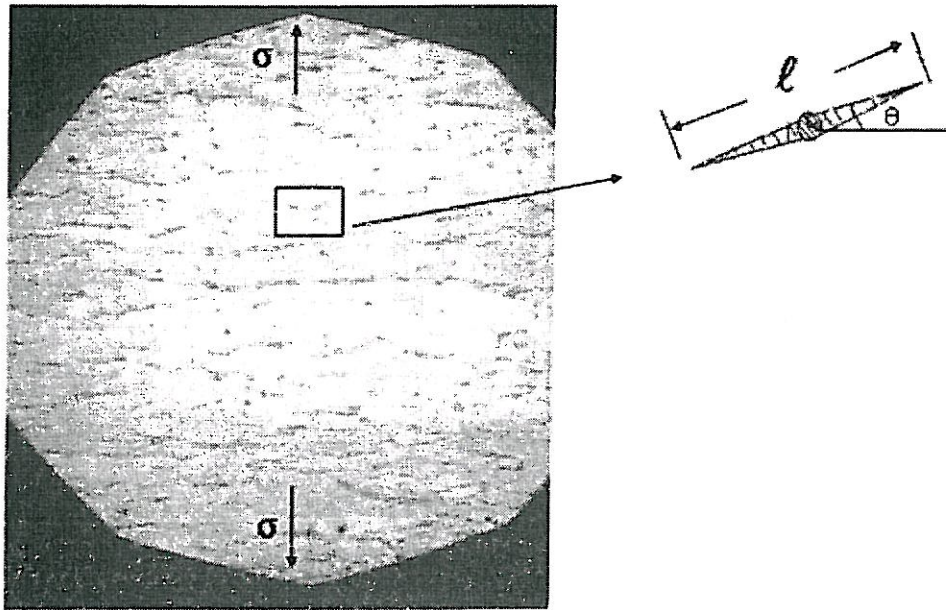


Figure 5.1.1: Optical Micrograph of Crazes in HIPS at $\varepsilon = 0.35$ (x 400).

6. MICROMECHANICS FOR RUBBER TOUGHENED HIPS AND OCCLUDED PARTICLE

In many rubber-toughened polymers, the second-phase particles are microcomposites themselves as a result of matrix phase sub-inclusions inside of the rubber particles. The amount of sub-inclusions determines both compliance and volume fraction of the second-phase particles which affects the mechanical properties of the polymer. For these reasons alone, it is essential to know effective properties of occluded particles.

Micromechanics may be used to obtain important information on effective properties of heterogeneous polymers. In this chapter, micromechanics models are employed and compared to evaluate properties of occluded particles in the HIPS.

The AFM images of high-impact polystyrene (Fig.4.1.1) have shown that it possesses a rather complex heterogeneous microstructure. The occluded particles are randomly dispersed in a polystyrene matrix. In addition, the occluded particles themselves are microscopic composite inclusions containing segregated phases of polybutadiene and polystyrene. Based on the AFM images, a HIPS microstructure may be viewed as a multi-scaled heterogeneous polymer composite as shown in Fig. 6.1.1. It has a constant particle volume fraction with an average size for the occluded particles, assuming that both the occluded particles and the polystyrene sub-inclusions are spherical.

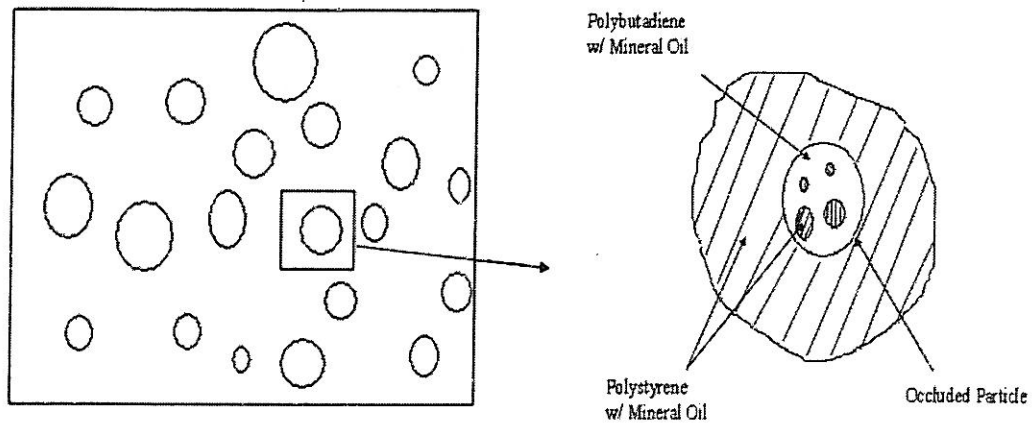


Figure 6.1.1: The Microstructure of a HIPS Polymer.

In this study, four different micromechanics approaches have been considered:

- (1) Halpin-Tsai Approach
- (2) Generalized SCM
- (3) Differential Scheme
- (4) Mori-Tanaka Approach.

A brief summary of the first two is given in this chapter and the others are presented in Appendix B where comparisons of different approaches along with experimental data are also given. Two micromechanics methods (i.e. the Halpin-Tsai approach [110] and the generalized SCM [111]) are selected to apply to the HIPS as a two-scale composite to estimate the average mechanical properties of the occluded particles. The occluded particles are considered as a composite consisting of an incompressible rubber phase as the matrix and polystyrene as inclusions. The overall HIPS is considered as a particulate composite with PS as the matrix phase and occluded particles are the inclusions. Corresponding micromechanics equations derived from both systems are solved

concurrently to determine the occluded volume fraction, C_{oc} , and effective properties of the occluded particles.

The reduced form of the generalized SCM, includes incompressible polybutadiene matrix in occluded particles and the Halpin-Tsai Equations with a modified spherical shape factor is used for the formulation of overall HIPS microstructure. Note that, material properties used for the calculations are modified to include the mineral oil effect. The ratio of solubility of mineral oil in rubber phase to matrix phase is taken as 1 to 3 based on the manufacturer's suggestion. The results are presented in Table 4.1.3.

6.1 Halpin-Tsai Equations

Halpin-Tsai equations are developed based on "self-consistent model" (introduced by R.Hill [112])-a fiber composite modeled as a single fiber surrounded by a cylinder of matrix with both phases embedded inside of an unbound homogeneous medium, which is equivalent to composite itself. Herman [113] employed this model and found a solution for composite moduli. Halpin-Tsai simplify the Herman's solution and extended it to composites with different reinforcement geometries

$$\frac{P}{P_m} = \frac{1 + \xi \eta C_f}{1 - \eta C_f} \quad (6.1)$$

where

$$\eta = \frac{(P_f / P_m) - 1}{(P_f / P_m) + \xi} \quad (6.2)$$

and

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

P_f = corresponding reinforcing material modulus E_f , G_f , or ν_f

P_m = corresponding matrix modulus E_m , G_m , or ν_m

In Eq. 6.4, the coefficient ξ is related with second-phase material packing geometry

$$\xi = \frac{7 - 5\nu_m}{8 - 10\nu_m}. \quad (\text{Particulate composite}) \quad (6.3)$$

Hewitt and de Malherbe [114] suggest a ξ to compensate the second-phase material volume fraction dependence of moduli. For spherical inclusions, the ξ is given as

$$\xi = 1 + 40C_f^{10}. \quad (6.4)$$

6.2 Three Phase Model with Generalized Self Consistent Method

The generalized self consistent method (Generalized SCM), which is referred to as Three Phase Model, is developed by Christensen and Lo [111] but in a slightly different form. The basic problem is defined as the spherical inclusion embedded in a concentric spherical annulus of the matrix material of the prescribed volume fraction, which in turn embedded in an infinite medium with the unknown effective properties.

The exact solution is given in a quadratic form as

$$A\left(\frac{\mu}{\mu_m}\right)^2 + 2B\left(\frac{\mu}{\mu_m}\right) + C = 0, \quad (6.5)$$

where

$$\begin{aligned} A = & 8\left(\frac{\mu_i}{\mu_m} - 1\right)(4 - 5\nu_m)\eta_1 c^{10/3} - 2\left[63\left(\frac{\mu_i}{\mu_m} - 1\right)\eta_2 + 2\eta_1\eta_3\right]c^{7/3} + 252\left(\frac{\mu_i}{\mu_m} - 1\right)\eta_2 c^{5/3} \\ & - 50\left(\frac{\mu_i}{\mu_m} - 1\right)(7 - 12\nu_m + 8\nu_m^2)\eta_2 c + 4(7 - 10\nu_m)\eta_2\eta_3 \end{aligned}$$

$$B = -2\left(\frac{\mu_i}{\mu_m} - 1\right)(1 - 5\nu_m)\eta_1 c^{10/3} + 2\left[63\left(\frac{\mu_i}{\mu_m} - 1\right)\eta_2 + 2\eta_1\eta_3\right]c^{7/3} - 252\left(\frac{\mu_i}{\mu_m} - 1\right)\eta_2 c^{5/3} \\ + 75\left(\frac{\mu_i}{\mu_m} - 1\right)(3 - \nu_m)\eta_2 c \nu_m + \frac{3}{2}(15\nu_m - 7)\eta_2\eta_3$$

$$C = 4\left(\frac{\mu_i}{\mu_m} - 1\right)(5\nu_m - 7)\eta_1 c^{10/3} - 2\left[63\left(\frac{\mu_i}{\mu_m} - 1\right)\eta_2 + 2\eta_1\eta_3\right]c^{7/3} + 252\left(\frac{\mu_i}{\mu_m} - 1\right)\eta_2 c^{5/3} \\ + 25\left(\frac{\mu_i}{\mu_m} - 1\right)(\nu_m^2 - 7)\eta_2 c - (7 + 5\nu_m)\eta_2\eta_3$$

with

$$\eta_1 = \left(\frac{\mu_i}{\mu_m} - 1\right)(7 - 10\nu_m)(7 + 5\nu_i) + 105(\nu_i - \nu_m)$$

$$\eta_2 = \left(\frac{\mu_i}{\mu_m} - 1\right)(7 + 5\nu_i) + 35(1 - \nu_i)$$

$$\eta_3 = \left(\frac{\mu_i}{\mu_m} - 1\right)(8 - 10\nu_m) + 15(1 - \nu_m),$$

where $c = \left(\frac{a}{b}\right)^3$, μ is the elastic shear modulus, and ν is the Poisson's ratio. The

subscripts i and m are referring to inclusion and matrix phases, respectively. Moreover,

solution for the effective bulk modulus K is given by

$$K = K_m + \frac{c(K_i - K_m)}{1 + (1 - c)\frac{(K_i - K_m)}{(K_m + \frac{4}{3}\mu_m)}}. \quad (6.6)$$

In the present case $\frac{\mu_{PB}}{\mu_{PS}} \approx 0(10^{-4} \sim 10^{-5})$ in the occluded particle where spherical polystyrene inclusions are rigid and polybutadiene matrix is incompressible, then occluded particle shear modulus is given as

$$\frac{\mu}{\mu_m} \rightarrow \frac{27}{16(1-c)^3}. \quad (6.7)$$

7. CONTINUUM DAMAGE MECHANICS FOR CRAZING DEVELOPMENT IN HIPS

Continuum Damage Mechanics (CDM) may be suitable for evaluation of craze evolution and associated property degradation. Continuum damage mechanics is a subject based on irreversible thermodynamics of kinetics, material microstructure change and property degradation under thermomechanical loading. It provides a (mathematically and experimentally) quantitative description of the process of material microstructural and associated property changes in the context of continuum mechanics. In this chapter, development of CDM on polymer crazing in glassy HIPS is presented. Fundamental variables and parameters are defined (also see Appendix C) for craze damage first. Thermodynamic development of damage mechanics on orthotropic crazing evolution in the heterogeneous HIPS is discussed.

7.1 Craze Damage in Glassy Polymers

Crazes occur in glassy polymer only in certain dilatational stress states (see Appendix D) and grow along the plane normal to the maximum principal stress direction. Crazes cause the damaged polymers to transmit and reflect light differing from that of cracks. They are stabilized by fibrils of oriented and drawn polymers (Fig. 7.1.1) from the bulk material surrounding them [46]. The fibrils are capable of transmitting loads across the craze's faces. Polymer fibrillation causes stress-induced flow of initial bulk polymer into fine aggregates of oriented macromolecules. The transformation of bulky polymer into fibril-like structures occurs irreversibly normal to the craze plane. The length of such

aggregates is estimated to be few micron, while their average diameter changes between tens to hundreds of angstroms [115].

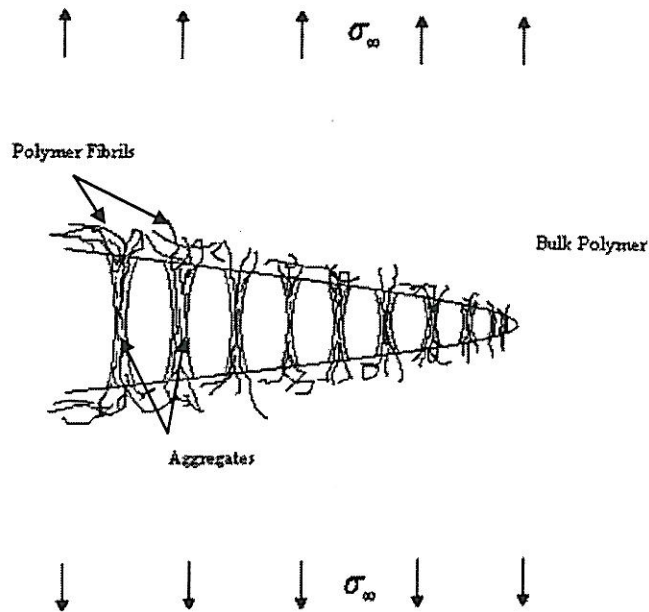


Figure 7.1.1: Fibril Development in a Craze.

7.2 Craze Damage Metric

Damage such as crazes is defined commonly as microstructural changes in a material under a given mechanical loading in an environment. This definition brings a necessity of introducing internal variables which represent a deteriorated state of the material. The craze damage metric gives a measure of the deterioration and could be an intrinsic variable for the problem. It relates the microstructure change (e.g., amount of crazes per unit volume or area) to mechanical or physical property degradation (e.g., modulus change or change of dielectric constant) [74].

With the introduction of the effective stress concept [68] and associated strain equivalence principle [70], the damage mechanics approach will be shown to be effective

in addressing a homogeneous craze distribution problem in glassy polymers. The strain equivalence principle is postulated at a mesoscale that craze degradation of the glassy polymer is only affected by craze damage associated effective stress. Deformation behavior of the polymer with craze is represented by the constitutive laws of the virgin material with the usual stress replaced with an effective stress.

7.3 A Theory for Orthotropic Craze Damage in Glassy Polymers

Under a uniaxial stress, craze formation exhibits strong directionality. Craze growth occurs in planes normal to the applied stress direction and the damaged material becomes orthotropic.

In this chapter, an orthotropic craze damage model is developed based on elastic continuum damage mechanics formulation. A fourth-order damage tensor representing material degradation and coupling between damage variables (e.g., D_{12} and D_{21}) are derived in terms of the elastic properties of the virgin and damaged, orthotropic, polymer. The effective stress concept and the strain equivalence principle are employed to establish constitutive equations of the damaged polymer. Thermodynamic driving force for craze damage growth is obtained using complimentary strain energy density function.

7.3.1 Craze Damage Matrix

Using the effective stress concept and the strain equivalence principle, constitutive equations of damaged polymer may be written as

$$\tilde{\sigma} = [I - D]^{-1} \sigma \quad \text{and} \quad \tilde{\sigma}_{ij} = C_{ijkl} \varepsilon_{kl}^e$$

(7.1)

$$\begin{aligned}\sigma &= [I - D]C\varepsilon^e \\ \varepsilon^e &= S[I - D]^{-1}\sigma\end{aligned}\quad \text{with} \quad S_{ijkl} = C_{ijkl}^{-1}$$

where the damage tensor D is defined as

$$D = I - \tilde{C}C^{-1} \quad (7.2)$$

and $\tilde{C}$ represents the stiffness matrix of a craze damaged polymer.

The virgin HIPS is isotropic. Based on experimental observations (Figs. 4.2.5 and 5.1.1), the crazed damaged polymer becomes orthotropic. In this case, the damaged polymer's stiffness matrix, $\tilde{C}$, along with the virgin polymer stiffness in a plane stress condition is

$$\tilde{C} = \begin{bmatrix} \tilde{C}_{11} & \tilde{C}_{12} & 0 \\ \tilde{C}_{12} & \tilde{C}_{22} & 0 \\ 0 & 0 & \tilde{C}_{66} \end{bmatrix} \quad \text{and} \quad C^{-1} = S = \begin{bmatrix} S_{11} & S_{12} & 0 \\ S_{12} & S_{11} & 0 \\ 0 & 0 & 2(S_{11} - S_{22}) \end{bmatrix}.$$

Next, with Eq. (7.2), the damage matrix may be written as

$$D = I - \tilde{C}S$$

$$D_{ij} = \begin{bmatrix} 1 - (\tilde{C}_{11}S_{11} + \tilde{C}_{12}S_{12}) & -(\tilde{C}_{11}S_{12} + \tilde{C}_{12}S_{11}) & 0 \\ -(\tilde{C}_{12}S_{11} + \tilde{C}_{22}S_{12}) & 1 - (\tilde{C}_{12}S_{12} + \tilde{C}_{22}S_{11}) & 0 \\ 0 & 0 & 1 - 2\tilde{C}_{66}(S_{11} - S_{12}) \end{bmatrix} \quad (7.3)$$

where

$$S_{11} = \frac{1}{E_0}$$

$$S_{12} = \frac{-\nu}{E_0}$$

and

$$\tilde{C}_{11} = \frac{E_1}{1 - \nu_{12}\nu_{21}}, \quad \tilde{C}_{12} = \frac{\nu_{12}E_2}{1 - \nu_{12}\nu_{21}}, \quad \tilde{C}_{22} = \frac{E_2}{1 - \nu_{12}\nu_{21}}, \quad \tilde{C}_{66} = G_{12}.$$

Substituting the associated representations, one may obtain the damage components, D_{ij}

as:

$$\begin{aligned} D_{11} &= 1 - \frac{1}{E_0} \frac{1}{(1 - \nu_{12}\nu_{21})} (E_1 - \nu\nu_{12}E_2) \\ D_{12} &= \frac{1}{E_0} \frac{1}{(1 - \nu_{12}\nu_{21})} (\nu E_1 - \nu_{12}E_2) \\ D_{21} &= \frac{1}{E_0} \frac{1}{(1 - \nu_{12}\nu_{21})} (\nu E_2 - \nu_{12}E_2) \\ D_{22} &= 1 - \frac{1}{E_0} \frac{1}{(1 - \nu_{12}\nu_{21})} (E_2 - \nu\nu_{12}E_2) \\ D_{66} &= 1 - \frac{G_{12}}{G_0}. \end{aligned} \tag{7.4a,b,c,d}$$

In reference to a solid with distributed, parallel cracks, results from the homogenization theory [116] show that the D matrix is in the form of

$$[\mathcal{D}] = \begin{bmatrix} \mathcal{D}_{11} & 0 & 0 & 0 & 0 & 0 \\ \mathcal{D}_{21} & 0 & 0 & 0 & 0 & 0 \\ \mathcal{D}_{31} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \mathcal{D}_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & \mathcal{D}_{66} \end{bmatrix}, \tag{7.5}$$

where $\mathcal{D}_{ij}$ are components of a damage matrix for a solid with parallel cracks. One would expect a same form of damage tensor for distributed, parallel crazes under uniaxial loading, resulting $D_{12} = D_{22} = 0$. This means that

- For $D_{12} = 0$ and $\frac{\nu_{12}}{E_1} = \frac{\nu_{21}}{E_2}$

$$D_{12} = \frac{1}{E_0} \frac{1}{(1 - \nu_{12}\nu_{21})} (\nu E_1 - \nu_{12} E_2) = 0 \quad \text{and}$$

$$\nu_{21} = \nu \quad (7.6)$$

- For $D_{22} = 0$ with $\frac{\nu_{12}}{E_1} = \frac{\nu}{E_2}$

$$D_{22} = 1 - \frac{1}{E_0} \frac{1}{(1 - \nu_{12}\nu_{21})} (E_2 - \nu \nu_{12} E_2) = 0 \quad \text{and}$$

$$E_2 = E_0, \quad \nu_{12} = \frac{\nu E_1}{E_0}. \quad (7.7a,b)$$

Substituting the above results into Eq. (7.4), one obtains the non-zero damage D_{11} , D_{21} and D_{66} as:

$$D_{11} = \frac{1 - \frac{E_1}{E_0}}{1 - \frac{\nu^2 E_1}{E_0}} \quad D_{21} = \frac{\nu \left(1 - \frac{E_1}{E_0}\right)}{1 - \frac{\nu^2 E_1}{E_0}} = \nu D_{11} \quad D_{66} = 1 - \frac{G_{12}}{G_0}.$$

(7.8a,b,c)

7.3.2 Constitutive Equations For Craze Damaged Polymer

The constitutive equations for a craze damaged polymer are given as

$$\sigma = [I - D] C \varepsilon^e$$

$$\varepsilon^e = S[I - D]^{-1} \sigma.$$

In the above expression, the term, $S[I - D]^{-1}$, has to be symmetric.

Symmetrization according to Murakami and Ohno[116] requires

$$S' = \frac{1}{2} \{ S[I - D]^{-1} + [I - D]^{-T} S \}.$$

For a virgin, isotropic polymer,

$$S = \begin{bmatrix} S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & 2(S_{11} - S_{12}) & 0 & 0 \\ 0 & 0 & 0 & 0 & 2(S_{11} - S_{12}) & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(S_{11} - S_{12}) \end{bmatrix}$$

where

$$S_{11} = \frac{1}{E_0}$$

$$S_{12} = \frac{-\nu}{E_0}.$$

As mentioned in the previous section, the orthotropic damage matrix is in the form of

$$[D] = \begin{bmatrix} D_{11} & 0 & 0 & 0 & 0 & 0 \\ D_{21} & 0 & 0 & 0 & 0 & 0 \\ D_{31} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & D_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & D_{66} \end{bmatrix}.$$

Then,

$$S' = \begin{bmatrix} A & K & P & 0 & 0 & 0 \\ K & S_{11} & S_{12} & 0 & 0 & 0 \\ P & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & 2(S_{11} - S_{12}) & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{2(S_{11} - S_{12})}{1 - D_{55}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{2(S_{11} - S_{12})}{1 - D_{66}} \end{bmatrix}$$

where

$$A = \frac{S_{11}}{1 - D_{11}} + \frac{S_{12}}{1 - D_{11}}(D_{21} + D_{31})$$

$$K = \frac{1}{2} \left[S_{12} \left(1 + \frac{1}{1 - D_{11}} \right) + \frac{1}{1 - D_{11}} (S_{11} D_{21} + S_{12} D_{31}) \right]$$

$$P = \frac{1}{2} \left[S_{12} \left(1 + \frac{1}{1 - D_{11}} \right) + \frac{1}{1 - D_{11}} (S_{12} D_{21} + S_{11} D_{31}) \right].$$

The constitutive equations for the polymer with orthotropic craze damage may be derived as:

$$\varepsilon_{ij}^e = S'_{ijkl} \sigma_{kl}$$

$$\varepsilon_1 = \sigma_1 \left[\frac{S_{11}}{1-D_{11}} + \frac{S_{12}}{1-D_{11}} (D_{21} + D_{31}) \right] + \sigma_2 \left[\frac{1}{2} \left[S_{12} \left(1 + \frac{1}{1-D_{11}} \right) + \frac{1}{1-D_{11}} (S_{11} D_{21} + S_{12} D_{31}) \right] \right] \\ + \sigma_3 \left[\frac{1}{2} \left[S_{12} \left(1 + \frac{1}{1-D_{11}} \right) + \frac{1}{1-D_{11}} (S_{12} D_{21} + S_{11} D_{31}) \right] \right]$$

$$\varepsilon_2 = \sigma_1 \left[\frac{1}{2} \left[S_{12} \left(1 + \frac{1}{1-D_{11}} \right) + \frac{1}{1-D_{11}} (S_{11} D_{21} + S_{12} D_{31}) \right] \right] + \sigma_2 S_{11} + \sigma_3 S_{12}$$

$$\varepsilon_3 = \sigma_1 \left[\frac{1}{2} \left[S_{12} \left(1 + \frac{1}{1-D_{11}} \right) + \frac{1}{1-D_{11}} (S_{12} D_{21} + S_{11} D_{31}) \right] \right] + \sigma_2 S_{12} + \sigma_3 S_{11}$$

$$\gamma_{23} = \tau_{23} 2(S_{11} - S_{12})$$

$$\gamma_{31} = \tau_{31} \frac{2(S_{11} - S_{12})}{1-D_{55}} \quad (7.9 \text{ a,b,c,d,e,f})$$

$$\gamma_{21} = \tau_{21} \frac{2(S_{11} - S_{12})}{1-D_{66}}.$$

In plane stress case, the constitutive equations can be simplified further and the reduced non-zero strain components become:

$$\varepsilon_1 = \sigma_1 \left[\frac{S_{11}}{1-D_{11}} + \frac{S_{12} D_{21}}{1-D_{11}} \right] + \sigma_2 \left[\frac{1}{2} \left[S_{12} \left(1 + \frac{1}{1-D_{11}} \right) + \frac{S_{11} D_{21}}{1-D_{11}} \right] \right] \\ \varepsilon_2 = \sigma_1 \left[\frac{1}{2} \left[S_{12} \left(1 + \frac{1}{1-D_{11}} \right) + \frac{S_{11} D_{21}}{1-D_{11}} \right] \right] + \sigma_2 S_{11} \quad (7.10 \text{ a,b,c})$$

$$\gamma_{21} = \tau_{21} \frac{2(S_{11} - S_{12})}{1-D_{66}}.$$

In a uniaxial loading case ($\sigma_1 \neq 0$) and inserting the definitions for S_{11} and S_{22} , the constitutive relations (plane stress) case for a craze damaged polymer, are:

$$\begin{aligned}\varepsilon_1 &= \sigma_1 \left[\frac{1}{E_0(1-D_{11})} - \frac{\nu}{E_0} \frac{D_{21}}{(1-D_{11})} \right] = \frac{\sigma_1}{E_0(1-D_{11})} [1 - \nu D_{21}] \\ \varepsilon_2 &= \sigma_1 \left[\frac{1}{2} \left[S_{12} \left(1 + \frac{1}{1-D_{11}} \right) + \frac{S_{11} D_{21}}{1-D_{11}} \right] \right] = \frac{\nu \sigma_1}{2E_0(1-D_{11})} [D_{11} + D_{21} - 2] \\ \gamma_{21} &= 0\end{aligned}\tag{7.11 a,b,c}$$

where

$$D_{11} = \frac{1 - \frac{E_1}{E_0}}{1 - \frac{\nu^2 E_1}{E_0}} \quad D_{21} = \frac{\nu \left(1 - \frac{E_1}{E_0} \right)}{1 - \frac{\nu^2 E_1}{E_0}} = \nu D_{11}.$$

7.3.3 Energy Release Rate for Craze Growth in Glassy Polymers

The energy release rate for craze growth, i.e., the thermodynamic craze damage driving force, may be derived from the complimentary strain energy function, W_e^* ,

$$W_e^* = \frac{1}{2} (I - D)^{-1} S \sigma \sigma^T. \tag{7.12}$$

Using Eq. (7.12), one can derive the components of thermodynamic driving force for plane stress case as:

$$\begin{aligned}W_e^*(\sigma) &= \frac{1}{2} \left[\left(\frac{S_{11}}{1-D_{11}} + \frac{S_{11} D_{21}}{1-D_{11}} \right) \sigma_1^2 + \left(\frac{S_{12}}{1-D_{11}} + \left(\frac{S_{12} D_{21}}{1-D_{11}} + S_{11} \right) \right) \sigma_2^2 + \left(\frac{2(S_{11} - S_{12})}{1-D_{66}} \right) \tau_{12}^2 \right] \\ &+ \frac{1}{2} \left[\left(\frac{S_{12}}{1-D_{11}} + \frac{S_{11}}{1-D_{11}} + \left(\frac{S_{12} D_{21}}{1-D_{11}} + S_{11} \right) + \frac{S_{11} D_{21}}{1-D_{11}} \right) \sigma_1 \sigma_2 + \left(\frac{S_{11}}{1-D_{11}} + \frac{S_{12} D_{21}}{1-D_{11}} + \frac{2(S_{11} - S_{12})}{1-D_{66}} \right) \sigma_1 \tau_{12} \right] \\ &+ \frac{1}{2} \left[\left(\frac{S_{12}}{1-D_{11}} + \left(\frac{S_{12} D_{21}}{1-D_{11}} + S_{11} \right) + \frac{2(S_{11} - S_{12})}{1-D_{66}} \right) \sigma_2 \tau_{12} \right] \\ Y_{11} &= \frac{\partial W_e^*}{\partial D_{11}} = \frac{1 + D_{21}}{2E_0(1-D_{11})^2} \left[\sigma_1^2 - \nu \sigma_2^2 + (1-\nu) \sigma_1 \sigma_2 + \sigma_1 \tau_{12} - \nu \sigma_2 \tau_{12} \right] \\ Y_{21} &= \frac{\partial W_e^*}{\partial D_{21}} = \frac{1}{2E_0(1-D_{11})} \left[\sigma_1^2 - \nu \sigma_2^2 + (1-\nu) \sigma_1 \sigma_2 + \sigma_1 \tau_{12} - \nu \sigma_2 \tau_{12} \right]\end{aligned}\tag{7.13 a,b,c}$$

$$Y_{66} = \frac{\partial W^*}{\partial D_{66}} = \frac{(1-\nu)}{E_0(1-D_{66})^2} [\sigma_1 \tau_{12} + \sigma_2 \tau_{12} + \tau_{12}^2].$$

The above results can be further simplified for the uniaxial loading case ($\sigma_1 \neq 0$) as:

$$Y_{11} = \frac{\partial W^*}{\partial D_{11}} = \frac{1 + D_{21}}{2E_0(1 - D_{11})^2} \sigma_1^2$$

$$Y_{21} = \frac{\partial W^*}{\partial D_{21}} = \frac{1}{2E_0(1 - D_{11})} \sigma_1^2 \quad (7.14 \text{ a,b,c})$$

$$Y_{66} = \frac{\partial W^*}{\partial D_{66}} = 0.$$

7.3.4 Craze Damage Evolution

For a craze damaged polymer, the damage, D , represents inelastic deformation resulting from crazing. The dissipation function (see Appendix C) may be constructed for an isothermal and orthotropic damage case as

$$\dot{\phi}_D^* = -Y \dot{D} \geq 0 \quad (7.15 \text{ a,b})$$

$$\dot{\phi}_D^* = -Y_{11} \dot{D}_{11} - Y_{21} \dot{D}_{21} - Y_{66} \dot{D}_{66}$$

where

$$Y_{11} = \frac{\sigma_1^2}{2E_0(1 - D_{11})^2} (1 + D_{21}) ; \quad Y_{21} = \frac{\sigma_1^2}{2E_0(1 - D_{11})} \quad \text{and} \quad Y_{66} = 0.$$

8. COMPUTATIONAL MICROMECHANICS FOR CRAZE INITIATION AND INTERACTION IN HIPS

Owing to the complex microstructure of craze development in HIPS polymers, computational micromechanics is required in the present study. FEM modeling is needed for understanding the influence on craze formation and interactions by the occluded particle volume fraction and size distribution. In this chapter, appropriate models have been developed for the purpose. 2-D finite-element models have been employed for the analyses. Crazeing is 3-D in nature; however, 2-D modeling is simple (captures the HIPS microstructure) yet an effective way for a comparative study to explore the influence of the occluded particle volume fraction and size distribution on craze formation and interaction in HIPS polymers. Also, 2-D modeling is efficient in saving computing time. Validity and accuracy of the models with the suitable boundary conditions and numerical procedure have been verified with selected reference solutions. Material properties used for the calculations are given in Tables 4.1.2 and 4.1.3. In the Tab. 4.1.3, the light-scattering results were measured values and the AFM imaging results were extracted from AFM pictures taken directly from the HIPS samples (based on the ratio of the total area of occluded particles to the overall image area). In the modeling, micromechanics results which include mineral oil effect are used for effective properties of occluded particles.

8.1 HIPS Microstructure and Computational Micromechanics Models

Proper Finite-element models have been introduced to address the HIPS microstructure. A HIPS observed in an AFM is shown in Fig. 4.1.1. In addition, the following TEM pictures (Fig. 8.1.1) are also shown as a base for micromechanics modeling in the study.

In the current study, it is difficult in modeling exactly the occluded particles with a large number of randomly distributed sub-particles. Hence, a periodical microstructure is assumed. The advantage in dealing with the periodical arrangement is its simplicity. Multi-particle systems can then be modeled by a representative volume with only one or a few particles using symmetry conditions involved.

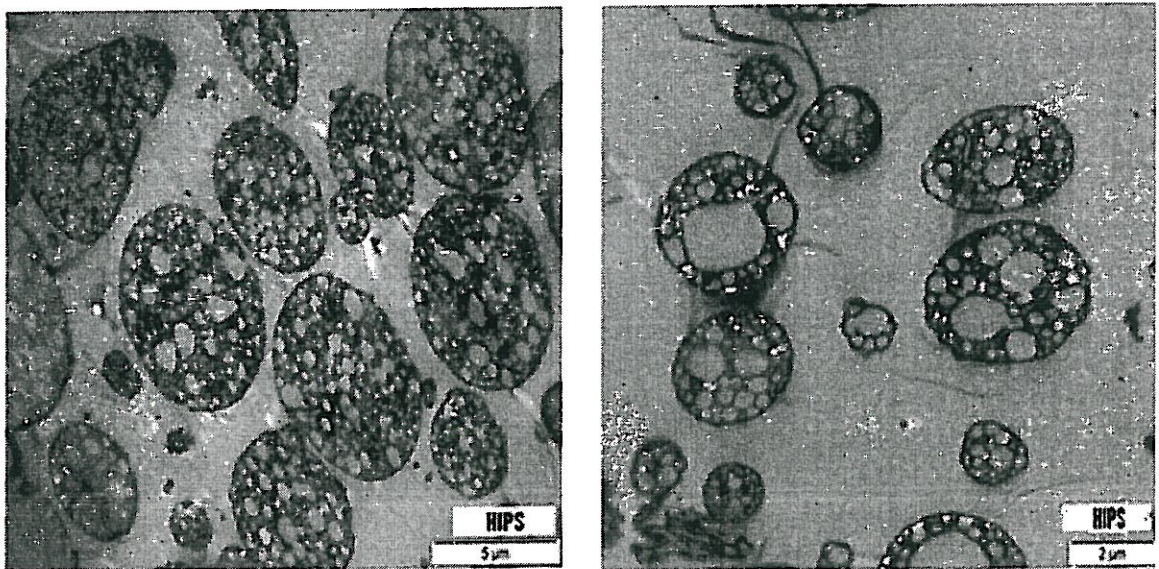


Figure 8.1.1: HIPS Microstructure. [Provided by Total Petrochemicals]

Microscopic observations are crucial to reveal the characteristics of continuous craze initiation, growth and possible craze interaction. Progressive craze growth

characteristics in HIPS are depicted in Fig. 8.1.2. Craze initiate from particles and grow out to neighboring particles by connecting them. This can be seen clearly in Fig. 8.1.3.

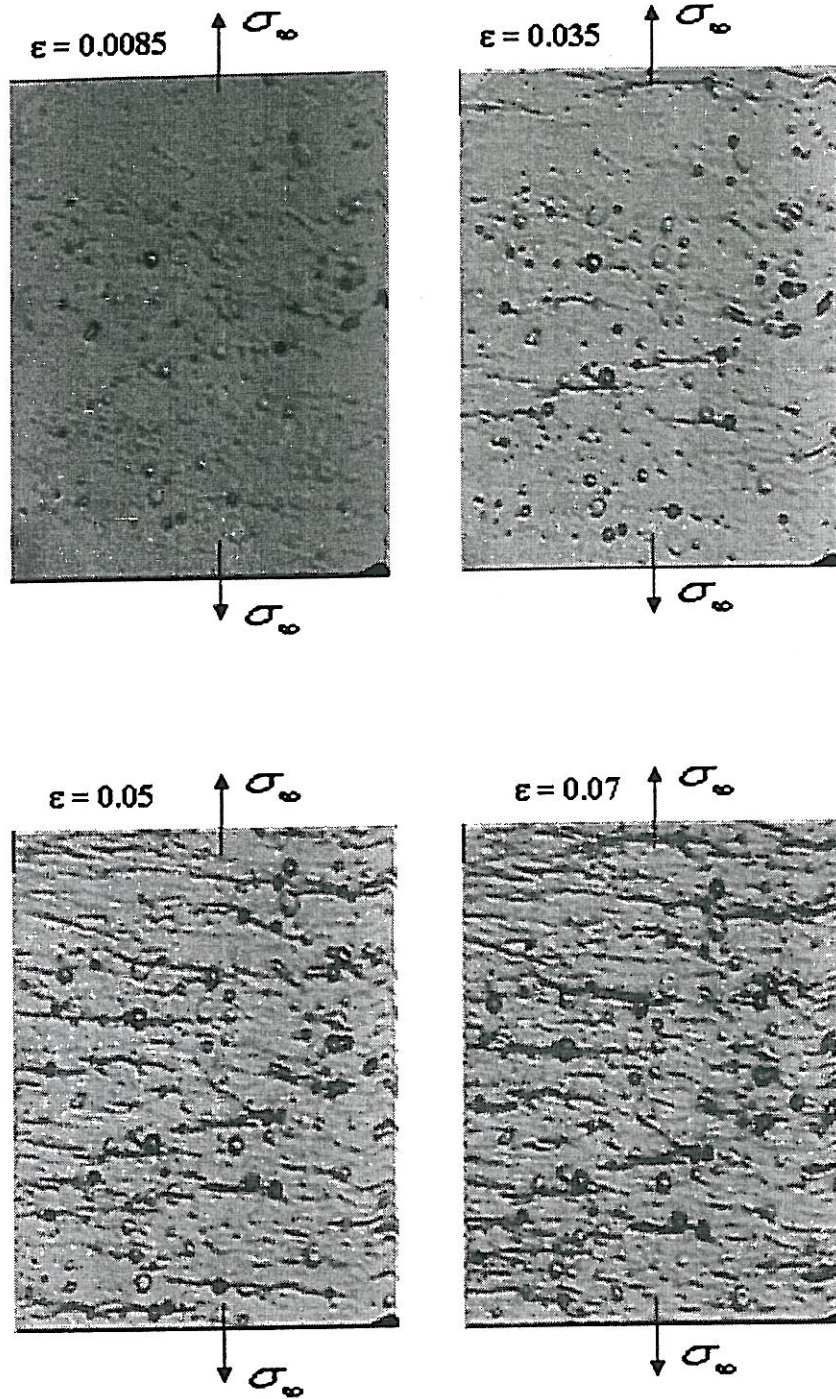


Figure 8.1.2: Progressive Craze Formation, Growth and Interaction in HIPS (x650).

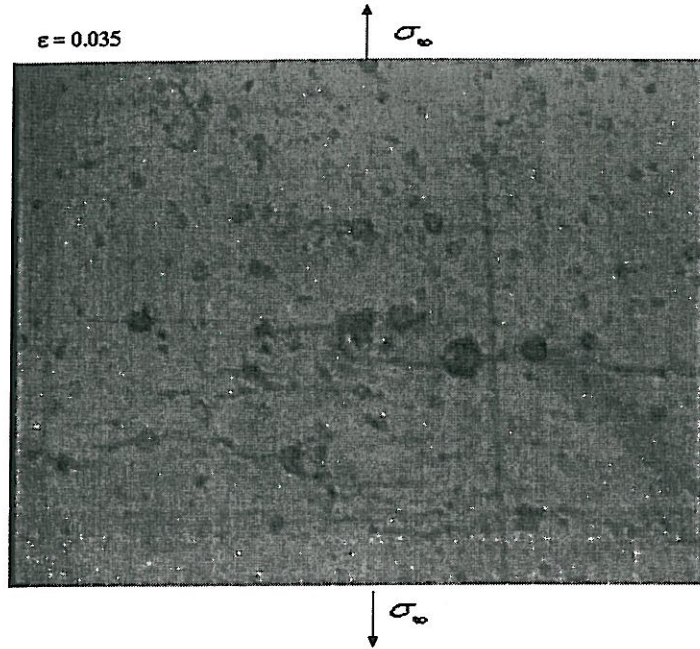


Figure 8.1.3: Craze Growth in HIPS (x1300).

8.2 Solution Accuracy and Convergence

i) Volume-Fraction Effect:

The solution accuracy and mesh quality of the computational model have been checked, considering a finite-width, thin plate with a circular hole. A reference solution, stress concentration factor, for the problem is given by Howland [117] as

$$K = 0.284 + \frac{2}{\left(1 - \frac{d}{H}\right)} - 0.600\left(1 - \frac{d}{H}\right) + 1.32\left(1 - \frac{d}{H}\right)^2, \quad (8.1)$$

where d and H are the diameter of the hole and the width of the plate as depicted in Fig. 8.2.1., respectively.

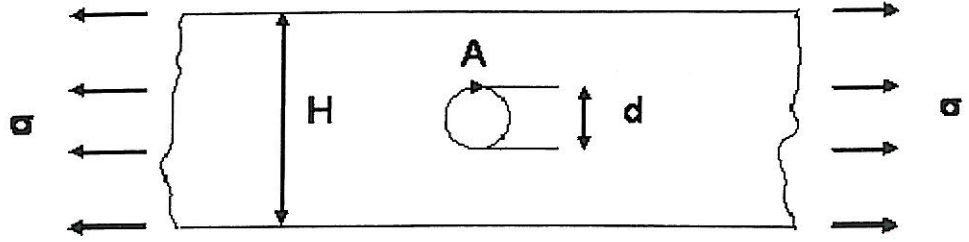


Figure 8.2.1: Thin Plate with a Circular Hole.

In Fig. 8.2.1, the maximum stress occurs at point A and the corresponding stress concentration is given as

$$\sigma_{\max} = \sigma_A \quad \text{and} \quad K = \frac{\sigma_{\max}}{\sigma}.$$

A quadrant of a plate with a circular hole is used for modeling the problem shown in Fig. 8.2.2.

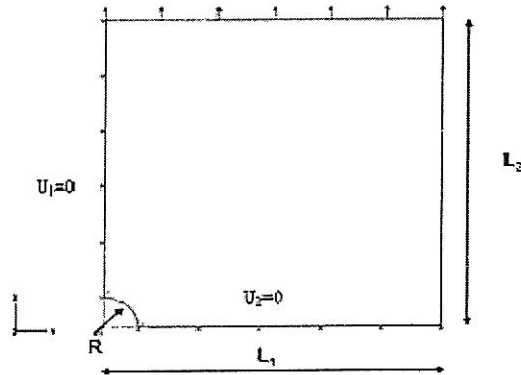


Figure 8.2.2: FEM Model for Studying Mesh Quality and Boundary Conditions.

The aspect ratio, $\lambda = \frac{L_1}{R}$, is chosen to be 10 (see Fig. 8.2.2) and two different cases are considered by changing L_2 ; taking $\frac{L_2}{R} = 10$ and $\frac{L_2}{R} = 20$. Only quadratic, eight-node quadrilateral elements are used for the study. The mesh quality is checked as the results converge to the true solution via refining the mesh by changing the number of elements,

ξ , and size of the elements, η . These variables are elucidated in Fig. 8.2.3. In the figure, for example, $\xi = 10$ and $\eta=10$ refer to that 10 elements are used on a given edge with element sizes (from a to b in Fig. 8.2.3) of 1, 2, 3, 4, 5...10 units, respectively.

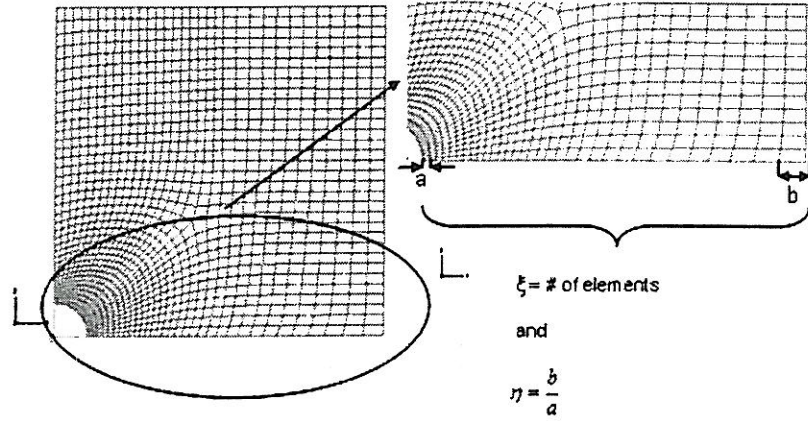


Figure 8.2.3: Mesh Refinement Parameters.

In Figs. 8.2.4 and 8.2.5, the convergence of the numerical solutions toward the true solution is shown as a function of ξ and η for both $\frac{L_2}{R} = 10$ and $\frac{L_2}{R} = 20$ cases. The calculated values for these cases are

$$K = \frac{\sigma_{\max}}{\sigma} = 3.085 \quad \text{and} \quad K = \frac{\sigma_{\max}}{\sigma} = 3.037$$

, respectively. The reference solution, calculated with Eq. (8.1), is

$$K_{ref} = \frac{\sigma_{\max}}{\sigma} = 3.036$$

and the solution accuracy from the FEM results for both cases are

$$\Delta = \frac{K - K_{Ref}}{K_{Ref}} \times 100 \approx 1.7\% \quad \text{and} \quad \Delta = \frac{K - K_{Ref}}{K_{Ref}} \times 100 \approx 0.03\%$$

, respectively.

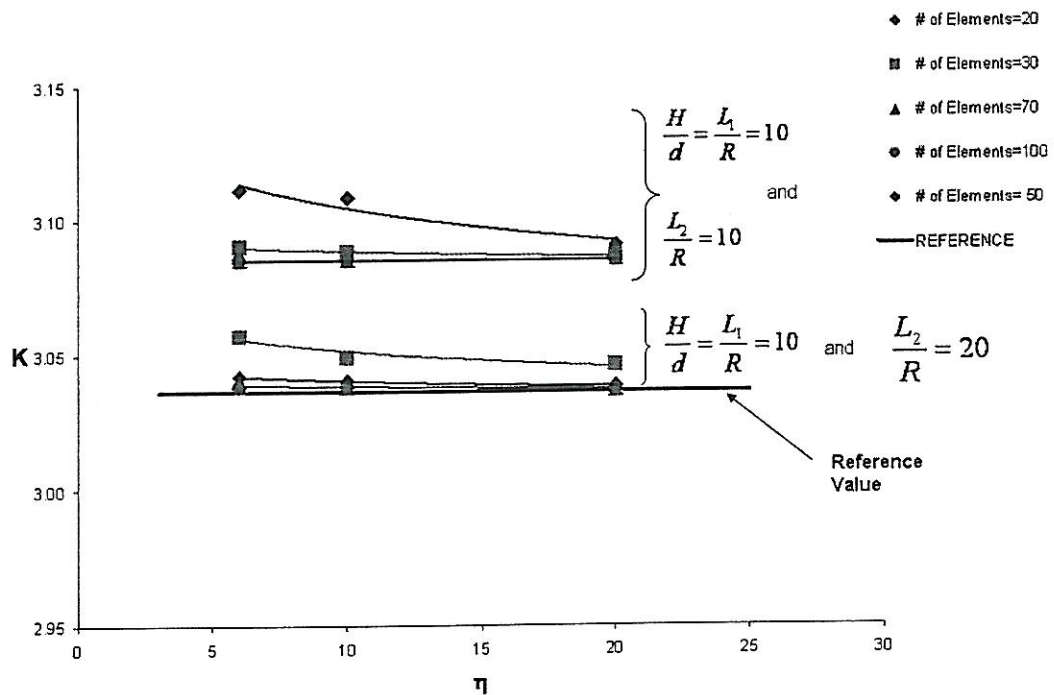


Figure 8.2.4: Stress Concentration Factor vs. Element Size.

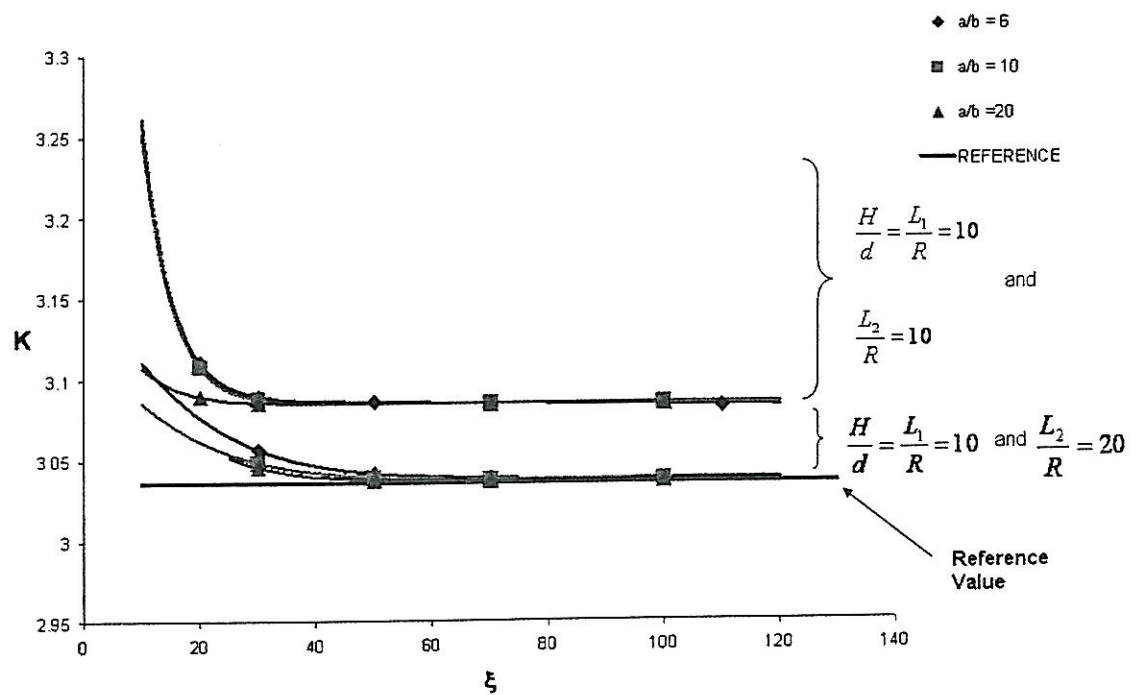


Figure 8.2.5: Stress Concentration Factor vs. Number of Element.

A higher accuracy is attained for the case $\frac{L_2}{R} = 20$ compared to the case $\frac{L_2}{R} = 10$ (Figs. 8.2.4 and 8.2.5). When $\frac{L_2}{R} = 20$, the model geometry is close to the reference solution geometry. Thus, the FEM results yield a higher accuracy. The optimum values for ξ and η are chosen to be 30 and 10, respectively, which give an average element aspect ratio, x , of 1.46 and result in a stress concentration K as

$$K = \frac{\sigma_{\max}}{\sigma} = 3.088,$$

with an error, ε , less than 0.1% for the case $\frac{L_2}{R} = 10$,

$$\varepsilon = \frac{K - K_{true}}{K_{true}} \times 100 \approx 0.1\%.$$

ii) Size Effect:

Currently, to the author's knowledge, there is no reference solution available in the open literature for the problem shown in Fig. 8.2.6 (b). However, the validity and accuracy of the micromechanics model are justified by starting with a limiting case, shown in Fig. 8.2.6 (a) and showing the convergence of the results to another limiting case (Fig. 9.2.6 (c)), through progressive steps of the current problem (Fig. 9.2.6 (b)). The calculation order is depicted with the arrows in Fig. 8.2.6, and it is executed with the same order, from left to right. In other word, first, a perforated plate (a square pattern) with circular holes is considered (Fig.9.2.6 (a)). A reference solution for this problem is given by Meijers [117]. The calculated values are presented in Fig. 8.2.7 along with the reference solution value.

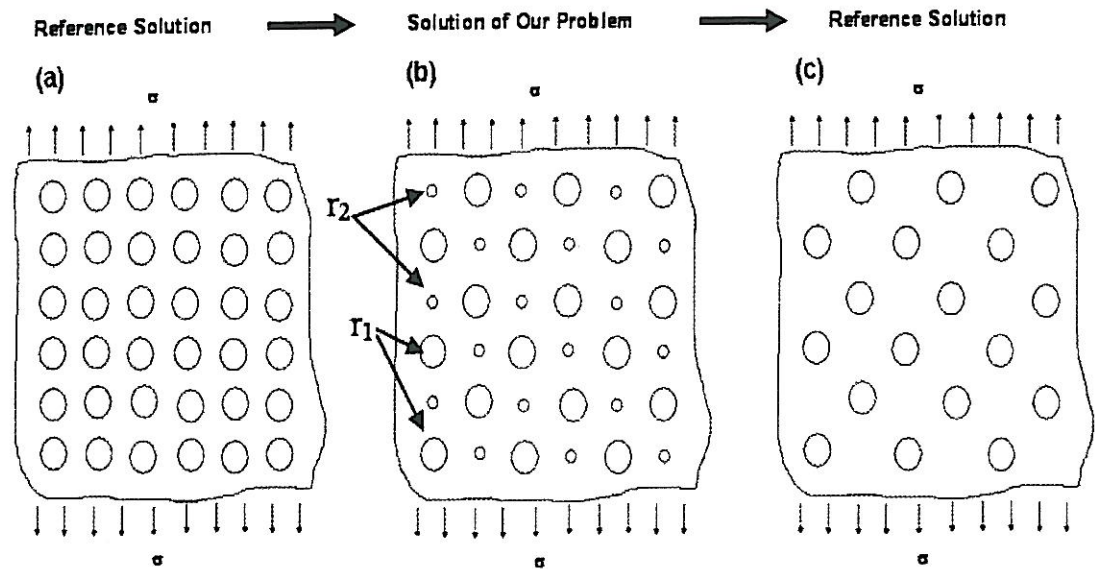
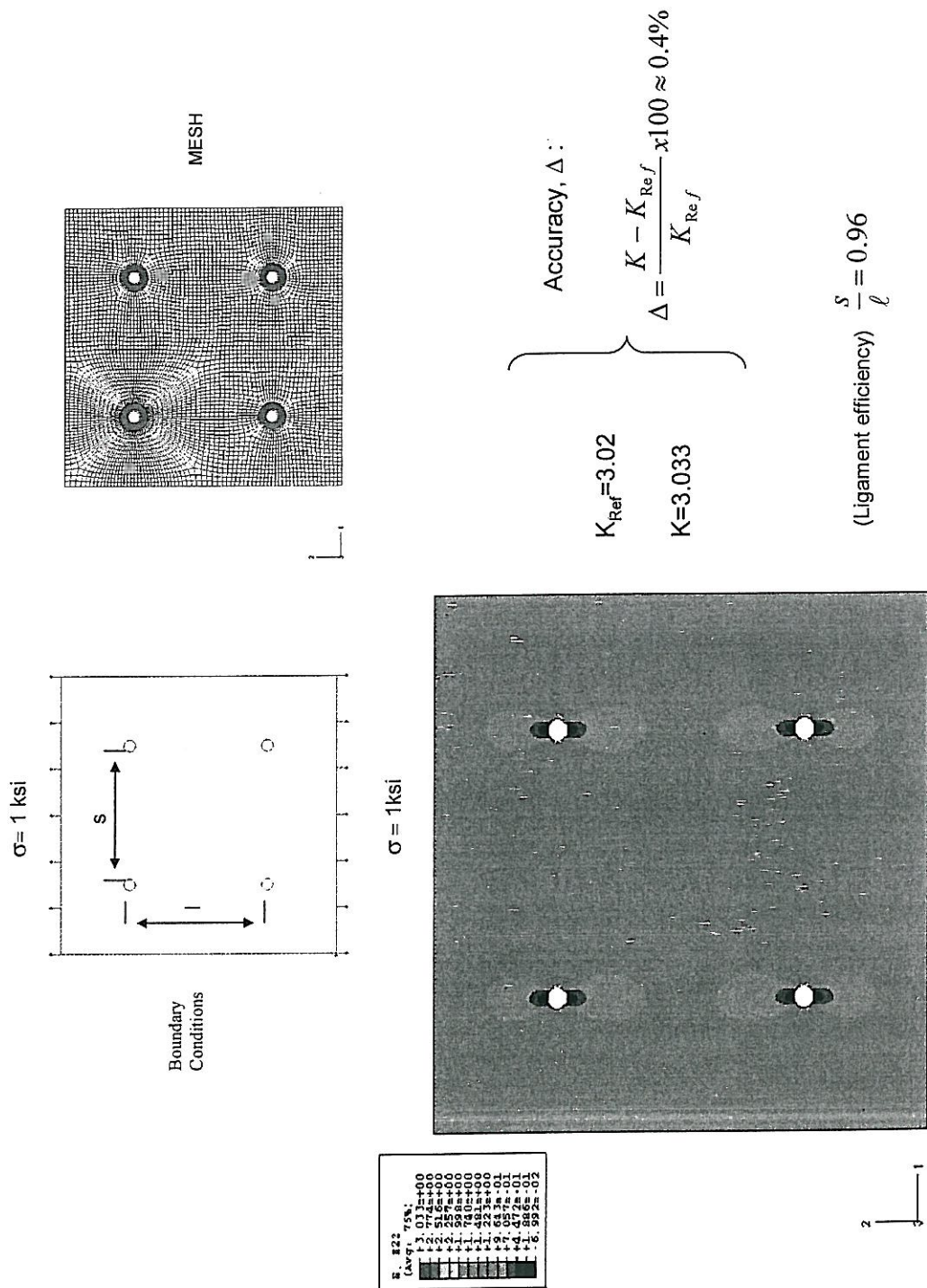


Figure 8.2.6: Validity of the Current Problem using Reference Solutions. a) A Thin Perforated Plate with a Square Pattern [117]; b) The Current Problem; c) A Thin Perforated Plate with a Diamond Pattern [117].

Then, reducing the radius of every other hole in Fig. 8.2.6 (a) (from r_1 to r_2), the current model is recovered (Fig. 8.2.6 (b)). The same process, gradually reducing the r_2 , is continued until $r_2=0$ and a perforated plate (a diamond pattern) with circular holes (Fig. 8.2.6 (c)) is recovered for which a reference solution is available [117].

Convergence of the results from one reference solution to another is depicted in Fig. 8.2.8.



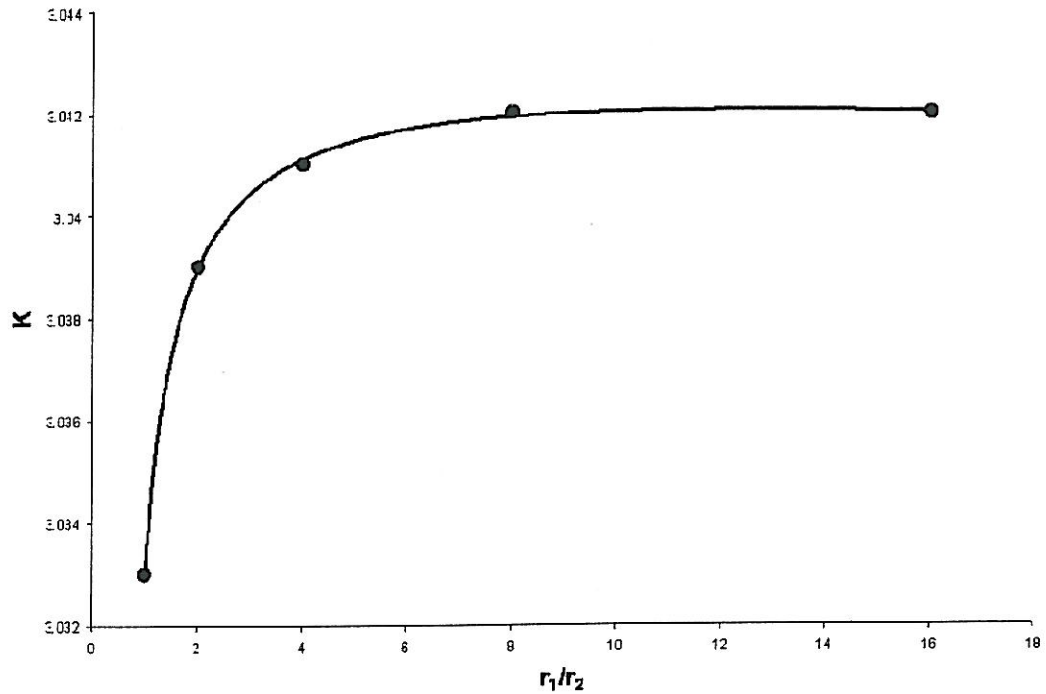


Figure 8.2.8: Stress Concentration, K , vs. Particle's Radius Ratio.

The radius, r_1 , is the initial radius of the holes and r_2 represents the reduced radius for the next progressive model (Fig. 8.2.9 a, b, c). Therefore, the reference solutions are available for the cases: $r_2 = r_1$ (Fig. 8.2.7) and $r_2 = 0$ (Fig. 8.2.10).

a)

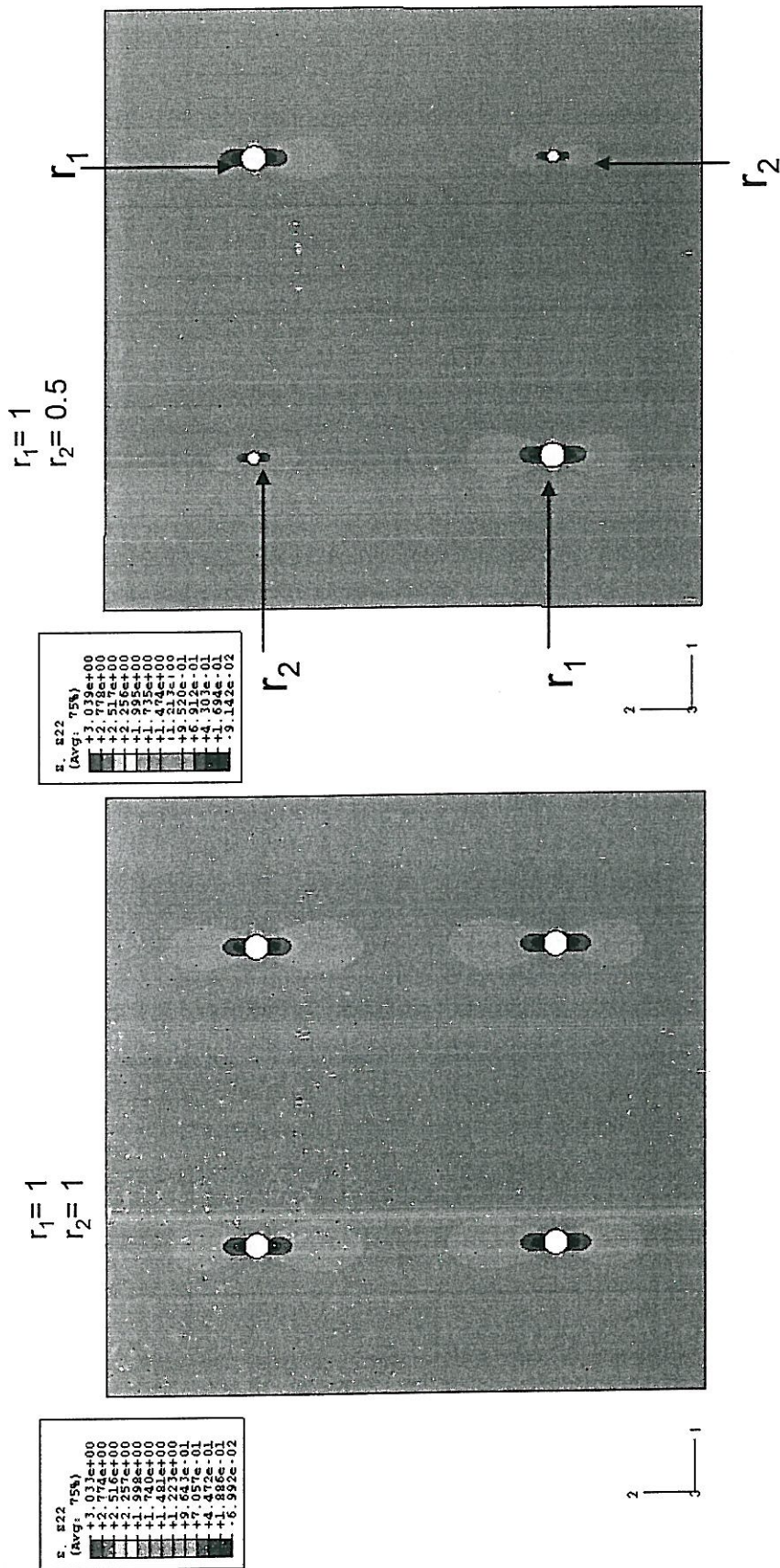


Figure 8.2.9 a: Convergence of Numerical Solutions Between the Reference Solutions Through Progressive Step Models.

a)

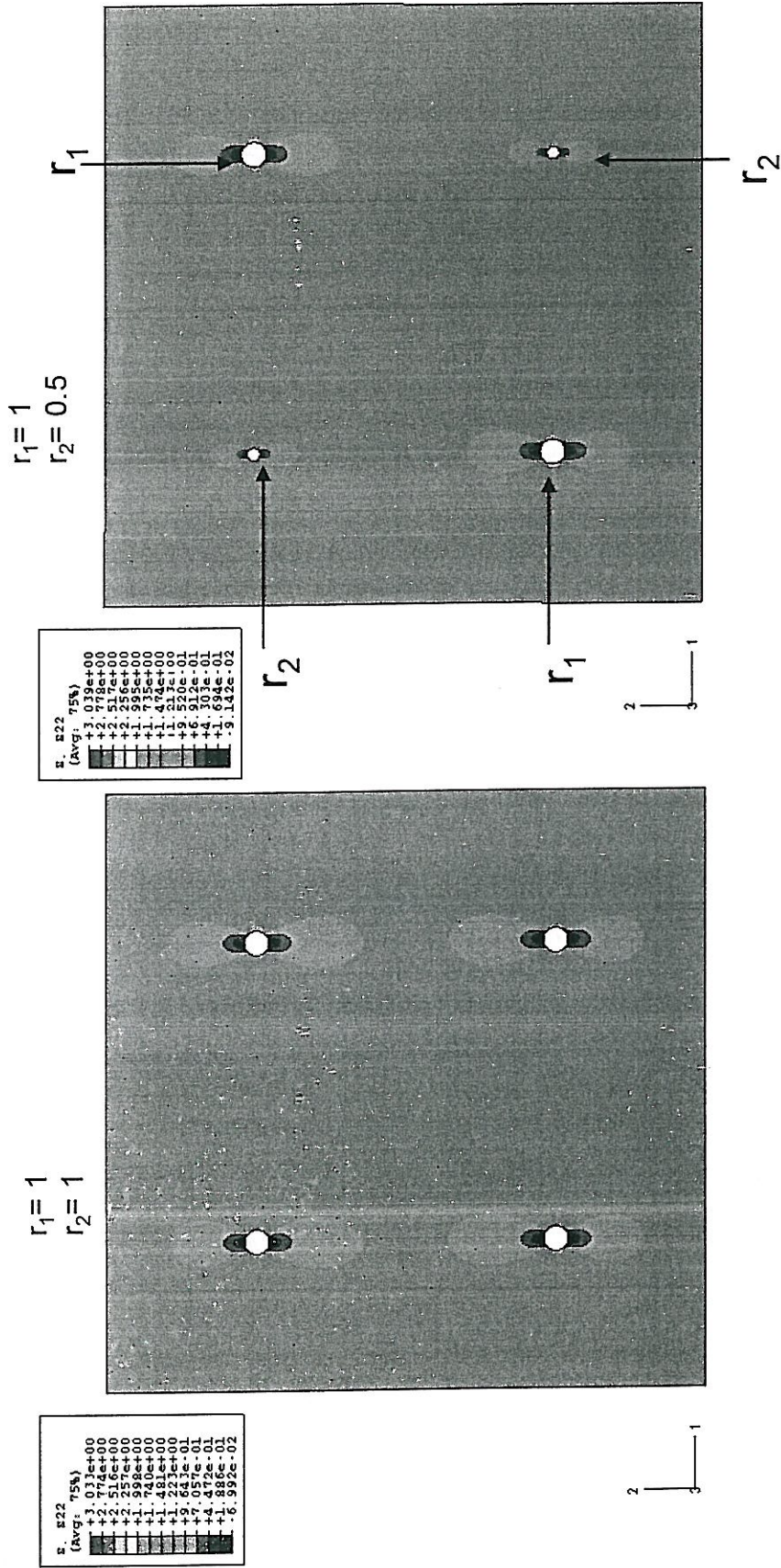


Figure 8.2.9 a: Convergence of Numerical Solutions Between the Reference Solutions Through Progressive Step Models.

b)

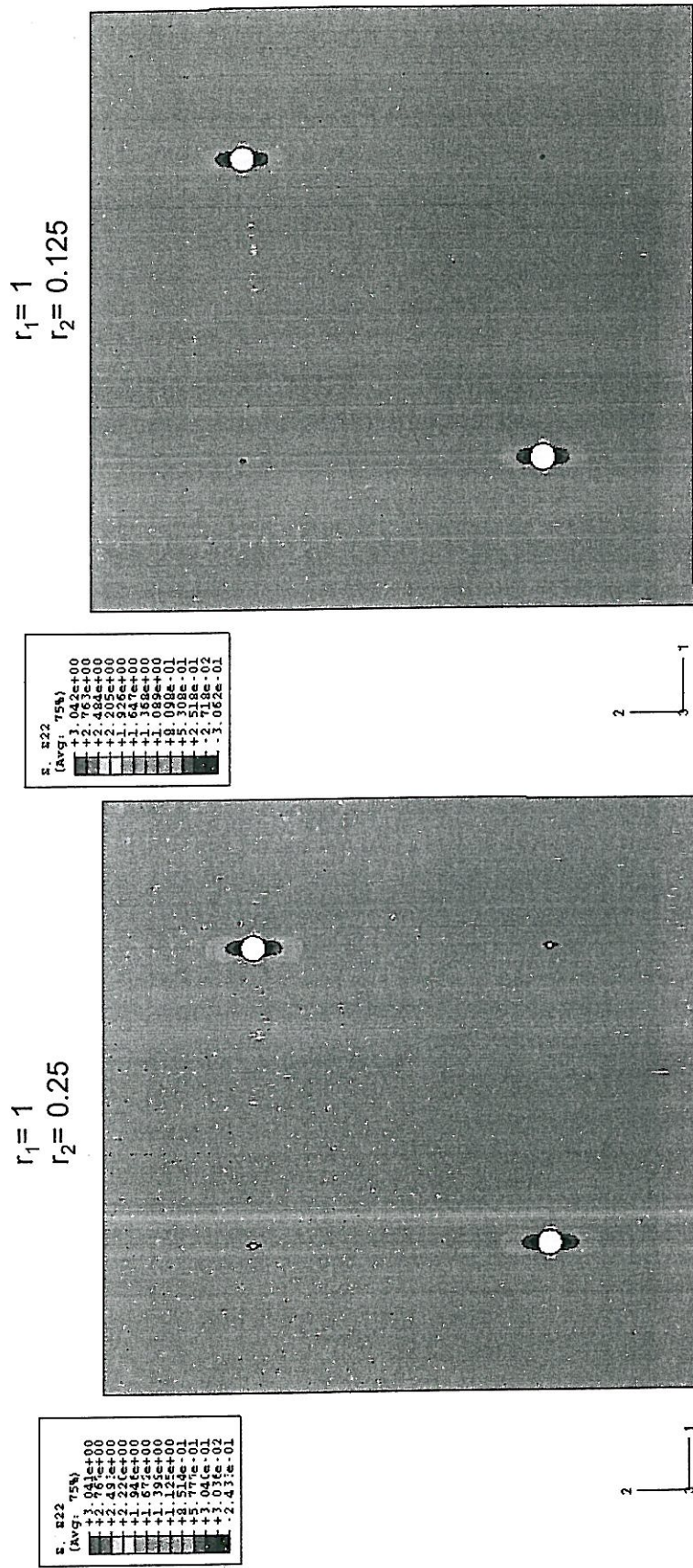
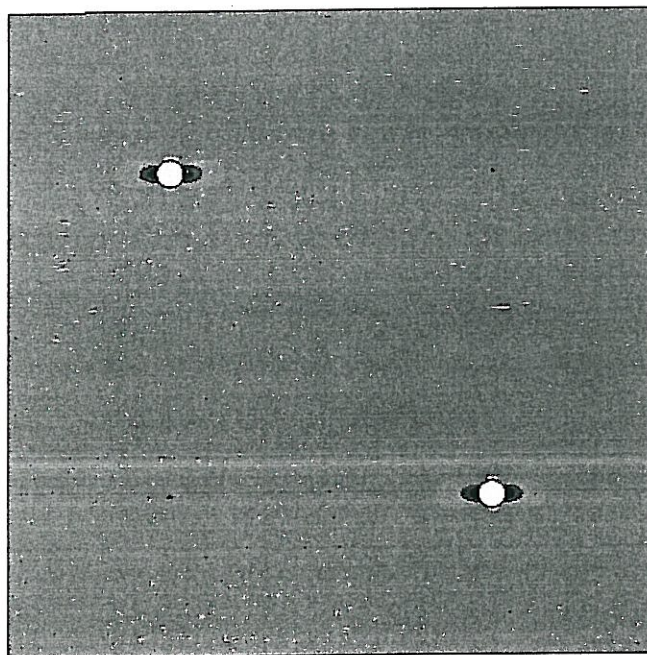
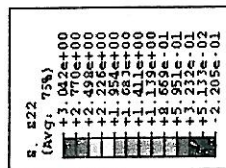


Figure 8.2.9 b: Convergence of Numerical Solutions Between the Reference Solutions Through Progressive Step Models.

c)

$$r_1 = 1$$

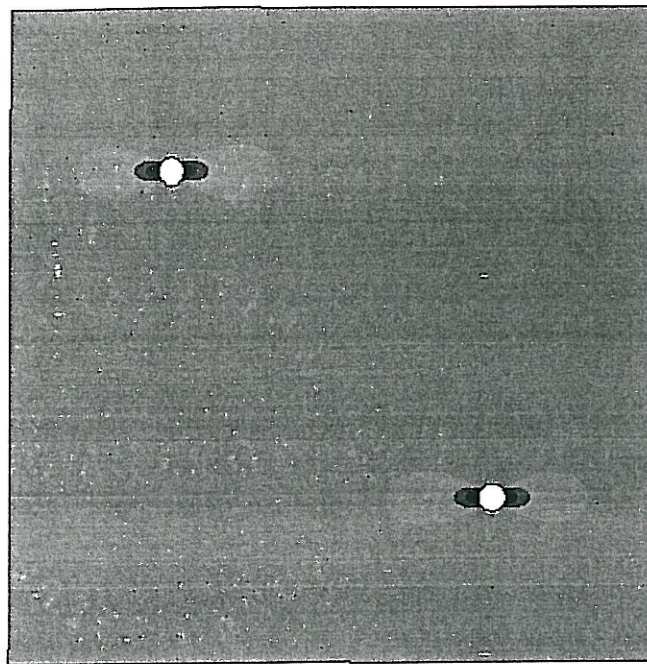
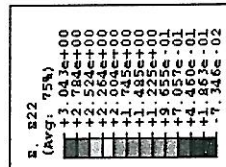
$$r_2 = 0.0625$$



2 1 1

$$r_1 = 1$$

$$r_2 = 0$$



2 1 1

Figure 8.2.9 c: Convergence of Numerical Solutions Between the Reference Solutions Through Progressive Step Models.

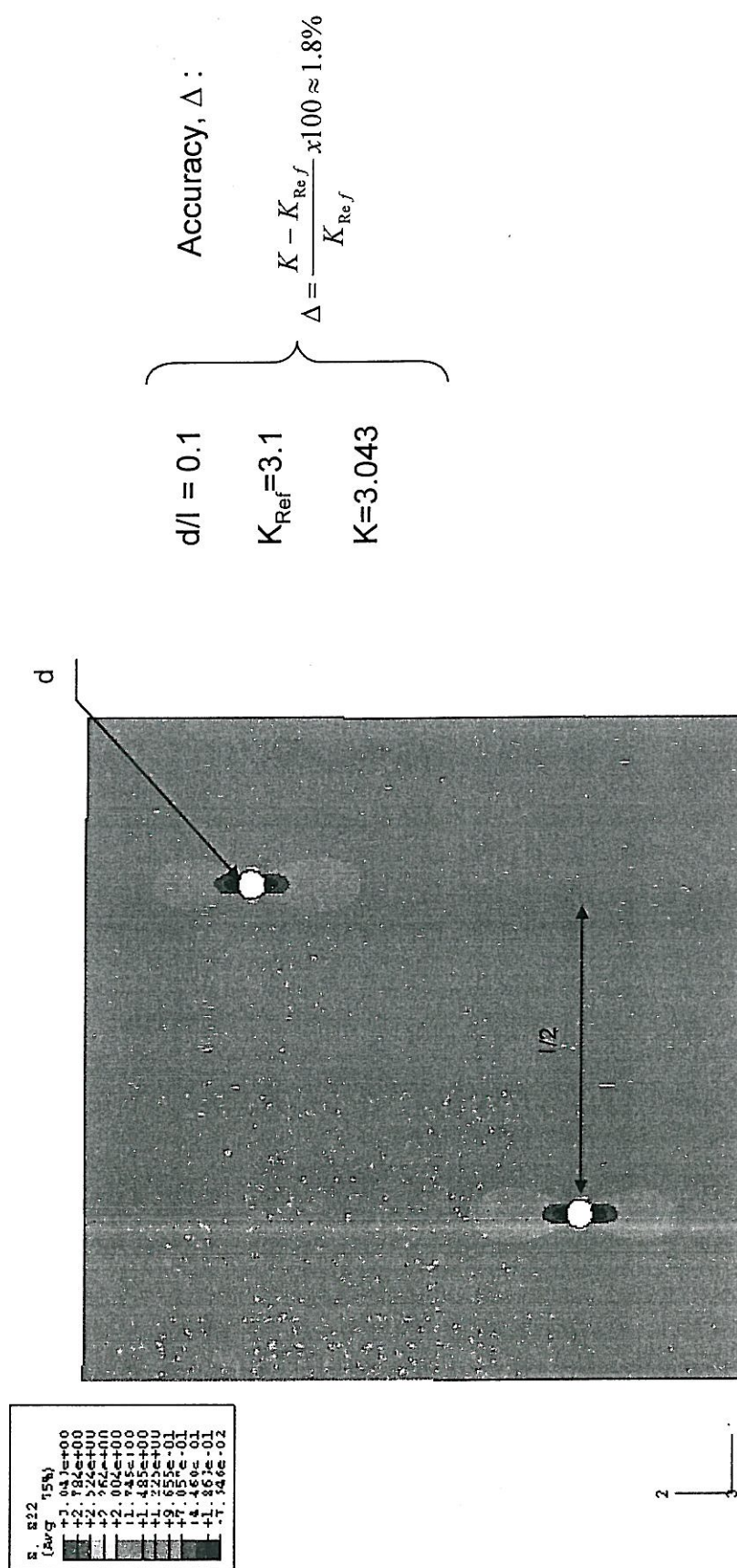


Figure 8.2.10: A Perforated Plate (a diamond pattern) with Circular Holes. [119]

Indeed, in the case of uniform-diameter circular holes (i.e., $r_1=r_2$), the prior model (volume effect model) is recovered and two models become identical (Fig. 8.2.11 a,b). This can also be seen in Fig. 8.2.12, where stress concentrations for both models at various occluded particle volume fractions are compared.

a) $V_f = 10\%$

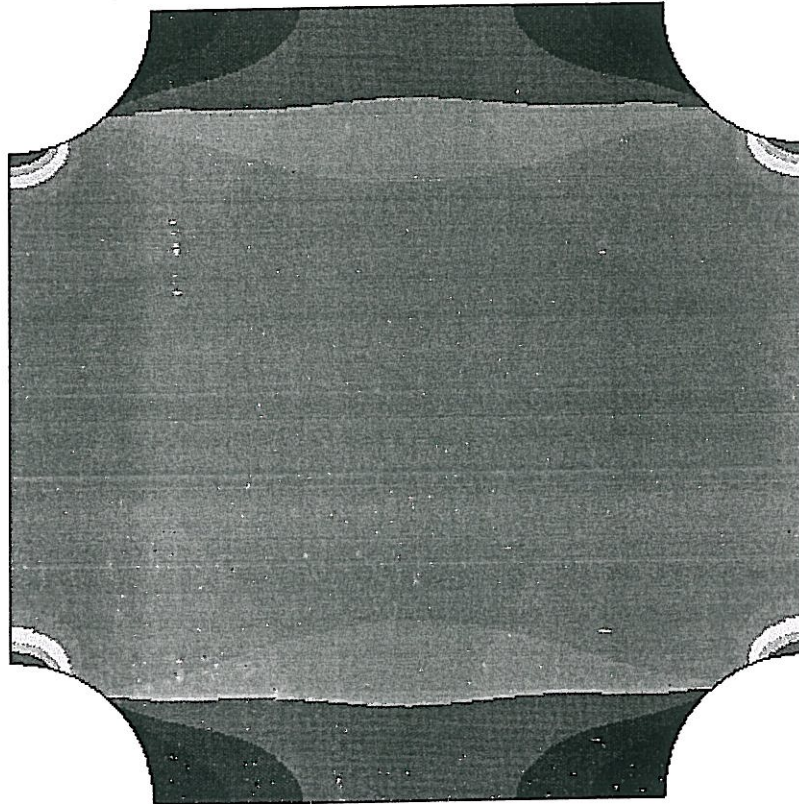
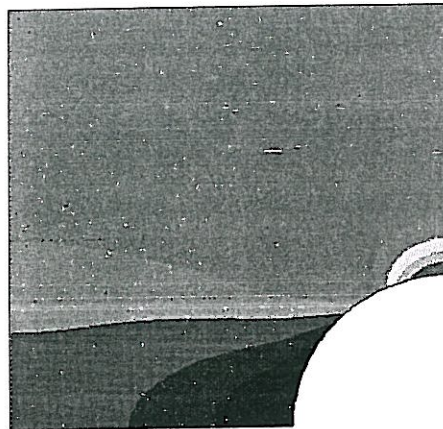
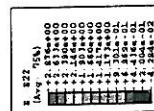
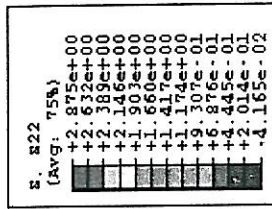


Figure 8.2.11 a: Comparison of Two Models: at $V_f = 10\%$.

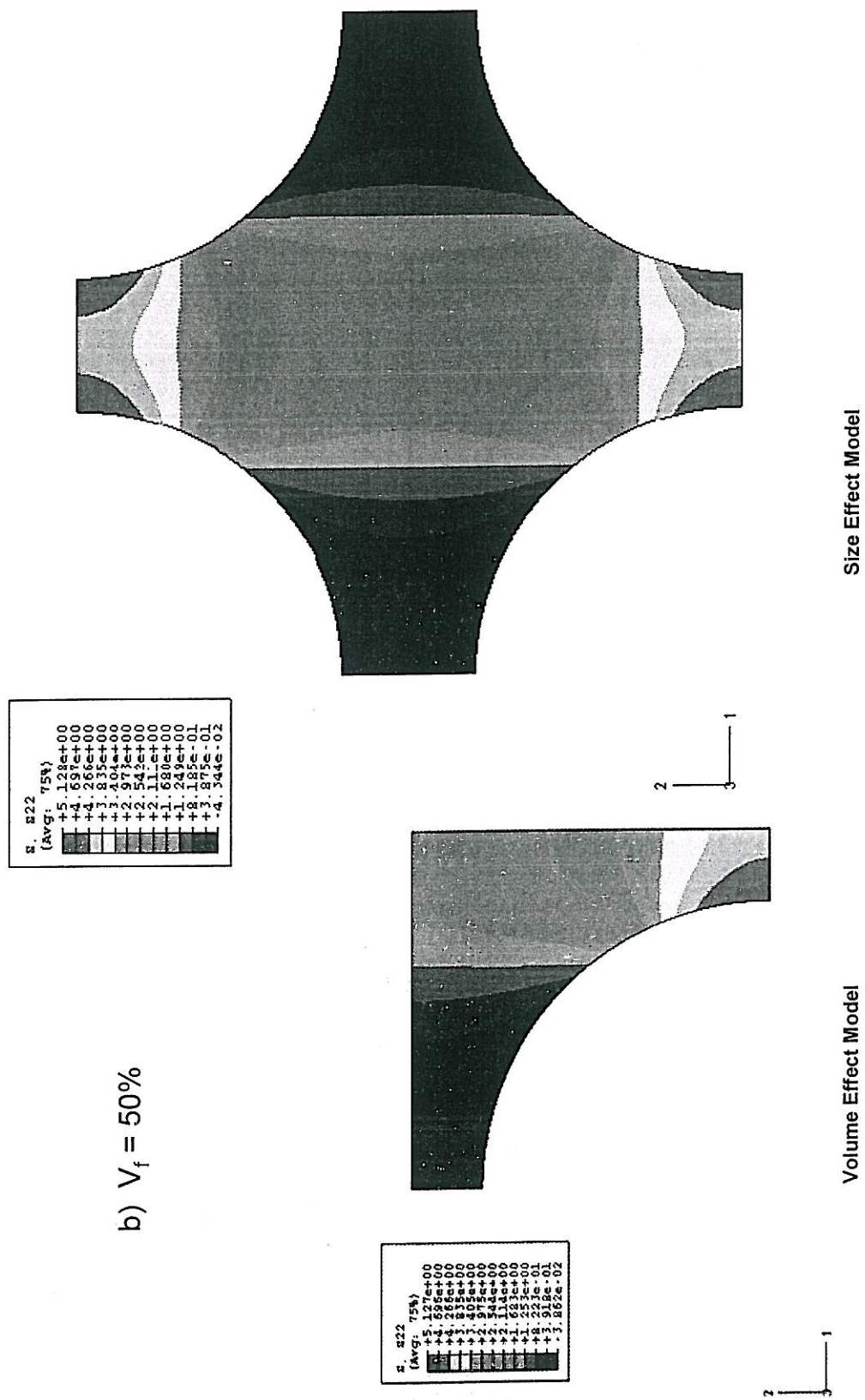


Figure 8.2.11 b: Comparison of Two Models: at $V_f=50\%$.

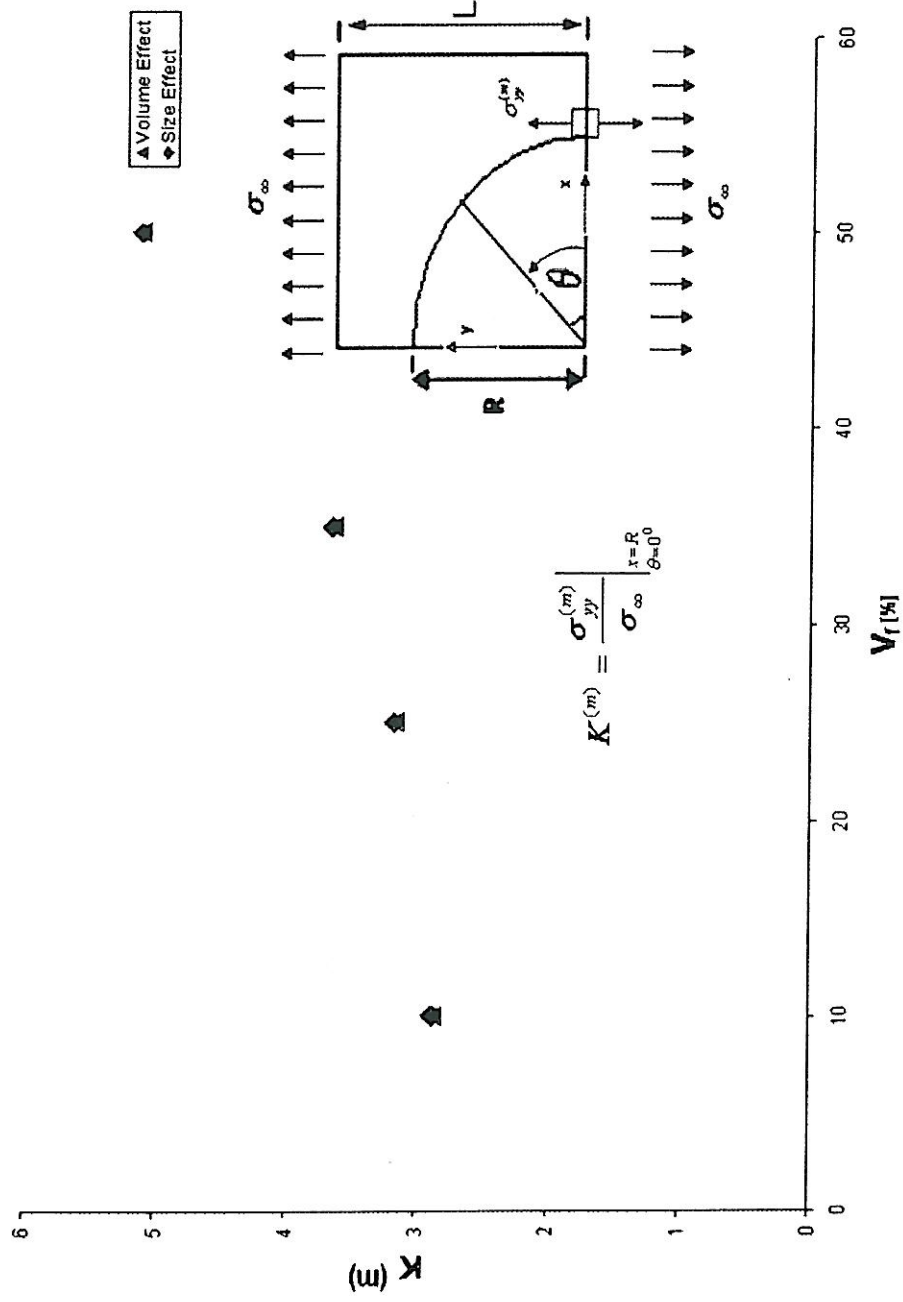


Figure 8.2.12: Stress Concentration, $K^{(m)}$, versus Particle Volume Fraction, V_f : Comparison of the Models.

ii) Craze Interaction:

The legitimacy and precision of the computational model has been vindicated via a reference solution [118]: a rectangular plate with a circular hole and two radial cracks emanating from the hole under uniaxial stress (Fig. 8.2.13).

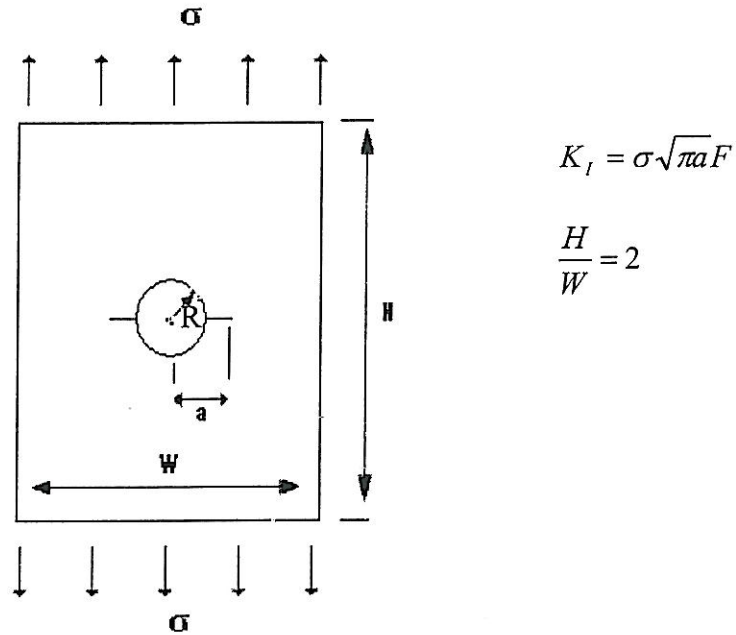


Figure 8.2.13: Cracks Emanating from a Circular Hole.

The expression for the stress intensity factor, K_I , is given above where F is the configuration correction factor (CCF). Its value changes depending on the crack size, a , and the radius of the hole, R .

A quadrant of a plate with a crack, shown in Fig. 8.2.14, is considered for modeling the problem. Contour integral, J -integral, is calculated, and the stress intensity factor is estimated assuming linear elasticity. For linear elastic case, J -integral is equal to the change in total potential energy due to a crack growth, and the following relation holds in a plane strain condition:

$$J = G \quad \text{and} \quad K^2 = G \frac{E}{1-\nu^2} \quad (\text{plane strain})$$

where G is strain energy release rate, E is elastic modulus and ν is Poisson's ratio.

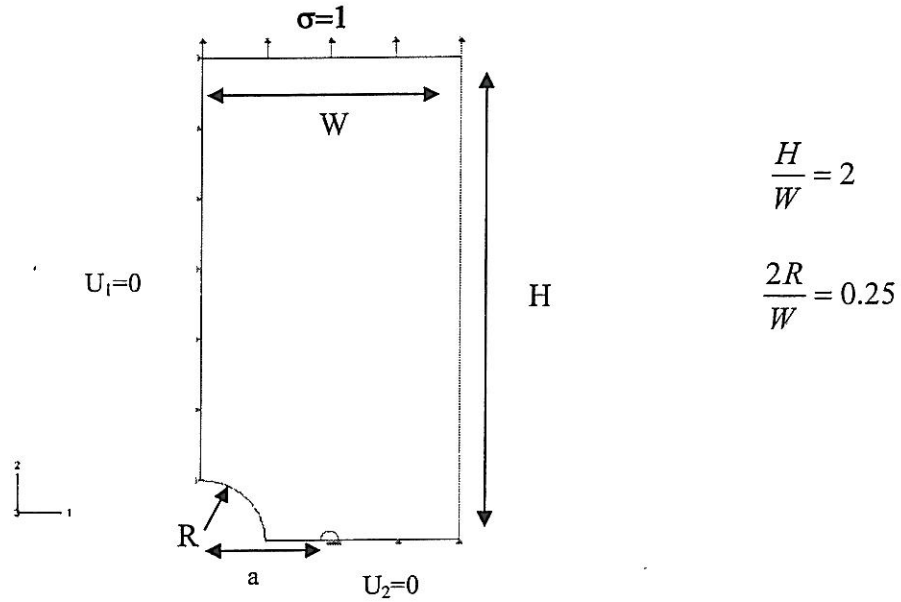


Figure 8.2.14: A Quadrant of the Plate with a Hole and a Crack.

The J -integral is path independent. However, owing to the approximate nature of the finite element solution, J -integral estimates from different rings may vary and thus the first few contours may be inaccurate [119]. In linear elastic problems, it is suggested that [119], the first and second contours should be ignored.

In the study, three different cases associated with different CCF values are calculated and the solutions are compared to the reference [118] values. J -integrals around the first five contours surrounding the crack-tip are evaluated. The value of a contour integral that appears approximately constant is used to estimate the corresponding stress intensity factor. In Fig. 8.2.15, the geometry and the mesh of all three cases are shown with the calculated stress intensity factors.

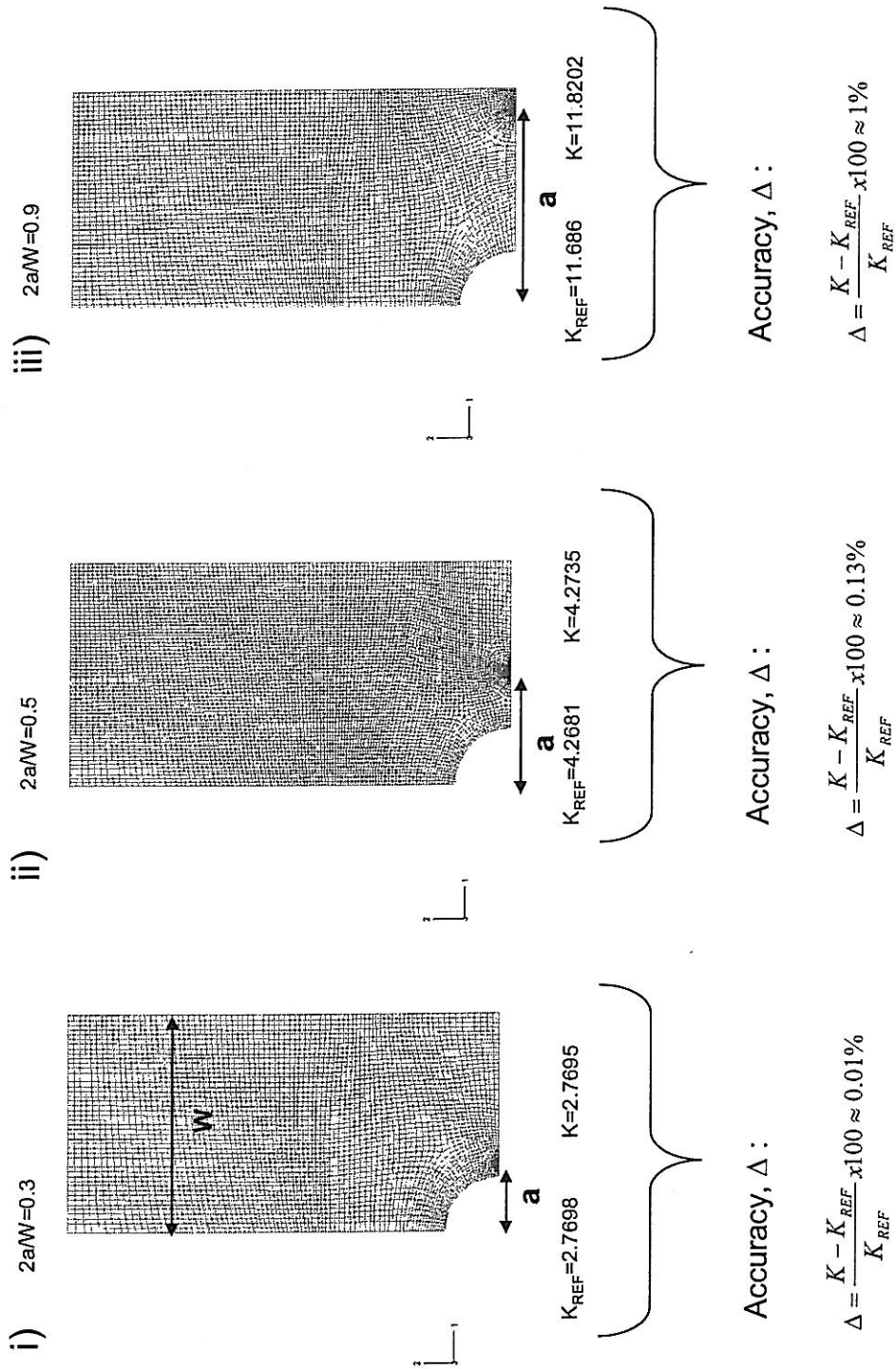


Figure 8.2.15: Three Cases Associated with Different CCF.

8.3 Craze Initiation in HIPS Polymer

Occluded particles in a HIPS may be considered as elastic inclusions in the polymer matrix and their interactions may be ignored at relatively low volume fractions. In this case, Eshelby's [87] and Goodier's [88] solutions are applicable. A common measure for particle interaction is taken as one diameter distance between particles, which corresponds to, for example, a volume fraction of 0.085 for body center cubic (BCC) periodic arrangement [120]. In a typical rubber-modified polymer, the occluded particle volume fraction is higher than 15%, resulting in a possible particle interaction. Therefore, analytical results are no longer valid and a numerical model is needed.

Craze initiation in a HIPS polymer is modeled such that effects of both second-phase particle volume fraction and size distribution are considered using two separate models, based on the observed polymer microstructure.

8.3.1 Craze Initiation Criteria in HIPS Polymer

Sternstein and Ongchin [6] have proposed the following multi-axial stress criterion for craze initiation.

$$\sigma_b = |\sigma_1 - \sigma_2| \geq A(T) + \frac{B(T)}{I_1}, \quad (8.2)$$

where σ_1, σ_2 are non-zero principal stresses; σ_b is the stress bias; $I_1 = \sigma_1 + \sigma_2 + \sigma_3$ is the first invariant of the stress tensor; and $A(T)$ and $B(T)$ are temperature-dependent material constants.

chemical grafting of polystyrene onto polybutadiene makes these phases inseparable. The current model is assumed to have a two-fold symmetry with respect to the x and y axes in the basic unit. A uniaxial loading case is modeled by a nominal loading on the HIPS. Analyses are carried out on only one quadrant of the region as shown in Fig. 8.3.3. A plane stress condition is assumed. A mesh refinement study (see Section 8.2) is conducted around the occluded particles. Quadratic, eight-node (with the total number of degrees of freedom is equal to 16), quadrilateral elements are used in the numerical analysis. The element size is chosen such that the results are least mesh-sensitive. The element aspect ratio, x , is kept within the limits of $\frac{1}{4} < x < 4$ [121] for the elements around the occluded particles. Particle interaction is also taken in to consideration.

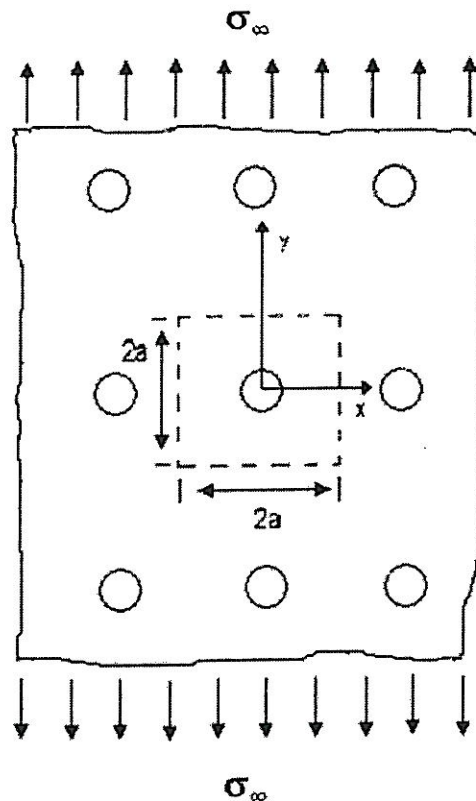


Figure 8.3.1: A HIPS with Occluded Particles Subjected to a Uniform Nominal Stress

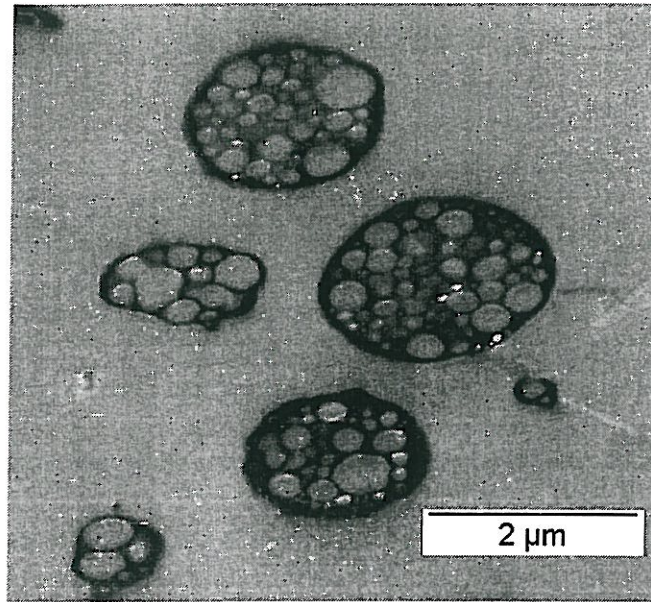


Figure 8.3.2: Interface Between an Occluded Particle and Its Surrounding.

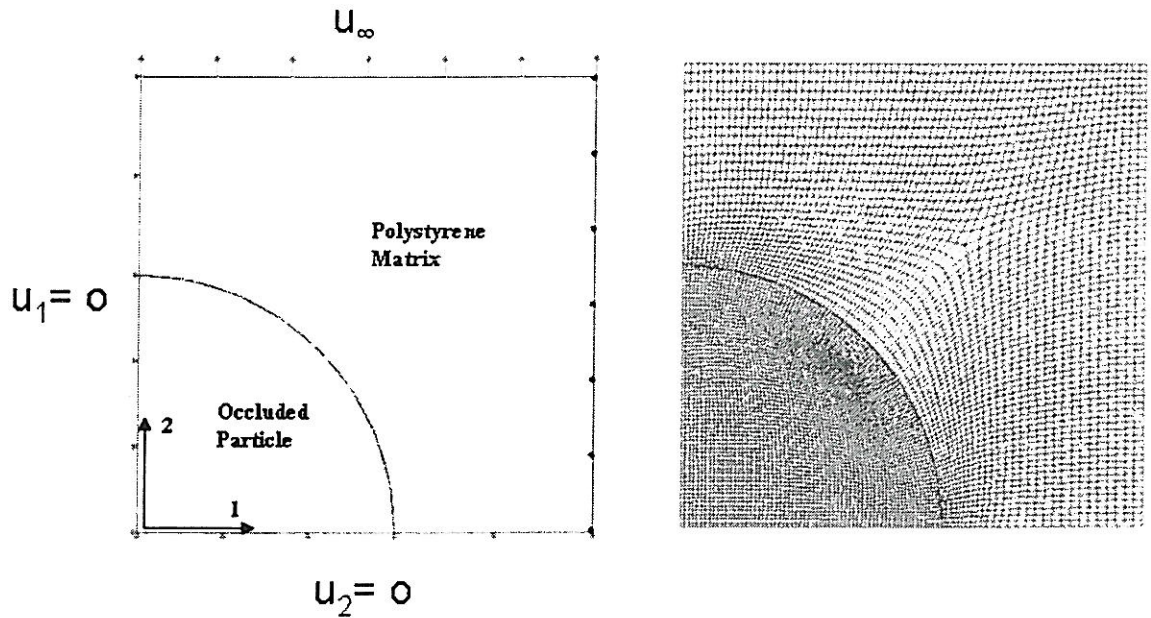


Figure 8.3.3: A Quadrant of the Representative Volume with Boundary Conditions and Mesh.

8.3.3 Modeling of Size Effect of Occluded Rubber Particles

Owing to its inherent complexity, the particle size distribution is modeled with consideration of a binomial size distribution. Having a bimodal size distribution is a simple yet an effective way to capture the particle size effect. In addition, experimental studies [53, 61] have shown that the bimodal size distribution enhances HIPS polymer toughness. In the study, the HIPS is considered as a polymer with homogeneously distributed occluded particles of two different sizes embedded in a PS matrix. In Fig. 8.3.4, the particle arrangement and a representative volume element (RVE) are depicted. Based on symmetry considerations, only the first quadrant of the RVE needs to be analyzed. Again, plane stress condition is assumed. Quadratic, eight-node (with the total number of degrees of freedom is equal to 16), quadrilateral elements are used for meshing (Fig. 8.3.5).

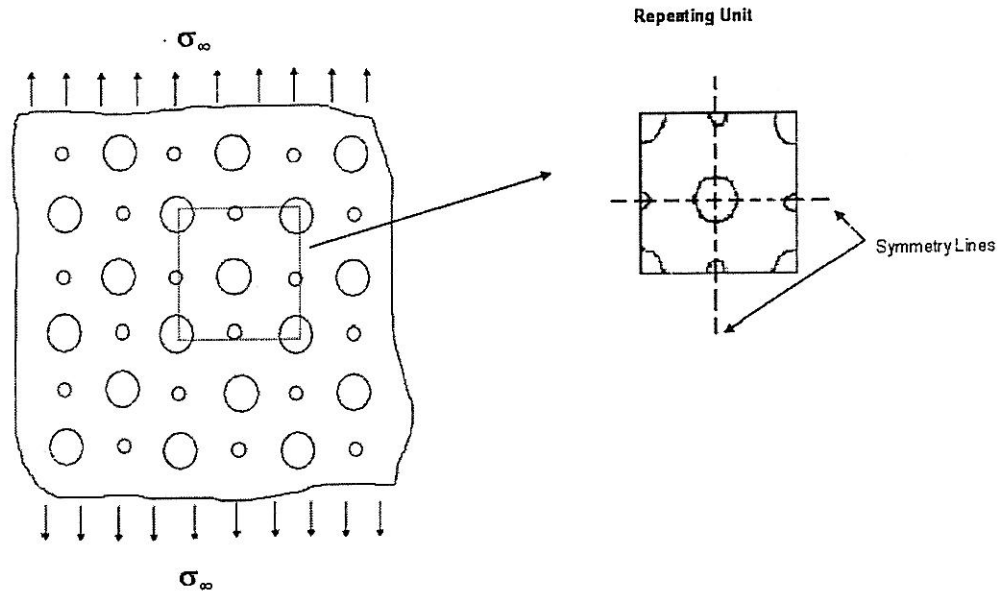


Figure 8.3.4: HIPS with Binomial Particle Size Distribution Subjected to Uniform Nominal Stress, σ_∞ .

In Fig. 8.3.5, the modeled quadrant with boundary conditions and finite element mesh is shown.

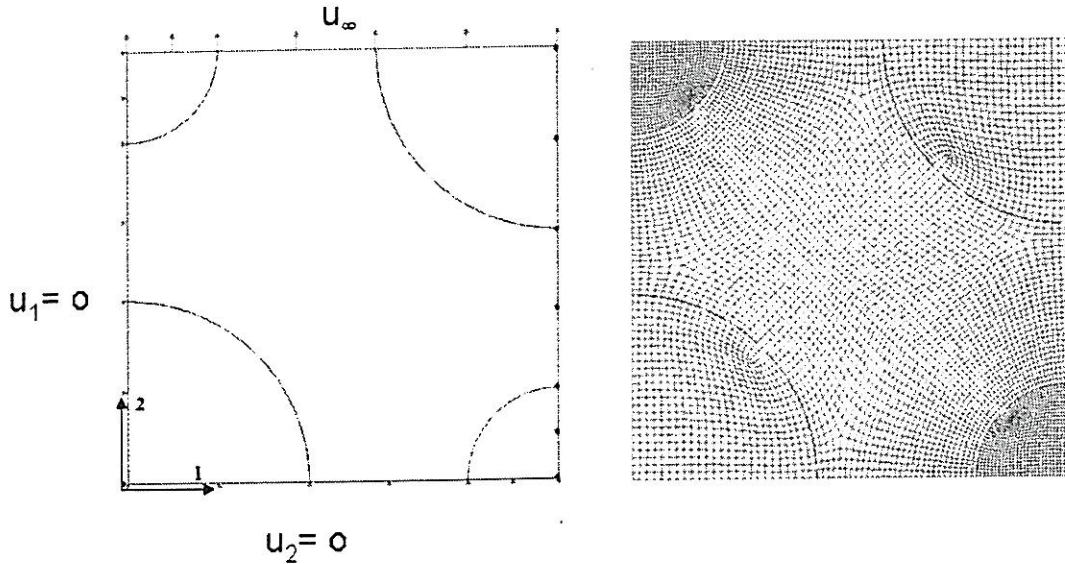


Figure 8.3.5: First Quadrant of the RVE with Boundary Conditions and FEM Mesh.

8.4 Craze Interaction

Generally, not a single craze, but a number of crazes initiate and grow simultaneously. Therefore, craze growth characteristics, eventually, are associated with craze interaction. The craze damage is influenced by craze interaction. As a result of the craze interaction, stress perturbation occurs and the stress state changes. Hence, the craze formation and growth is affected. It is essential to model the craze interaction to address the craze growth characteristics.

8.4.1 Craze Growth Criteria in HIPS

In the literature, craze growth studies are mainly based on one-dimensional plasticity theory, such as the Dugdale Model [122]. For example, in [16, 123] it is

assumed that plastic deformation concentrates in a strip in front of the craze and the material outside of the craze behaves linearly elastic.

In the study, craze interactions are explored without considering craze growth kinetics. A simple criterion is adapted based on the local maximum principal stress. It is assumed that craze will grow when the local maximum principal stress is equal to the yield stress of the polystyrene.

8.4.2 Modeling of Craze Interaction in HIPS

In this section, craze interaction is modeled by considering a HIPS microstructure and observed craze geometry (i.e., size and thickness). Owing to inherent complexity (Figs. 8.1.1 and 8.1.2), craze interaction is modeled assuming a regular arrangement and considering mono and bimodal size distributions only. A plane strain condition is applied. Quadratic, eight-node (with the total number of degrees of freedom is equal to 16), quadrilateral elements are used for meshing. The element size is chosen such that the results are least mesh-sensitive. The element aspect ratio, x , is kept within the limits of $\frac{1}{4} < x < 4$ [121] for the elements around and at the tip of a craze emanating from an occluded particle. Symmetry conditions are identified and only the first quadrant of the repeating unit is analyzed. Craze is modeled as a crack with a constant normal traction force applied on its surfaces depicting load carrying fibrils. The craze size estimation is made by using craze-length density distribution curves constructed based on microscopic craze damage observations. At a given deformation, the craze length, ℓ , appearing with the highest frequency is used in the model. The surface traction force is calculated using

the applied load and the observed craze geometry. At a given strain (knowing the applied load and the corresponding observed craze length), traction force, σ_t , on the craze surfaces is increased gradually until the craze thickness is equal to the observed value of that strain level.

In Fig. 8.4.1, a representative volume element for a mono-size system is shown with boundary conditions and finite element mesh.

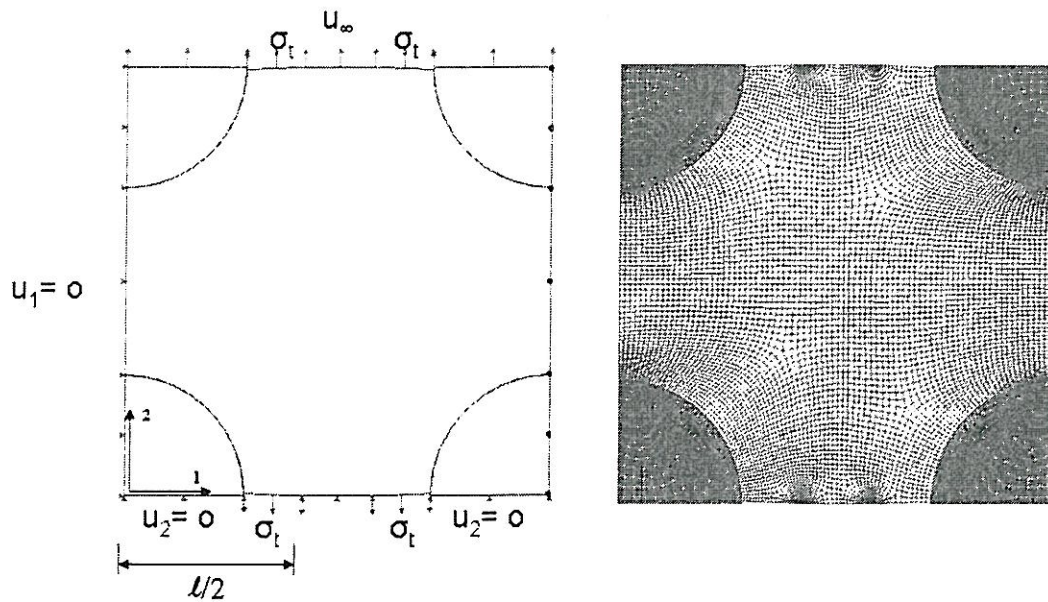


Figure 8.4.1: A Quadrant of the Representative Volume with Boundary Conditions and FEM Mesh.

9. RESULTS AND DISCUSSION

In this chapter, results of experimental, theoretical and numerical investigation on craze formation and growth in HIPS are presented. The mechanical behavior of unmodified PS and HIPS are discussed and compared. Craze formation is observed with an optical microscopy during plastic deformation and a statistical description of craze damage in the HIPS is conducted. Craze length and orientation distributions are found to follow well defined statistical functions. Comparisons are made among various HIPS systems differ by a second-phase particle volume fraction and/or particle microstructure.

The results of damage-mechanics experiments are given in detail. The associated material property degradation is reported. Craze damage accumulation and evolution are investigated. Based on the irreversible thermodynamics formulation given in Section 7.3, damage mechanics variables and associated driving forces for damage formation in HIPS are determined. The orthotropic nature of craze damage in the HIPS polymer is also investigated. The important characteristics of damage formation and growth in HIPS are explored by a computational micromechanics method. The effects of second-phase particle volume fraction and size on the craze formation are discussed.

9.1 Basic Stress-Strain Relationship of HIPS

Typical stress-strain responses of an unmodified polystyrene and HIPS are shown in Fig. 9.1.1. The experiments were conducted in the same conditions. [Test specimens were loaded in a strain-rate control mode ($\dot{\epsilon} = 0.00007 \text{ in/in/sec}$) and the test were conducted in air at room temperature until failure.]

The PS showed almost linear behavior and broke in a brittle manner. The HIPS had a linear elastic response only up to 1% strain. Apparently, the occluded particles had a drastic effect on macroscopic properties. As can be seen, a typical stress-strain response of the HIPS showed a small-strain elastic response before yielding, followed by strain softening and strain hardening. There was a negligible change in the cross-sectional area during testing with no sign of necking.

As expected, strength and modulus of the unmodified PS were higher than those of the HIPS. The difference was more than three times in material's strengths. The strength of the PS was 6.6 ksi, and it was approximately 1.9 ksi for the HIPS. Failure strain of the HIPS was approximately fifteen times larger than that of the PS. [Failure strain for the PS was 0.022 and 0.33 in/in for the HIPS.]

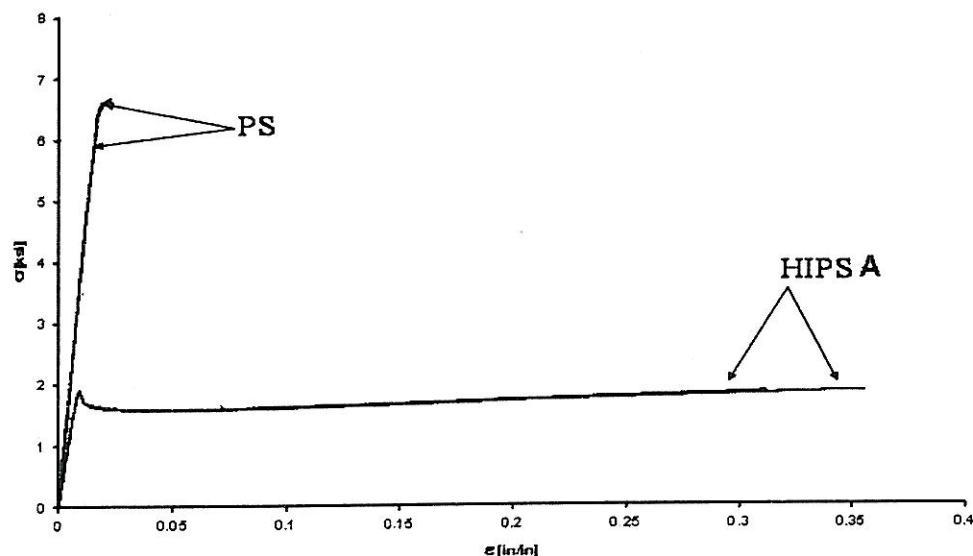


Figure 9.1.1: Stress-Strain Relationship of PS & HIPS at RT [$\dot{\epsilon} = 0.00007 \text{ in/in/sec}$].

All six different kinds of HIPS used in this study were tested first to establish their base-line mechanical properties for subsequent analytical studies. For comparison, the stress-strain behavior of three HIPS grades (i.e., HIPS A, HIPS E and HIPS F) from different manufacturers were obtained and shown in Fig. 9.1.2. The HIPS F had a soft initial elastic response, a low yield strength, followed by a shallow strain softening and a substantial strain hardening. Reductions in stiffness and yield strength were consistent with expectations and they may be attributed to HIPS F's high occluded particle volume fraction.

At least three mechanical tests for each grade HIPS were conducted. Their mechanical properties are given in Table 4.1.2 for all the HIPS used.

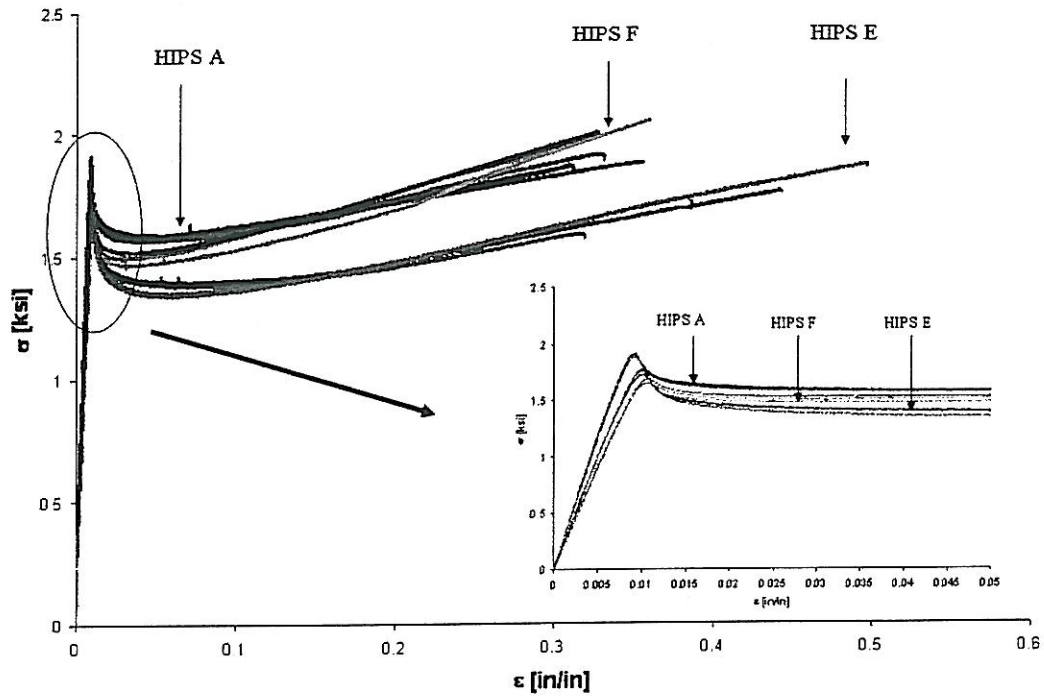


Figure 9.1.2: Stress-Strain Relationship of Different HIPS at RT
 $[\dot{\epsilon} = 0.00007 \text{ in/in/sec}]$

9.2 Craze Damage Observations on HIPS

Earlier observations [36, 124] of HIPS polymers conducted under TEM reveal a cellular structure of rubber particles, with sub-inclusions of the PS dispersed in particles with a continuum rubber phase. Crazes connected the rubber particles but did not go through them.

In this study, microscopic characterization of crazing was done by means of SEM and optical-microscope observations. Analyses were conducted on images of test specimens both under loads and with no load. Images given in Fig. 9.2.1 were taken in an optical microscope. The micrographs reveal whitened surfaces of fractured samples in a no load condition, depicting high craze concentrations prior to the failure of HIPS. As can

be seen, crazes were generated from the rubber particles and possessed a strong directionality. The crazes grew in the direction perpendicular to the applied load although few deviated from the expected direction. Many crazes were too close to distinguish themselves under optical microscope observations.

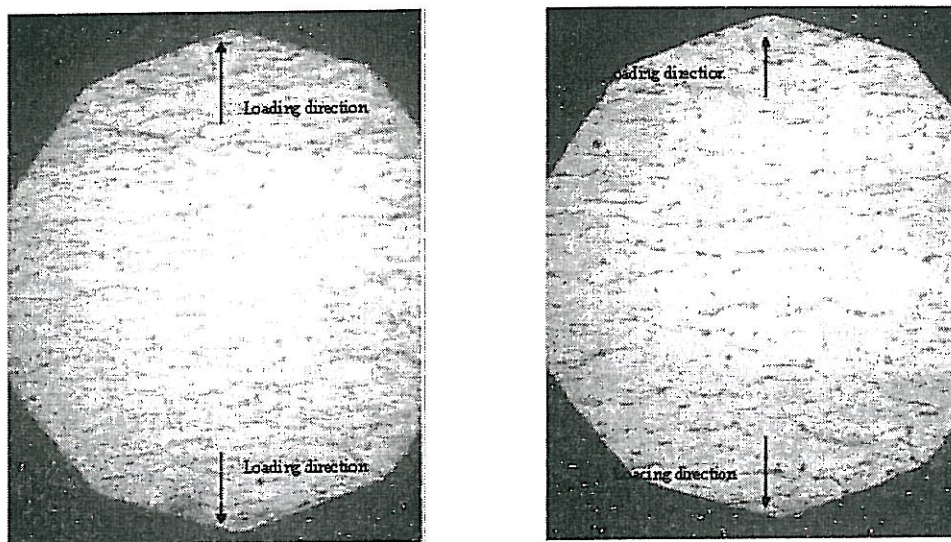


Figure 9.2.1: Optical Microscope Images of Crazes in HIPS (x400).

In Fig. 9.2.2, craze formation and evolution are shown along a stress-strain curve. Craze formation started at the strain level of 0.0085 in/in where craze initiation was detected the first time. Whitening became more intense as the load increased and higher craze densities were observed.

SEM images (e.g., Figs. 9.2.3 and 9.2.4) with better resolutions are shown here for a subsequent analysis. The micrograph in Fig. 9.2.3 was taken in a broken sample, no load condition. Approximate length, width, and orientation associated with the craze are clearly visible. Micrographs in Fig. 9.2.4 were taken from a surface of a loaded HIPS specimen by using specially designed tensile loading stage. These pictures were taken somewhere in the same region but at different strain levels.

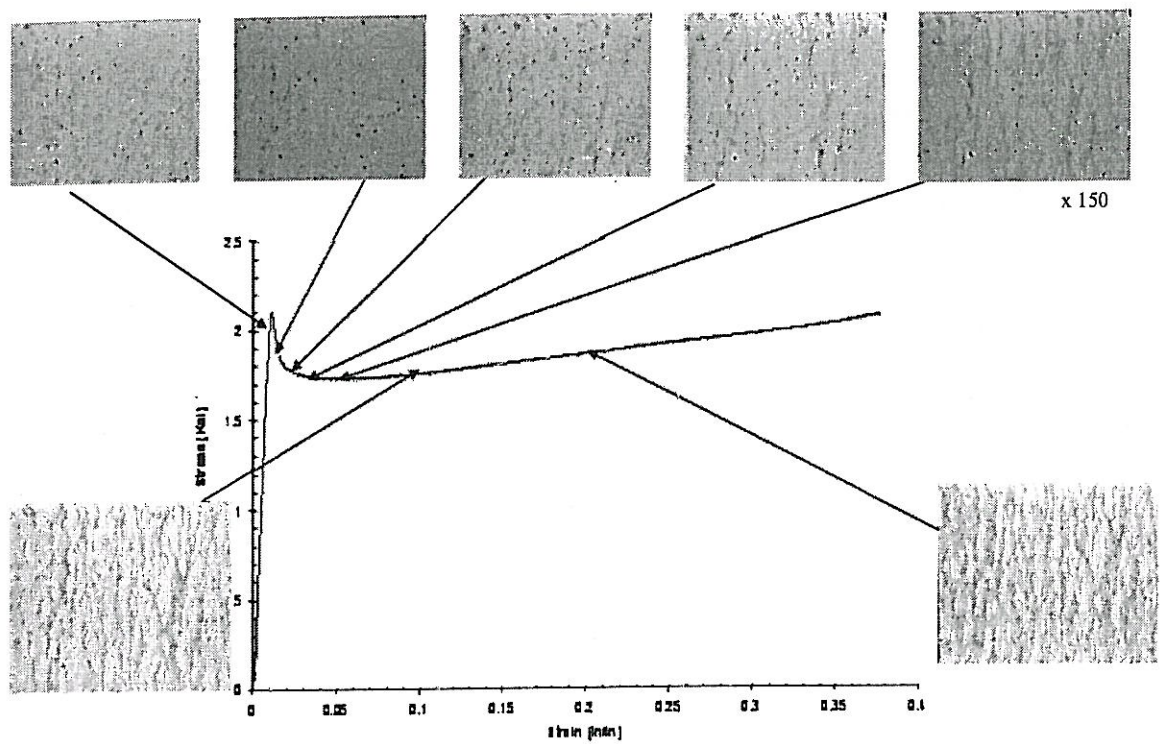


Figure 9.2.2: Craze Evolution in HIPS at RT [$\dot{\epsilon} = 0.002 \text{ in/min}$].



Figure 9.2.3: SEM Micrograph of a Craze Emanating from a Rubber Particle in HIPS.

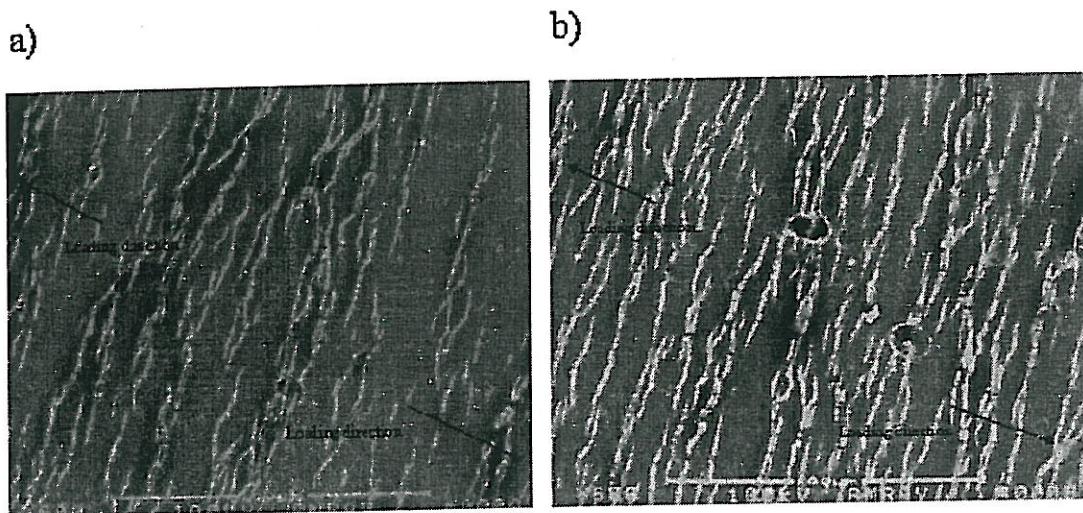


Figure 9.2.4: SEM Images of a Crazed Surface in a HIPS under Mechanical Loading.

As can be seen, the crazes were normal to the applied load with variety of lengths. They had somewhat uniform craze width ($1.5\text{--}2\text{ }\mu\text{m}$). The craze density increase is obvious when the two images are compared. The micrograph on the right, Fig. 9.2.4 (b) was taken at a higher strain level; thus, the observed craze density is higher compared to the one on the left.

9.3 Microscopic Craze Damage Characterization

Microscopic characteristics of craze damage were studied and are presented in this Section. Craze accumulation was analyzed quantitatively by measurements of craze density, orientation and size as discussed in Chap. 5. Their quantities were extracted from experiments, and corresponding statistical distribution functions were constructed. The images captured at 1300x magnification were used for the detailed analyses. The limit of accuracy of the results is set by the microscope's magnification.

Even though experiments and associated statistical analyses were carried out for all six kinds of HIPS materials, the general discussion is mostly focused on HIPS A. Some results were compared with other two grades (HIPS E and HIPS F). The information on the other HIPS grades is to be covered in the later sections.

9.3.1 Density and Cumulative Functions of Craze Length

Experimental data for cumulative distribution functions of craze length, $F(\ell)$, in a HIPS at strain levels of 0.0095, 0.02, 0.05 and 0.1 are shown in Fig. 9.3.1. In these plots, the y-axis, $F(\ell)$, represents the total number of crazes per unit area. These data were extracted from three specimens (HIPS A) using images taken at the different strain levels. The cumulative distribution functions in HIPS A, HIPS E and HIPS F at different strain levels are given in Fig. 9.3.2.

From the figures, for example in HIPS A, it can be seen that $F(\ell)$ became saturated beyond 0.035 mm. Almost 85-90 % of the crazes have their lengths smaller than 0.035 mm. The saturation state gets smaller at a lower strain level ($\ell \approx 0.02\text{mm}$ for $\varepsilon = 0.01$). In general, $F(\ell)$ increased rapidly with the craze length, ℓ , between 0 and 0.015mm, which was an indication of a high craze length concentration in that range. The $F(\ell)$ curves also increased with deformation (Fig. 9.3.2), implying that the number of crazes increased with the applied strain. The statistical data appeared to follow the following Weibull function [125]:

$$F(\ell) = N(1 - e^{-(\frac{\ell - \ell_0}{\beta})^\alpha}), \quad (9.1)$$

where N is the total number of crazes observed on a sampled surface area; 2β is a measure of the craze length; and α is a shape parameter, representing the spread of the distribution function. The least square curve fitting method was used to determine α and β .

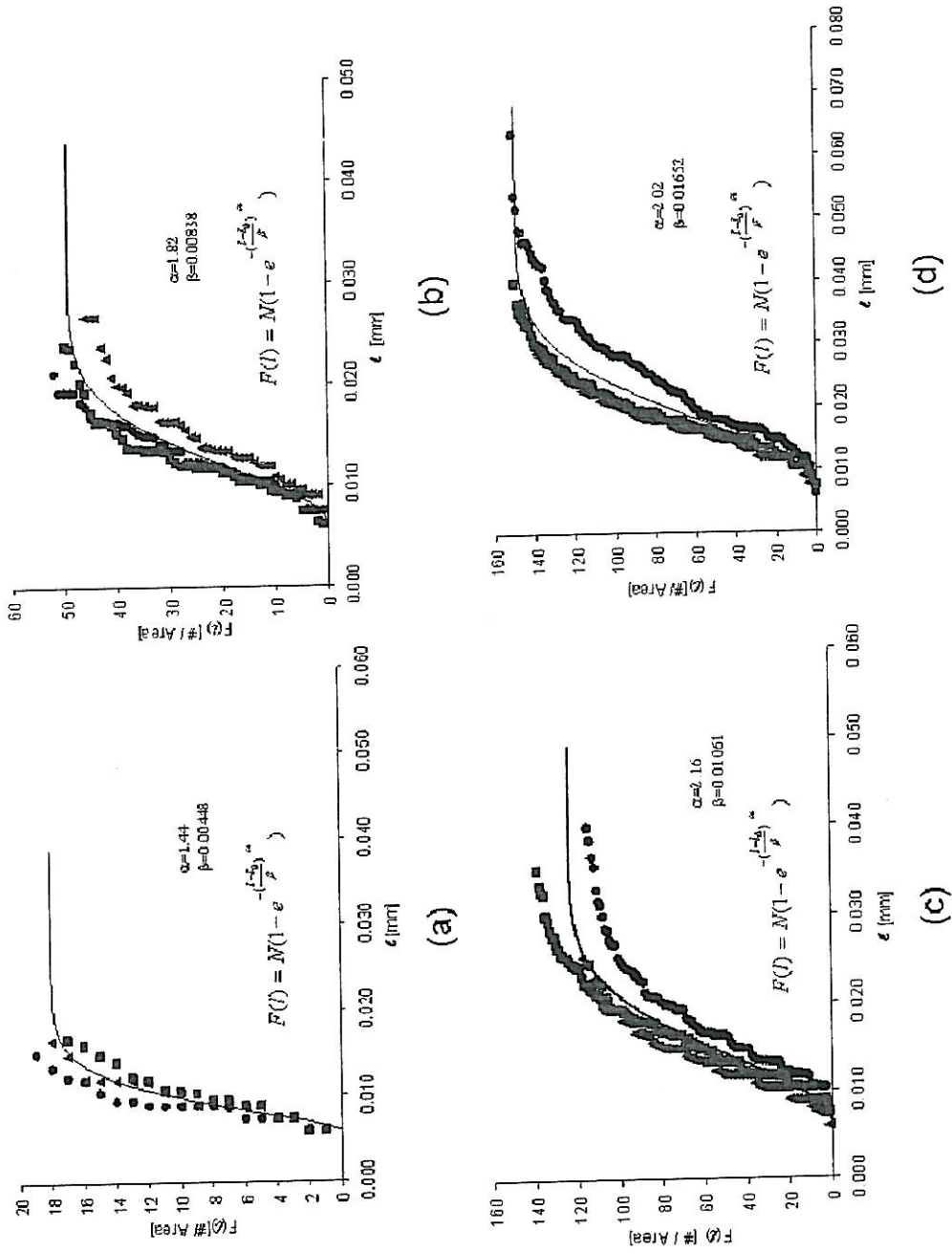


Figure 9.3.1: Cumulative Distribution Function, $F(l)$, versus Craze Length [HIPS A] at Various Strains: a) $\epsilon = 0.0095$, b) $\epsilon = 0.02$, c) $\epsilon = 0.05$, d) $\epsilon = 0.1$. [T= RT; $\dot{\epsilon} = 0.00007 \text{ in/in/sec}$]

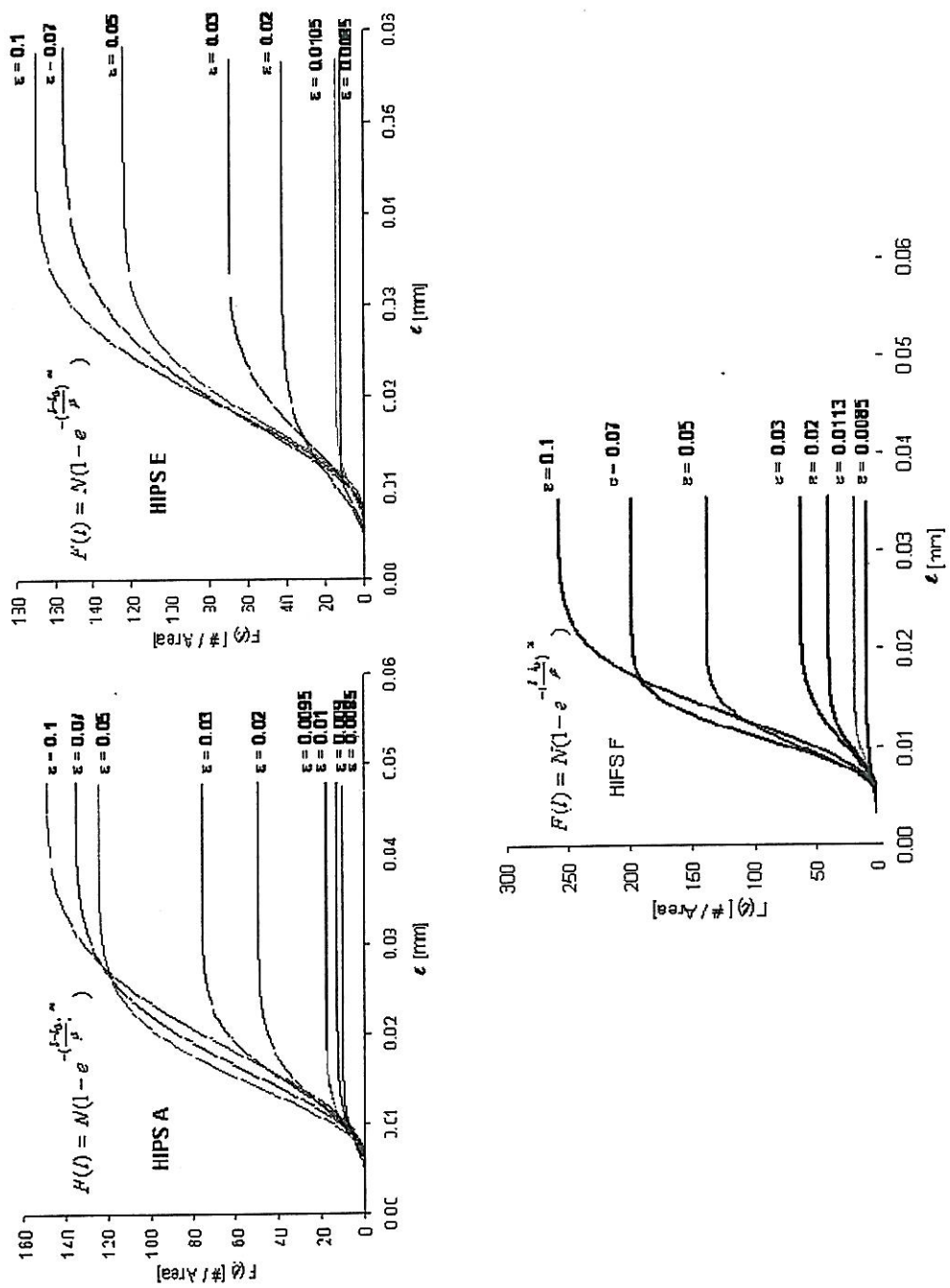


Figure 9.3.2: Cumulative Distribution Function, $F(l)$, versus Craze Length in HIPS at Different Strains.
 [T= RT; $\dot{\epsilon} = 0.00007 \text{ in / in / sec}$]

The density function for craze length distribution was obtained by differentiating Eq. (9.1) with respect to l and has the following form

$$f(l) = N \frac{\alpha}{\beta^\alpha} (l - l_0)^{\alpha-1} e^{-\left(\frac{l-l_0}{\beta}\right)^\alpha} \quad (9.2)$$

For the cases of $\epsilon = 0.0095, 0.02, 0.05$ and 0.1 , experimental data of the craze length density distribution functions, $f(l)$, for HIPS A are given in Fig. 9.3.3. (All data were plotted in a $\Delta x = 0.006$ mm increments.) The craze density functions at different strain levels are given in Fig. 9.3.4 and the results for HIPS E and HIPS F are also included.

The characteristic craze length, $\hat{l}$, defined as the craze length appearing with the highest frequency, can be extracted from the craze-length density distribution functions at given strain levels. A slight right shift of the peak of each progressive density distribution curve indicates that the characteristic craze length increased with the applied strain. As the same procedures were used for all six HIPS grades, similar trends were observed.

Variations of N , β , α , and the characteristic length, $\hat{l}$, with the applied strain are shown in Figs. 9.3.5, 9.3.6, 9.3.7, and 9.3.8 respectively. Results for the other two HIPS grades (HIPS E and HIPS F) are also included in these graphs.

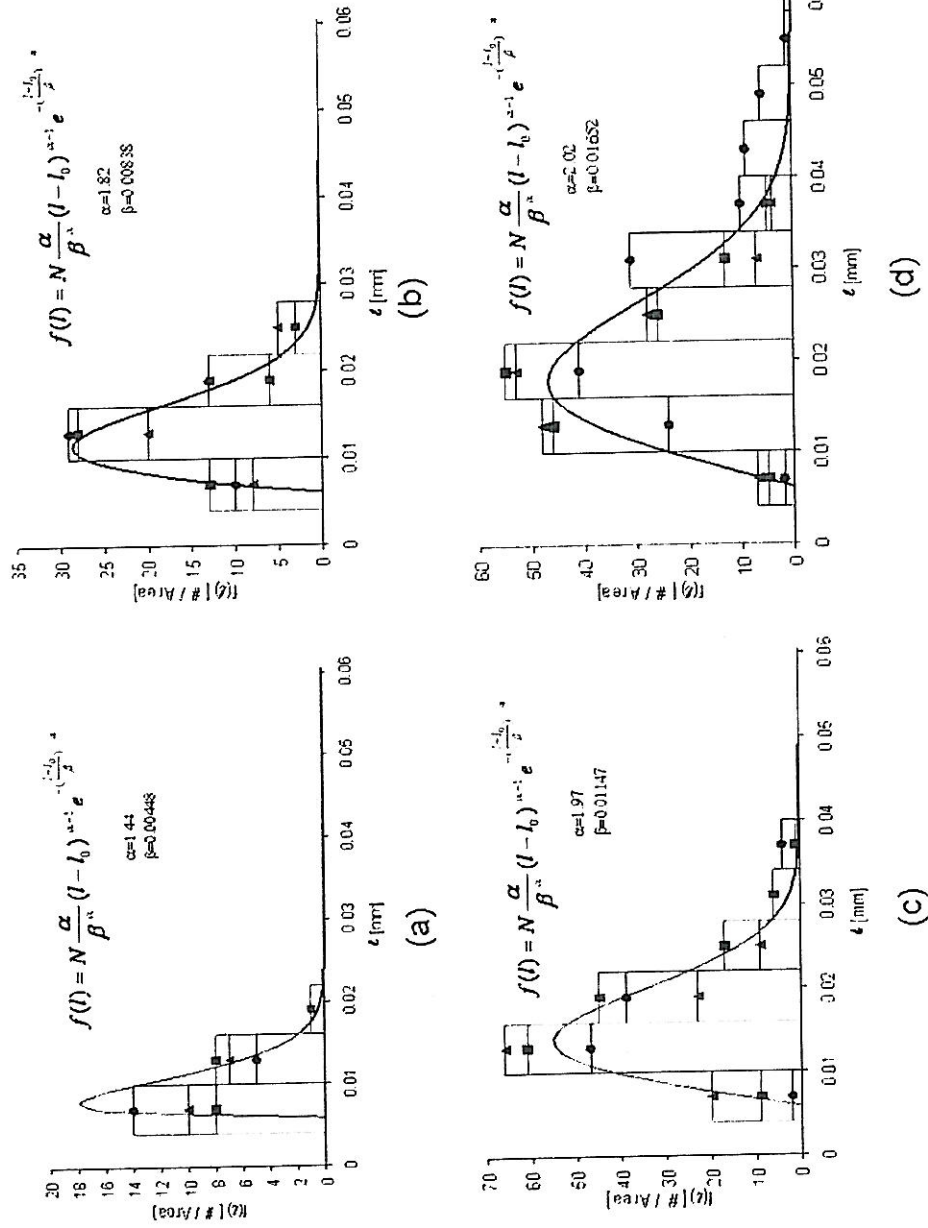


Figure 9.3.3: Frequency of Craze Length Density Function, $f(l)$, vs. Craze Length in HIPS [HIPS A] at Various Strains: a) $\epsilon = 0.0095$, b) $\epsilon = 0.02$, c) $\epsilon = 0.05$, d) $\epsilon = 0.1$. [T= RT; $\dot{\epsilon} = 0.00007 in / in / sec$]

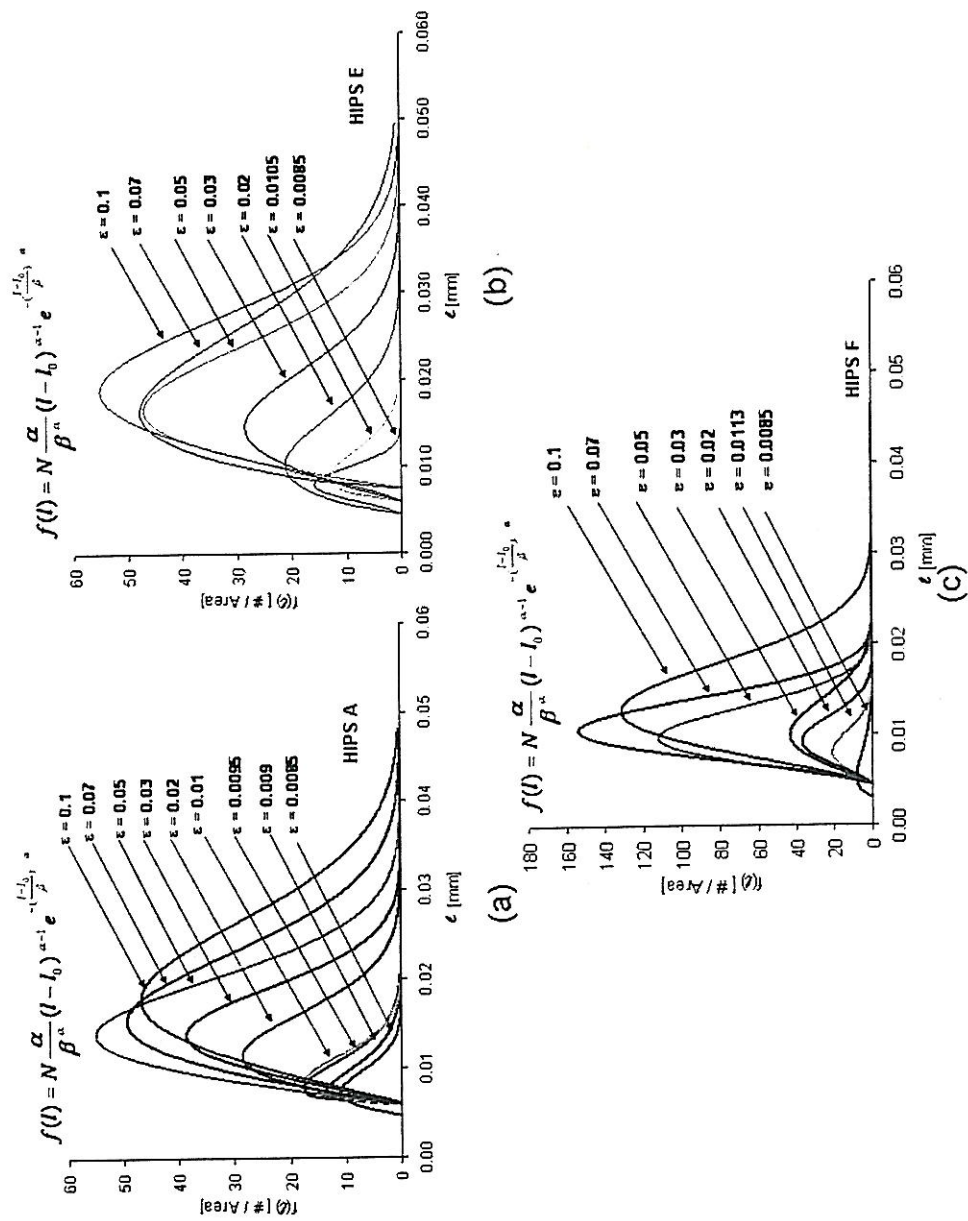


Figure 9.3.4: Density Distribution Functions of Craze Length in HIPS at Different Strains: a)HIPS A, b)HIPS E, c) HIPS F.
[T= RT; $\dot{\epsilon} = 0.00007 \text{ in / in / sec}$]

As expected, a higher number of crazes, N , was observed for higher applied strain, implying that more crazes were initiated as the deformation increased. Among the three HIPS grades, at a given strain, the highest craze density was observed in HIPS F, which also contained the highest volume fraction of occluded particles.

The value of β increased with the strain and tended to reach an asymptotic level eventually. The craze density distribution function, $f(l)$, spread wider with a larger value of scaling parameter as seen in Fig. 9.3.4. Apparently, crazes grew into larger sizes in the HIPS E. In Fig. 9.3.9, the aforementioned characteristics are shown by comparing the spreads of the three grades at various strains. This can also be seen in Fig. 9.3.8, where HIPS E had a higher characteristic craze length. On the contrary, shorter crazes were characteristic of HIPS F.

The Weibull shape parameter, α , were related to the craze density and the nature of craze growth. Larger α generated more pointed $f(l)$ curves, as seen in Fig. 9.3.9, represented a higher craze population and indicated a higher degree of craze growth homogeneity. In Fig. 9.3.7, an increase in shape parameter, α , with applied strain was not surprising because the number of crazes, N , also increased (Fig. 9.3.5). In the same figure, higher number of craze was formed and grew more homogeneously in the HIPS F compared to the other grades.

Briefly, a higher number but shorter crazes were generated in the HIPS F. and they grew together, more homogeneously than those of the HIPS A and HIPS E. HIPS A and HIPS E were comparable in terms of the number of crazes formed and their growth nature but larger crazes were characteristic of HIPS E.

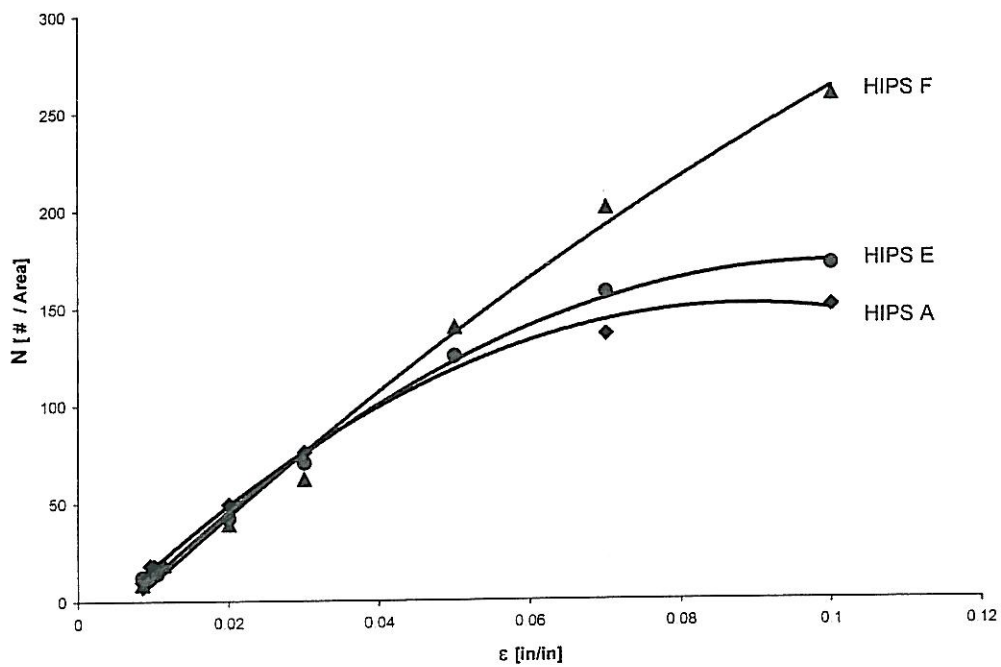


Figure 9.3.5 : Craze Density, N , as a Function of Applied Strain in HIPS.
 $[T = RT ; \dot{\epsilon} = 0.00007 \text{ in/in/sec}]$

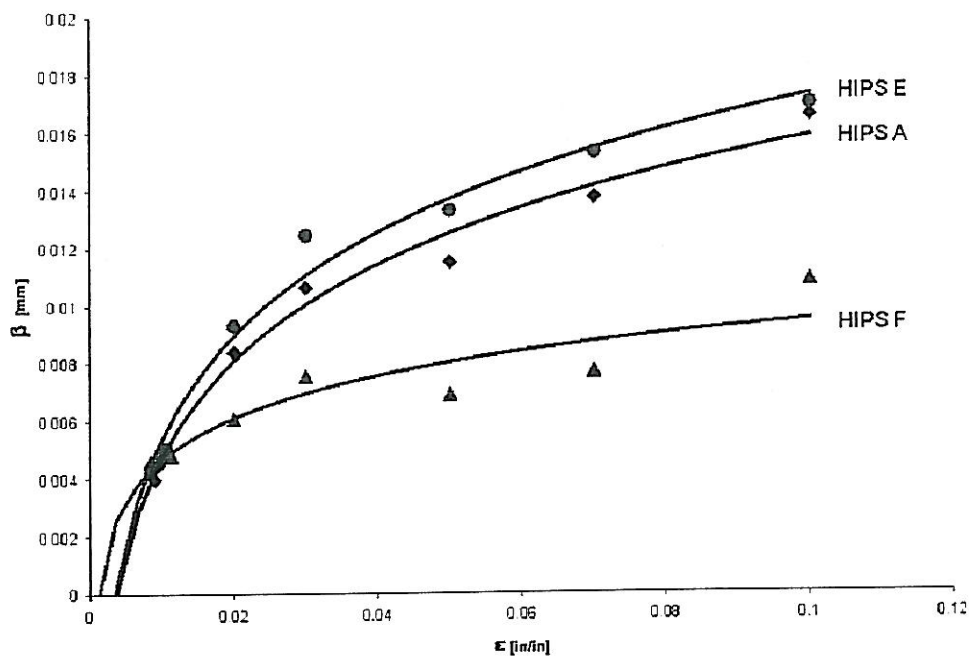


Figure 9.3.6 : Variation of Weibull's Scaling Parameter, β , as a Function of Applied Strain in HIPS. $[T = RT ; \dot{\epsilon} = 0.00007 \text{ in/in/sec}]$

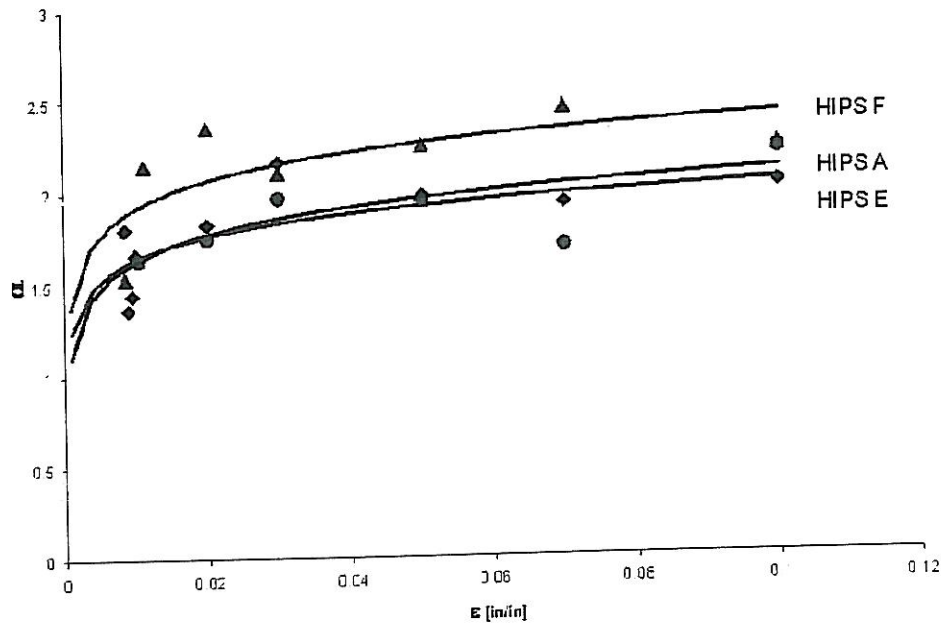


Figure 9.3.7 : Variation of Weibull's Scaling Parameter, α , as a Function of Applied Strain in HIPS. [T= RT ; $\dot{\epsilon}$ = 0.00007 in/in/sec]

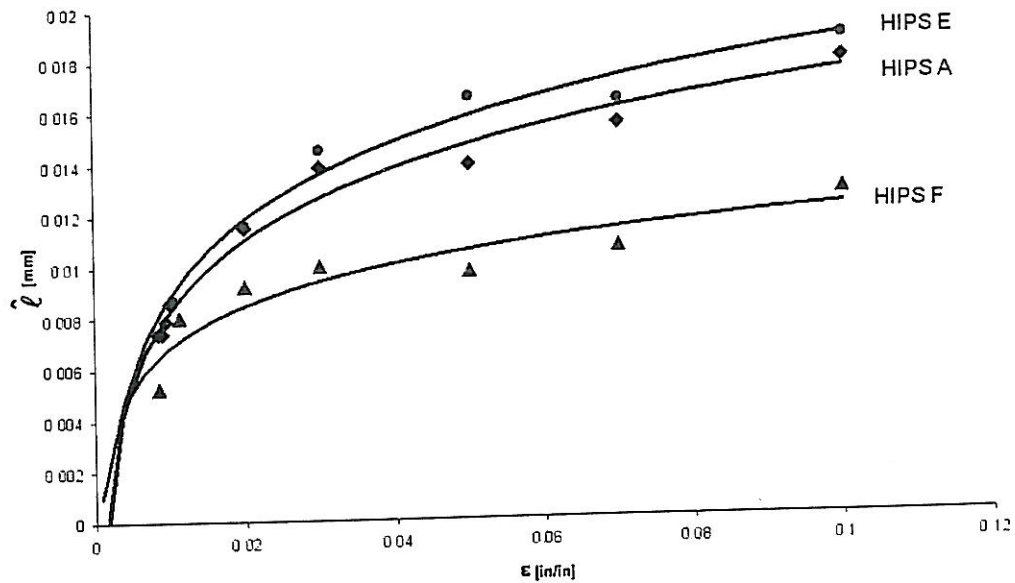


Figure 9.3.8 : Variation of Characteristic Craze Length, $\hat{\ell}$, as a Function of Applied Strain in HIPS. [T= RT ; $\dot{\epsilon}$ = 0.00007 in/in/sec]

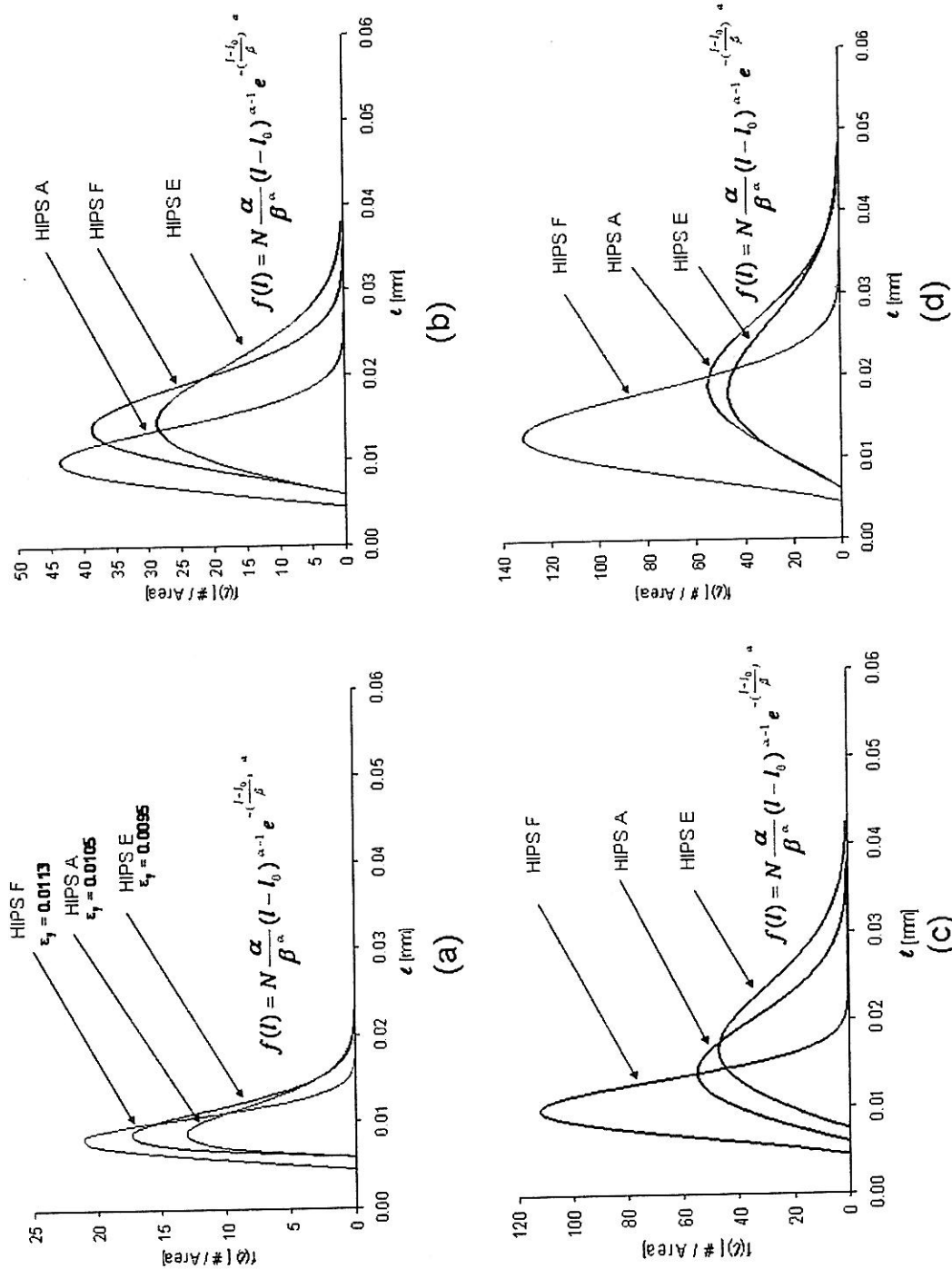


Figure 9.3.9: Craze Length Density Functions, $f(l)$, in HIPS at Different Strains: a) $\epsilon = \epsilon_y$, b) $\epsilon = 0.03$, c) $\epsilon = 0.05$, d) $\epsilon = 0.1$.
 [T= RT; $\dot{\epsilon} = 0.00007 \text{ in/in/sec}$]

9.3.2 Density and Cumulative Functions of Craze Orientation

In Fig. 9.3.10, experimental data are given for the cumulative distribution functions, $G(\theta)$, for the cases with $\varepsilon = 0.0095, 0.03, 0.05$ and 0.1 for HIPS A. In these graphs, the vertical axis, $G(\theta)$, represents the total number of crazes per unit area and the horizontal axis represents the craze orientation. The $G(\theta)$ curves increased with deformation (Fig. 9.3.10), implying that the number of crazes increased with the applied strain. The cumulative distribution functions of craze orientation at different strain levels are shown in Fig. 9.3.11. The results of HIPS E and HIPS F are also included in the figure.

Although craze density and lengths increased with the applied strain, orientations of the crazes were almost unchanged. The 90-95% of the crazes had orientations in the angle range of -35° and 35° . The $G(\theta)$ became saturated beyond 35° implying that the crazes had preferred orientations. The experimental data follow the standard Gaussian distribution function as

$$G(\theta) = \frac{N}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\theta} e^{-\frac{(\xi-a)^2}{2\sigma^2}} d\xi, \quad (9.3)$$

where N is the total number of crazes observed on the test specimen surface; a is the mean; and σ is the standard deviation.

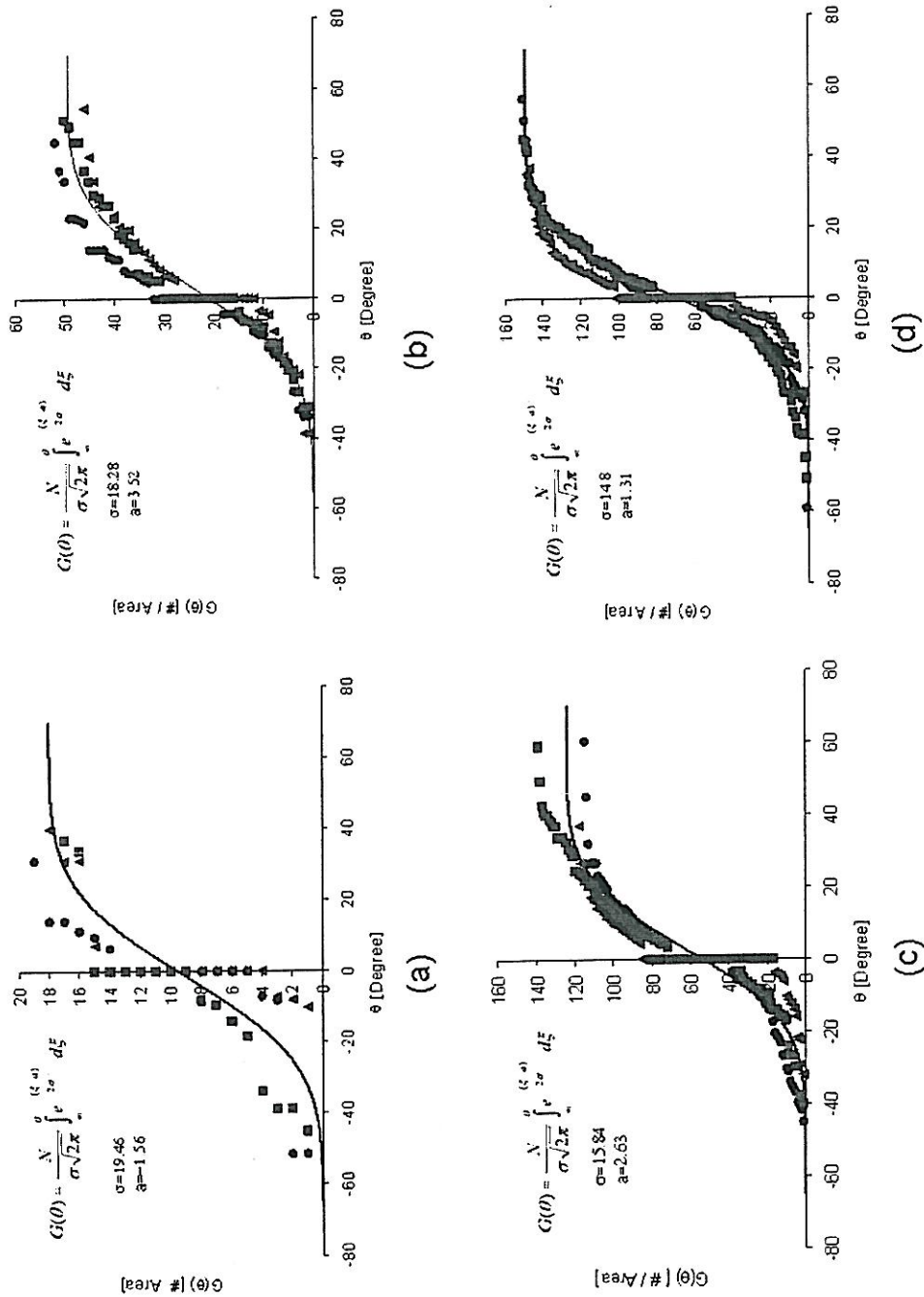


Figure 9.3.10: Cumulative Distribution Function, $G(\theta)$, versus Craze Orientation in HIPS [HIPS A] at Different Strains: a) $\epsilon = 0.0095$, b) $\epsilon = 0.02$, c) $\epsilon = 0.05$, d) $\epsilon = 0.1$. [T = RT; $\dot{\epsilon} = 0.00007 \text{ in/in/sec}$]

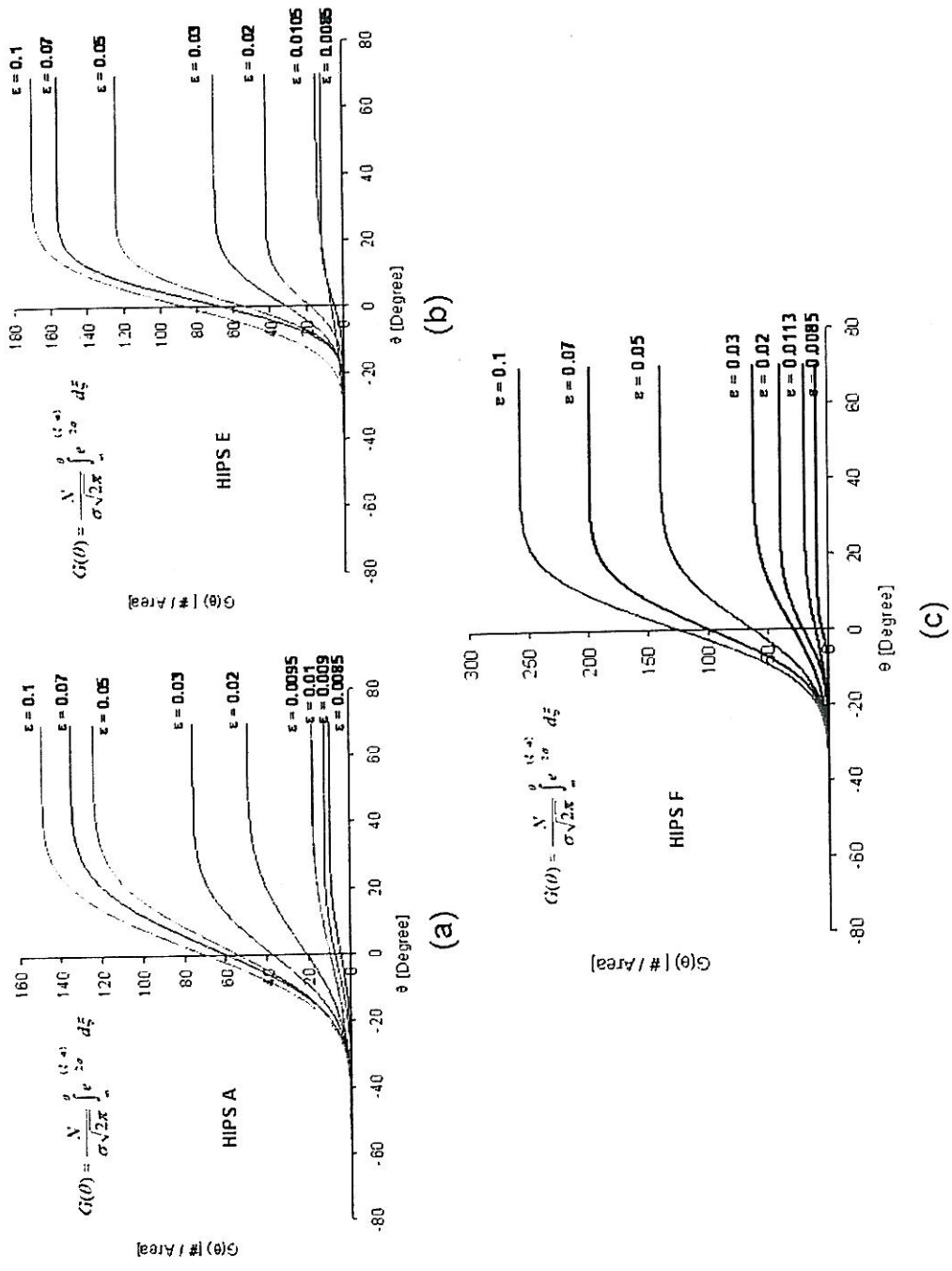


Figure 9.3.11: Cumulative Distribution Function, $G(\theta)$, versus Craze Orientation in HIPS at Different Strains: a)HIPS A, b)HIPS E, c) HIPS F.[T= RT; $\dot{\epsilon} = 0.00007in/in/sec$]

By differentiating the craze orientation distribution function, $G(\theta)$, with respect to θ the craze orientation density function, $g(\theta)$, has the following form,

$$g(\theta) = \frac{N}{\sqrt{2\pi}\sigma} e^{-(\theta-\alpha)^2 / 2\sigma^2} . \quad (9.4)$$

For the cases of $\epsilon = 0.0095, 0.02, 0.05$ and 0.1 , experimental data for the density distribution functions, $g(\theta)$, are given in Fig. 9.3.12. In the figures, symmetry of the distribution function, $g(\theta)$, about $\theta=0^\circ$ can be seen.

The craze orientation density functions at different strain levels are given in Fig. 9.3.13 and the results for HIPS E and HIPS F are also included.

The characteristic craze orientation, $\hat{\theta}$, which is the angle with the highest appearing frequency, can be extracted from the experimental data at a given strain level. Variation of $\hat{\theta}$ with the strain is shown in Fig. 9.3.14, and the results for HIPS E and HIPS F are also shown. A constant trend for all the HIPS grades can be seen from the figure: the characteristic craze orientation did not change with the applied strain and was about 0° (i.e., perpendicular to the loading direction). The initially observed θ scattering (around 2° for HIPS A) might be a result of surface and material inhomogeneity causing microscopic stress variation, in return, a deviation from 0° . The scattering diminished as the load increased, and crazes grew normal to principal stress direction.

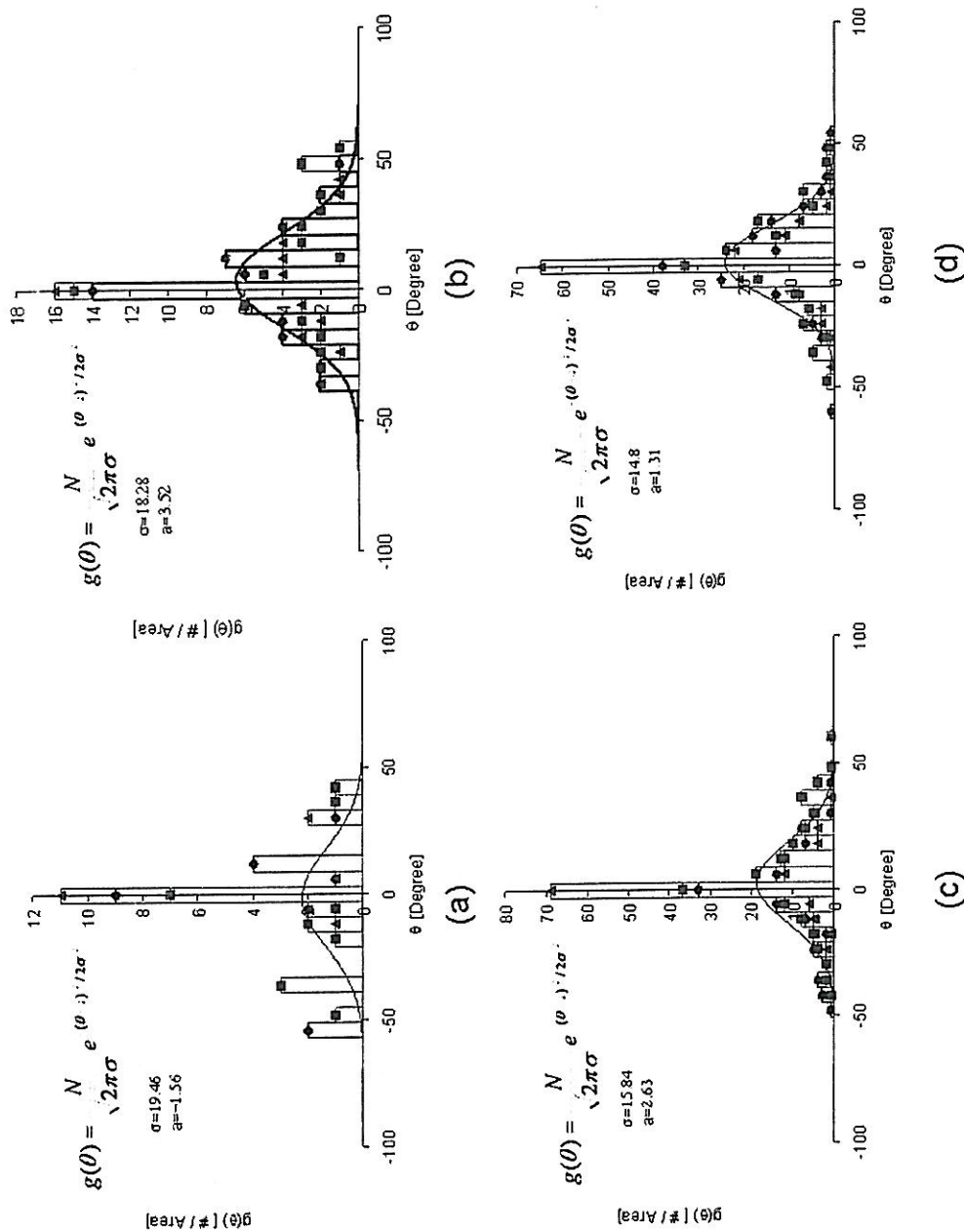


Figure 9.3.12: Craze Orientation Density Function, $g(\theta)$, vs. Craze Orientation in HIPS [HIPS A] at Various Strains: a) $\epsilon = 0.0095$, b) $\epsilon = 0.02$, c) $\epsilon = 0.05$, d) $\epsilon = 0.1$. [T = RT; $\dot{\epsilon} = 0.00007$ in / in / sec]

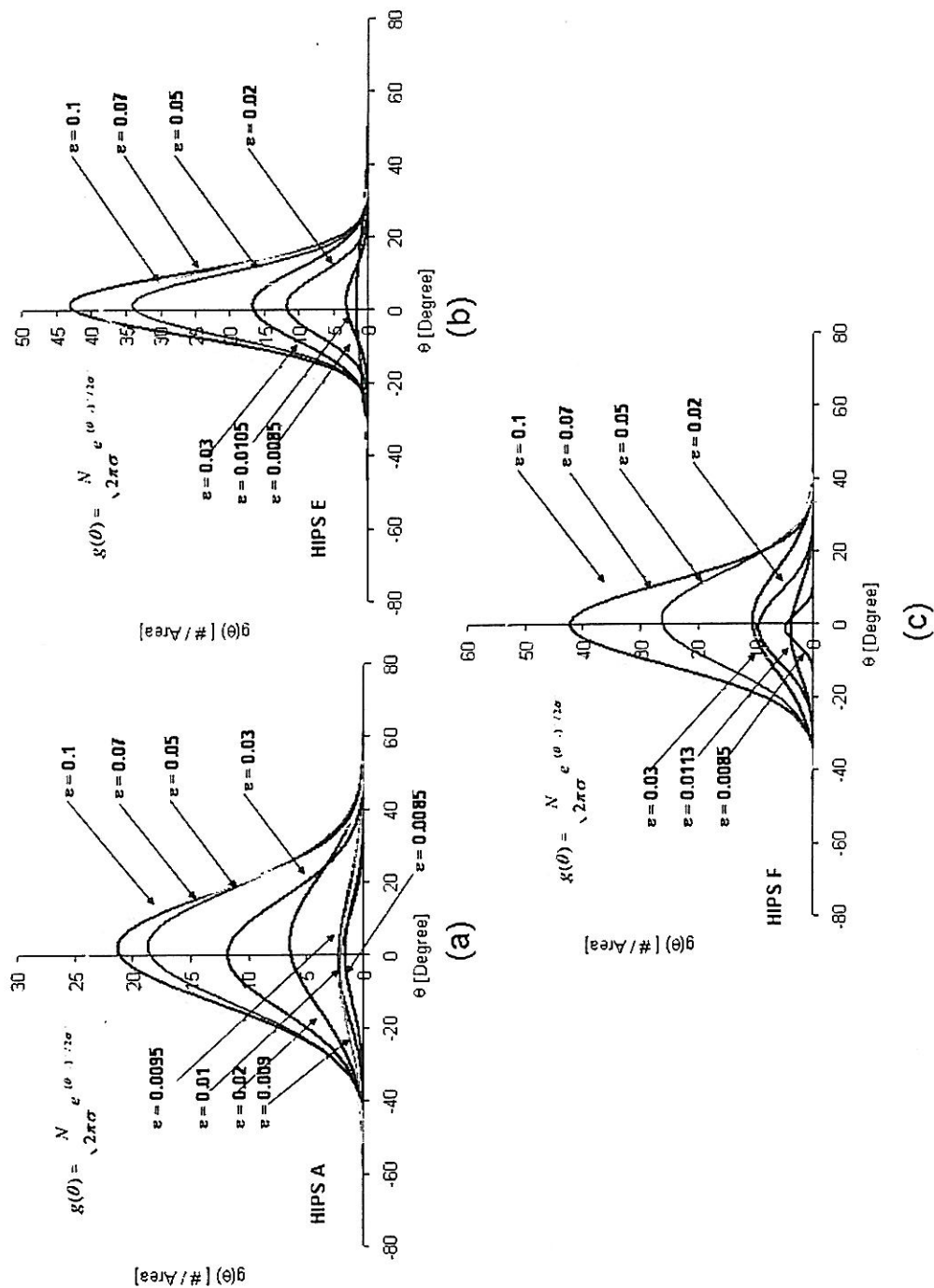


Figure 9.3.13: Craze Orientation Density Distribution Function, $g(\theta)$, in HIPS at Different Strains: a)HIPS A, b)HIPS E, c) HIPS F. [T= RT; $\dot{\epsilon} = 0.00007 \text{ in / in / sec}$]

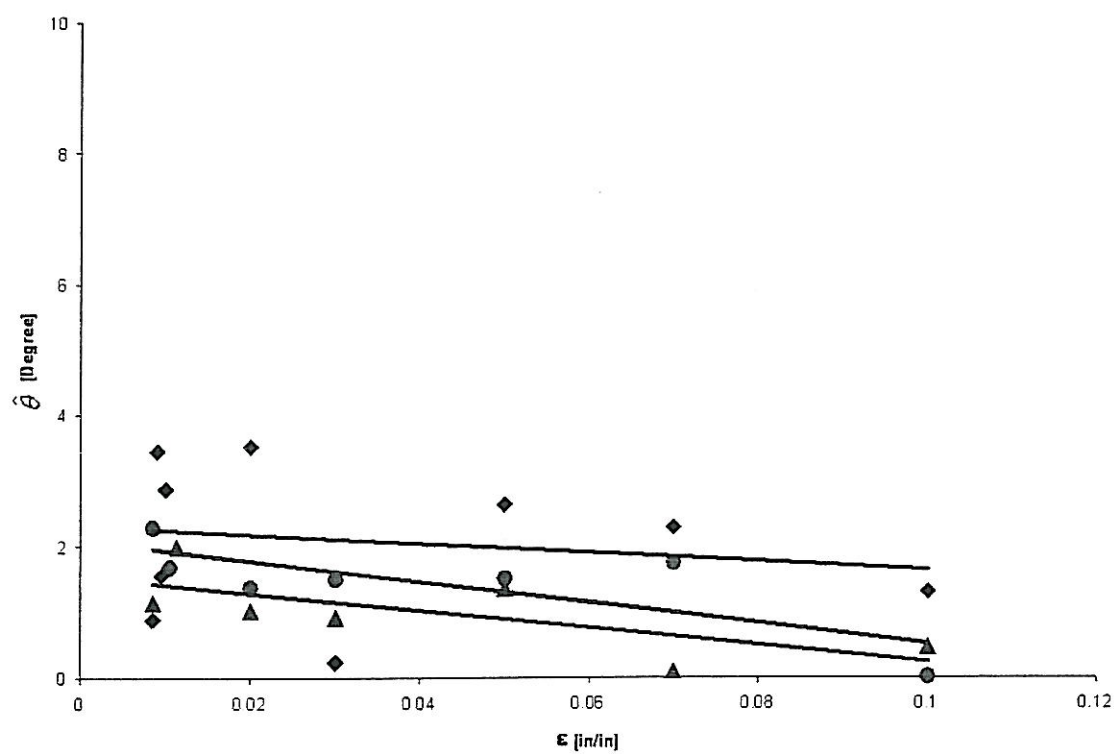


Figure 9.3.14: Variation of Characteristic Angle, $\hat{\theta}$, as a Function of the Applied Strain.
 [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

9.4 Craze Damage Development and Associated CDM Parameters

In this section, the results of experimental and theoretical study on damage mechanics are presented. Mechanical property degradation with crazing is reported. Craze damage accumulation and evolution in HIPS is addressed. Associated continuum damage mechanics parameters are determined. Possible correlations between microscopic (i.e., microstructural craze damage parameters) and resulting macroscopic (i.e., CDM Variables) craze damage are investigated.

Even though experiments and calculations were carried out for all six HIPS polymers, the general discussion given in this Section is limited to HIPS A, HIPS E and HIPS F. Damage mechanics experiments conducted for the grades are shown in Fig. 9.4.1.

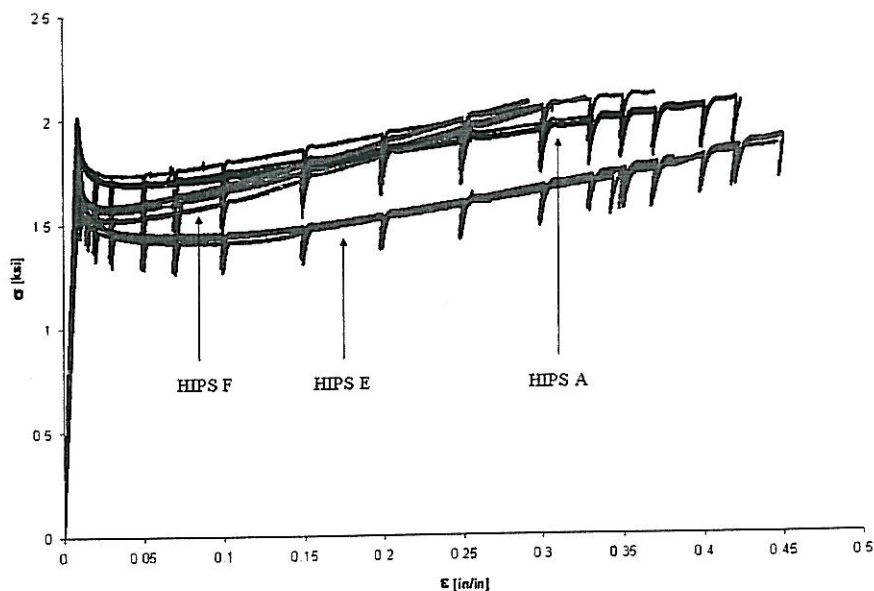


Figure 9.4.1: Stress-strain Behavior of HIPS with Loading-unloading-reloading Interruptions. [T=RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

9.4.1 Degradation of Mechanical Properties with Crazing

The microscopic craze damage has a preferred orientation distribution, as mentioned in the preceding sections. This leads to damaged-induced orthotropy (see Section 7.3) of material properties. In this part, degradations of in-plane material constants are reported. The Young's modulus change along the loading direction was recorded during damage mechanics experiments. Degradations of the other in-plane properties, E_2 , ν_{12} , ν_{21} , were calculated analytically, as discussed in Sec. 7.3. In Figs. 9.4.2 and 9.4.3, Young's moduli and Poisson's ratio change with the craze damage in HIPS are shown. In Fig. 9.4.2, significant material softening in the loading direction is obvious. For example, at a 35% strain, a total stiffness reduction of about 80% from the reference value was found prior to failure. However, the predicted results revealed no change in E_{22} with the craze formation and growth implying that there was no softening in the transverse direction. Supportive numerical findings and experimental observations are reported [79-81, 126] in the literature.

A similar trend was predicted in Poisson's ratio change with craze development. Major Poisson's ratio, ν_{12} , degraded with the craze damage, while minor Poisson's ratio, ν_{21} , was found unchanged (Fig. 9.4.3).

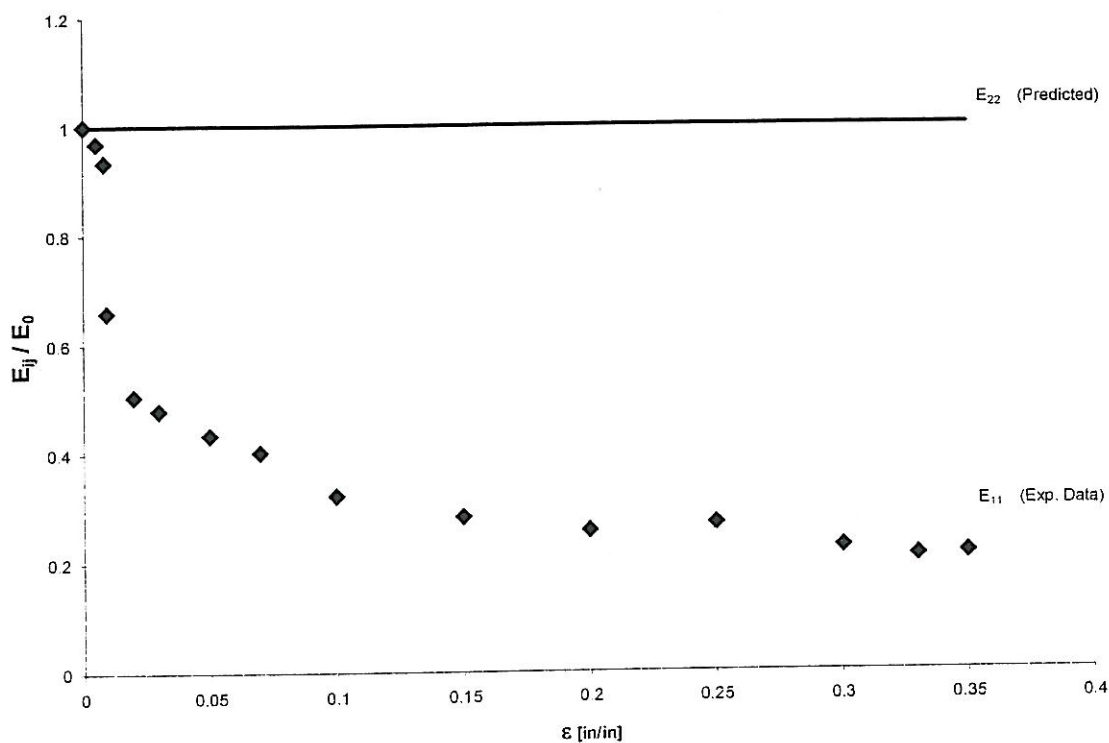


Figure 9.4.2: Young's Moduli Degradation with Applied Strain.
[HIPS A, $T = RT$; $\dot{\epsilon} = 0.00007$ in/in/sec]

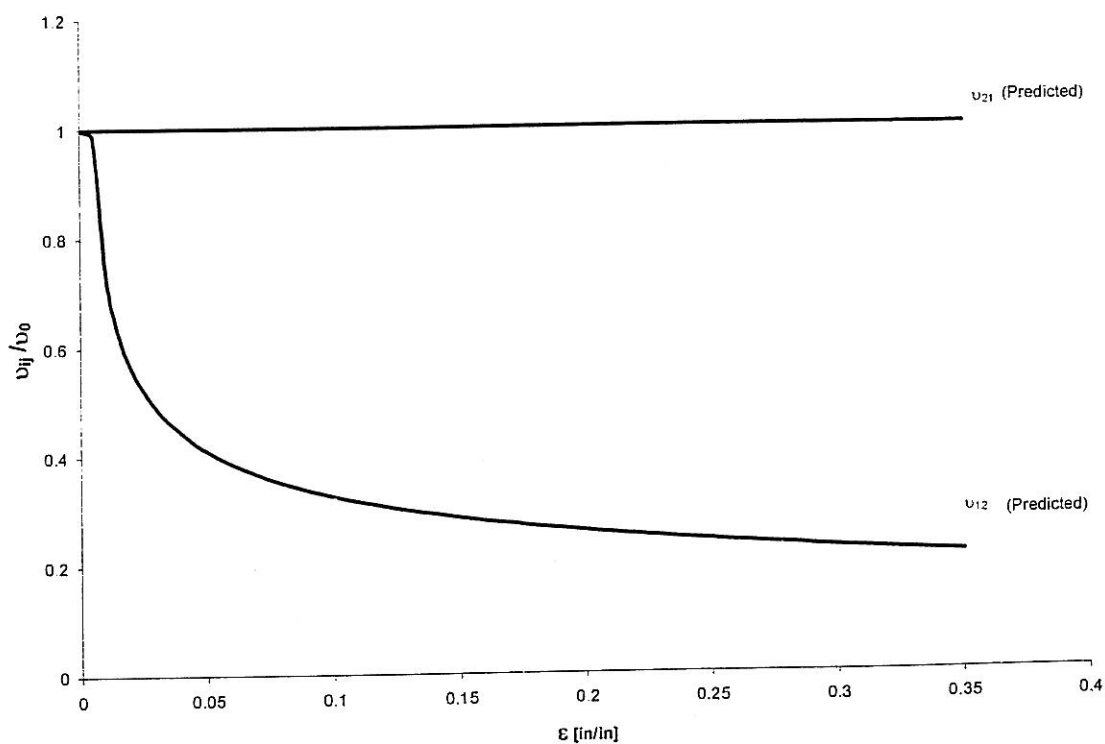


Figure 9.4.3: Poisson's Ratio Degradation with Applied Strain.
[HIPS A, $T = RT$; $\dot{\epsilon} = 0.00007$ in/in/sec]

9.4.2 Craze Damage Accumulation and Evolution

In Fig. 9.4.4, craze damage development in HIPS under increasing strain in air at room temperature is shown. The craze damage, D_{11} , increased rapidly over the first 2% strain then kept increasing slowly to 25% strain. At a later stage of deformation, damage accumulation rate started increasing again until the HIPS failed at the end.

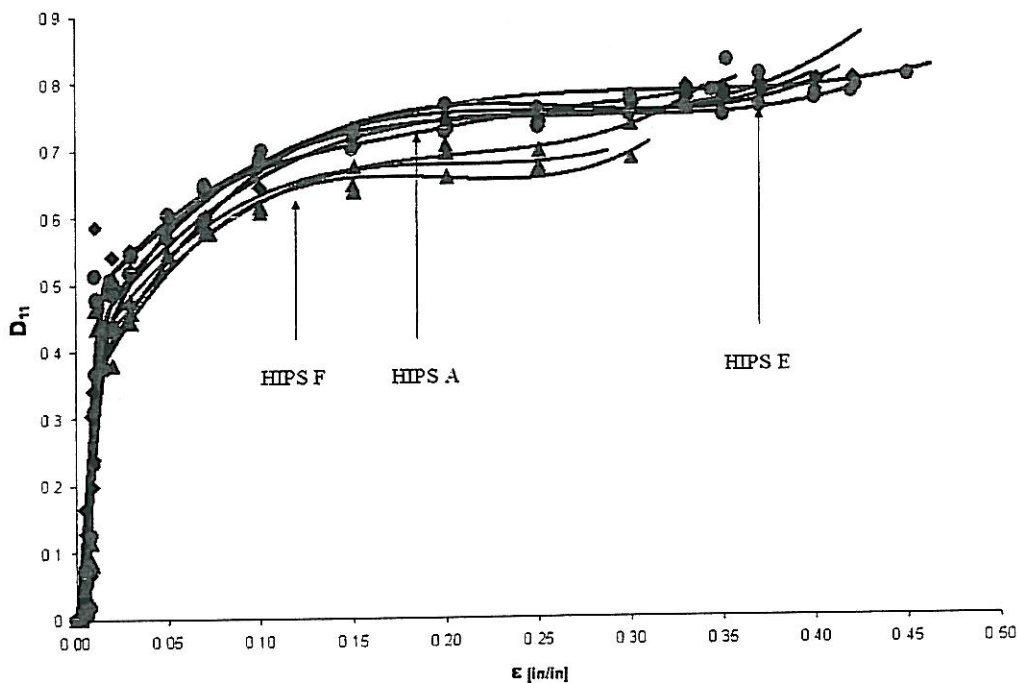


Figure 9.4.4: Craze Damage Development in HIPS Under Increasing Strain.
[T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

The severity of craze damage is related to its microstructure parameters (i.e., craze density, size, orientation and their distributions). The craze density is the number of crazes per unit volume. Its formulation is given in Chap. 5. In the study, the craze population, size and orientation data were acquired up to 10 % strain, and some of the

results have already been reported in Sec. 10.3. In this part, possible correlations between the craze damage microstructure parameters and CDM variables are reported.

In Figs. 9.4.5 and 9.4.6, variation of craze damage with craze density, λ , and characteristic craze length, $\hat{\ell}$, up to 10% strain are shown, respectively. Damage accumulation with craze density was not linear and increased slowly. However, the craze damage increased somewhat linearly with characteristic craze length.

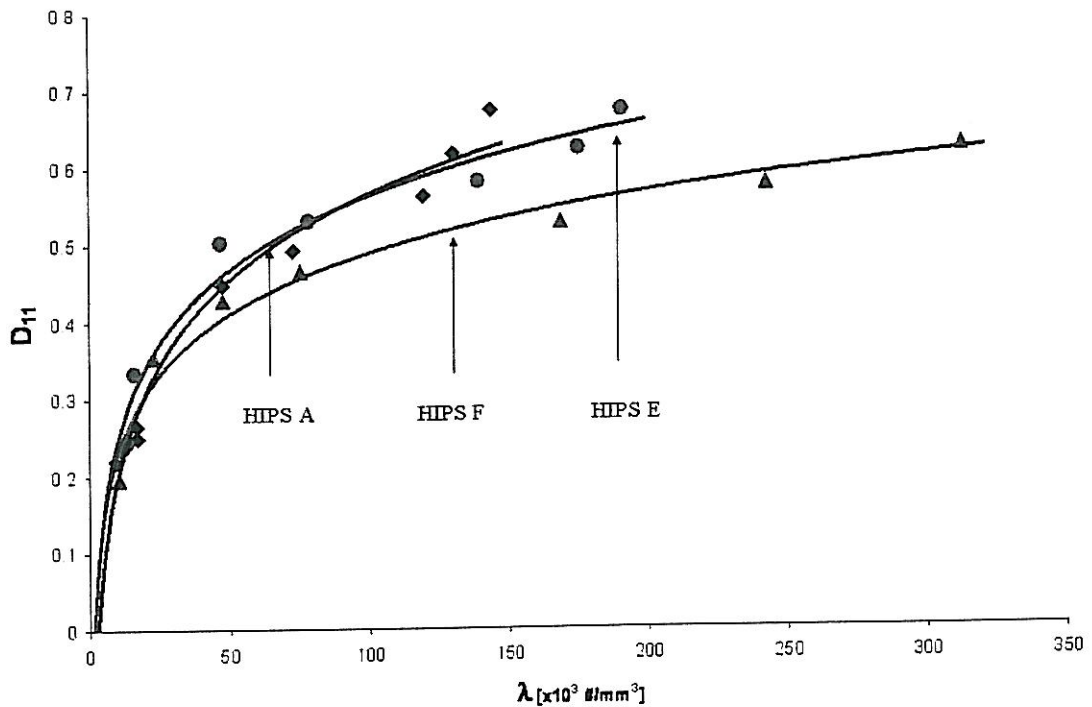


Figure 9.4.5: Craze Damage Accumulation with Craze Density.
 [T= RT; $\dot{\epsilon}$ = 0.00007 in/in/sec]

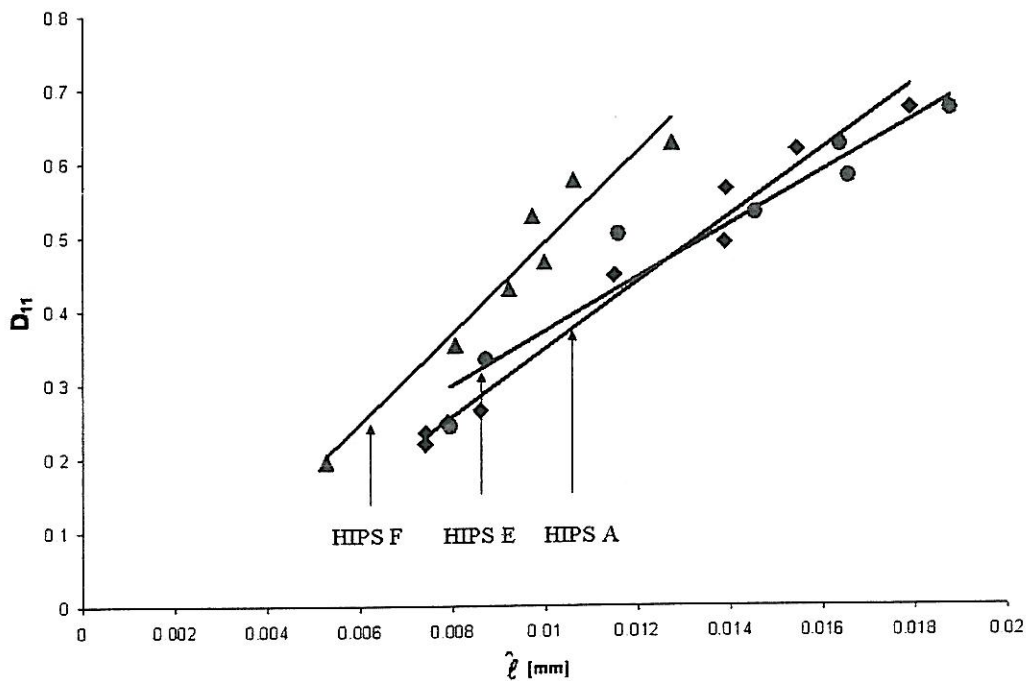


Figure 9.4.6: Craze Damage Accumulation with Characteristic Craze Length.
 [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

When all three HIPS grades were considered (Fig.9.4.4), at any given strain, less damage was developed in HIPS F. Fracture of HIPS A and HIPS E did not occur until D_{II} approached 90%. For HIPS F, fracture occurred at D_{II} less than 75%. Apparently, the HIPS with a higher craze density but shorter craze sizes was more resistant to craze damage accumulation.

9.4.3 Thermodynamic Driving Force for Craze Damage Development

Thermodynamic driving force, $-Y_{II}$, corresponds to the energy released during craze growth as a result of craze formation. The thermodynamic driving force for craze

development in HIPS under an increasing strain at room temperature is shown in Fig. 9.4.7. The damage strain energy release rate increased continually with the applied loading. As expected, relationship was not linear because of the nature of the Eq. C.3 (see Appendix C). Thermodynamic driving force may be correlated to the applied stress and the corresponding damage state. It is, indeed, a quadratic function of the applied stress (Sec. 7.3.3). In Fig. 9.4.7, at any given strain level, the magnitude of strain energy release rate for HIPS A was found to be larger compared to HIPS E and HIPS F.

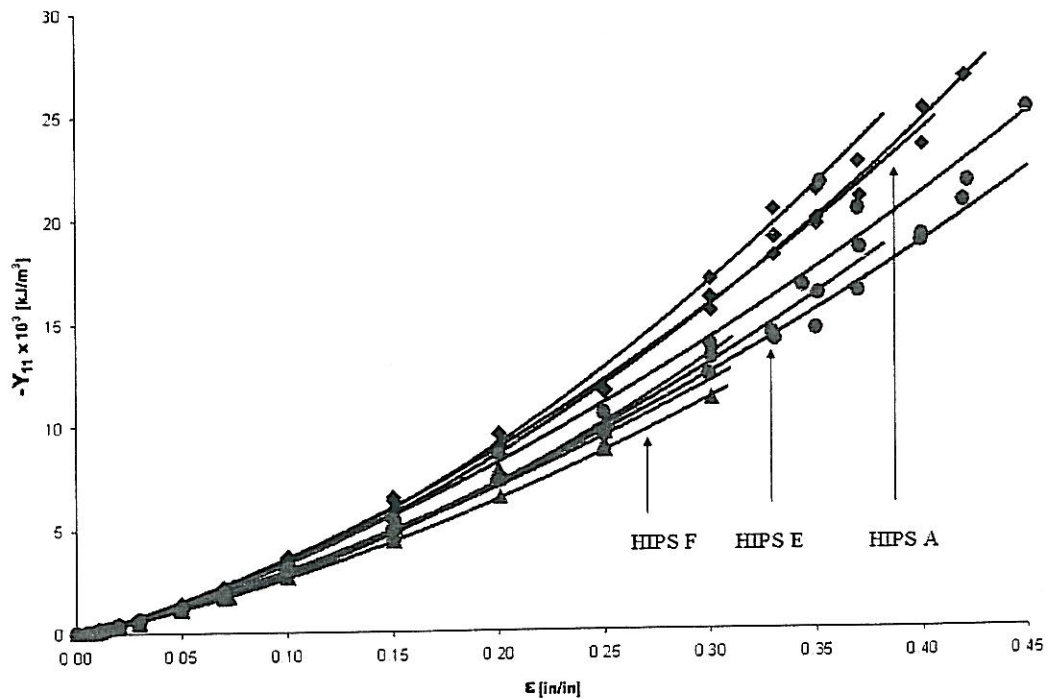


Figure 9.4.7: Thermodynamic Driving Force for Craze Development in HIPS under Increasing Strain. [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

In Fig. 9.4.8, the relationship was determined for HIPS between craze damage and the thermodynamic driving force. The craze damage increased quickly with increasing thermodynamic force.

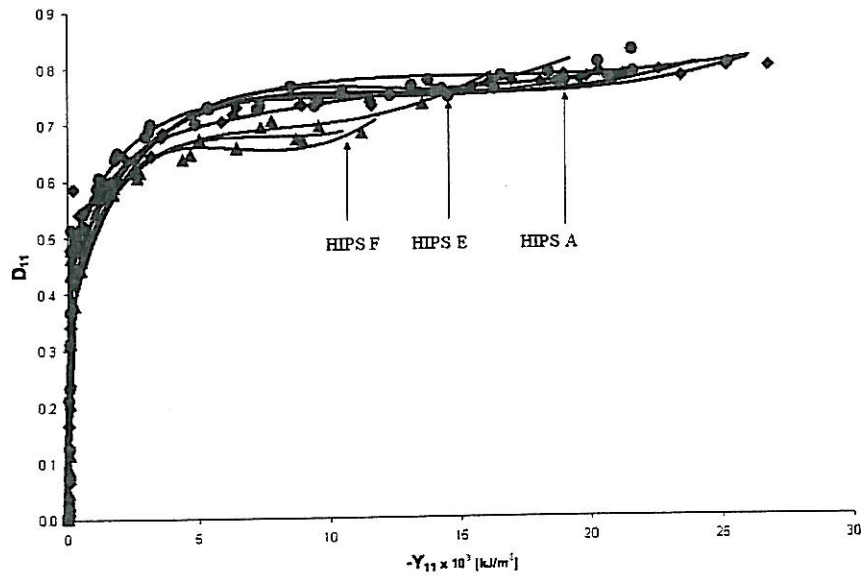


Figure 9.4.8: Craze Damage Developments in HIPS under Increasing Thermodynamic Driving Force. [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

In Figs. 9.4.9 and 9.4.10, craze density, λ , and the characteristic craze length, $\hat{\ell}$, change are correlated with the thermodynamic driving force.

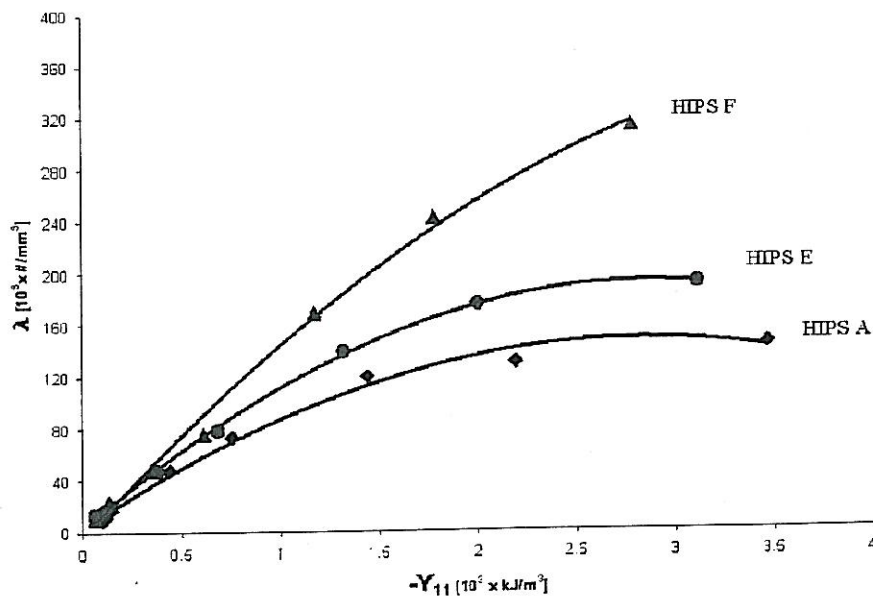


Figure 9.4.9: Craze Density as a Function of Thermodynamic Driving Force. [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

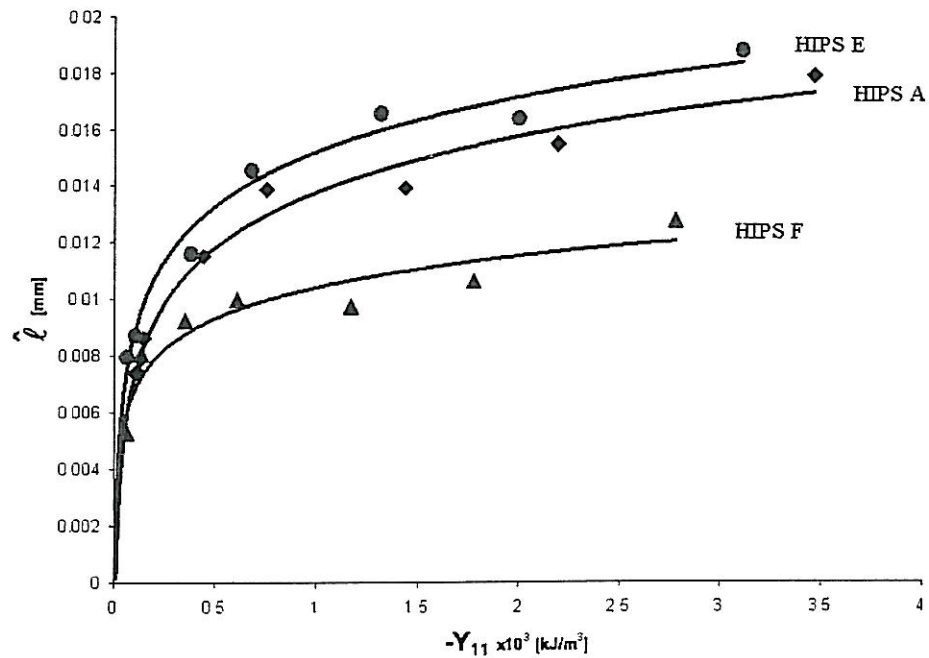


Figure 9.4.10: Characteristic Craze Length as a Function of Thermodynamic Driving Force. [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

As can be seen from the figures, the values of craze density and characteristic craze length both increased with an increasing thermodynamic driving force.

9.4.4 Craze Damage Evolution Rate

Craze damage evolution gives physical processes of craze damage development. The rate of change of craze damage may be evaluated from the mechanical property degradation data obtained in the damage mechanics experiments. The craze damage evolution of the HIPS was determined in the study from the damage accumulation results. In Figs. 9.4.11 and 10.9.12, craze damage evolution in HIPS is given. The results show

that the craze damage rate changed with the applied loading in a complex manner. The craze damage rate increased sharply and reached its peak value around 1% strain which is the limit of thermodynamic reversible deformation. The craze damage rate decreased immediately with the material hardening with subsequent slow down. The craze fibrils in the loading direction might have provided additional load carrying and material resistance.

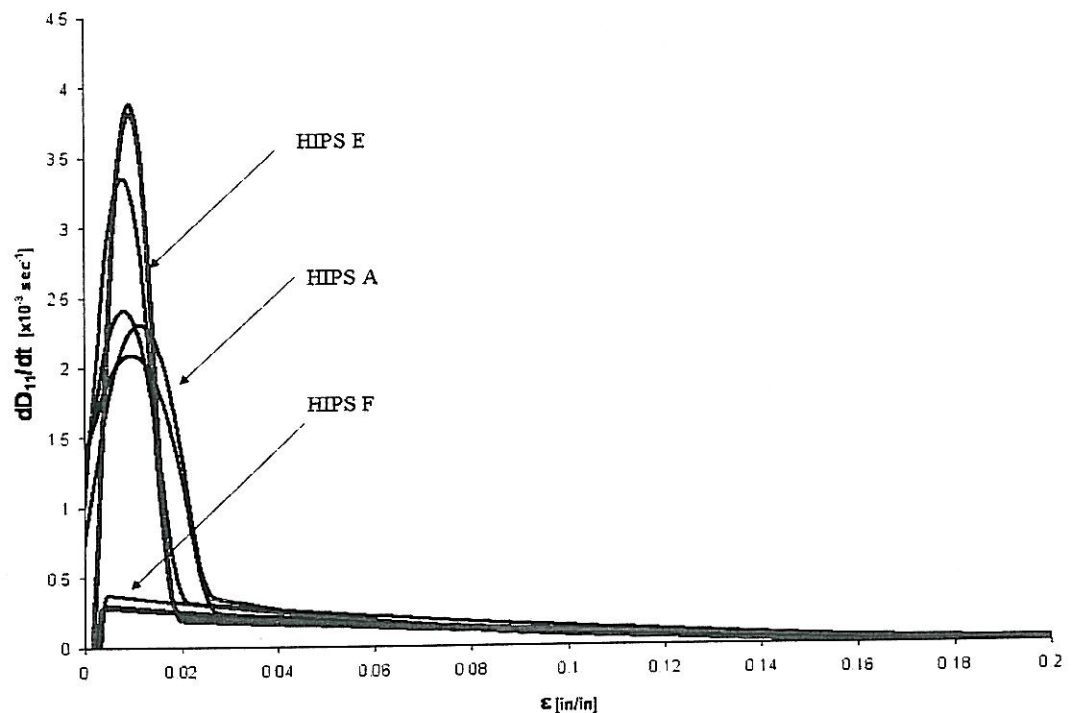


Figure 9.4.11: Craze Damage Rate, $\dot{D}_{11}$, in HIPS under Increasing Strain.

[T= RT; $\dot{\epsilon} = 0.00007 \text{ in/in/sec}$]

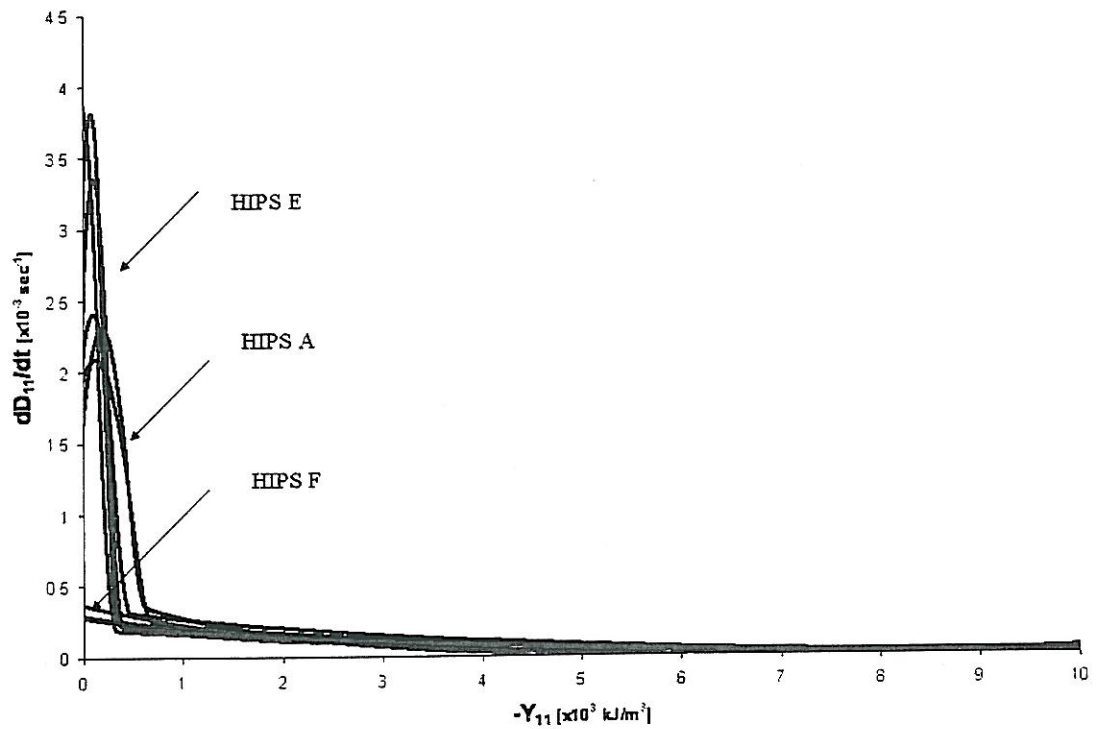


Figure 9.4.12: Relationship Between Craze Damage Rate in HIPS and Thermodynamic Driving Force. [T= RT ; $\dot{\epsilon}$ = 0.00007 in/in/sec]

In Figs. 9.4.13 and 9.4.14, the craze density change and craze growth rate are shown. In the figures, the decreases in the rate of formation of new crazes and their growth are obvious. The craze damage rate characteristics for all grades were similar except at the early stage of deformation, where higher rates were observed for HIPS E.

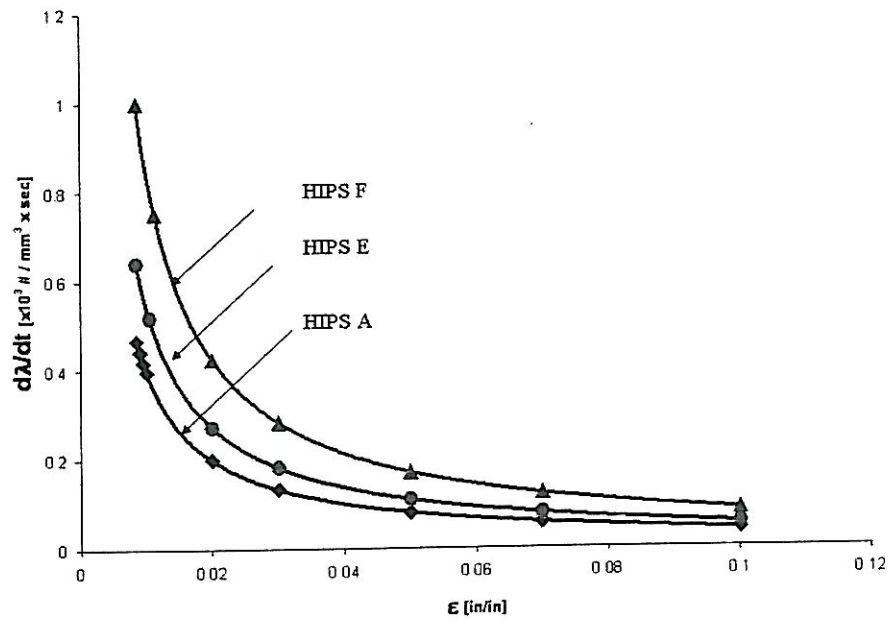


Figure 9.4.13: The Rate Change of Craze Density in HIPS Subjected to Increasing Strain. [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

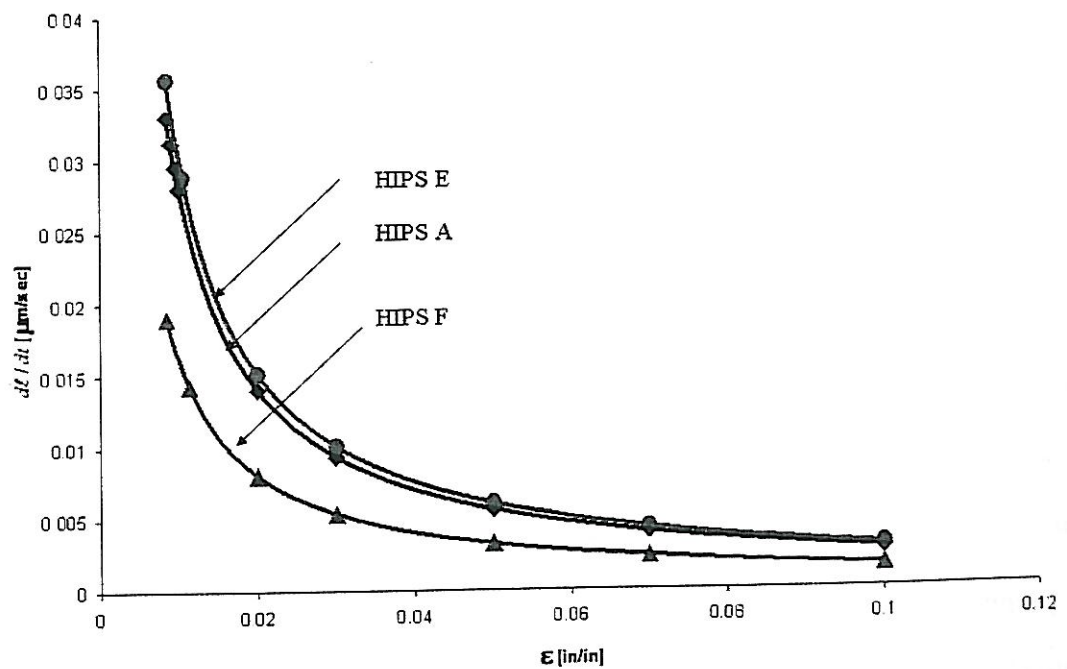


Figure 9.4.14: Craze Growth Rate versus Strain. [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

9.5 Effect of Microstructure on Craze Damage

Mechanical properties of HIPS depend on the microstructure of the HIPS. Controlling the volume fraction, properties, size and dispersion of the second phase in the HIPS polymer are critical to achieve a desired HIPS microstructure. The effects of particle size and distribution on craze damage in the HIPS are studied and reported in this section. Four HIPS grades were investigated comparatively. Among the cases studied, two HIPS grades had similar particle sizes but with different dispersions, and other two had similar particle dispersions but with different sizes. The statistical nature of craze formation and evolution, as well as craze damage and its evolution, under uniaxial loading were evaluated. The relationships between microscopic statistical features and continuum damage mechanics results for the HIPS were addressed.

9.5.1 Effect of Rubber Particle Size

Mechanical properties of rubber-toughened polymers are recognized to be affected by the size of the second-phase particles. For the convenience of the study, the amount of occluded particle was kept fixed, the effect of rubber particle size was studied here. For example, the number of reinforcing particles increased, when the particle size decreased; thereby more stress concentration sites for craze formation were generated.

In this part, results for the two HIPS grades, namely HIPS C and HIPS D, with similar particle size distributions but different sizes are presented. A summary of chemical compositions and selected mechanical properties of the HIPS polymers is given

in Tables 4.1.1 and 4.1.2, respectively. The microstructures of the polymers are shown in Fig. 4.1.1 and corresponding particle size distributions can be found in Appendix A (Fig. A3) after Saltykov's correction [59]. In Table A1, statistical parameters of the rubber particle size distributions are also given.

Stress-strain responses of both grades of the HIPS were compared and shown in Fig. 9.5.1. Apparently, the two HIPS polymers were relatively close in terms of their mechanical responses to applied loads. Both of the HIPS grades had similar chemical compositions and microstructures; thus, their mechanical properties were comparable. These experiments were conducted under the same conditions. [Samples were loaded in a strain-rate control mode ($\dot{\epsilon} = 0.00007 \text{ in/in/sec}$) in air at room temperature until failure.]

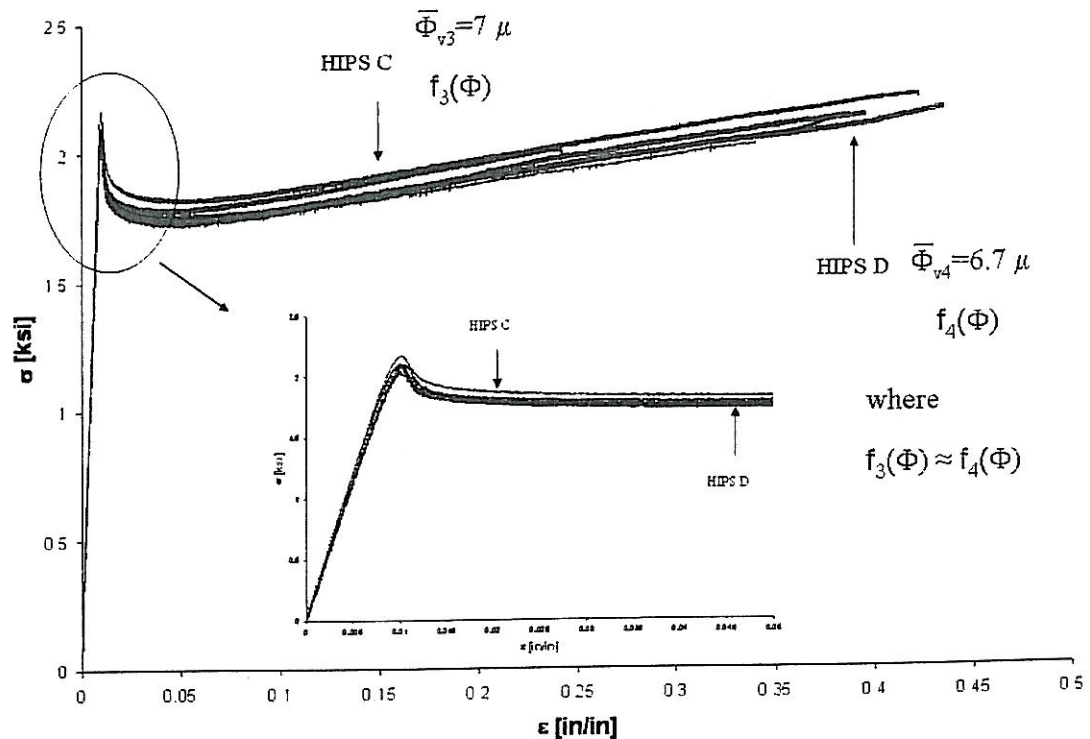


Figure 9.5.1: Stress-strain Behavior of Selected HIPS. [T= RT; $\dot{\epsilon} = 0.00007 \text{ in/in/sec}$]

Microscopic craze features were observed and given in Figs. 9.5.2 and 9.5.3. In Fig. 9.5.2, the craze density, λ , was found to be associated with the applied strain, ε , the damage variable, D_{11} , and the thermodynamic force, $-Y_{11}$: λ increased with ε and $-Y_{11}$. The relationship between the damage variable, D_{11} , and the craze density was found to be nonlinear. At a given strain, the craze density was higher in HIPS C, but the amount of damage in the two HIPS appeared to be close (Fig. 9.5.3). In Figs. 9.5.4 and 9.5.5, Weibull's parameters for craze size distribution functions are determined.

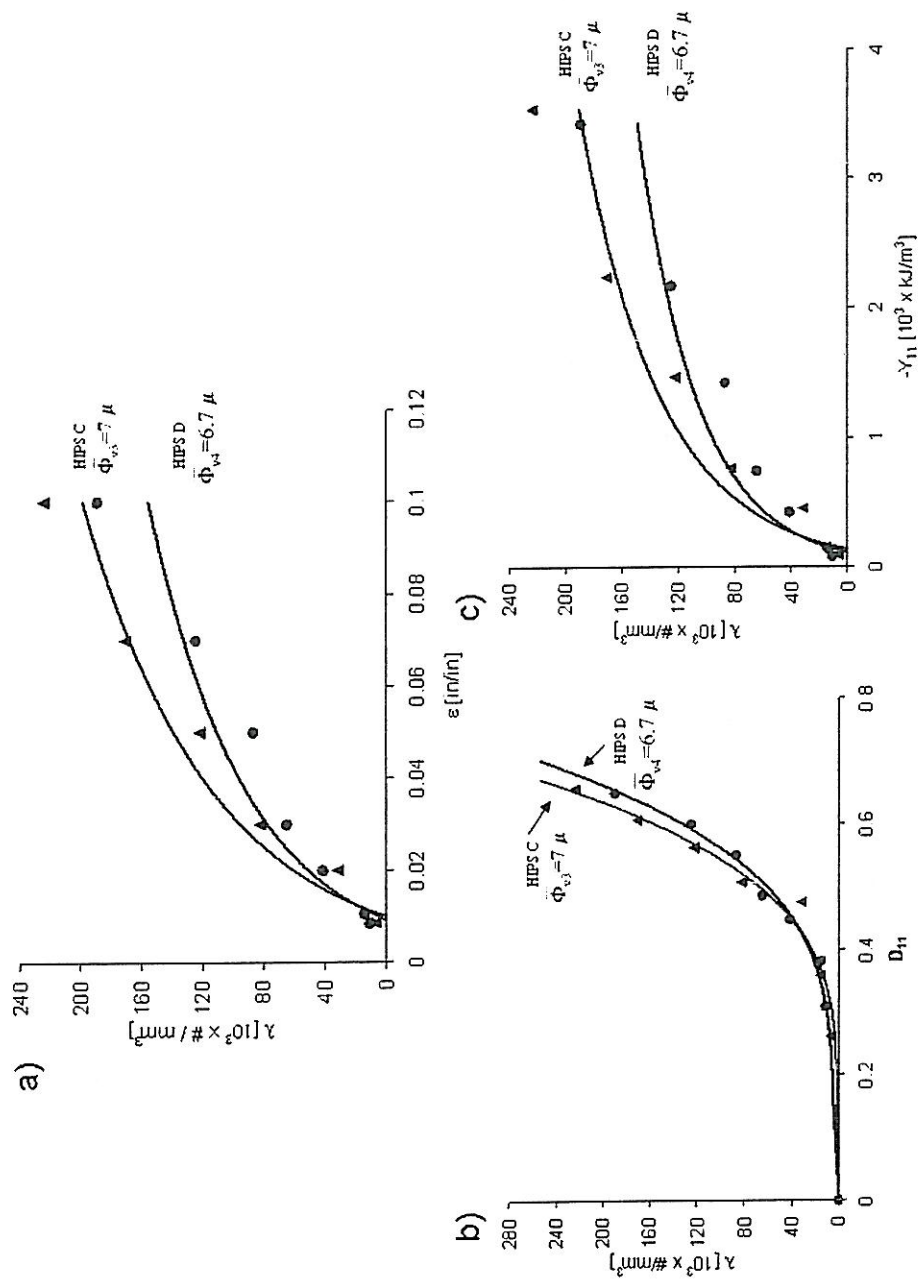


Figure 9.5.2: Craze Density, λ , in HIPS Polymers: a) Under Increasing Strain, b) Relation with Damage, D_{11} , c) Under Thermodynamic Driving Force. [$T = RT$; $\dot{\epsilon} = 0.00007 \text{ in/in/sec}$]

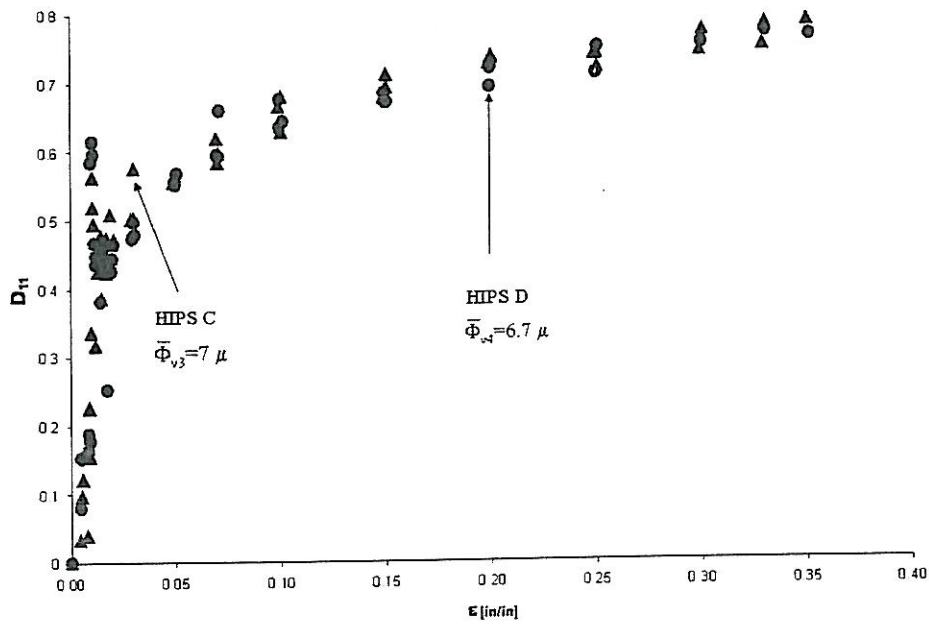


Figure 9.5.3: Craze Damage Developments in HIPS under Applied Strain, ϵ .
[T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

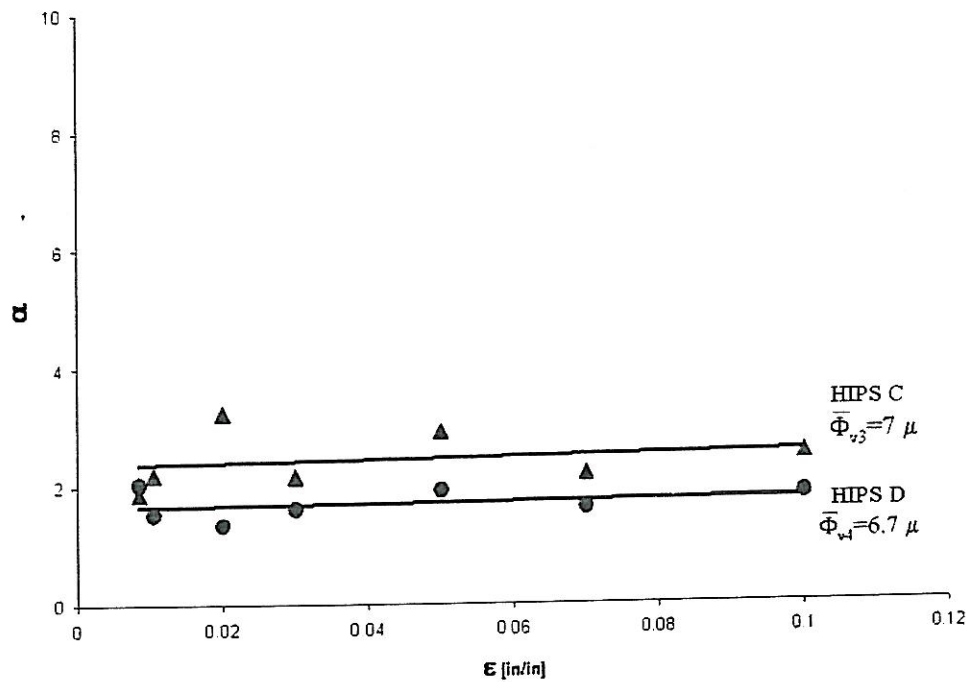


Figure 9.5.4: Weibull's Shape Parameter, α , for Craze Length Statistics in HIPS Polymers. [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

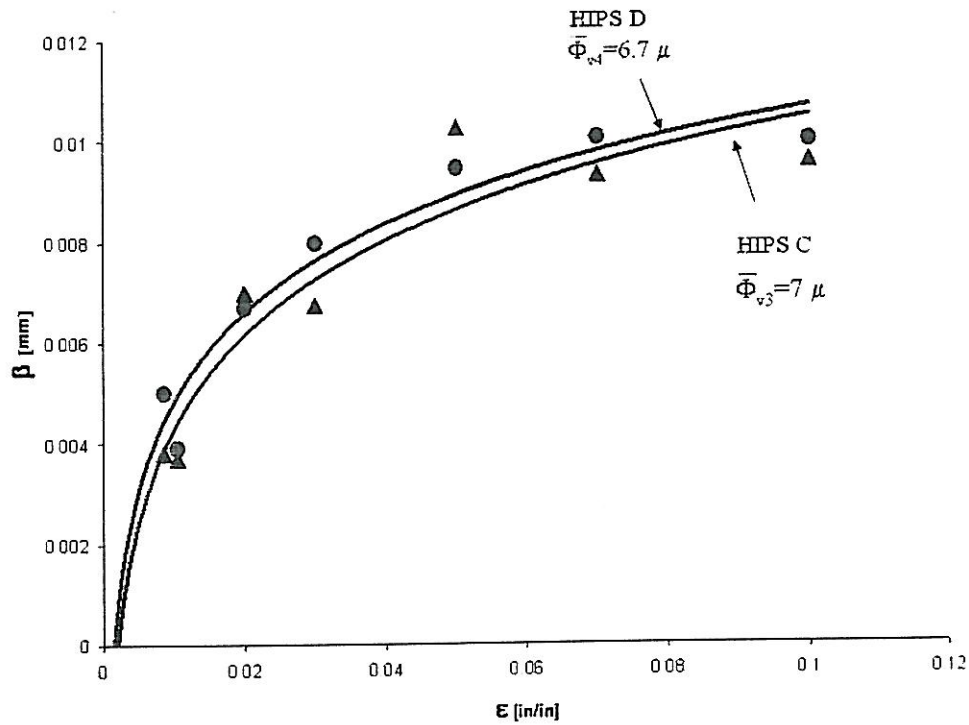


Figure 9.5.5: Weibull's Scaling Parameter, β , for Craze Length Statistics in HIPS Polymers. [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

The HIPS C had slightly lower scaling parameter, β , at a given applied strain. Based on Fig. 9.5.5, a similar distribution of craze size was expected in the HIPS polymers, as shown in Fig. 9.5.6, where the characteristic craze length changed with the applied strain, thermodynamic force, and the resulting damage, D_{II} .

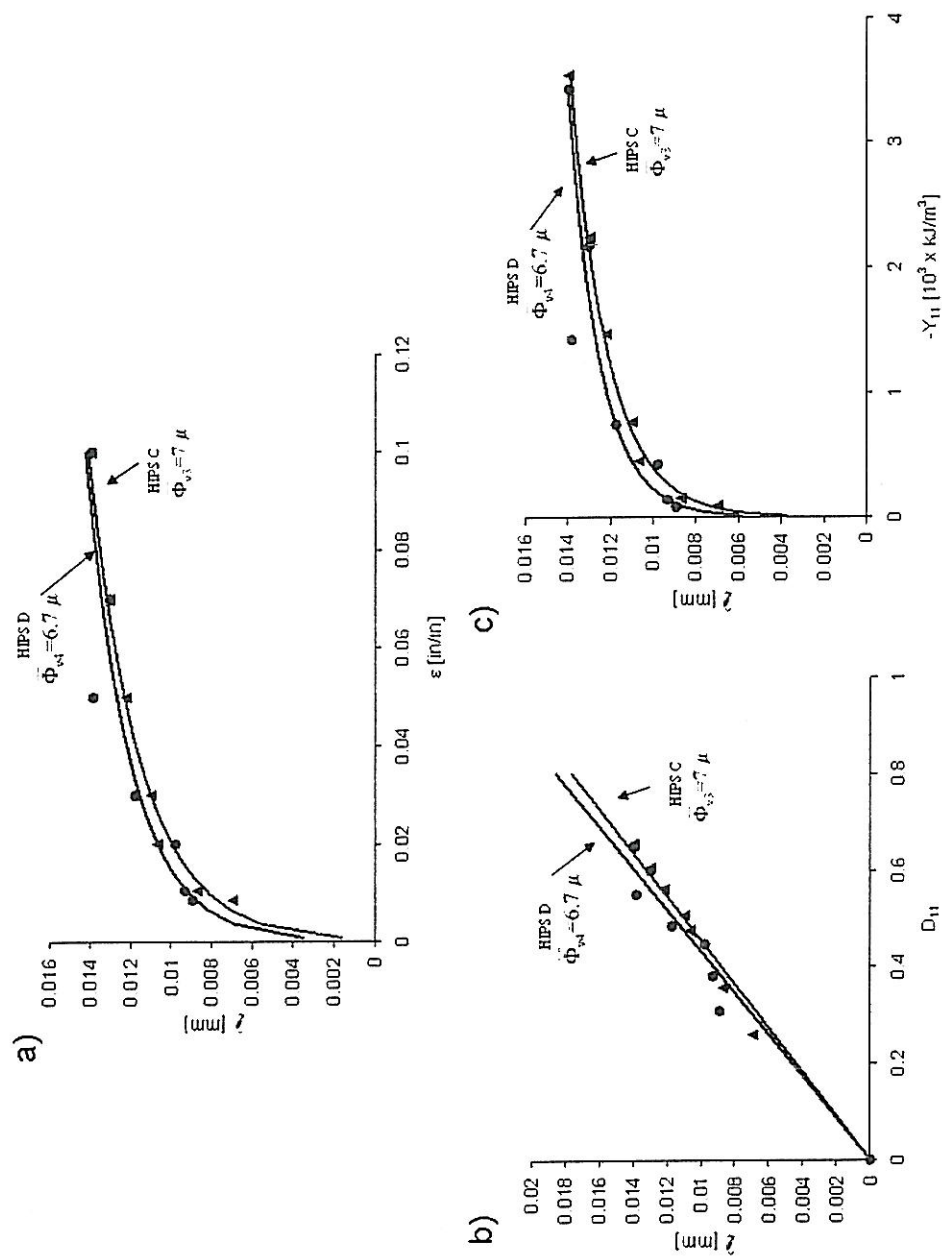


Figure 9.5.6: Characteristic Craze Length in HIPS Polymers: a) Under Increasing Strain, b) Relation with, D_{11} , c) Under Thermodynamic Driving Force. [$T = \text{RT}$; $\dot{\epsilon} = 0.00007 \text{ in/in/sec}$]

9.5.2 Effect of Particle Size Distribution

Occluded particle dispersion is an important factor in toughening the PS polymer. Owing to its inherent complexity, the effect of particle size distribution on toughening is not completely understood. Earlier studies [53, 61] have been conducted mostly on simpler systems like those with a binomial size distribution.

In this section, HIPS polymers with similar average particle sizes but with different size distributions were studied and results are presented. The chemical compositions and mechanical properties for the test grade HIPS, namely HIPS A and HIPS B, are given in Tables 4.1.1 and 4.1.2, respectively. The HIPS material microstructures are presented in Fig. 4.1.1, and the associated particle size distributions can be found in Appendix A (Fig. A2) [with Saltykov's correction[59]]. Also, in Table A1, statistical parameters of the rubber particle size distributions in HIPS are summarized and presented.

In Fig. 9.5.7, stress-strain behavior of the HIPS polymers is shown. Their mechanical properties were close, owing to similar chemical compositions and microstructures. All experiments were conducted in the same conditions. [Samples were loaded in a strain-rate control mode ($\dot{\epsilon} = 0.00007 \text{ in/in/sec}$) in air at room temperature until failure.]

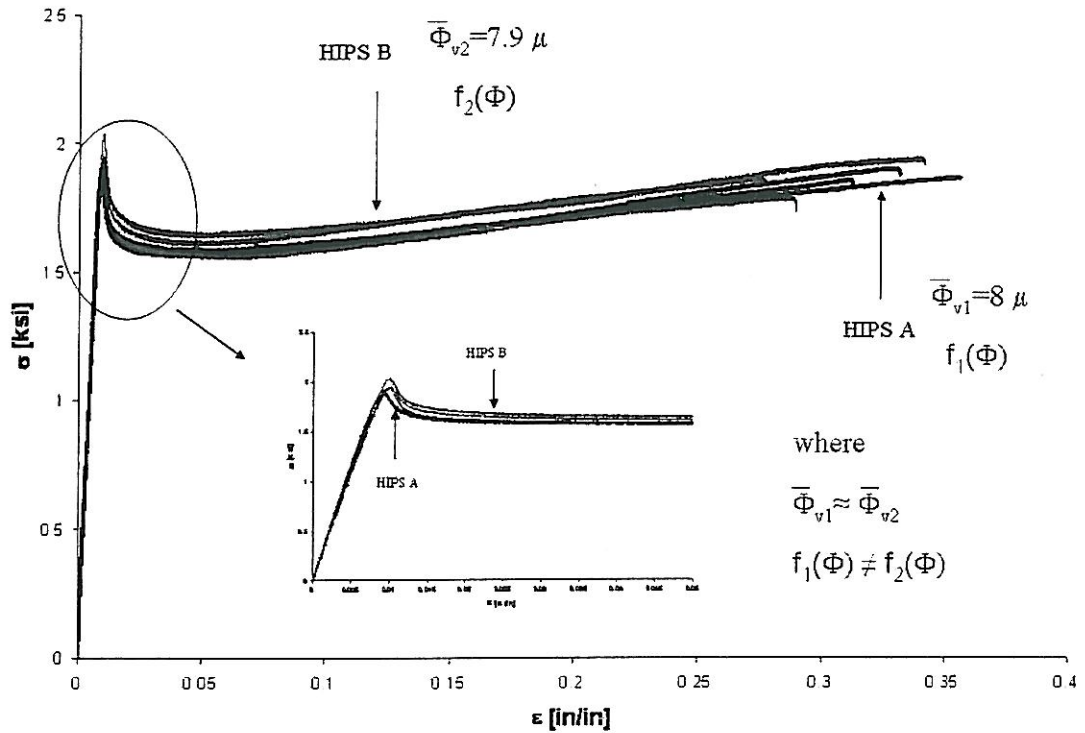


Figure 9.5.7.: Stress-strain Behavior of HIPS Polymers.
 [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

Comparisons of microscopic craze formation and growth characteristics between the two HIPS are given in Figs. 9.5.8 and 9.5.9. Craze density changes with the applied strain, ϵ , damage variable, D_{II} , and thermodynamic force, $-Y_{II}$, are determined shown in Fig. 9.5.8.

As anticipated, the craze density in the HIPS increased with the applied strain and the thermodynamic driving force, but its rate of change decreased. Again, the craze density change with the damage variable, D_{II} , was nonlinear. While a higher craze population was observed for HIPS A, damage developments for both grades were fairly close as shown in Fig. 9.5.9.

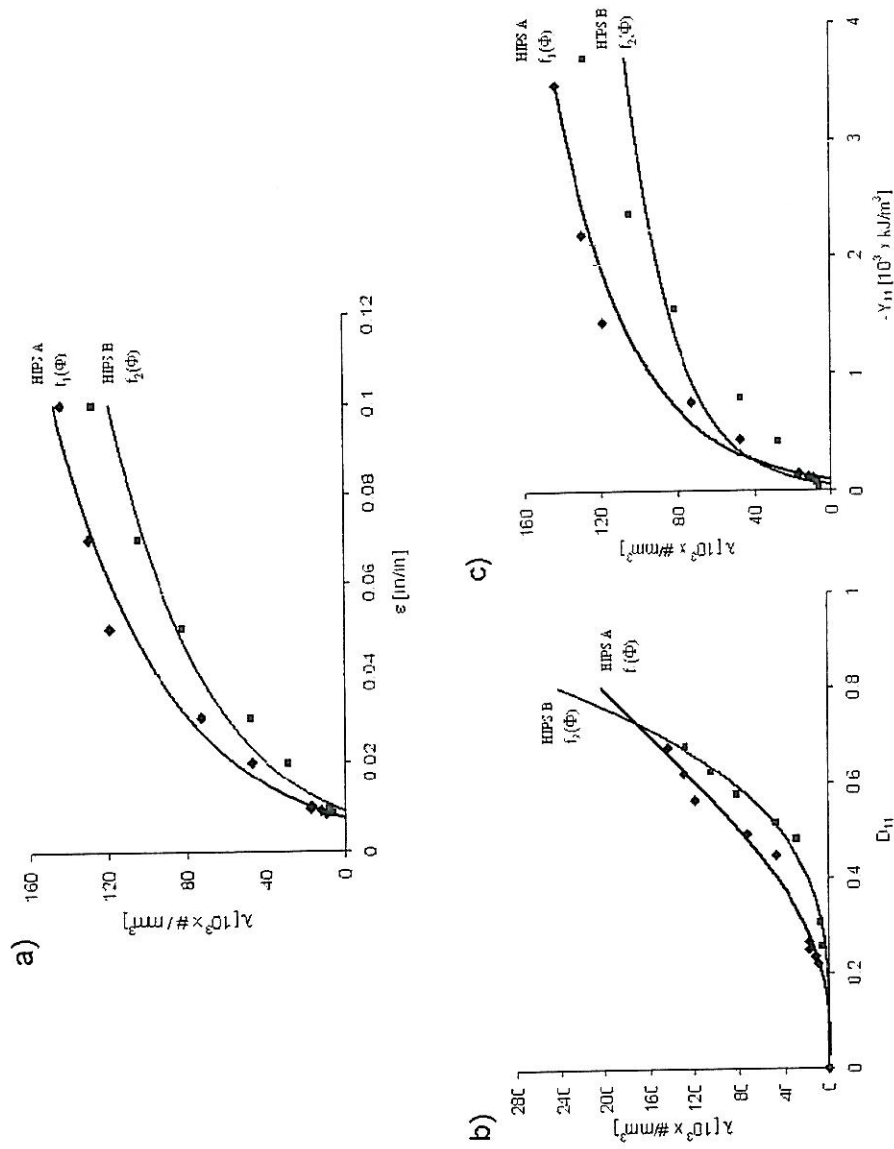


Figure 9.5.8.: Craze Density Change in HIPS Polymers: a) Under Increasing Strain, b) Relation with Damage, D_{11} , c) Under Thermodynamic Driving Force. [$T = \text{RT}$; $\dot{\epsilon} = 0.00007 \text{ in/in/sec}$]

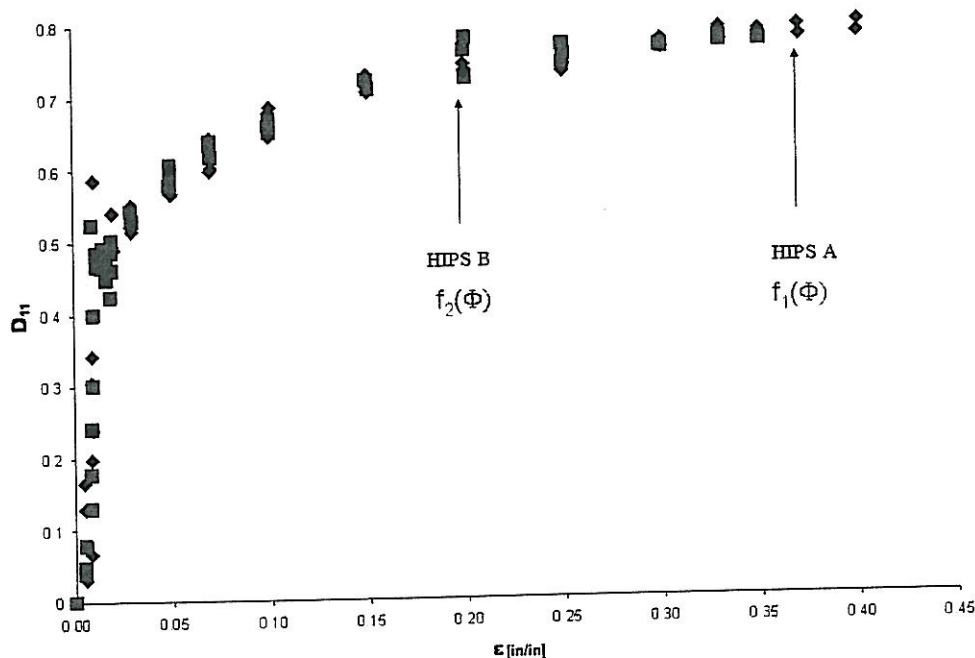


Figure 9.5.9: Effect of Particle Size Distribution in HIPS on Craze Damage Subjected to Increasing Strain. [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

Weibull's shape and scaling parameters of craze-length distributions in HIPS A and HIPS B are presented in Figs. 9.5.10 and 9.5.11, respectively. The HIPS A had a slightly larger shape parameter, whereas the HIPS B held a higher scale parameter. In Fig.9.5.12, the characteristic craze length development is shown with an increasing strain, thermodynamic force and damage variable, D_{11} . Characteristic craze length exhibited similar trends: it increased gradually and eventually reached an asymptotic value. The relationship between the damage variable, D_{11} , and characteristic length appeared to be linear with a larger craze size, $\hat{\ell}$, in HIPS B.

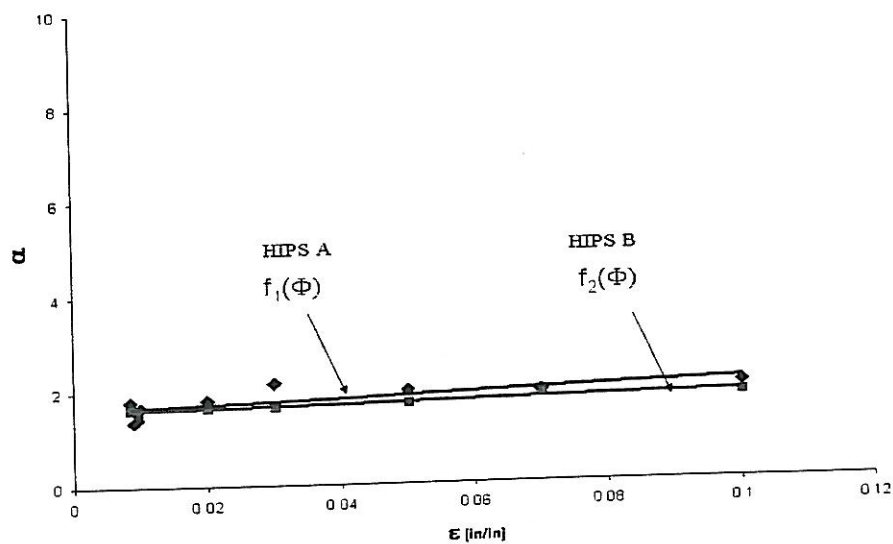


Figure 9.5.10: Weibull's Shape Parameter, α , in HIPS Polymers.
 [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

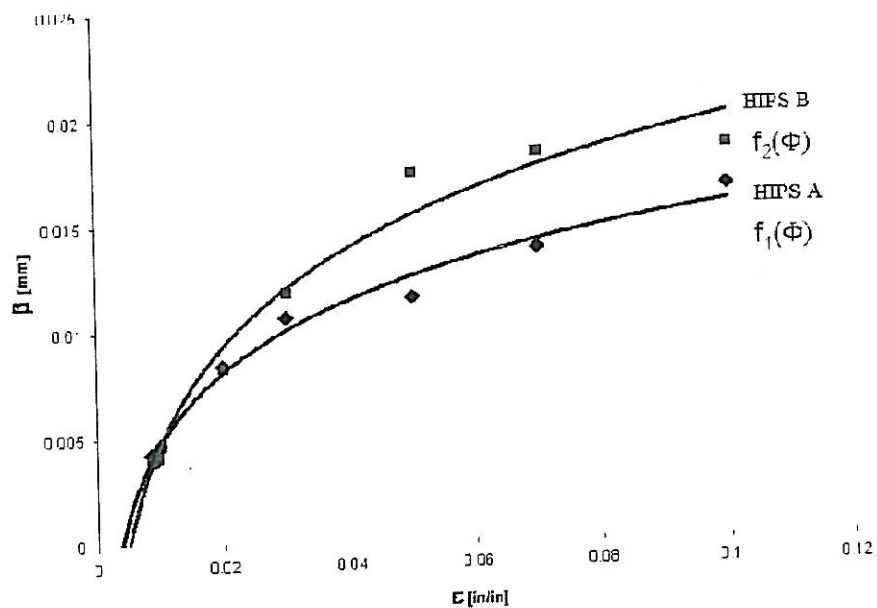


Figure 9.5.11: Weibull's Scaling Parameter, β , in HIPS Polymer.
 [T= RT; $\dot{\epsilon} = 0.00007$ in/in/sec]

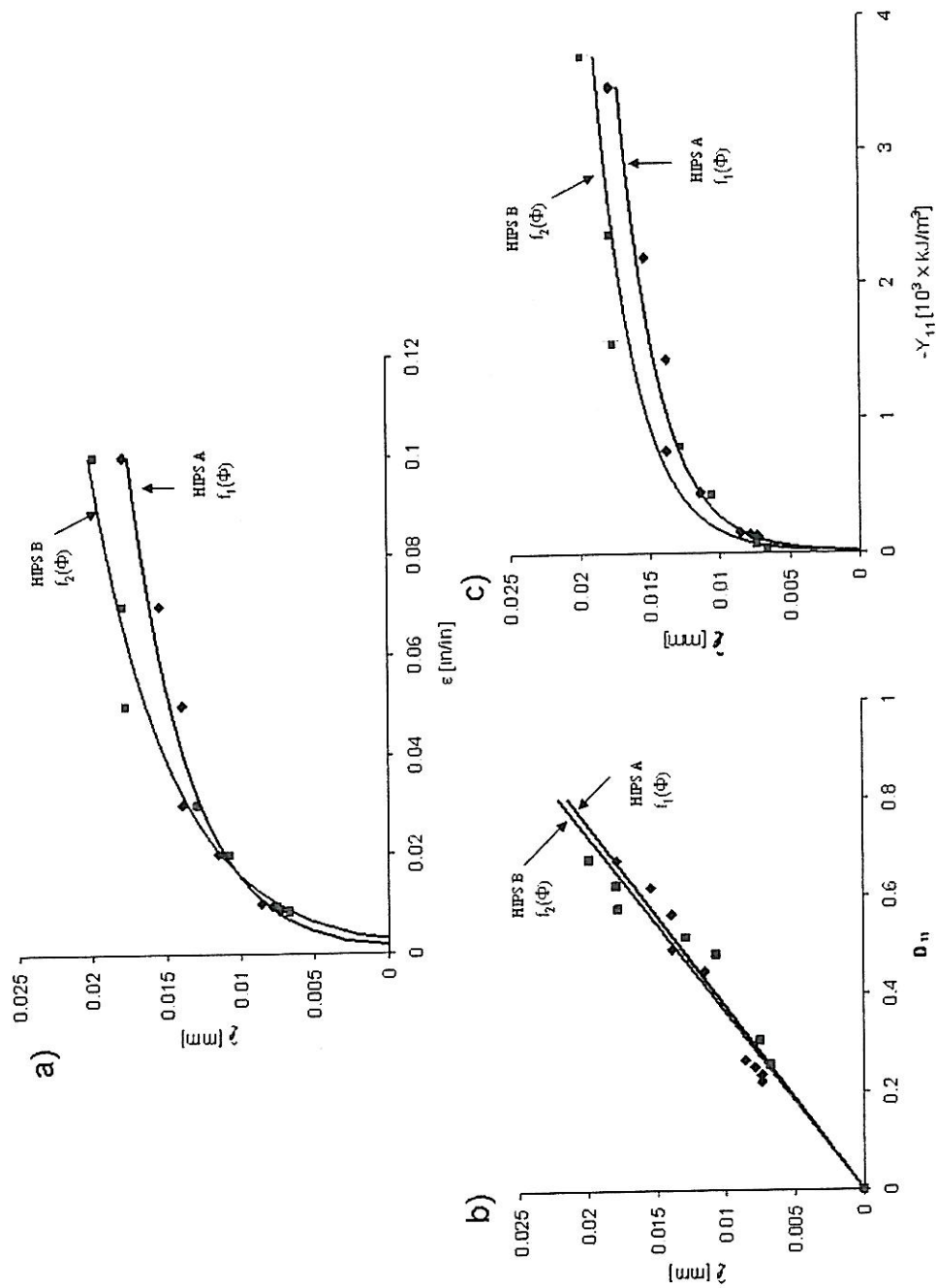
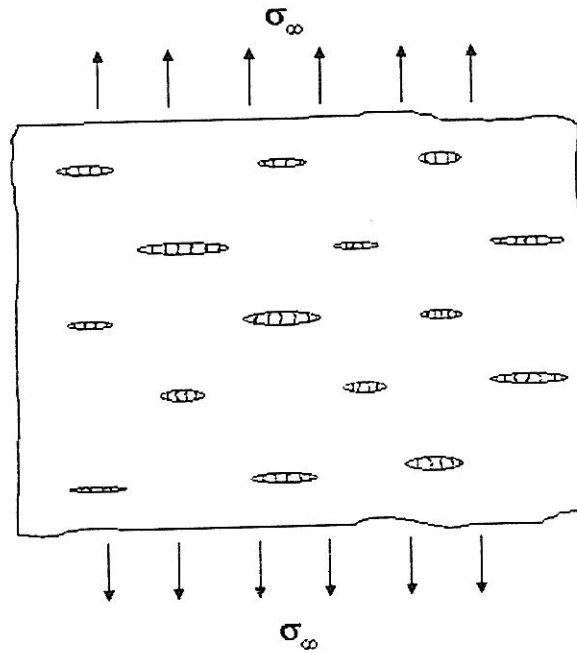


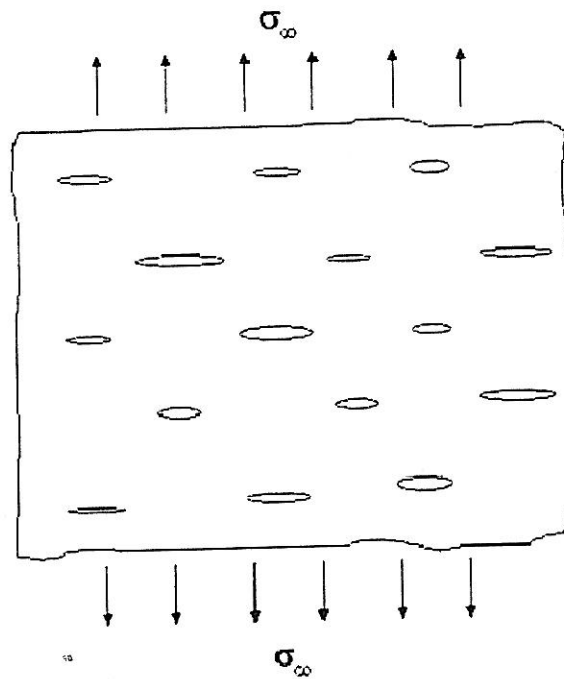
Figure 9.5.12: Characteristic Craze Length in HIPS Polymers: a) Under Increasing Strain, b) Relation with Damage, D_{11} , c) Under Thermodynamic Driving Force. [$T = \text{RT}$; $\dot{\epsilon} = 0.00007$ in/in/sec]

9.6 Effect of Orthotropic Nature of Craze Damage in HIPS Polymers

An orthotropic damage theory has been formulated in Sec. 7.3 based on continuum damage mechanics. From the theory and experimental observations, crazes grow perpendicularly to the maximum principal stress direction and craze damage becomes highly orthotropic. A similar problem of a polymeric solid with aligned cracks has also been previously studied, for example, Refs. [127-131]. The case of aligned microcracks may be viewed as the limiting case (in theory) of aligned crazes distributed in the polymer. A comparison of these two problems (Fig. 9.6.1) sheds light on the nature of craze damage in glassy polymers.



a) aligned crazes ($\perp$ to max. principal stress direction) in glassy HIPS.



b) aligned microcracks in glassy HIPS.

Figure 9.6.1: A Comparison of a Cracked and a Crazed HIPS Polymer.

In Fig. 9.6.2, damage variable, D_{11} , obtained by current theory and various crack models is shown. Experimental results are also included for comparison.

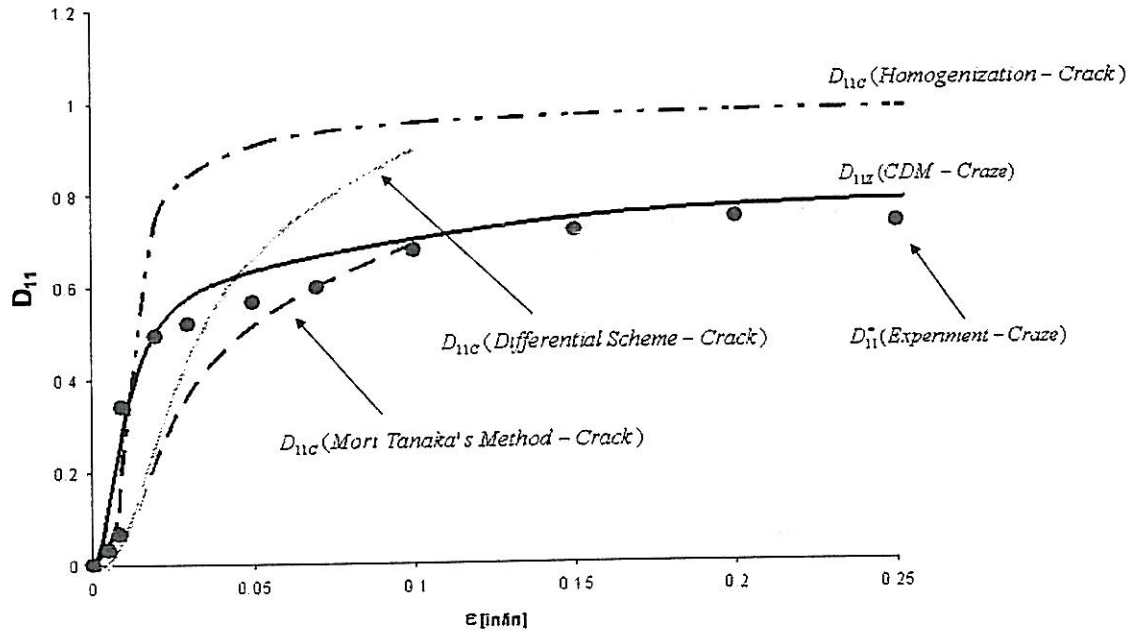


Figure 9.6.2: Craze Damage Variable, D_{11} , in HIPS under Increasing Strain, ϵ .
[Experimental data, theoretical results and comparison with various crack models].

It is clear from the figure that the experimental data and the results from the craze mechanics theory developed in Sec. 7.3 are consistent. The results from different micromechanics crack approaches apparently overestimate the damage effect by the distributed crazes. Different than both the differential scheme and Mori-Tanaka's method, the homogenization theory [116] accounts crack interactions through periodical boundary conditions of the unit cells. Homogenization theory on aligned microcracks

provides the results initially close to experimental data. However, at higher loads, it overestimates the effect, as expected.

In Sec. 7.3, a craze damage tensor has been introduced; thus, the non-zero damage components, D_{11} , D_{21} , and D_{66} , give the orthotropic nature of the craze damage. The subscript “1” represents the direction normal to the plane of a craze. D_{11} and D_{66} are related to Young’s modulus and shear modulus degradations. D_{21} is a coupling term caused by the Poisson’s effect. It represents the material property change in “1” direction due to the presence of crazes in the orthogonal direction. In Fig. 9.6.3, damage variables, D_{11} and D_{21} are determined for the HIPS craze problem with the aforementioned craze damage.

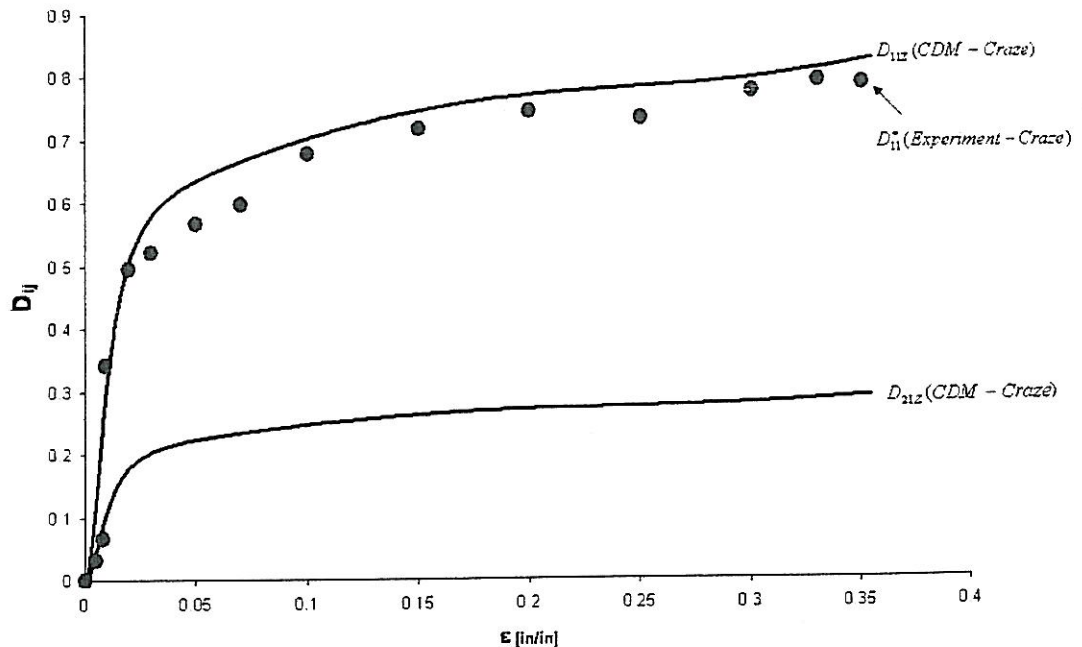


Figure 9.6.3: Orthotropic Damage, D_{ij} , in HIPS under Increasing Strain, ϵ .

In the following figure, Fig. 9.6.4, the results for the HIPS with parallel cracks are also included for comparison.

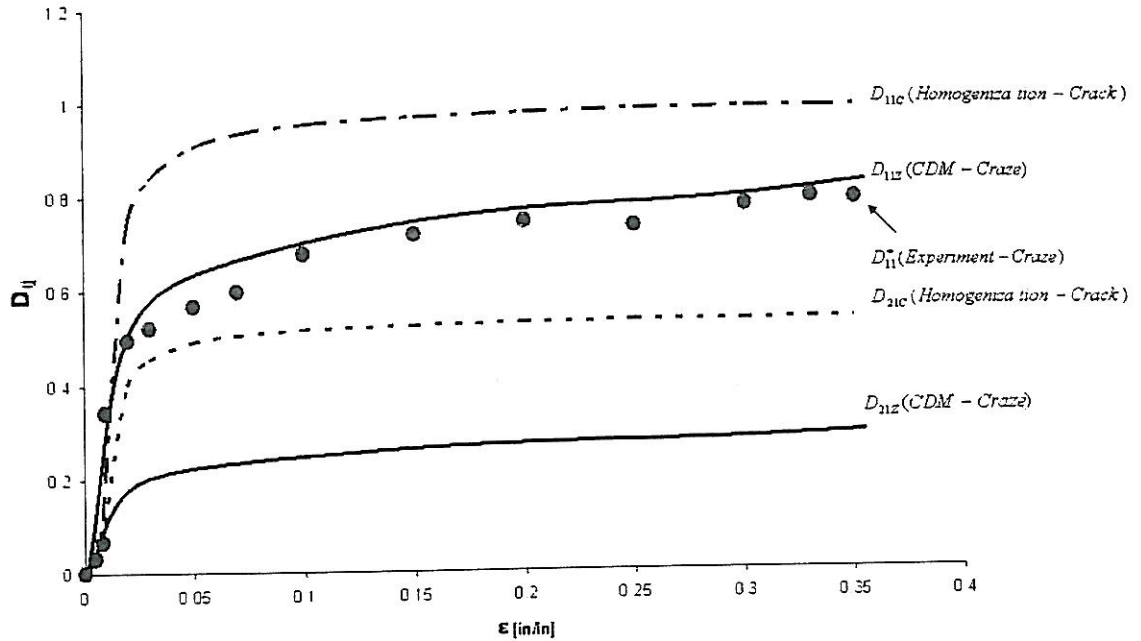


Figure 9.6.4: Orthotropic Damage, D_{ij} , in HIPS under Increasing Strain, ϵ .
[Results from micromechanics crack approaches are also given for comparison].

The craze damage evolution in the HIPS is studied by direct differentiation of the damage growth in Fig. 9.6.3. The results are shown in Fig. 9.6.5 in which the experimental data obtained in the study are also included. In Fig. 9.6.6, related microcrack damage evolution curves are included for comparison.

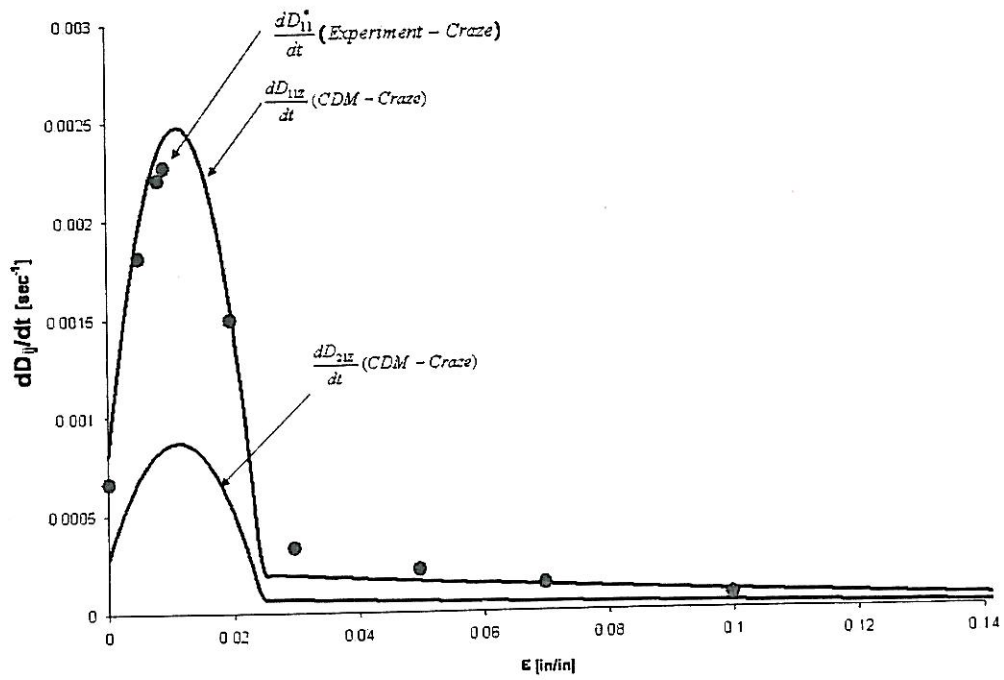


Figure 9.6.5: Orthotropic Nature of Damage Evolution in HIPS Polymers.

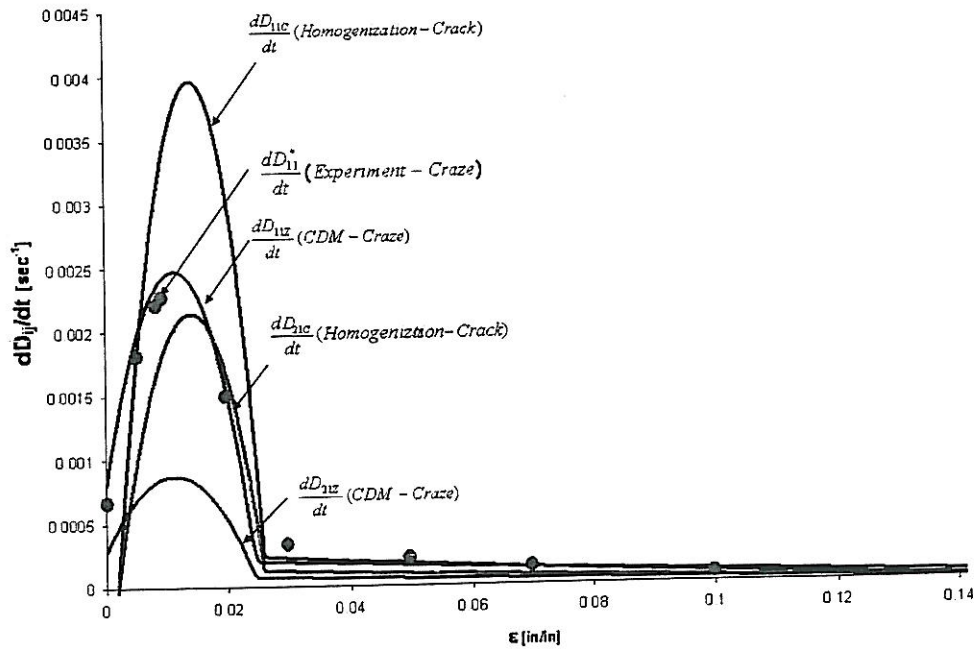


Figure 9.6.6: Orthotropic Nature of Damage Evolution in HIPS Polymers.
[Results from micromechanics crack approaches are also given for comparison].

The associated thermodynamic driving forces for craze growth in the HIPS, $-Y_{11}$, $-Y_{21}$, $-Y_{66}$, are derived in Sec. 7.3. In a uniaxial damage mechanics experiment, their values are shown in Fig. 9.6.7. As expected, crack models conferred greater results and strain energy release rates are higher for parallel cracks compared to crazes. Possibly, load bearing fibrillation between craze surfaces augments the damage endurance and results in an additional craze damage resistance.

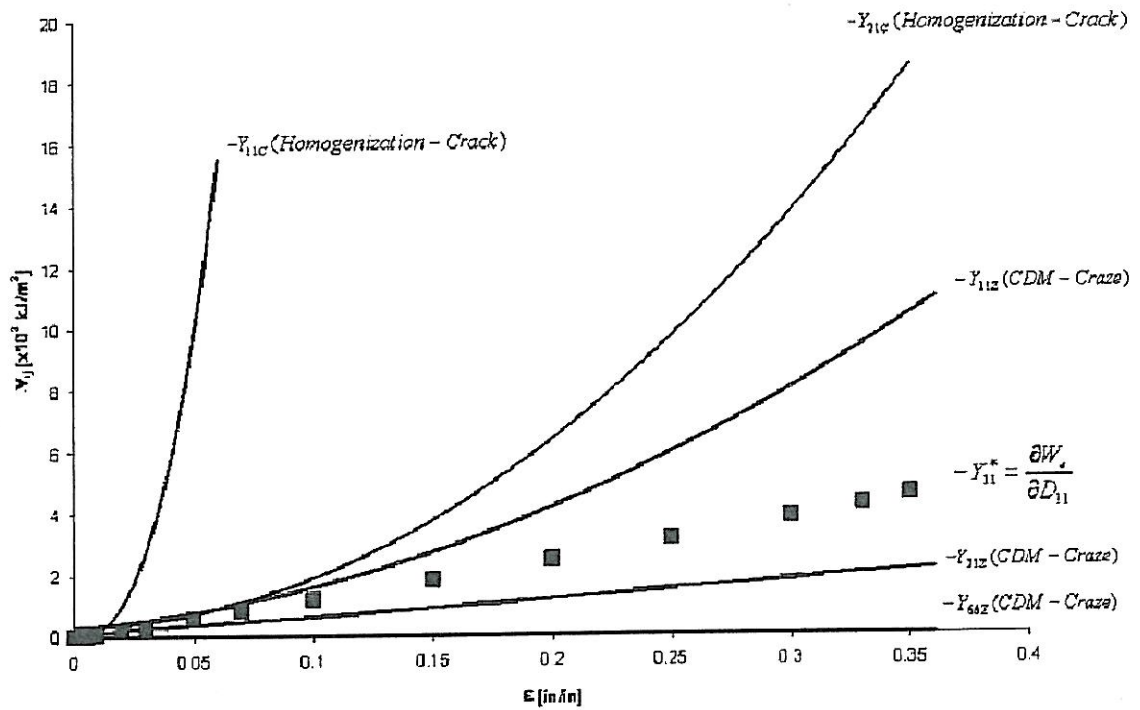


Figure 9.6.7: Orthotropic Nature of Thermodynamic Craze Damage Driving Forces in HIPS.

9.7 Craze Initiation

Micromechanics on craze development in particle-filled HIPS polymers has been carried out with finite element methods. Effects of volume fraction and size distribution of occluded particles on craze formation in HIPS have been investigated. In Chapter 8, two dimensional micromechanics models have been introduced to determine local stress and deformation fields associated with the embedded occluded particles for craze initiation. Comparative evaluation has been made on craze formation in HIPS polymers with different sizes and volume fractions of the rubber toughened PS systems.

9.7.1 Volume-Fraction Effect of Occluded Particles

A finite element model is used to investigate the particle volume fraction effect on craze formation in HIPS polymers. HIPS polymers with three different volume fractions are considered (Fig. 9.7.1). The HIPS is subjected to a nominal tensile stress along the axial direction. Eight-node, quadrilateral elements with displacement based formulation are used in the micromechanics modeling (Fig. 9.3.2). A plane stress condition is assumed. [The difference between the plane stress and plane strain assumptions is approximately 10%. A case study in which results of the plane stress and plane strain conditions are compared is given in Appendix E.]

Numerical results are presented in terms of local stress concentration factors, i.e., ratios of the local stresses to the applied nominal stress. Stress concentrations are shown as a function of particle volume fraction at the locations of interest.

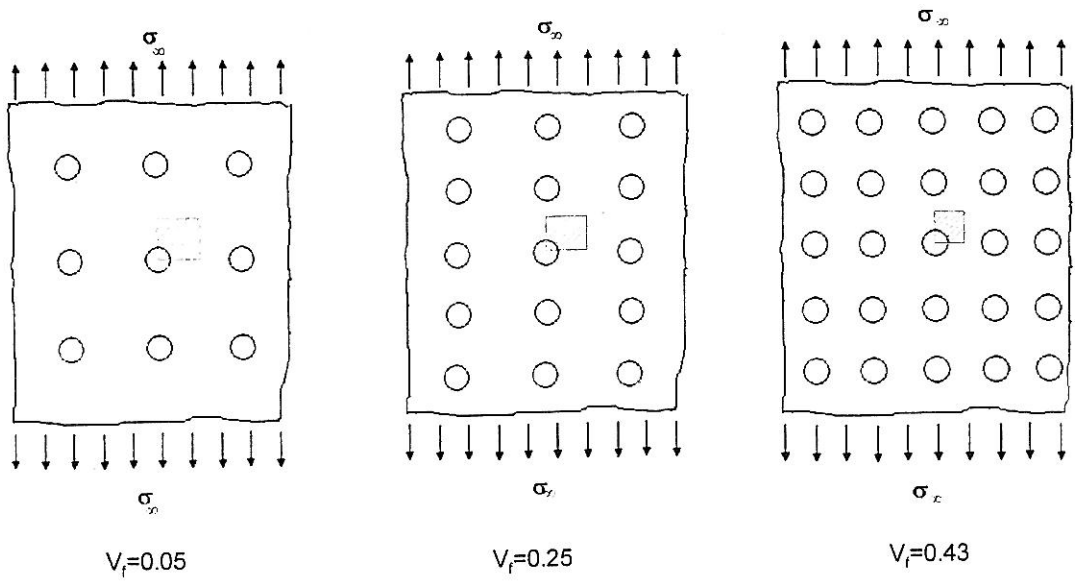
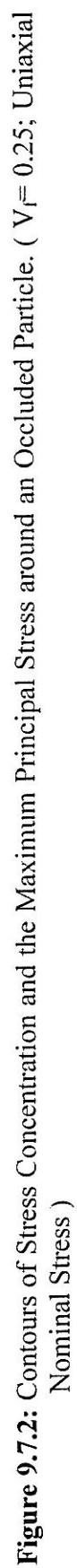


Figure 9.7.1: Representative Volume Element in HIPS with Different Particle Volume Fractions.

In Fig. 9.7.2, contours of stress concentration, $\frac{\sigma_{22}}{\sigma_x}$, and the maximum principal stress, $\frac{\sigma_{\max}}{\sigma_x}$, are shown for the case of an HIPS with a 25% volume fraction of particles.



The highest stress concentration occurs at the equator of the occluded particle. The maximum principal stress also occurs parallel to the applied stress at the equator. This is illustrated in Fig. 9.7.3 in which maximum principal stresses around a particle at different circular paths are shown. Previous theoretical predictions and experimental results [88, 120, 132-134] are in accord with the findings, indicating craze initiation and growth are most likely to start from a particle equator.

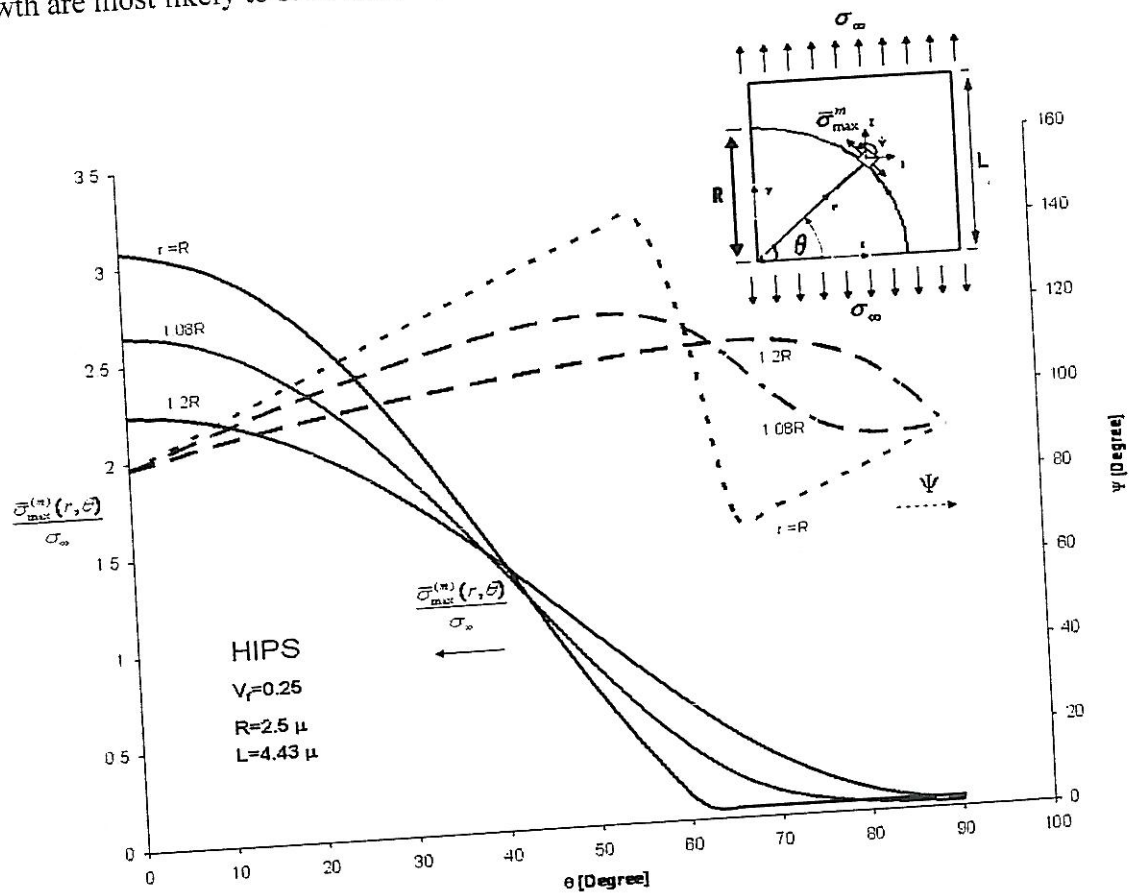


Figure 9.7.3: Maximum Principal Stresses and Their Directions at Various Circular Paths Around an Occluded Particles. (Uniaxial Nominal Stress)

In Fig. 9.7.4, the maximum principal stresses (in a vector form) are shown around an occluded particle.

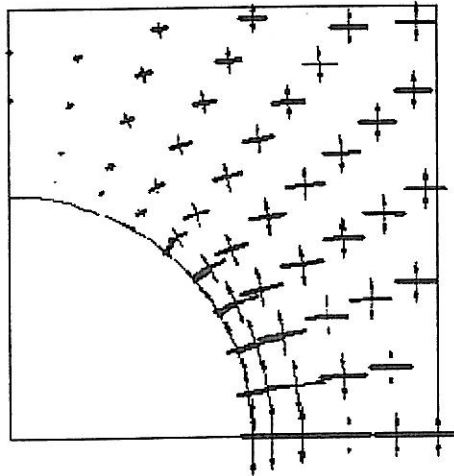


Figure 9.7.4: Maximum Principal Stress and Craze Growth Directions. ($V_f = 0.25$; Uniaxial Nominal Stress)

Blue arrows in the figure (Fig.9.7.4) are representing the local principal stresses while red lines, normal to the principal stress directions, are drawn to illustrate possible craze directions. (Lengths of the lines are proportional to their magnitudes.)

The maximum stress concentration increases with the occluded particle volume fraction (Fig. 9.7.5). Assuming that the size of the particle is uniform, an increase in particle volume fraction results in a higher number of particles with shorter inter particle distance; thus, promotes particle interaction; hence, higher stress concentrations. Also, having a uniform size, all the particles have the same probability to initiate a craze. Two limit cases, i.e., unmodified polystyrene and polystyrene with holes, are also shown for comparison. The stress concentrations are noted to decrease as the occlusion (polystyrene) amount in the rubber particle increases (Fig. 9.7.6).

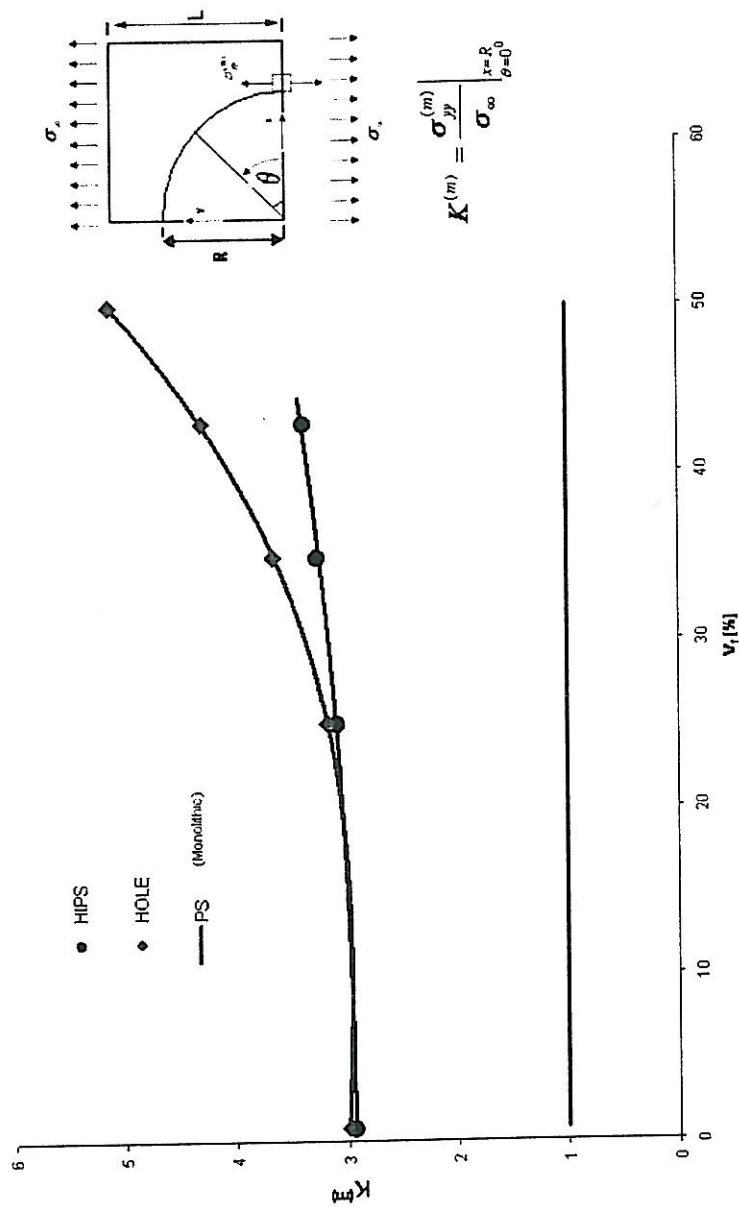


Figure 9.7.5: Stress Concentrations at the Equator of a Particle in HIPS with Different Volume Fractions.

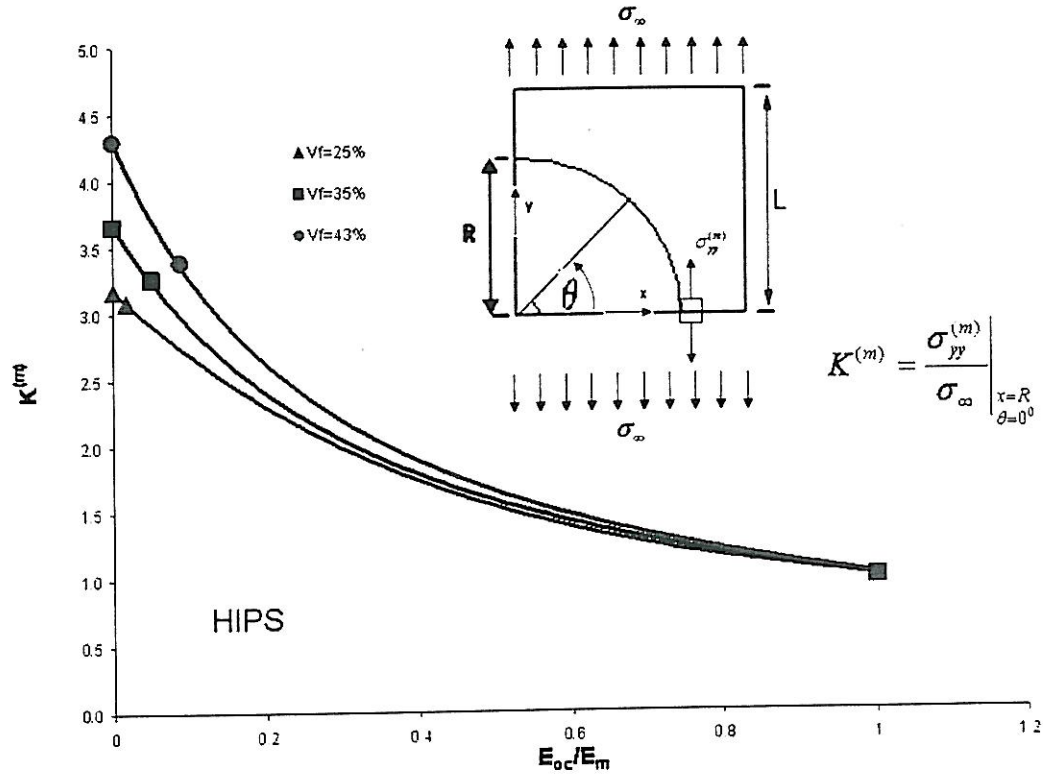


Figure 9.7.6: Stress Concentrations at a Particle Equator in HIPS with Different Occluded Particle Moduli.

In Figs. 9.7.7 and 9.7.8, stresses around an occluded particle are shown in polar coordinates for an HIPS with a particle volume fraction of 0.25. The radial and shear stresses at the interface (i.e., in the resin and in the particle along the interface) are continuous. The only significant stress component is the circumferential stress, $\sigma_{\theta\theta}$, in the matrix and it has its maximum at the equator. Its value decreases towards particle's pole and becomes negative around 63° . Similar trends are found in the HIPS with other volume fractions. At a lower volume fraction, the value of the circumferential stress converges to -1 (its theoretical value).

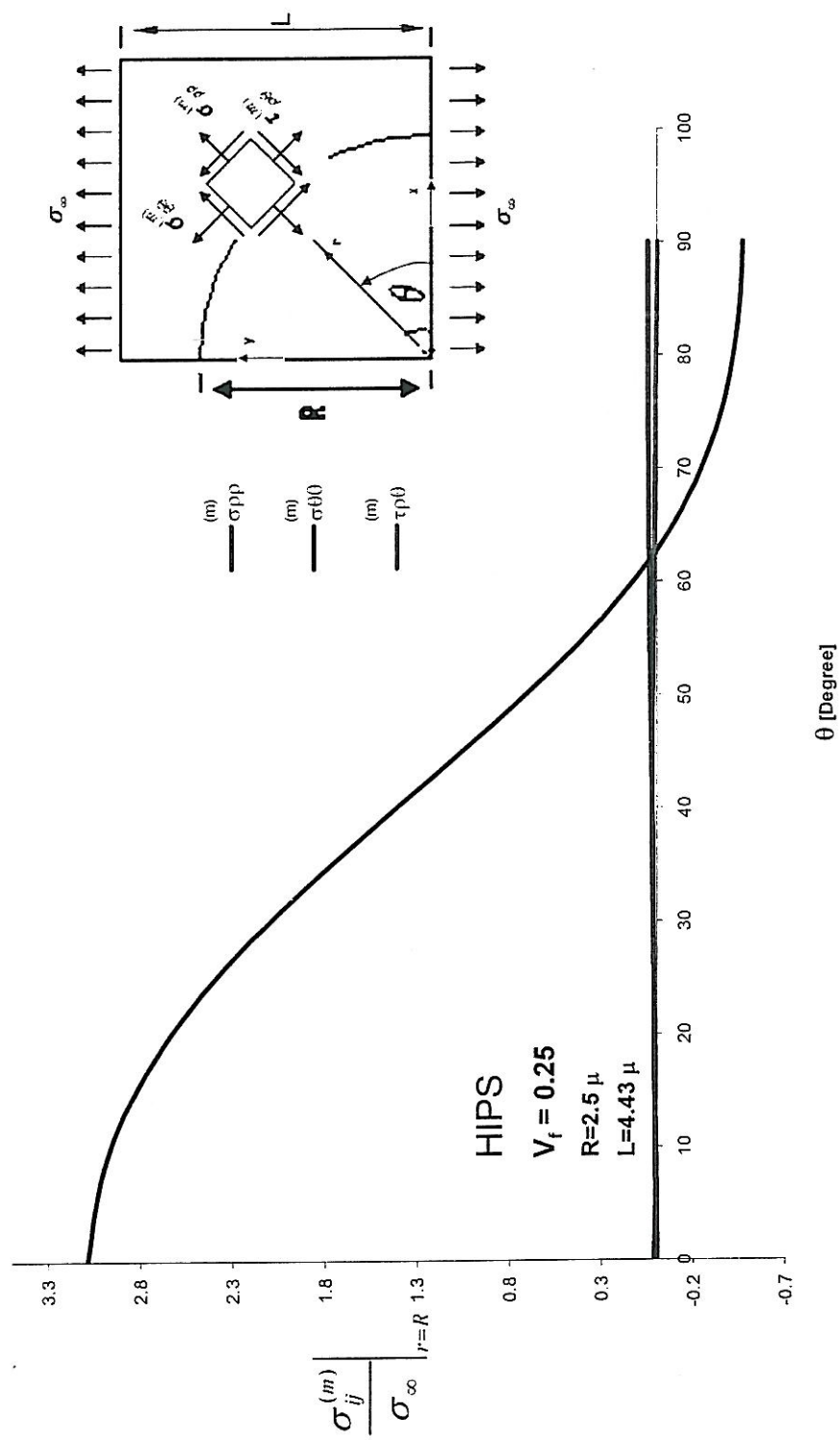


Figure 9.7.7: Stresses in PS Matrix Around an Occluded Particle in HIPS Polymers.

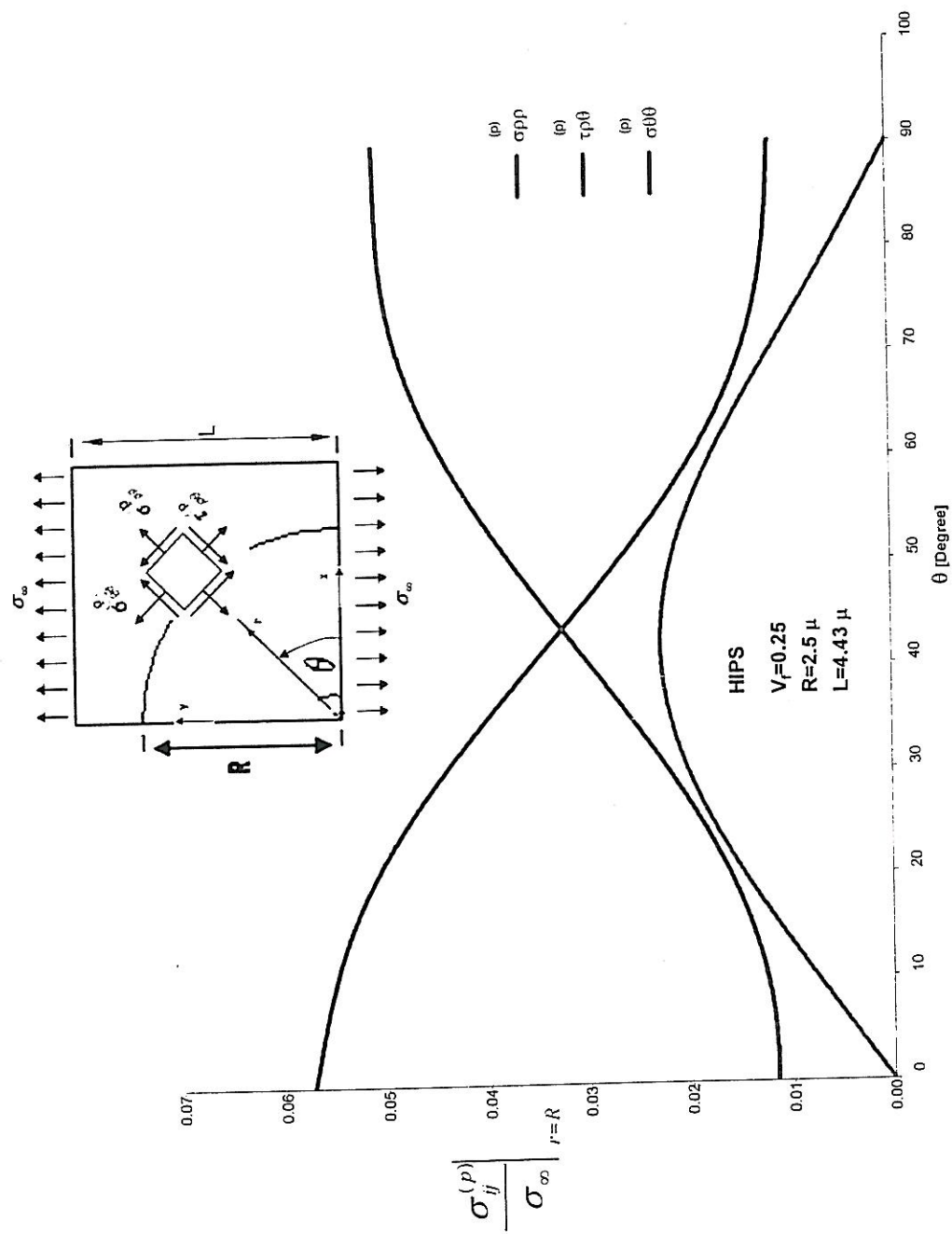


Figure 9.7.8: Stresses in Rubber Phase Around an Occluded Particle in HIPS Polymers.

In Fig. 9.7.9, the maximum principal stresses in the PS matrix around an occluded particle in HIPS with various volume fractions are presented. In the figure, the right-hand y-axis shows the directions of the maximum principal stresses. As can be seen, the maximum principal stresses increase with the particle volume fraction and their directions are parallel to the applied load direction, both at the equator and at the pole.

Stress distributions in the polystyrene matrix containing occluded particles are found to be similar to the ones containing holes. This can be seen in Fig. 9.7.10 in which the maximum principal stresses in the matrix are compared along particle-matrix and hole-matrix interfaces.

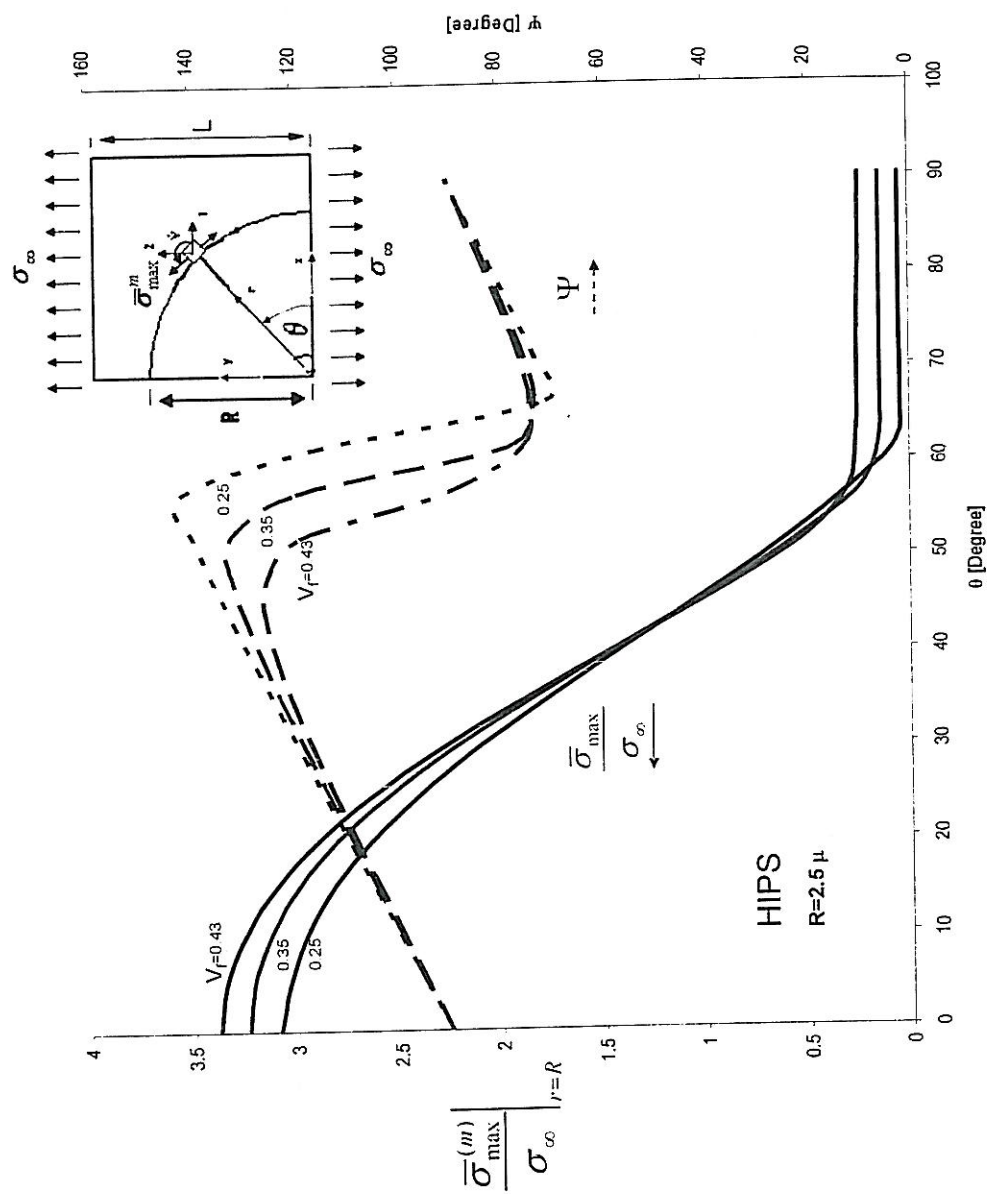


Figure 9.7.9: Maximum Principal Stresses Around an Occluded Particle in HIPS with Various Volume Fractions.

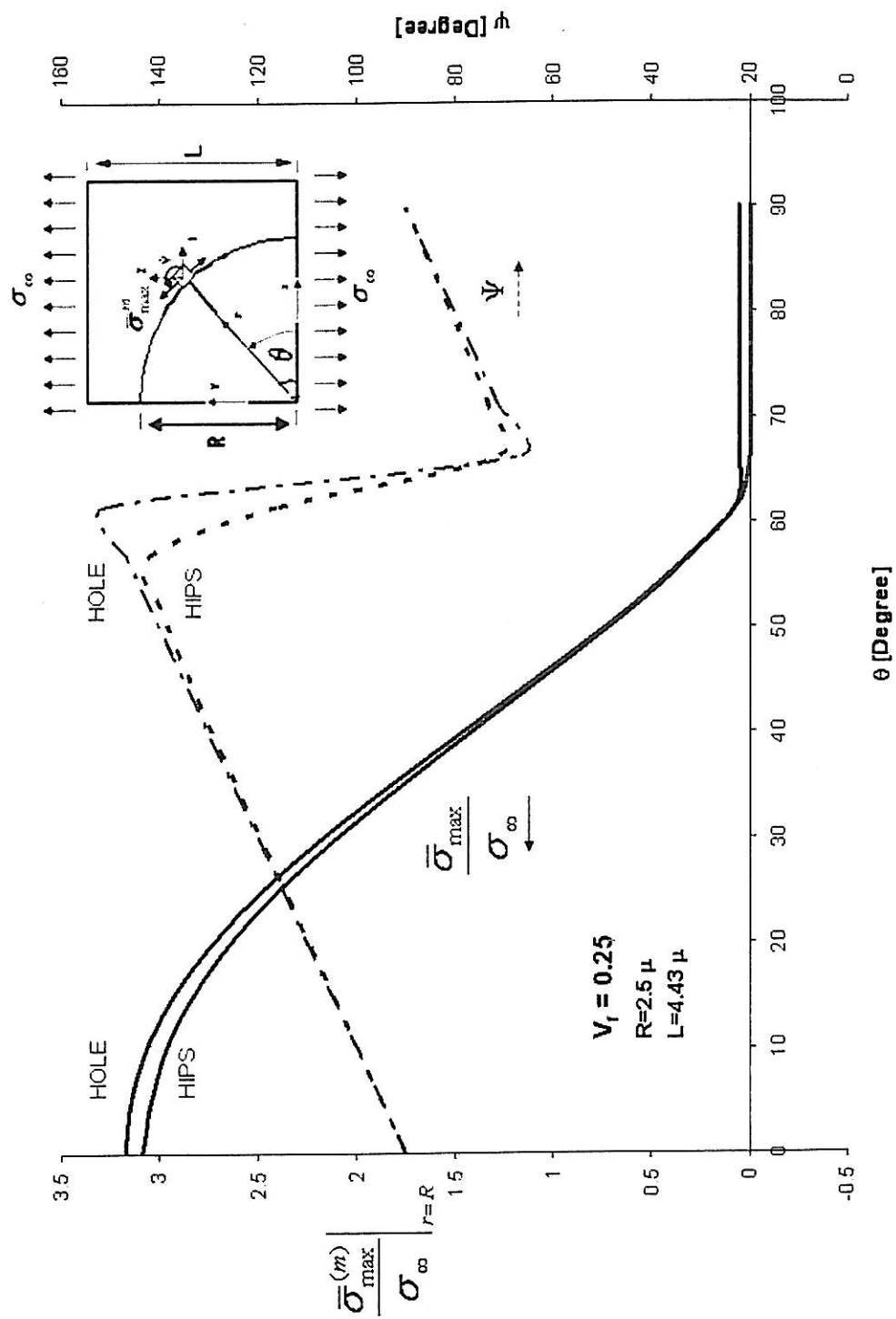


Figure 9.7.10: Maximum Principal Stresses Along Interfaces of Occluded Particle-PS and Hole-PS.

The stress field between occluded particles is given in Fig. 9.7.11. In the figure, the horizontal axis represents the normalized, center to center, half distance between the particles. For example, $\frac{x}{R} = 1$ corresponds to the polystyrene matrix-particle interface.

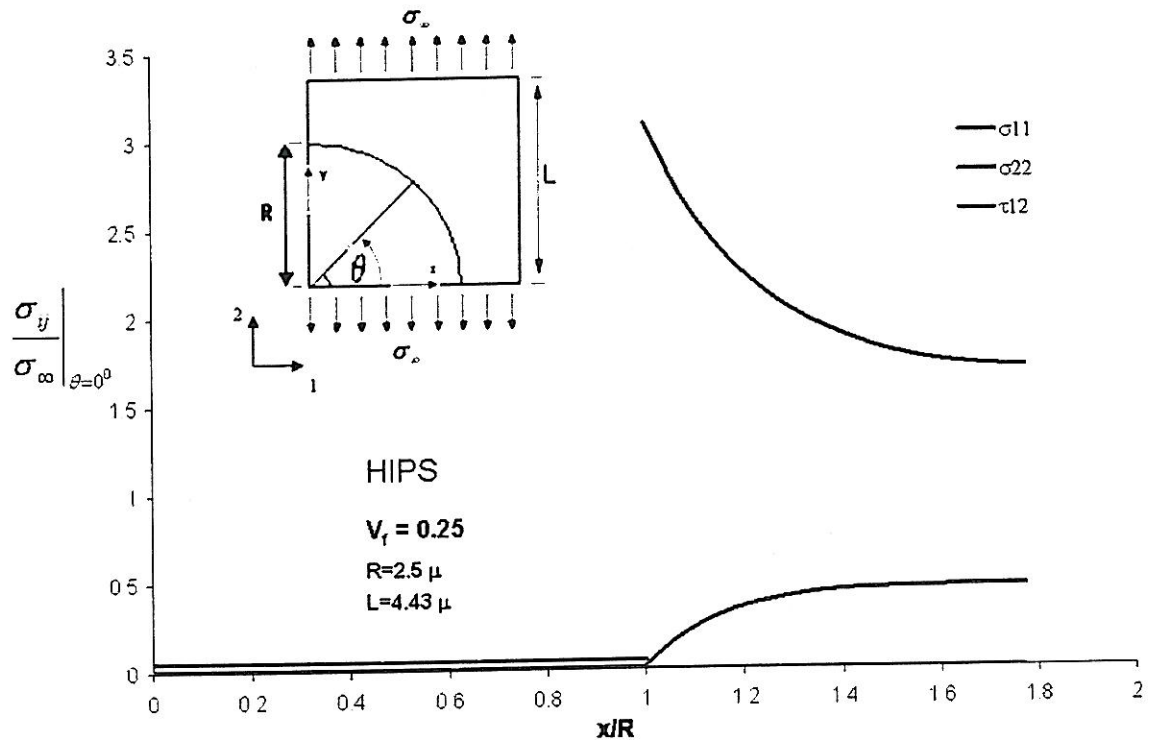


Figure 9.7.11: Stress Field Between Occluded Particles in HIPS Polymers.

As can be seen, shear stresses are zero due to symmetry and the value of σ_{11} is not significant in the occluded particle. Only a small amount of stress is transmitted to the occluded particles. The stress component, σ_{22} , has a maximum value at the interface and its value drops away from the particle.

In Fig. 9.7.12, the maximum principal stress distributions between particles in HIPS with various volume fractions are shown. The right vertical-axis indicates directions of associated stresses.

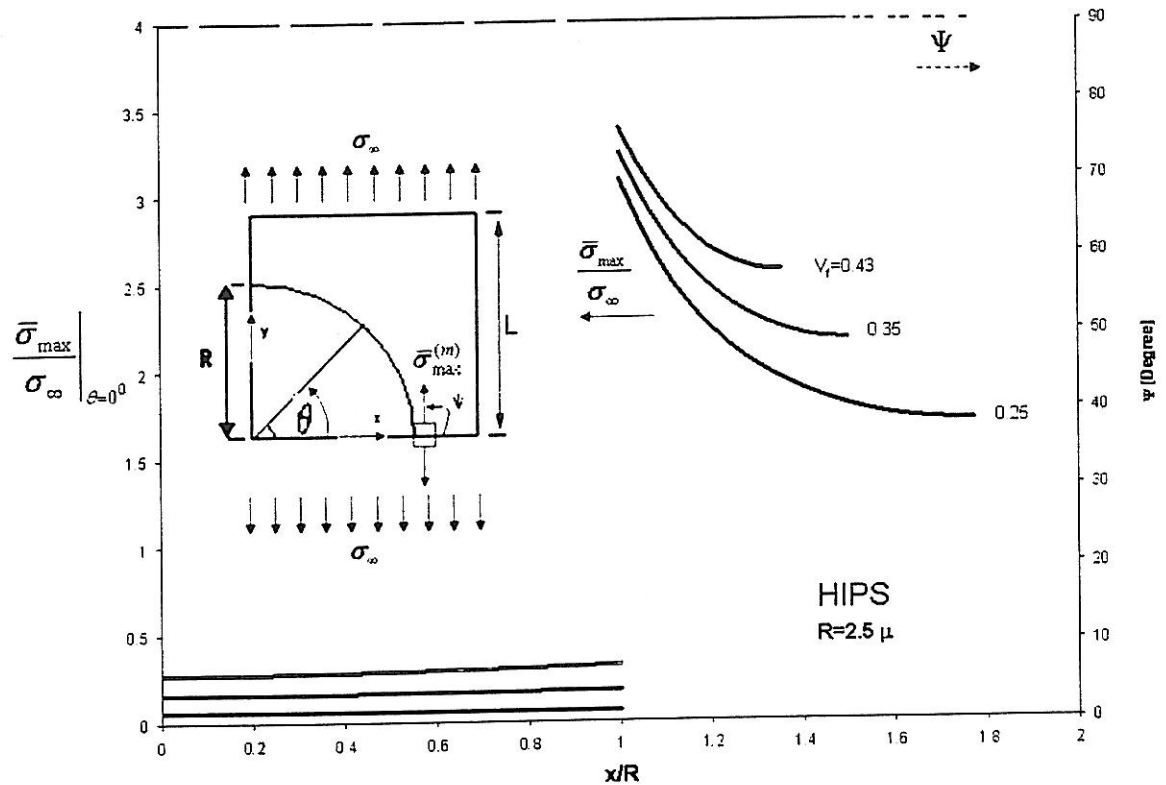


Figure 9.7.12: Maximum Principal Stresses Between Particles in HIPS at Various Volume Fractions.

The maximum principal stresses increase with the particle volume fraction, possibly, as a result of the shorter interparticle distance and particle interaction. However, the maximum principal stress directions are all the same in the applied load direction. The highest principal stress is at the particle interface; even though, it gradually decreases away from the particle.

Theoretically, stresses inside of the occluded particles need to be uniform [87] and almost perfectly hydrostatic in this case. This is because of high Poisson's ratio of the occluded particles (ν_{oc} is around 0.4) and the applied tensile stress state. At relatively

high volume fractions and for less compliant particles, stresses inside of the occluded particle are not always uniform. This can be seen clearly in Fig. 9.7.13.

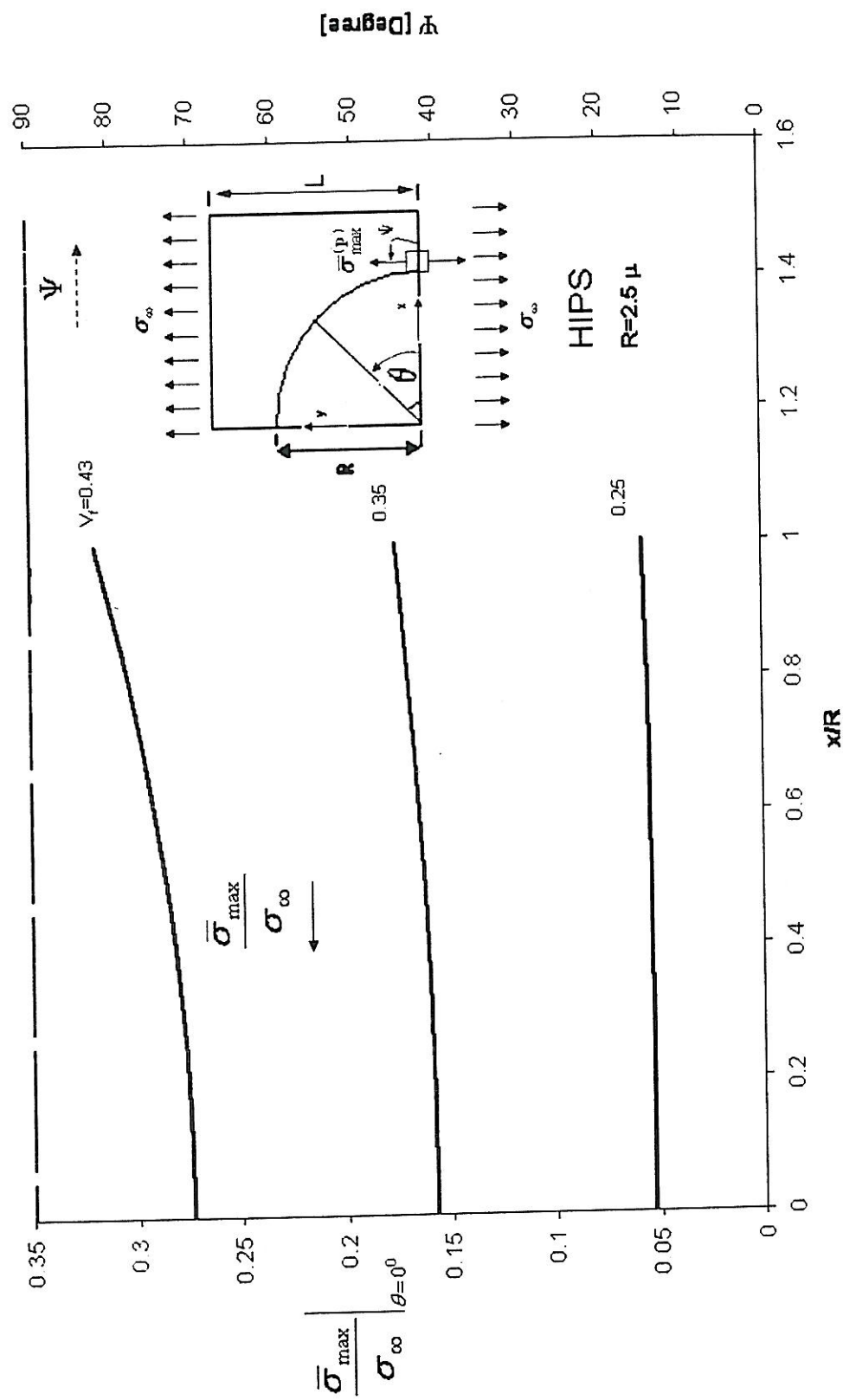


Figure 9.7.13: Maximum Principal Stresses Inside an Occluded Particle.

9.7.2 Effects of Particle Sizes and Interactions

In this section, the effects of particle sizes and their interactions on craze formation in HIPS are explored. In this study, a bimodal distribution of occluded particles is considered as it has been commonly used in toughened polymers. Thus the micromechanics model addresses a HIPS with a homogeneously distributed rubber particles with two different sizes embedded in polystyrene matrix. Details of the computational micromechanics modeling are given in Section 8.1.2. In a representative volume element as shown in Fig. 9.7.14, a particle of diameter $2r_1$ is placed next to the second particle of diameter 5μ , which is the average diameter of occluded particles in HIPS. Various bimodal systems in the HIPS are investigated by changing the bimodal ratio, k (Fig. 9.7.14). Numerical examples on a HIPS with a bimodal distribution of particles ($V_f = 25\%$) are conducted in the study. A uniform nominal displacement boundary condition corresponding to a unit axial stress is applied on the upper boundary of the representative volume element.

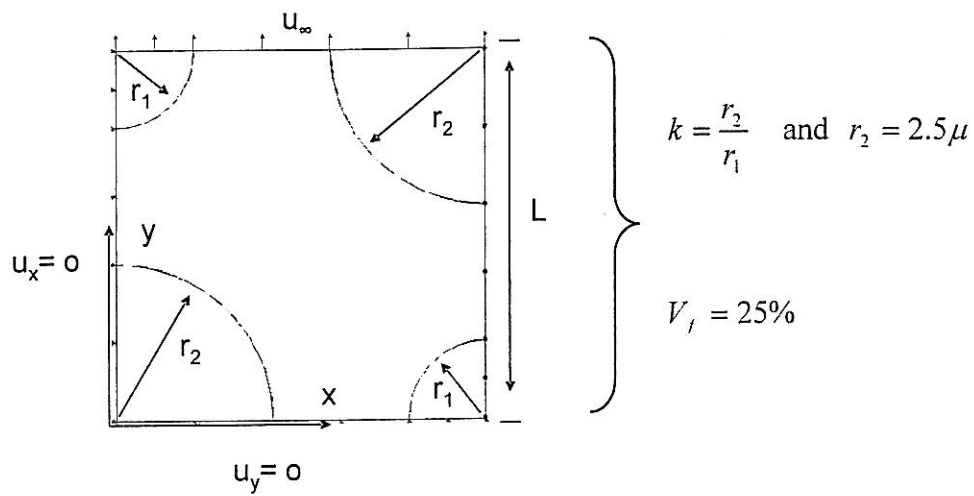


Figure 9.7.14: Representative Volume Element of Bimodal Particle Distribution in HIPS Polymers.

Results are presented in terms of stress concentrations, the ratio of local stress to the nominal stress, and the maximum principal stresses.

In Fig. 9.7.15, maximum stress concentrations change with the first particle size, r_1 , are shown at particles-matrix interfaces.

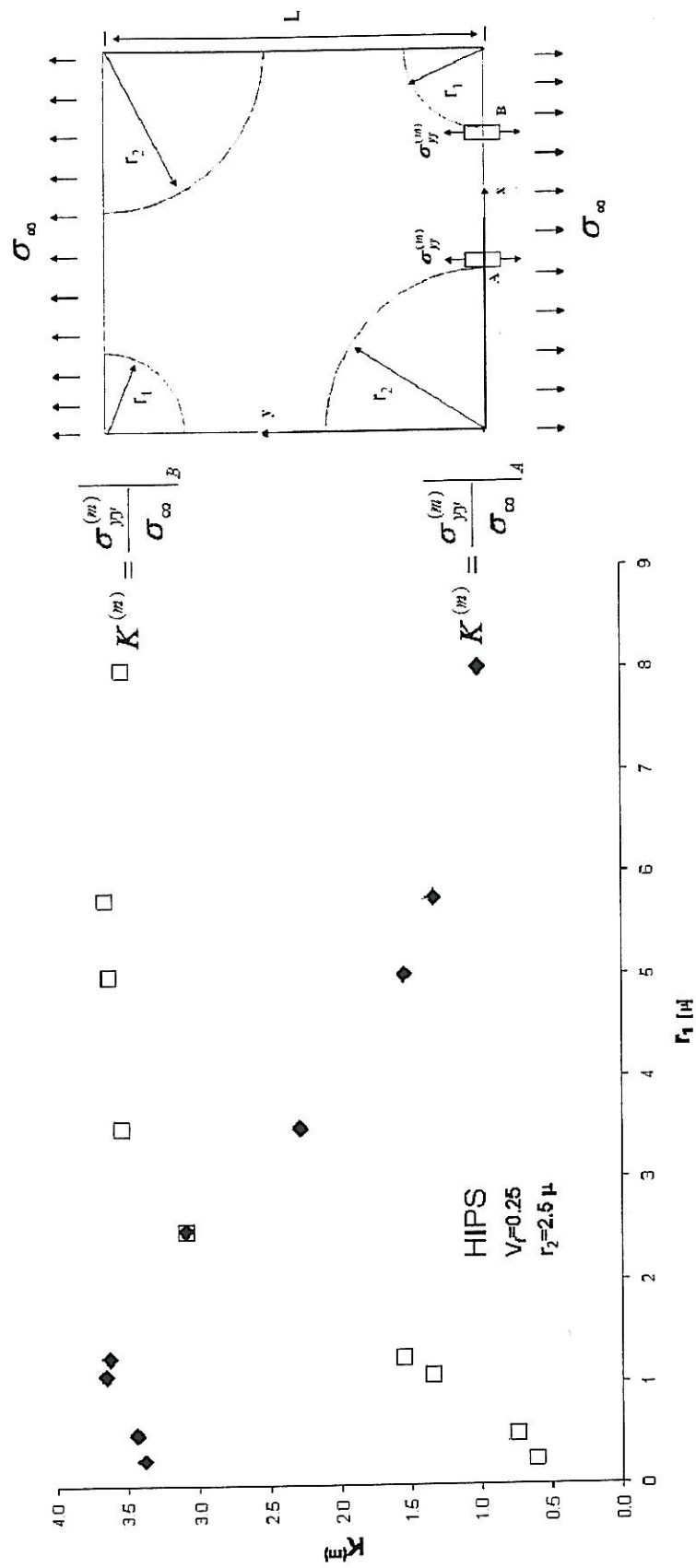


Figure 9.7.15: Maximum Stress Concentrations Around Occluded Particles.

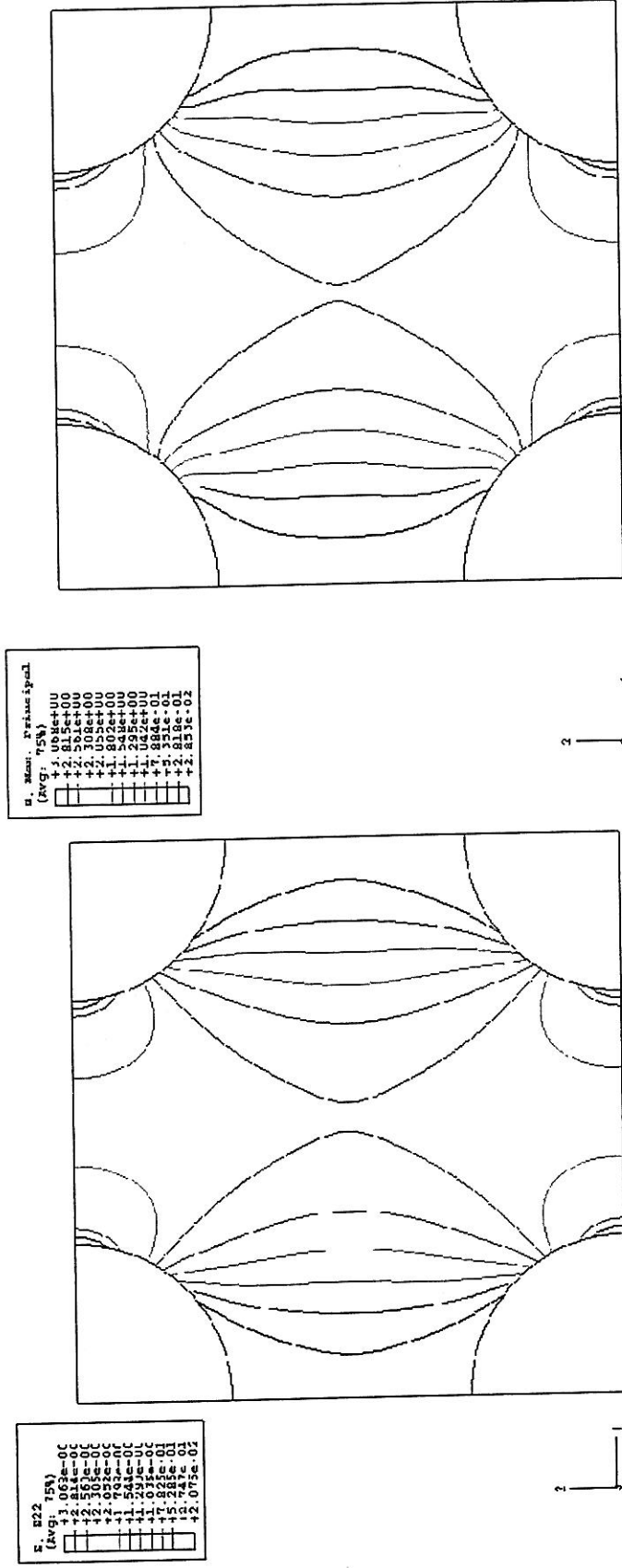
In the HIPS polymer with particles of bimodal sizes, the maximum stress concentration is obtained at the equator of the larger particle. Its value increases with particle size and reaches a maximum at $k \approx 2.3$ (Fig. 9.7.15). In fact, this is the critical bimodal ratio which gives the smallest interparticle distance, i.e., the surface-to-surface distance between two particles for $V_f = 25\%$. As the first particle size increases further, the maximum stress concentration factor at A (see Fig. 9.7.15) start to decrease. As expected, maximum stress concentrations are the same for $k=1$ (mono-modal particles in HIPS). After this point, the size of the first particle is larger than the 5 micron diameter; thus, higher stress concentrations are observed at the equator of the first particle, i.e., the larger particle.

Conclusively, stresses are concentrated at the equator of a large particle. Therefore, crazes may be initiated at the large particle's equator. The same phenomenon has been observed under a transmission electron microscope and reported in the literature [48, 53].

In the four selected bimodal ratio, the contour diagrams of stress concentrations and the maximum principal stresses are shown in Fig. 9.7.16. These figures represent a full description of the stress state in HIPS with bimodal particles.

In Figs. 9.7.17 and 9.7.18, the corresponding maximum principal stresses around particles are shown with their associated directions.

a) $k=1$



b) $k=2$

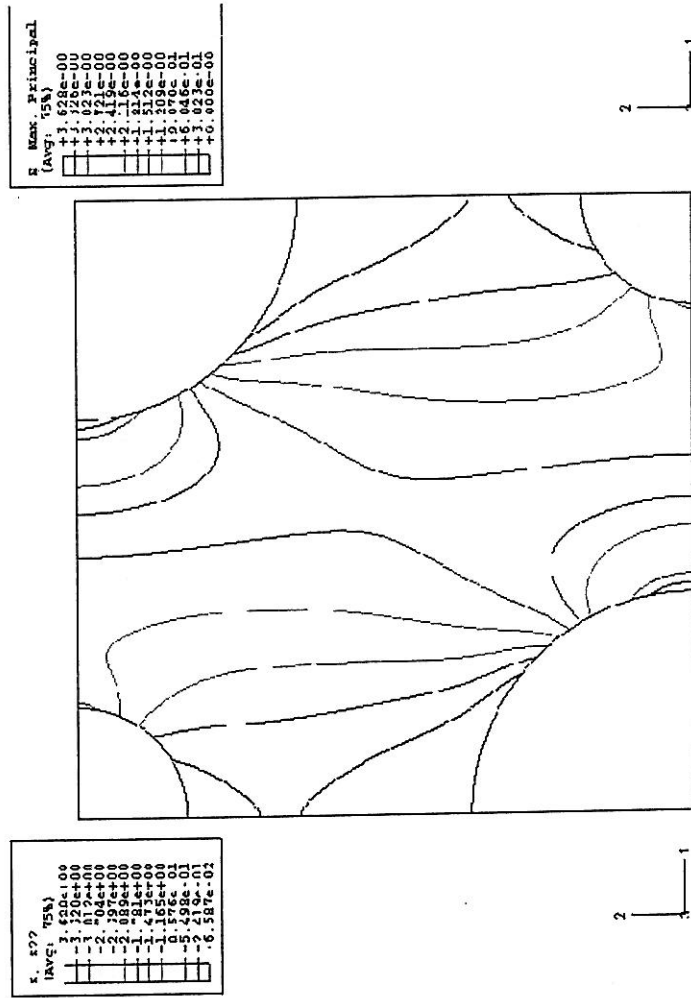


Figure 9.7.16b: Stress Concentrations and Maximum Principal Stress in HIPS with Different Bimodal Particle Size: b) $k=2$. ($V_f=0.25$; Uniaxial Nominal Stress)

c) $k=5$

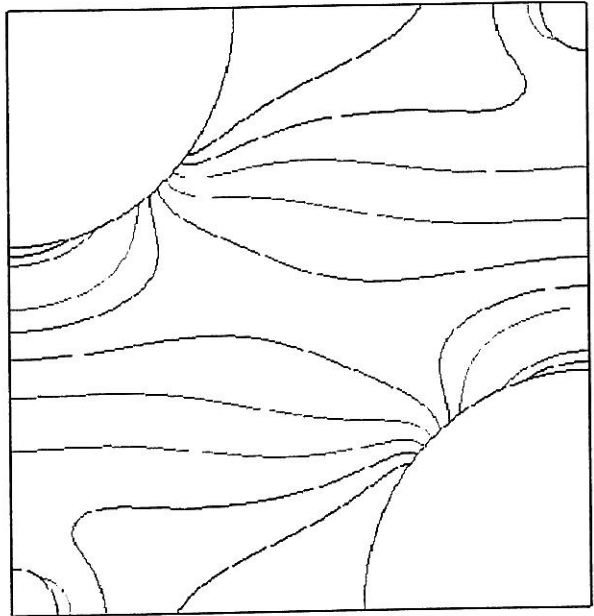
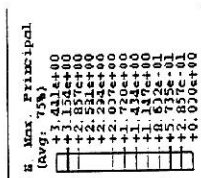
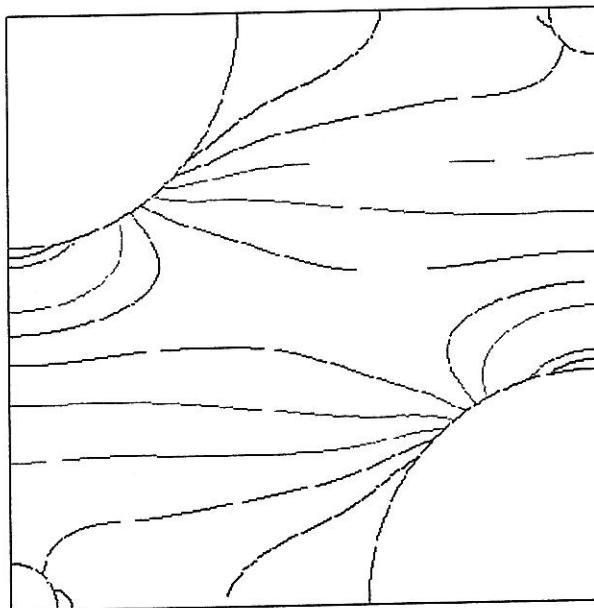
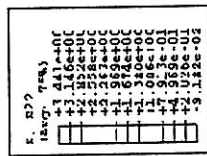


Figure 9.7.16c: Stress Concentrations and Maximum Principal Stress in HIPS with Different Bimodal Particle Size: c) $k=5$. ($V_f=0.25$; Uniaxial Nominal Stress)

d) $k=10$

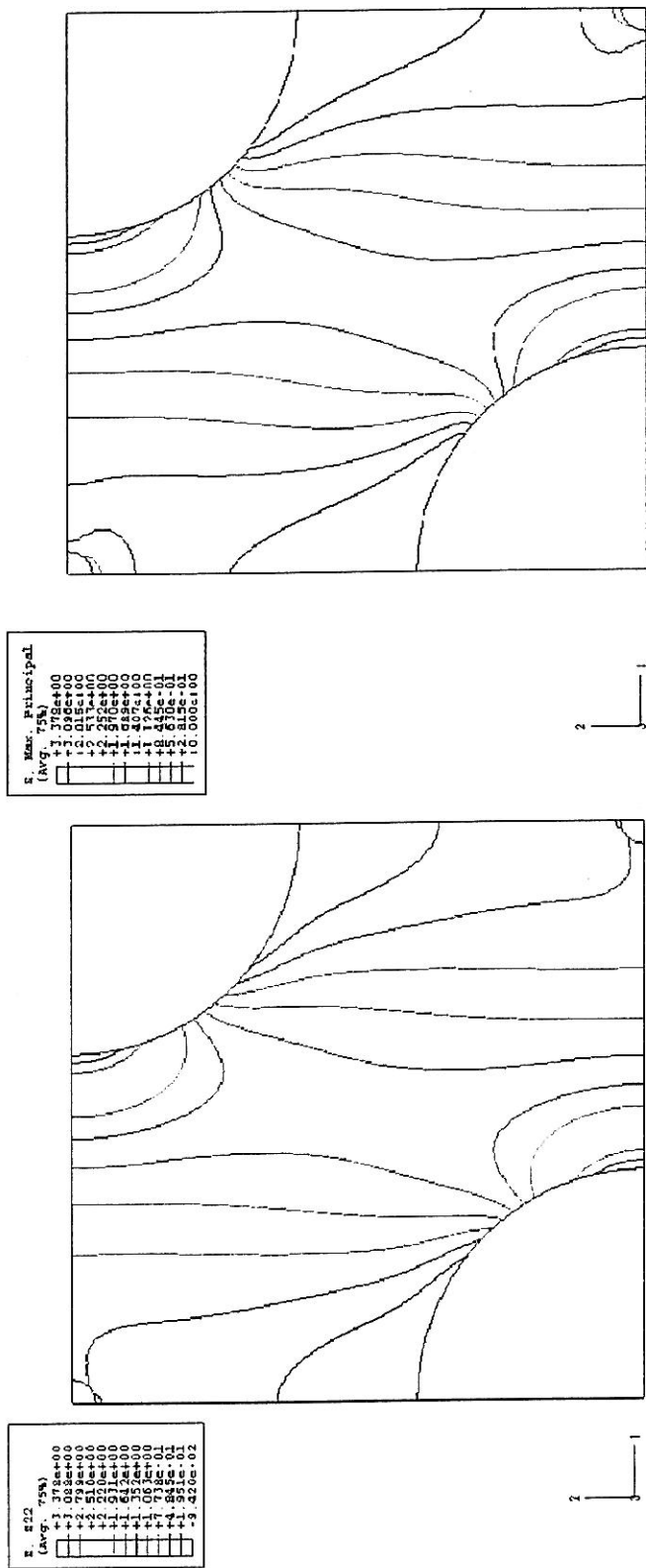


Figure 9.7.16d: Stress Concentrations and Maximum Principal Stress in HIPS with Different Bimodal Particle Size: d) $k=10$. ($V_f=0.25$; Uniaxial Nominal Stress)

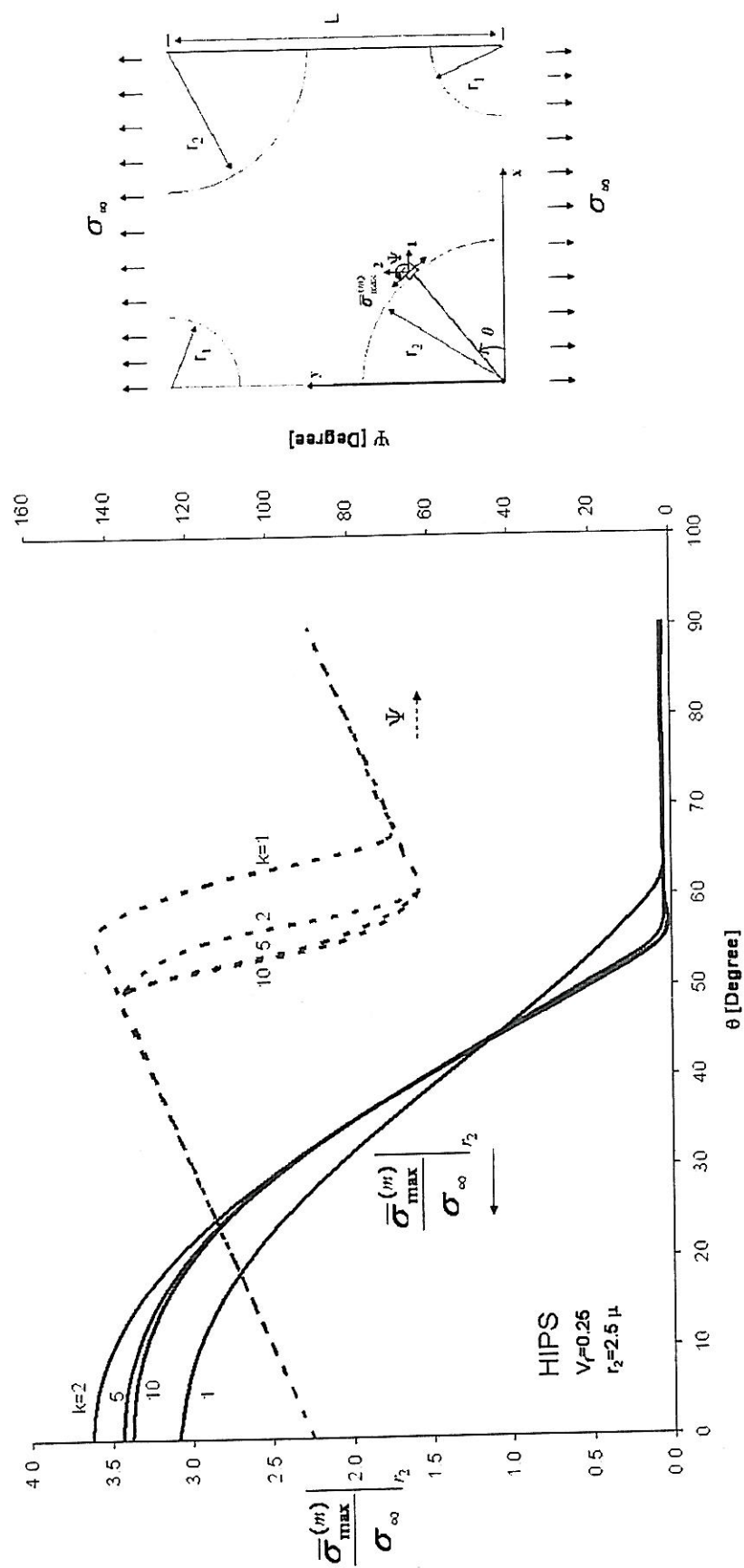


Figure 9.7.17: Maximum Principal Stress Around the Fixed Particle in HIPS with Various Bimodal Ratios.

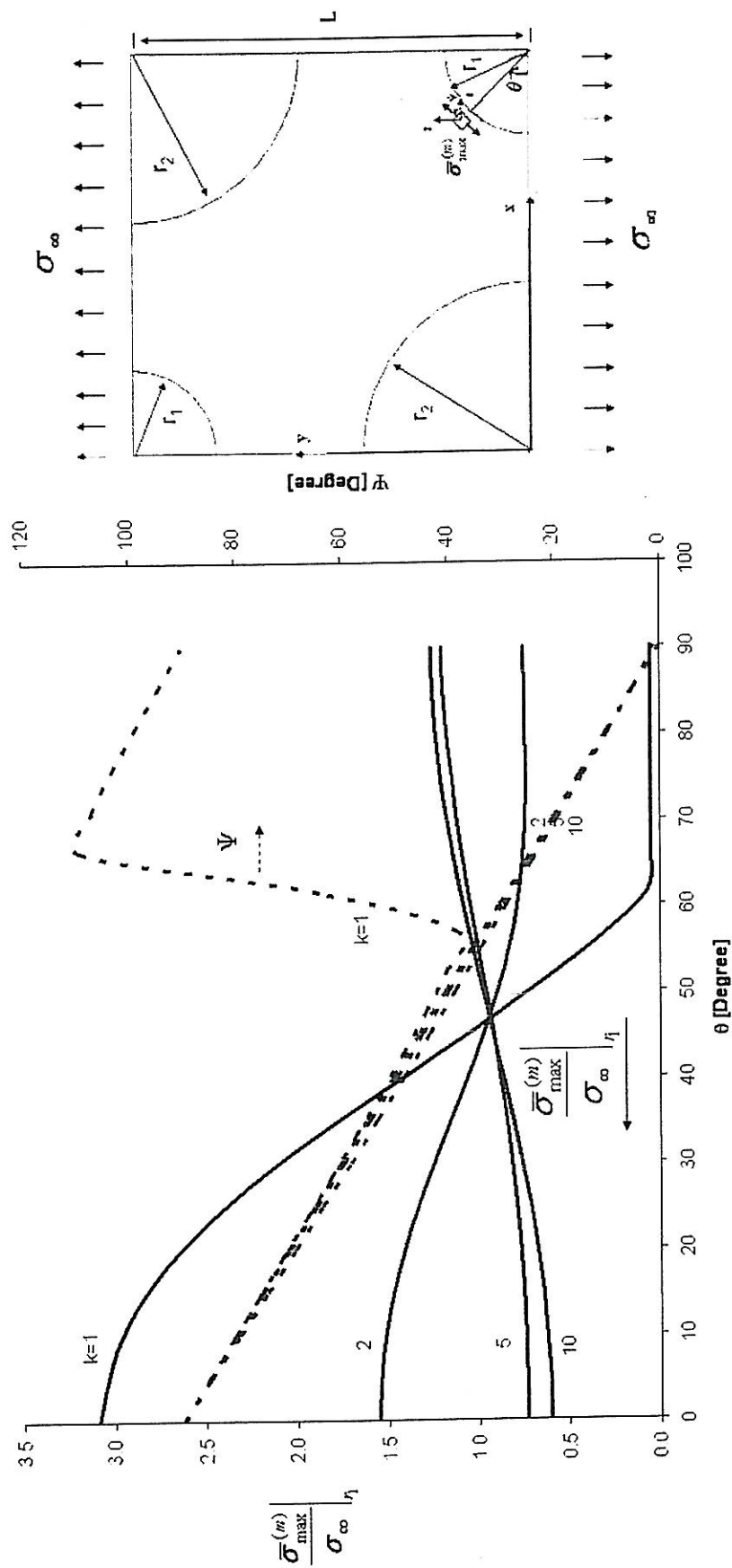


Figure 9.7.18: Maximum Principal Stress Around the First Particle in HIPS with Various Bimodal Ratios.

In the figures, the left vertical-axis gives the maximum principle stress. The right vertical-axis shows their associated directions.

In Fig. 9.7.18, the highest maximum principal stress occurs at the particle's equator along the particle-matrix interface in a monomodal HIPS ($k=1$). Its direction is parallel to the applied load, with a value decreasing gradually from the equator to the pole. As mentioned before, in a bimodal HIPS, the highest maximum principal stress is found at the large particle's equator (i.e., the second particle). However, for the small particles, depending on the bimodal ratio, a higher local maximum principal stress is found at the particle's pole (Fig. 9.7.18, $k=5$ and $k=10$) rather than that at its equator. Along the small particle-matrix interface, the direction of the maximum principal stress decreases from 90° at the equator (where $\theta = 0^\circ$) to 0° at the pole (where $\theta = 90^\circ$).

In Figs. 9.7.19, 9.7.20 and 9.7.21, maximum principal stresses are shown along three different paths, i.e., along the x-axis, along the y-axis and along the first diagonal (along the r direction at $\theta = 45^\circ$). Again, in the figures, the right y-axis is for the stress and the left y-axis is for its associated stress direction.

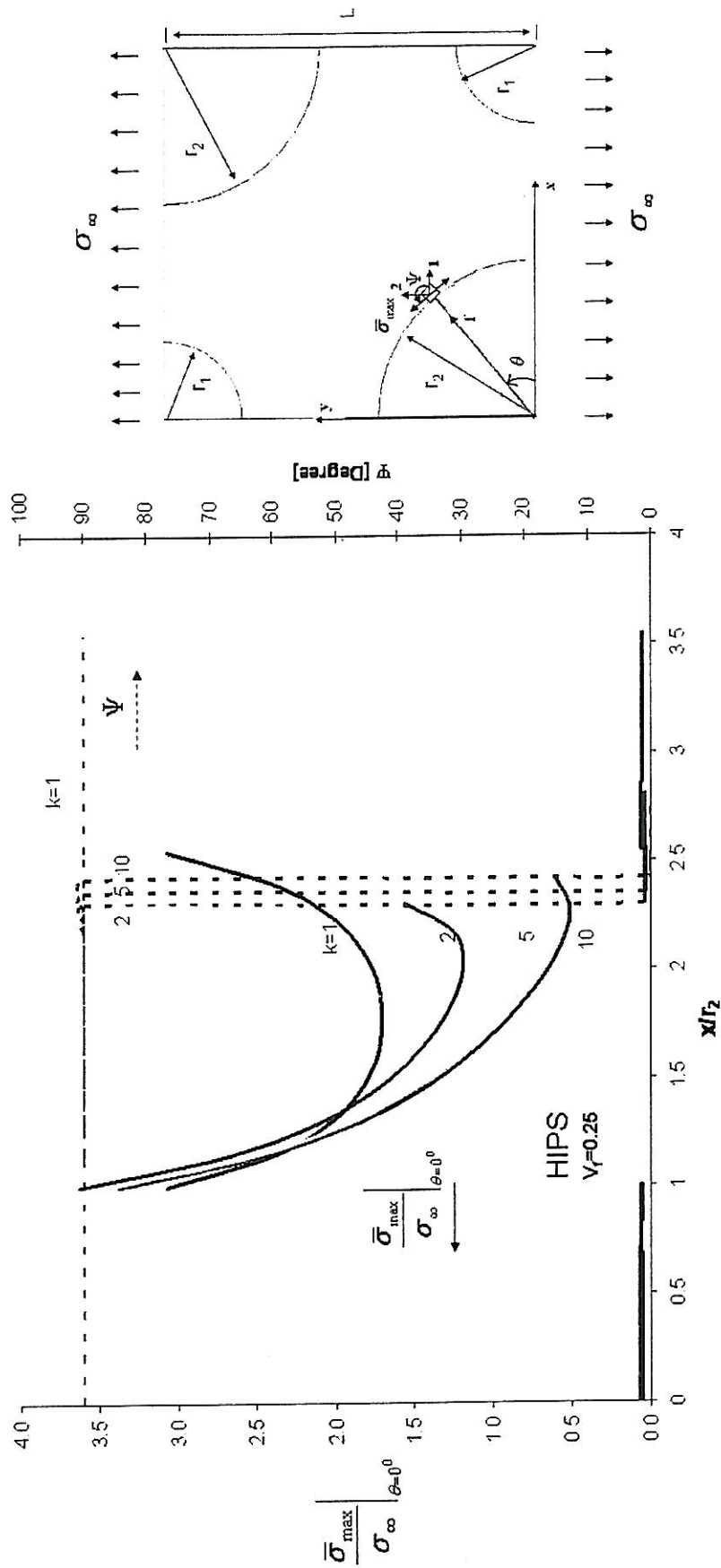


Figure 9.7.19: Maximum Principal Stress Along the x-axis in HIPS with Various Bimodal Ratios.

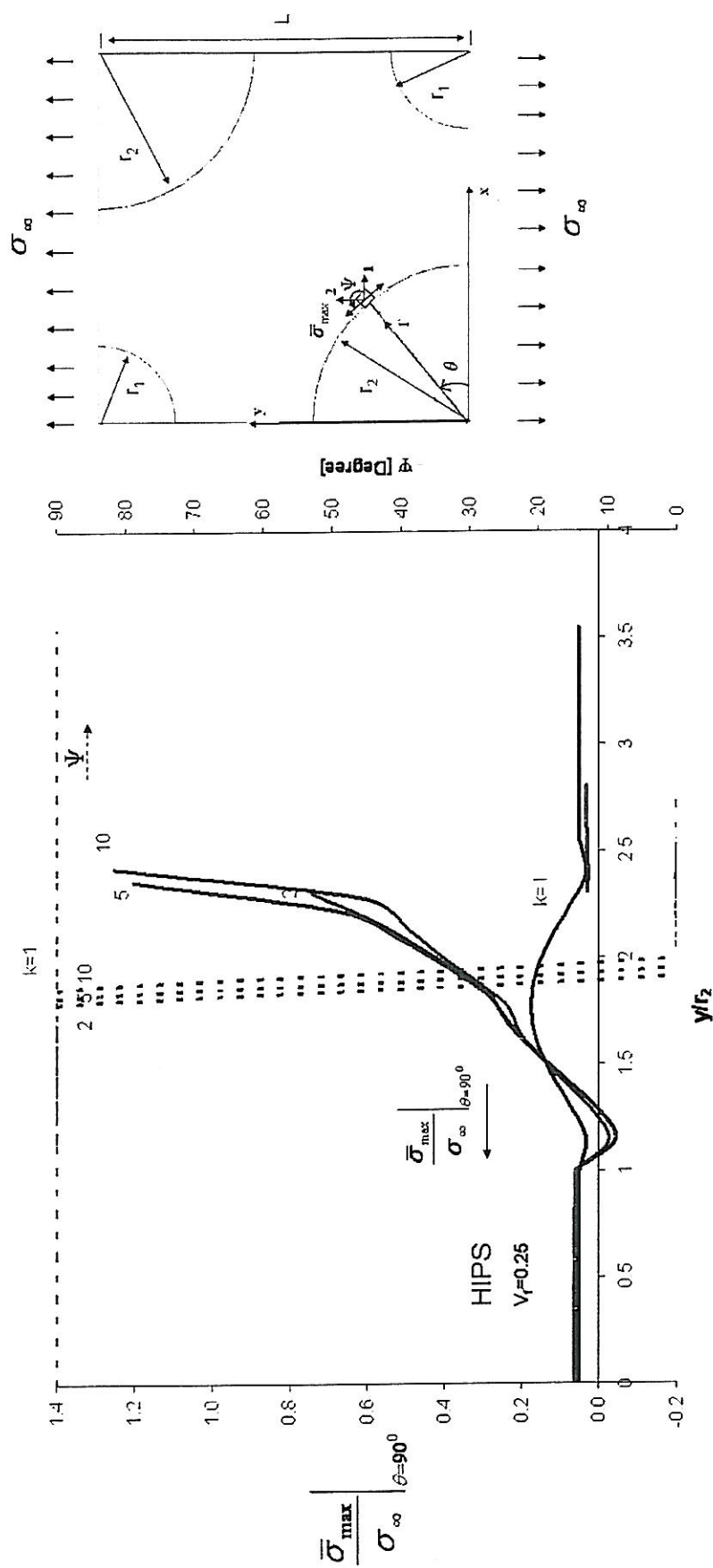


Figure 9.7.20: Maximum Principal Stress Along the y-axis in HIPS with Various Bimodal Ratios.

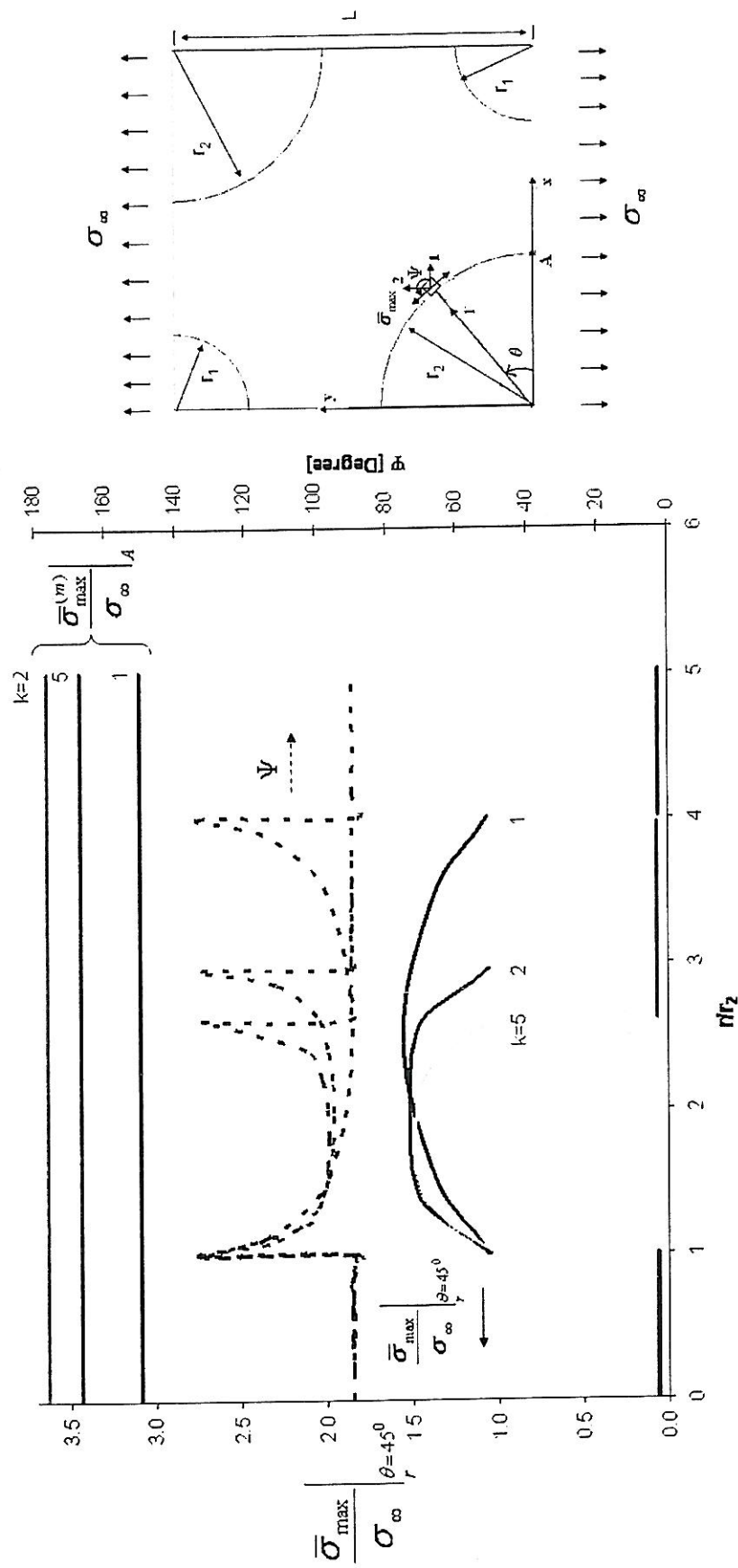
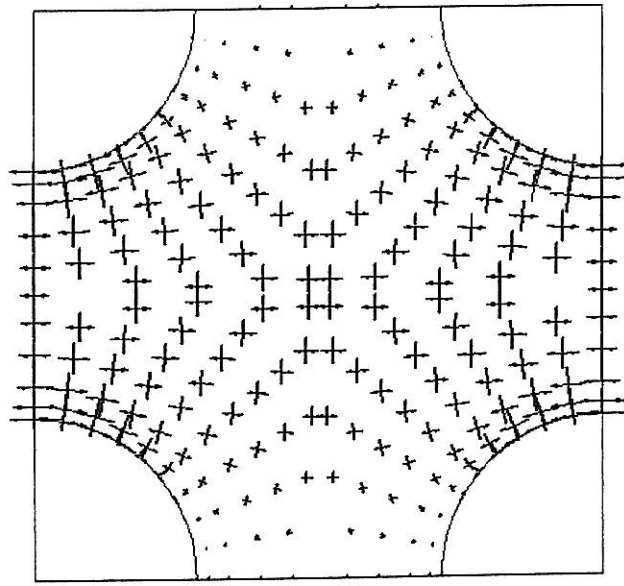


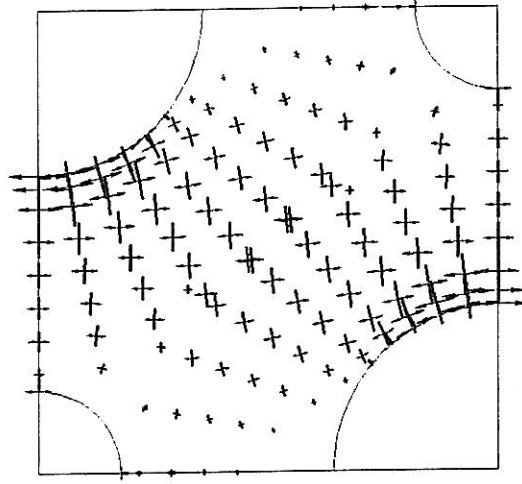
Figure 9.7.21: Maximum Principal Stress Along the First Diagonal (along the r at $\theta = 45^\circ$) in HIPS with Various Bimodal Ratios.

A uniform, maximum principal stress is found inside of the particles. Different from the Figs. 9.7.19 and 9.7.20, the distributions of principal stresses in Fig. 9.7.21 are symmetric to its diagonals. In the figure, the solid lines represent the highest values, i.e., values at the equator of the large particle. Thus, the large particles are crucial for craze formation. In Fig. 9.7.22, distributions of the maximum principal stress are shown in representative volume elements of different bimodal HIPS systems. In the figures, blue arrows represent the maximum principal stress vectors whereas red lines show the possible craze directions. The length of each craze line is proportional to the magnitude of the maximum principal stress.

$k=1$



2



5

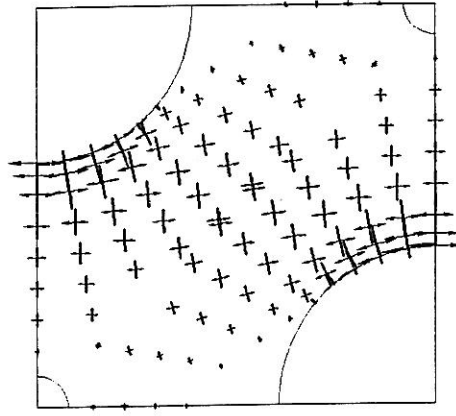


Figure 9.7.22: Distributions of Maximum Principal Stress in HIPS with Various Bimodal Ratios.

9.8 Interaction among Crazes Emanating from Rubber Particles

In this Section, a micromechanics study on interaction of crazes emanating from adjacent rubber particles (Fig. 9.8.1) is reported. The maximum principal stresses and possible craze growth trajectories are obtained in a vicinity of a craze tip emanating from occluded particles.

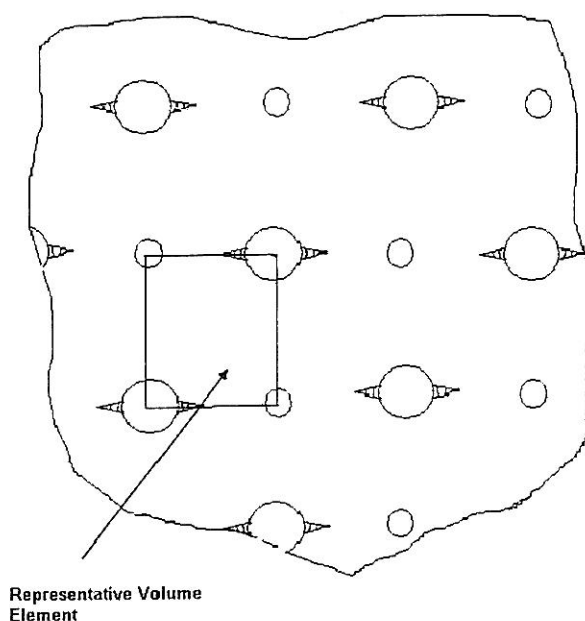


Figure 9.8.1: Interaction of Crazes Emanating from adjacent Rubber Particle in HIPS Polymers.

The maximum principal stress criterion is used to estimate the craze growth direction in a HIPS polymer with a rubber particle volume fraction of 25%. Computational micromechanics are carried out for HIPS polymers with mono-modal and bimodal particle systems. Nominal displacements on representative elements for these cases are made, using the damage variables obtained at selected strain levels. Details of the micromechanics modeling are discussed in Section 8.2.2.

In Fig. 9.8.2, the maximum principal stresses and possible craze growth and new craze formation are shown in the vicinity of existing crazes emanating from rubber particles in a HIPS polymer with mono-modal particle dispersion ($\epsilon_{\infty} = 0.0085$).

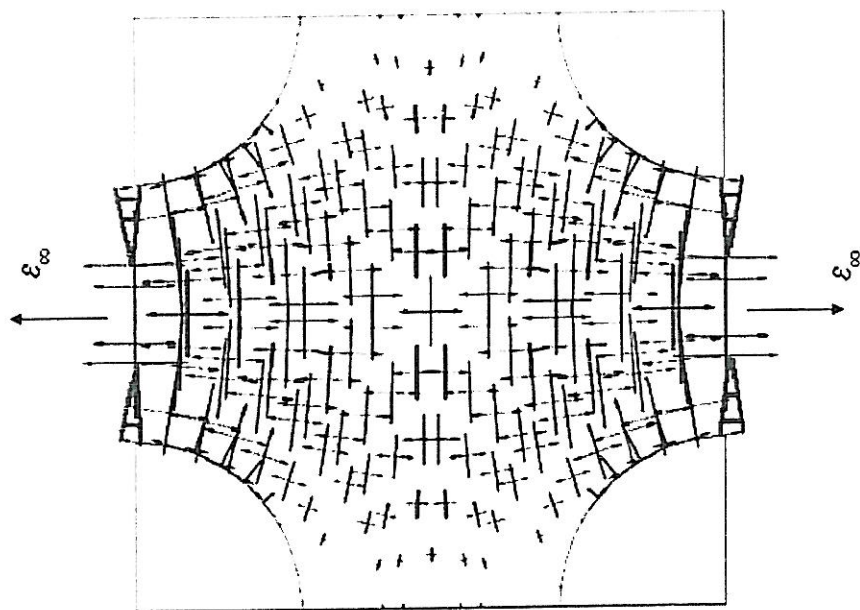


Figure 9.8.2: Maximum Principal Stress (blue) in the Vicinity of Crazes Emanating from Rubber Particles, and Possible Craze Formation and Growth (red) in HIPS. [$V_f=0.25$; $\epsilon_c=0.0085$; Mono-modal Particle Dispersion]

In the figure, maximum principal stresses are shown in blue and new craze formation and growth in red. All particles have the same size; thus, the same probability to have crazes. At $\epsilon_o = 0.0085$, the length of each craze is estimated to be $3.7 \mu\text{m}$, based on the craze statistics experiments reported in Section 4.2.

High stress concentrations occur at the craze tip and, craze growth and new craze formation are expected to occur in the direction perpendicular to the principal stress direction. SEM micrographs (Fig.9.8.3) taken from a 25% particle filled HIPS reveal the craze growth and formation patterns that are suggested by the micromechanics results (Fig. 9.8.2).

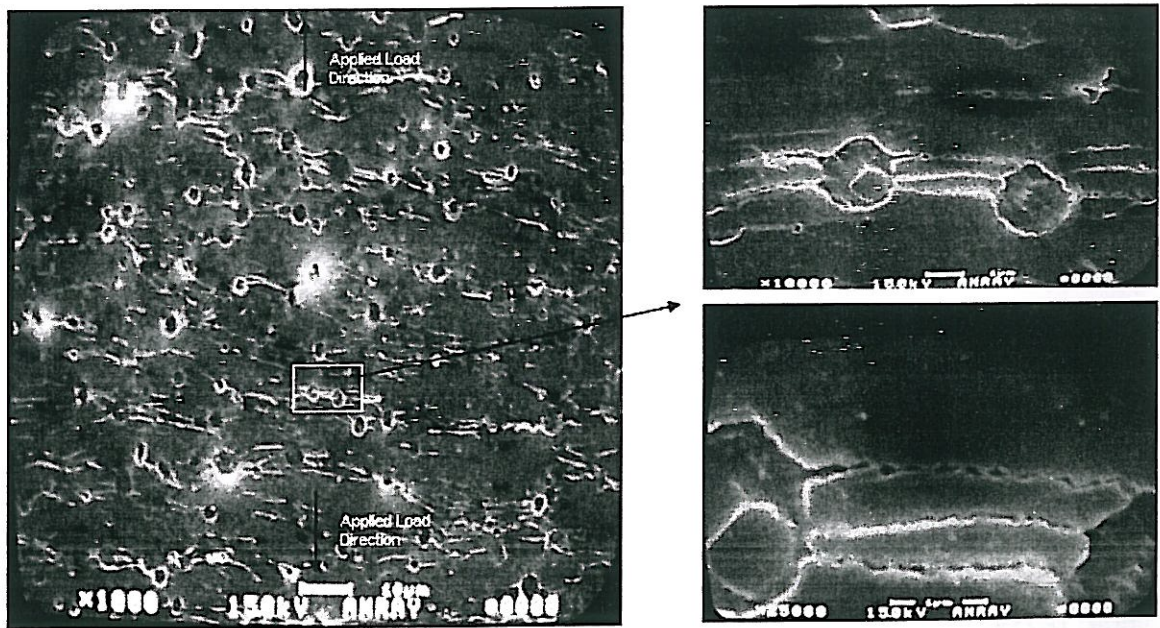


Figure 9.8.3: Initiation of Crazes Emanating from Rubber Particles in HIPS Polymers.
[$V_f=0.25$; $\epsilon=0.35$]

In Fig. 9.8.4, interaction among crazes and their growth around the rubber particles are shown in a mono-modal dispersed rubber-particle filled HIPS polymer under

two different levels of strain. At $\epsilon_\infty = 0.01$, a larger initial craze length and nominal load are employed in the micromechanics modeling, based on experiments in assessing craze statistics and craze damage.

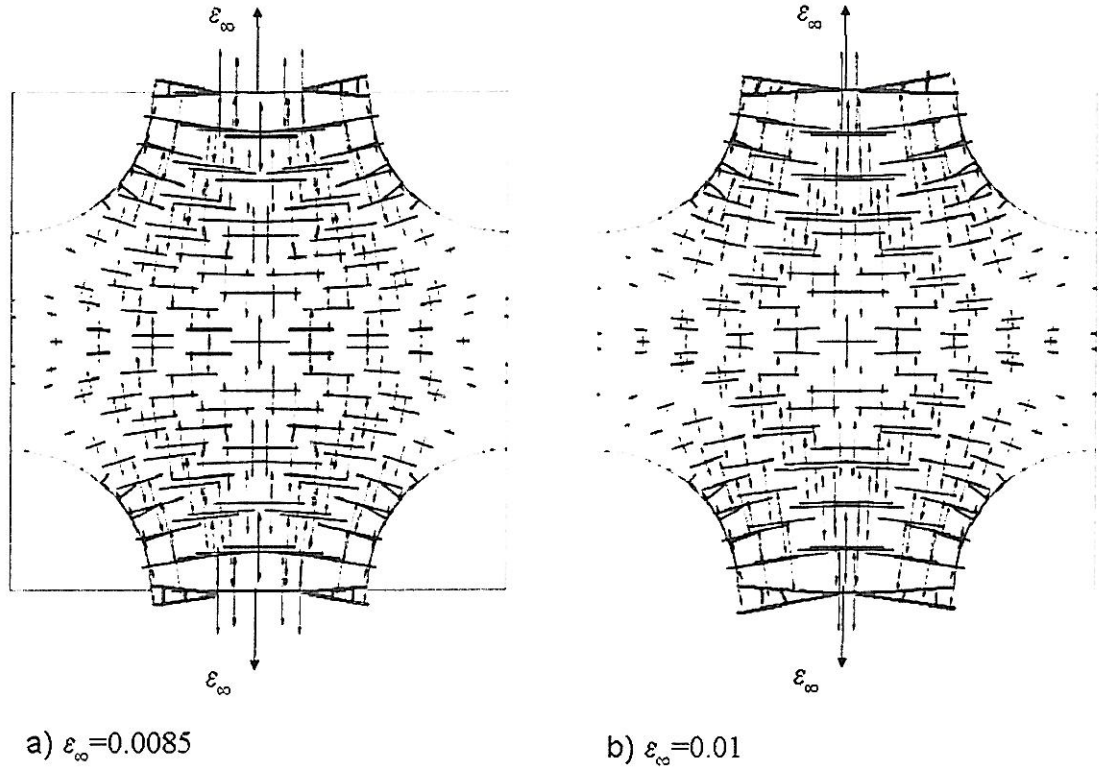


Figure 9.8.4:Maximum Principal Stress (blue) in the Vicinity of Crazes Emanating from Rubber Particles and Possible Craze Formation and Growth (red) in HIPS at: a) $\epsilon_\infty = 0.0085$; b) $\epsilon_\infty = 0.01$. [$V_f=0.25$; Mono-modal, $k=1$, Particle Dispersion]

In Fig. 9.8.5, interaction of crazes emanating from rubber particles and potential craze formation and growth paths around rubber particles in a bimodal dispersed rubber particle filled HIPS ($k=2$) are shown at a loading level, $\epsilon_\infty = 0.0085$. In the micromechanics model, only larger particles emanate crazes (based on the results obtained in Section 9.7.2). Compared to the mono-modal dispersion HIPS, two crazes are introduced at the equator of the larger particles. Computational micromechanics

procedures used are the same as those carried out in the craze interaction problems on mono-modal dispersion HIPS polymers.

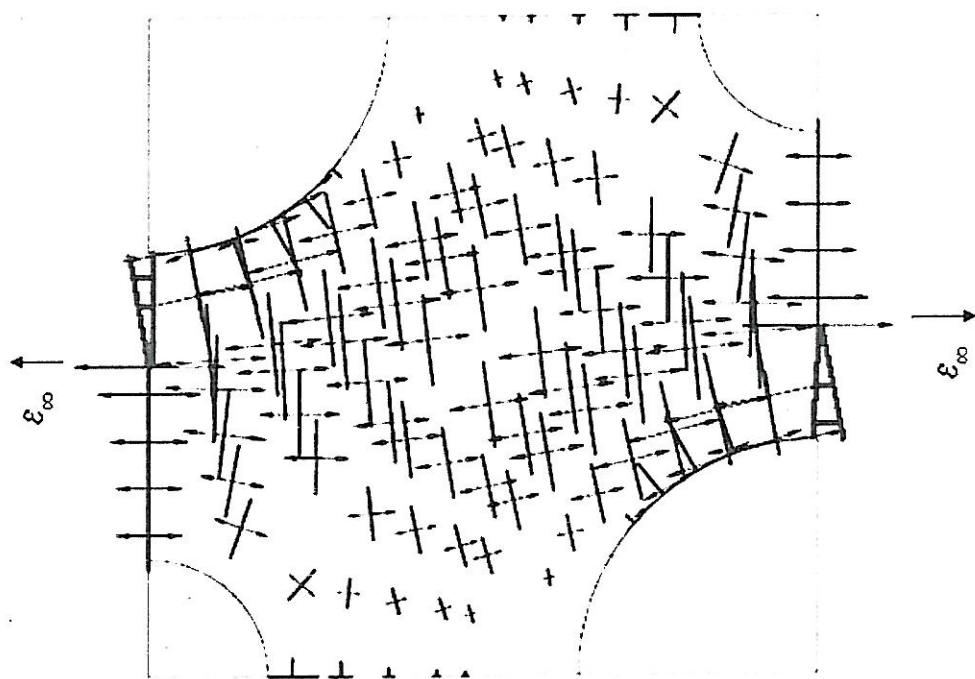


Figure 9.8.5: Maximum Principal Stress (blue) in the Vicinity of Crazes Emanating from Rubber Particles and Possible Craze Formation and Growth (red) in HIPS. [$V_f=0.25$; $\epsilon_{cr}=0.0085$; Bimodal, $k=2$, Particle Dispersion]

As can be seen in Fig.9.8.5, the interaction of crazes emanating from particles affects new craze formation and growth in the bimodal HIPS. The bimodal HIPS system does not have a microstructure symmetry. The craze interaction affects the local stress field (Fig.9.8.6) and may cause a shift in the craze growth and formation. Craze formation and growth are not orthogonal to applied load direction.

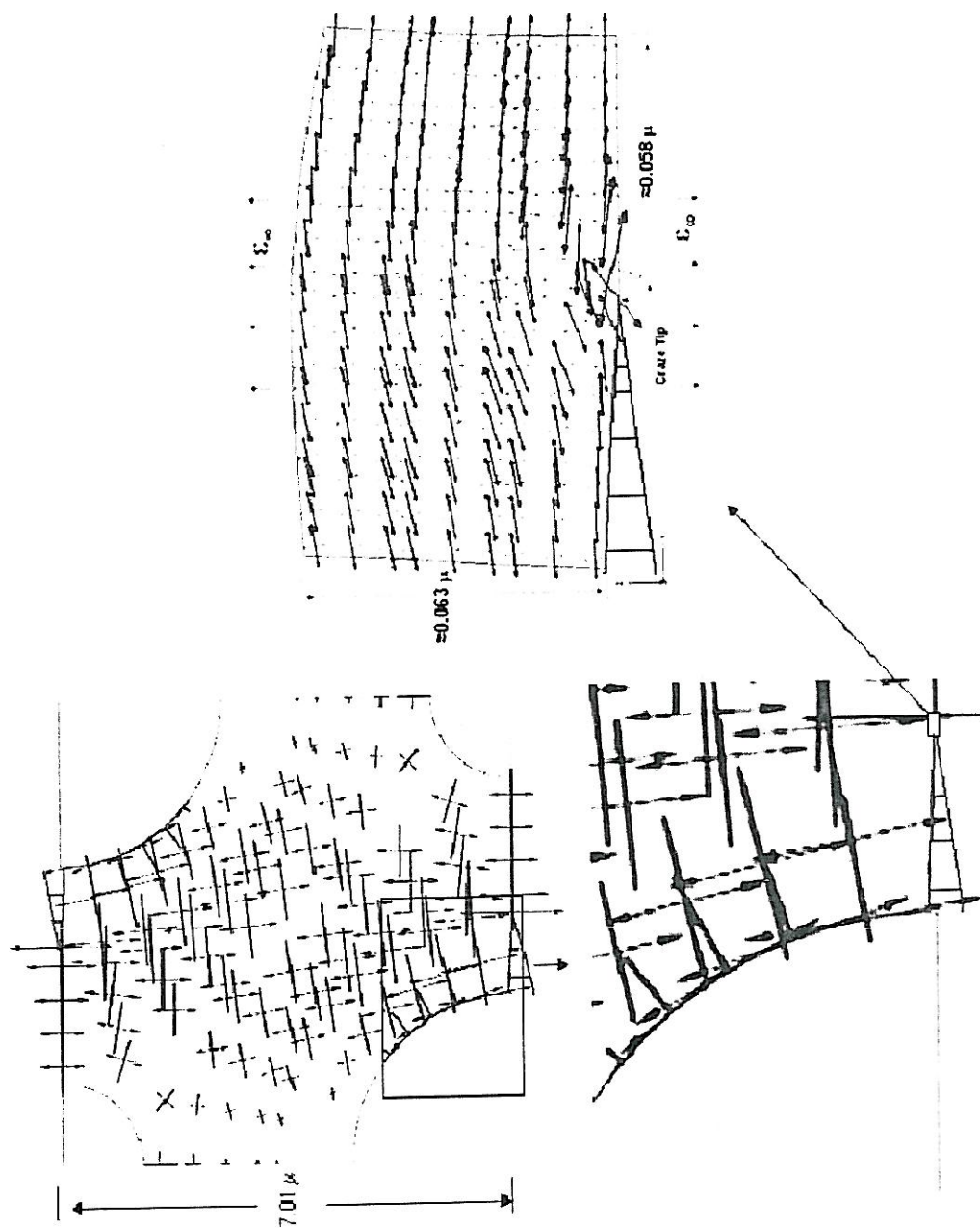


Figure 9.8.6: Maximum Principal Stresses and Possible Craze Formation and Growth in the Vicinity of a Craze Emanating from a Bimodal HIPS Polymer. [$V_f=0.25$; $\varepsilon_c=0.0085$; Bimodal, $k=2$, Particle Dispersion]

In Fig. 9.8.6, around the particle and in the vicinity of an existing craze, maximum principal stresses and possible craze formation and growth trajectories under uniaxial tensile load are shown. Blue arrows are the maximum principal stress directions and red lines are possible craze formation and growth trails. The stress field shown in the figure corresponds to the applied nominal load of 1.86 ksi and all the obtained maximum principal stresses are shown. However, only the ones exceed the yield stress of polystyrene ($\sigma_{ys} = 6.6$ ksi) will cause craze formation. In Fig. 9.8.7 (a), those maximum principal stresses higher than the polystyrene yield stress are given along with the crazes formed at several load levels. Craze damage growth under three different loading, i.e., $\epsilon_x = 0.0085$, $\epsilon_x = 0.01$ and $\epsilon_x = 0.02$, are investigated and possible craze damage zone growth is shown in Fig. 9.8.7(b). In micromechanics modeling, employed nominal displacements are based on obtained damage variables at given strain levels. Also, at a given strain level, characteristic craze length, l , and thickness, δ , are estimated from direct microscopic observations (see Section 4.2).

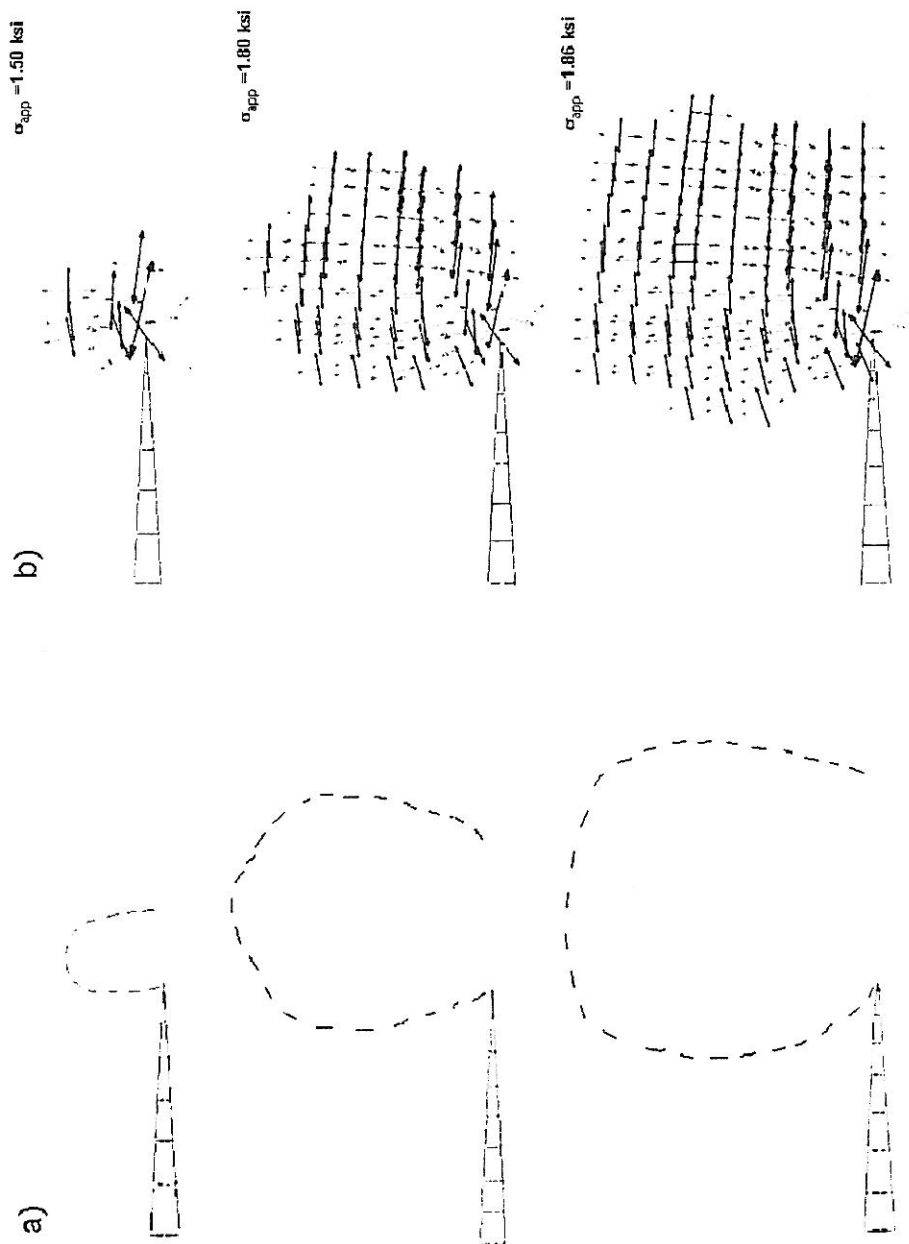


Figure 9.8.7(a): Craze Development in HIPS under Increasing Loading. a) Craze Damage Zone; b) Maximum Principal Stresses (blue) which exceed σ_{ys} and Possible Craze Formation (red). $[V]=0.25$; $\epsilon_{cr}=0.0085$; Bimodal, $k=2$, Particle Dispersion]

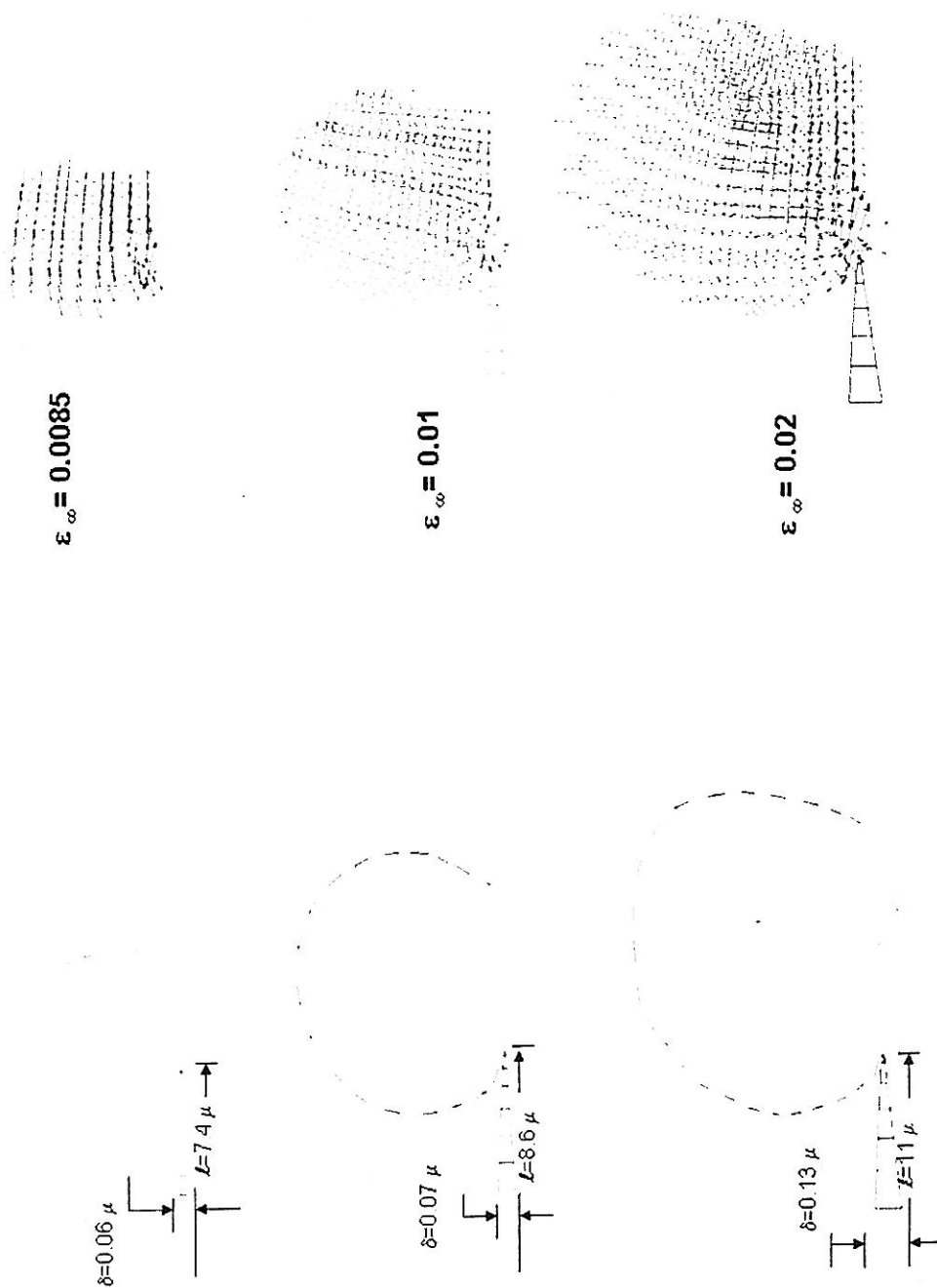


Figure 9.8.7(b): Craze Development in HIPS under Increasing Strain. a) Craze Damage Zone Growth; b) Maximum Principal Stresses (blue) and Possible Craze Formation (red). [$V_f=0.25$; Bimodal, $k=2$, Particle Dispersion]

In a HIPS polymer with a stationary craze emanating from a rubber particle, new crazes are formed adjacent parallel to the existing one under an increasing load. Craze damage appears to grow both upward and forward. The evolving craze damage zone eventually gets connected to the next one and causing large stress whitening areas as observed in experiments.

Comparisons the case of $k=2$ with those of $k=1$ and $k=10$ ($V_f=0.25$ and $\epsilon_x=0.0085$) reveal that the bimodal ($k=2$) HIPS system is more critical in that the maximum principal stresses and the corresponding craze growth zone size are greater than those of $k=1$ and $k=10$. For the $k=1$ and $k=2$ cases, maximum principal stresses and craze damage formation in the craze-tip vicinity are shown in Figs. 9.8.8 and 9.8.9, respectively.

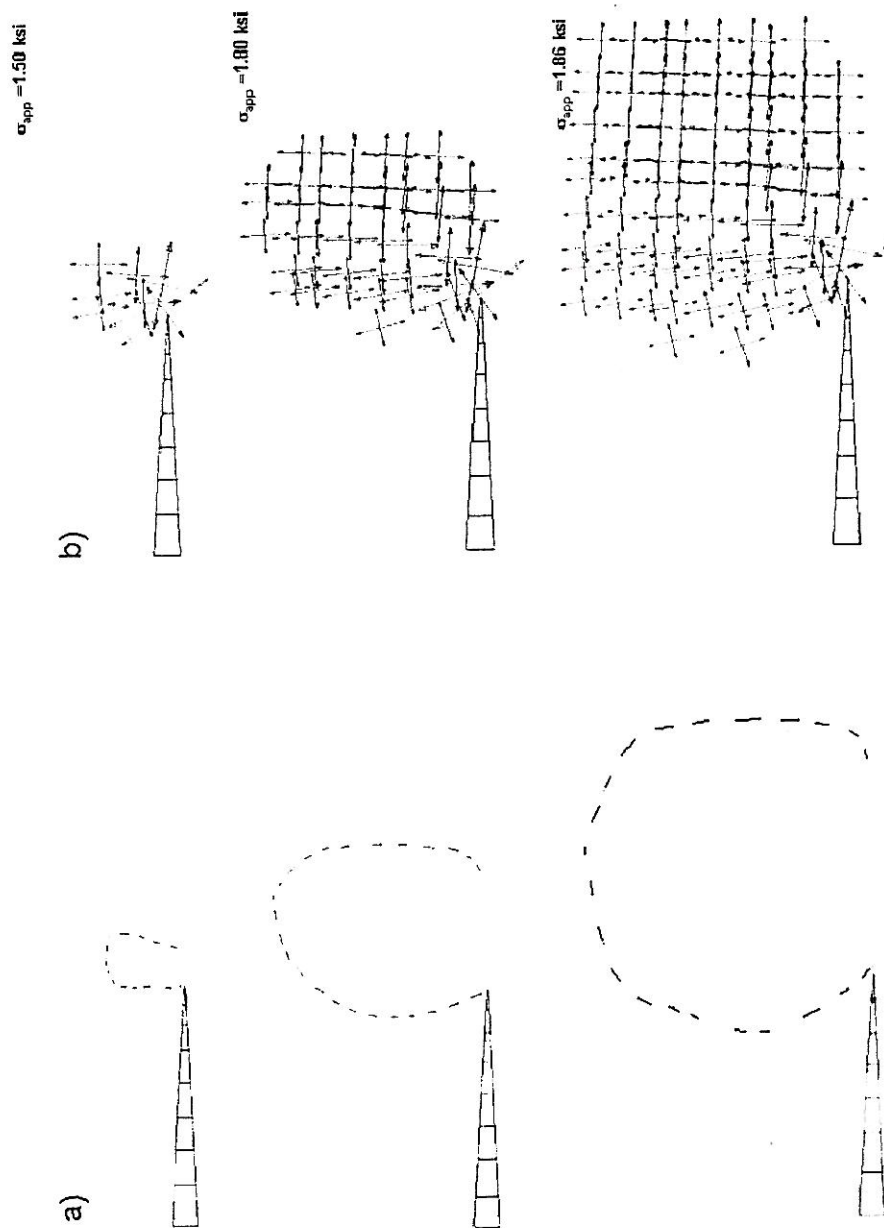


Figure 9.8.8: Craze Development in HIPS under Increasing Loading. a) Craze Damage Zone; b) Maximum Principal Stresses (blue) which exceed σ_{ys} and Possible Craze Formation (red). [$V_f=0.25$; $\epsilon=0.0085$; Mono-modal, $k=1$, Particle Dispersion]

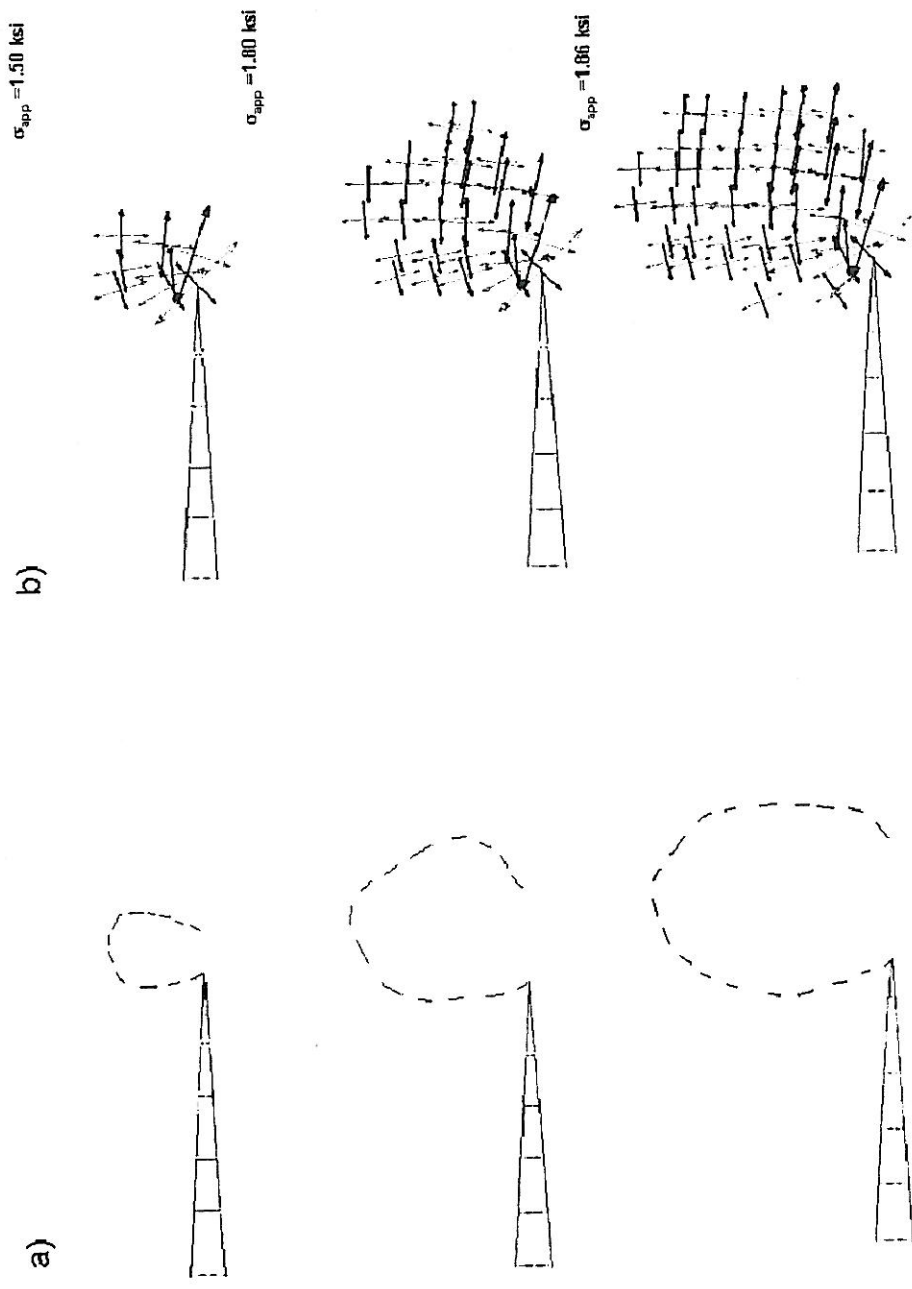


Figure 9.8.9: Craze Development in HIPS under Increasing Loading. a) Craze Damage Zone; b) Maximum Principal Stresses (blue) which exceed σ_y and Possible Craze Formation (red). [$V_f=0.25$; $\epsilon=0.0085$; Bimodal, $k=10$, Particle Dispersion]

10. CONCLUSIONS

Craze damage development in high-impact polystyrene (HIPS) has been studied experimentally, theoretically and numerically from continuum and microscopic points of view. The following conclusions have been drawn based on the results obtained in the study:

1. A series of monotonic tensile experiments have been conducted. Important microstructure parameters, e.g., craze density, orientation, size and their distributions have been obtained during craze damage evolution in HIPS.
2. A proper experimental method, using a loading-unloading-reloading test scheme, has been introduced. Macroscopic craze damage development and resulting property degradation of HIPS have been measured.
3. Microscopic craze damage evolution in HIPS can be characterized by density and cumulative distribution functions of craze length and orientation.
4. Cumulative and density distributions of craze length can be described with a three-parameter Weibull-form function. The Weibull shape and scale parameters, α and β , are found to be related to the craze density, size and the nature of craze growth. Cumulative and density distributions of craze orientation followed the standard Gaussian distribution function.
5. A comparative study on micromechanics of rubber toughened polymer has been made for proper evaluation of effective properties of occluded particles in the HIPS.

6. A generalized SCM, including incompressible polybutadiene matrix in occluded particles, has been used to account for the HIPS microstructure details. Constitutive properties used in the micromechanics formulation have been modified to include the mineral oil effect.
7. The effect of craze damage on mechanical property degradation has been studied with the aid of experimentally measured modulus reductions. The maximum degradation of the modulus is about 20%. Transverse Young modulus, E_2 , and Poisson's ratio, ν_{21} , are not expected to change with the craze formation and growth under uniaxial tensile loading.
8. Craze orthotropy has been investigated with a craze damage model, based on continuum damage mechanics formulation. A fourth-order damage tensor representing material degradation and coupling between damage variables (e.g., D_{12} and D_{21}) has been derived. The effective stress concept and the strain equivalence principle are employed to formulate constitutive equations of the damaged polymer. Also, thermodynamic driving force for craze damage growth is obtained using a complementary strain energy density function.
9. Computational micromechanics modeling, based on a finite element method, has been developed to study the influence of the occluded particle volume fraction and size distribution on craze formation in HIPS. The maximum stress concentration increases with the occluded particle volume fraction, but decreases as the occlusion (polystyrene) amount in the rubber particle increases. In a HIPS polymer with occluded particles of bimodal sizes, the maximum stress

concentration is found to be located at the equator of the larger particle. Thus, crazes are expected to initiate at the equators of large particles.

10. Craze interaction has also been modeled with the HIPS microstructure and craze geometry. The associated craze growth characteristics in HIPS have been studied. In a HIPS polymer with mono-modal particle dispersion, craze growth and new craze formation are found to occur in the direction perpendicular to the maximum principal stress direction. In a bimodal HIPS system, craze interaction affects the local stress field and causes a shift in the craze growth and formation. The strong interaction causes craze formation and growth not to occur orthogonal to applied load direction. The crazes appear to attract and grow into each other under increasing loading.

11. FUTURE RESEARCH

The following recommendations may be considered in the future research to extend the current experimental, analytical and numerical studies on investigate craze damage development in HIPS:

1. The predicted in-plane properties, E_{22} , ν_{12} , ν_{21} , need to be validated with additional experiments. Development of new experimental methods is essential to assess the damage components, D_{22} and D_{66} and to confirm the analytical estimates.
2. Non-zero thermodynamic driving force components, $-Y_{11}$, $-Y_{21}$, associated with the corresponding damage variables have been formulated. However, the critical thermodynamic driving force, Y_c , which is a measure of material damage resistance has not been measured. It is essential to develop new experimental methods to measure Y_c .
3. The orthotropic damage formulation based on continuum damage mechanics (CDM) for uniaxial loading can be extended to general anisotropic damage in multiaxial loading states.
4. Constitutive equations of the damaged polymer have been derived for only uniaxial tensile loading condition. Further studies are necessary to expand the study to cover various loading conditions.
5. In computational micromechanics modeling, occluded particles are assumed to be miscible and effective material properties are used (ignoring polystyrene sub-inclusions; hence, it's real microstructure). It is also assumed that the particles are

perfectly bonded to the matrix and dispersed in a regular arrangement. Current models need to be improved to account all of these.

6. The occluded particle size effect has been studied considering a bimodal HIPS only. General models, which include other particle size distributions, are needed to ascertain the relationship between the particle size dispersion and the craze formation.
7. This research has covered only a small aspect of craze damage in HIPS. All the experimental methods, theoretical and numerical analyses have been formulated for the simple, uniaxial tensile loading condition in air at room temperature. Craze development in HIPS subjected to other environments (i.e., temperature, fluid etc.) and stress states should also be investigated.

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13 APPENDICES

APPENDIX A: Rubber Particle Size Modification

Accurate rubber particle size distributions data are necessary to investigate second-phase particle size and distribution effect. There are two commonly used methods to measure particle size distributions: Light-scattering Method and Image Analysis Method.

These methods are approximate. The light-scattering is based on measurements done in a liquid suspension (Toluene or MEK) which causes particle swelling; thus, observed particle sizes and corresponding distributions are not accurate. Image analysis method is a direct method; however, three dimensional particle size distributions are estimated from size dispersion data extracted using 2-D images.

In the study, occluded particle size distributions measured by light-scattering method are corrected by a correction factor, a swelling factor, given by R. A. Hall [107]. He studies swelling of rubber particles in MEK solvent experimentally and gives an estimated swelling factor of 1.64. Also, occluded particle size distributions extracted from AFM images are corrected via Saltykov's Method. Details of the correction procedure are given elsewhere [59].

In Fig.A1, measured occluded particle size distribution (by light-scattering method) and particle size dispersion data (by AFM imaging analysis) are shown for HIPS A. In the figure, corrected particle size distribution curve and size dispersion data are also included for comparison.

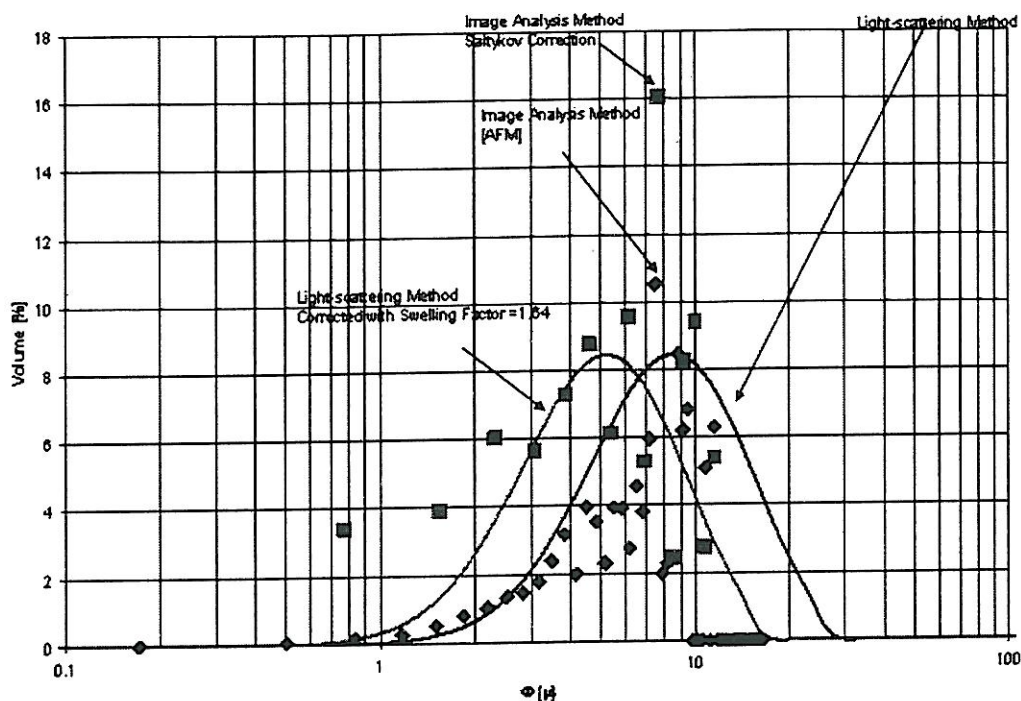


Figure A1: Original and corrected Particle Size Distributions for HIPS A.

For the study, particle size dispersion data were available only by AFM imaging. Thus, supplied particle size distribution data for all six grades of HIPS used for the study are corrected using Saltykov's method.

In the following figures, Figs.A2-A4, particle size distribution functions (analysis in number) estimated after Saltykov's correction are shown for all the HIPS grades comparatively. Overall results are summarized in Table A1.

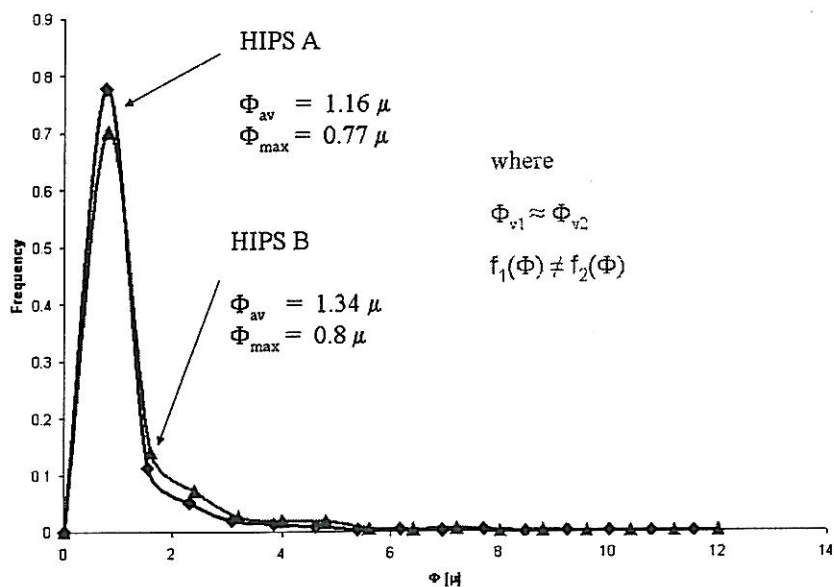


Figure A2: HIPS Grades with Similar Average Particle Sizes, but Different Size Distributions.

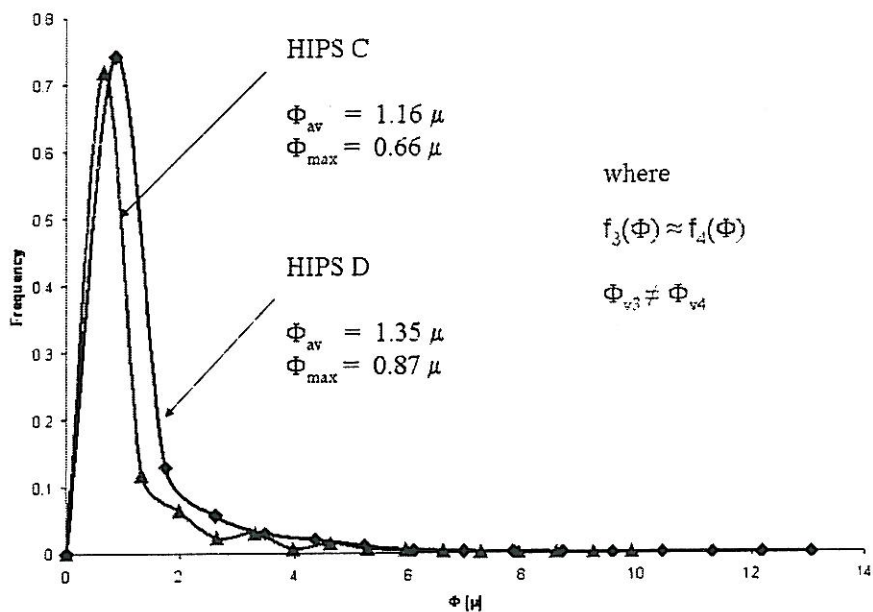


Figure A3: HIPS Grades with a Similar Particle Size Distribution, but Different Average Particle Sizes.

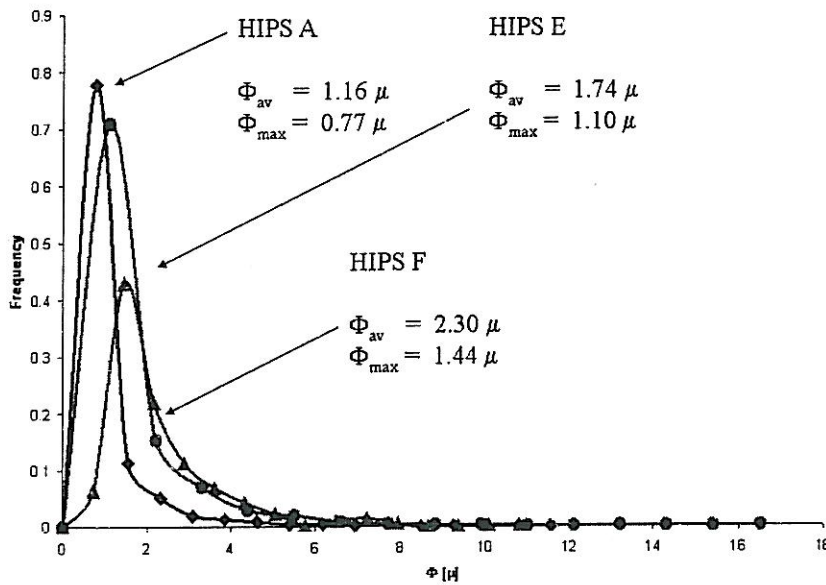


Figure A4: Particle Size Distributions of HIPS Grades by Different Manufacturers.

Table A1: Summary of Rubber Particle Size Distribution after Saltykov's Correction
(Analysis in Number)

Φ [μ] Rubber Particle Size Dist. (Analysis by Number)	HIPS A Φ_{v1} $f_1(\Phi)$	HIPS B $\Phi_{v1} \approx \Phi_{v2}$ $f_2(\Phi)$	HIPS C Φ_{v3} $f_3(\Phi)$	HIPS D Φ_{v4} $f_4(\Phi) \approx f_3'(\Phi)$	HIPS E Φ_{v5} $f_5(\Phi)$	HIPS F Φ_{v6} $f_6(\Phi)$
Average	1.16	1.34	1.16	1.35	1.74	2.30
Mode	0.77	0.80	0.66	0.87	1.10	1.44
Median	0.39	0.47	0.49	0.29	0.37	1.00
Standard Deviation	2.27	2.21	1.79	2.50	3.13	2.82

APPENDIX B: Micromechanics Models

B.1 Differential Method

Bruggeman [135] performed the first study related to Differential Method of modeling. However, it was not in the context of mechanics. Later, the Differential Method was applied by Roscoe [136] on modeling the behavior of fluid suspensions even though the method was equally good for both fluid and solid suspensions.

The starting point of the Differential Method is based on the elastic solution of dilute suspension given by Goodier [137]

$$\begin{aligned}\frac{\mu}{\mu_m} &= 1 - \frac{15(1-\nu_m)[1-(\mu_i/\mu_m)]}{7-5\nu_m+2(4-5\nu_m)\frac{\mu_i}{\mu_m}}c \\ K &= K_m + \frac{(K_i - K_m)}{1+[(K_i - K_m)/(K_m + \frac{4}{3}\mu_m)]}c\end{aligned}\quad , \quad (B.1 \text{ a, b})$$

where, $c = \left(\frac{a}{b}\right)^3$ is the volume fraction of the spherical particles under dilute conditions

($c \ll 1$), μ is the elastic shear modulus, K is the bulk modulus, and ν is the Poisson's ratio.

Subscripts i and m are referring to inclusion and matrix phases respectively.

The basic idea behind the method is viewing the whole composite as a sequence of dilute suspensions when a new increment of inclusions is added each time. In this step wise process, new effective properties are calculated from suitably modified homogeneous medium of the previous step. This process is continued until the volume fraction of the inclusion phase reaches to 1. Mathematically, it comes to a point where the

increments of the added inclusions become infinitesimal and a differential form results.

The end result of this process gives the following governing equations [138]

$$\frac{d\mu}{dc} + \frac{15(1-\nu)(\mu - \mu_i)}{(1-c) \left[7 - 5\nu + 2(4-5\nu) \frac{\mu_i}{\mu} \right]} = 0$$

and

(B.2 a, b)

$$\frac{dK}{dc} + \frac{(K - K_i)}{(1-c) \left[1 + \frac{K_i - K}{K + \frac{4}{3}\mu} \right]} = 0$$

where effective Poisson's ratio, ν , is related to K and μ through

$$\nu = \frac{3K - 2\mu}{2(3K + \mu)}. \quad (B.3)$$

These differential equations are coupled and non-linear. They need to be solved simultaneously for the values K , μ , and ν by satisfying the following boundary conditions [138]

$$\begin{aligned} \text{at } c=0 \quad \mu &= \mu_m \\ &K = K_m \\ \text{at } c=1 \quad \mu &= \mu_i \\ &K = K_i. \end{aligned}$$

In the case of perfectly rigid inclusions and incompressible matrix phase where $K_m \gg \mu_m$ the above equations take the simpler forms

$$\frac{\mu}{\mu_m} = \frac{1}{(1-c)^{5/2}}$$

and

(B.4 a,b)

$$\frac{K}{K_m} = \frac{1}{(1-c)}.$$

B.2 Mori-Tanaka Method

Different than both the Differential Method and the Three Phase Model, Mori-Tanaka model is a mathematical formulation. It involves rather complex manipulations of the field variable in the context of eigenstrain and backstress. Even though the Mori-Tanaka Method made numerous contributions in micromechanics analysis, Benveniste [139] gave the simplest derivation of the Mori-Tanaka's formulation.

When applied to the spherical inclusion problem under non-dilute conditions, following equations are given by Benveniste [139]

$$\mu = \mu_m + c(\mu_i - \mu_m) \frac{1}{1 + (1-c) \left[\frac{\mu_i - \mu_m}{\mu_m + \frac{\mu_m(9K_m + 8\mu_m)}{6(K_m - 2\mu_m)}} \right]} \quad (B.5)$$

and

$$K = K_m + \frac{c(K_i - K_m)}{1 + (1-c) \frac{(K_i - K_m)}{(K_m + \frac{4}{3}\mu_m)}} \quad (B.6)$$

In case of perfectly rigid inclusions and nearly incompressible matrix phase Eqs.(B.5) and (B.6) become

$$\frac{\mu}{\mu_m} = \frac{1 + (\frac{3}{2})c}{(1-c)} \quad (B.7)$$

and

$$\frac{K}{K_m} = \frac{1}{(1-c)}. \quad (\text{B.8})$$

B.3 Comparison Among Different Approaches

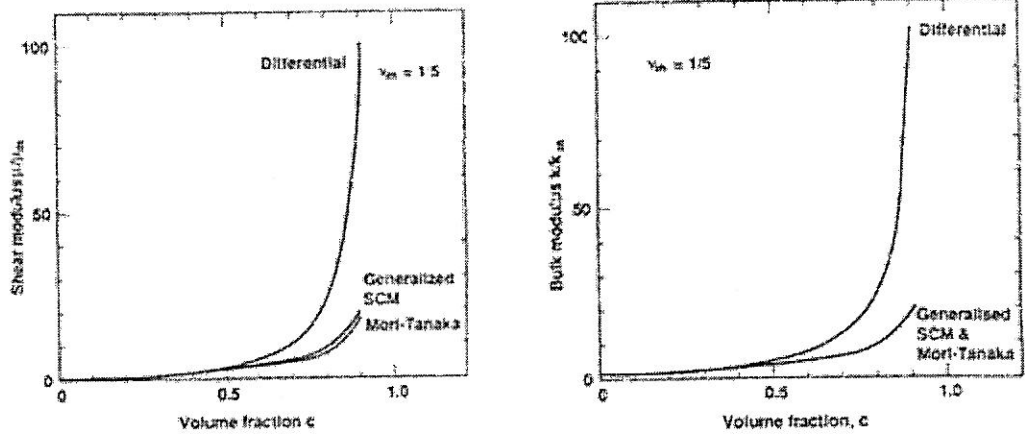
Among all the micromechanics models considered for occluded particle and HIPS polymer, Halpin-Tsai Equations are applicable to elastic cases only and incompressibility is not included in the formulation. Different than the Halpin-Tsai Equations, the Differential Scheme, the Generalized Self-Consistent Method and the Mori-Tanaka Method can be used both for elastic and incompressible materials. These three methods are summarized in Table B.1 and their reduced forms are given for the cases of an incompressible matrix with rigid inclusions.

For comparison, the reduced forms are useful in the sense that they allow one to have a simple analytical form rather than a graphical assessment [138]. The dominant characteristic of these models (Table B.1) is the exponent of the $(1-c)$ term. The solutions diverge as $c \rightarrow 1$, which is similar to order of singularities in elastic problems. While the Differential Method and the Generalized Self Consistent Method show higher order effect for incompressible matrix case than for the compressible case, the Mori-Tanaka Method predicts same order effect for the both cases. As explained in [138] that strain gradients have higher order in the incompressible case than in compressible case; thus, the Mori-Tanaka Method can be divergence based on this argument by orders of magnitude as $c \rightarrow 1$.

Table B.1: Summary of Micromechanics Models which Include Rubber Phase Incompressibility

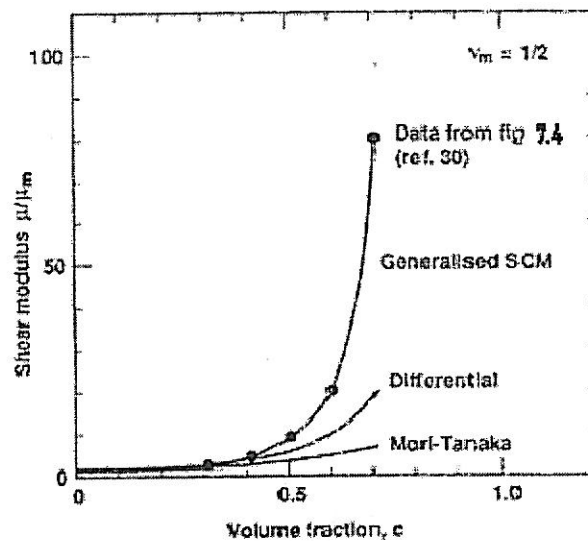
Micro-Mechanical Method	Elastic Matrix	Incompressible Matrix with Rigid Inclusions
Differential Method	$\frac{d\mu}{dc} + \frac{15(1-\nu)(\mu - \mu_i)}{(1-c) \left[7 - 5\nu + 2(4-5\nu) \frac{\mu_i}{\mu} \right]} = 0$ $\frac{dk}{dc} + \frac{(k - k_i)}{(1-c) \left[1 + \frac{k_i - k}{k + \frac{4}{3}\mu} \right]} = 0$	$\frac{\mu}{\mu_m} = \frac{1}{(1-c)^{5/2}}$ $\frac{k}{k_m} = \frac{1}{(1-c)}$
Three Phase Method	$A \left(\frac{\mu}{\mu_m} \right)^2 + 2B \left(\frac{\mu}{\mu_m} \right) + C = 0$ $k = k_m + \frac{c(k_i - k_m)}{1 + (1-c) \frac{(k_i - k_m)}{(k_m + \frac{4}{3}\mu_m)}}$	$\frac{\mu}{\mu_m} \rightarrow \frac{27}{16(1-c)^3}$
Mori-Tanaka Method	$\mu = \mu_m + c(\mu_i - \mu_m) \frac{1}{1 + (1-c) \left[\frac{\mu_i - \mu_m}{\mu_m + \frac{\mu_m(9k_m + 8\mu_m)}{6(k_m - 2\mu_m)}} \right]}$ $k = k_m + \frac{c(k_i - k_m)}{1 + (1-c) \frac{(k_i - k_m)}{(k_m + \frac{4}{3}\mu_m)}}$	$\frac{\mu}{\mu_m} = \frac{1 + (\frac{3}{2})c}{(1-c)}$ $\frac{k}{k_m} = \frac{1}{(1-c)}$

With regard to the Differential Method, Norris [140] and Milton [141] mention the Differential Method is a step wise method. Initial dilute suspension is homogenized to a new dilute suspension. Then the homogenization of the previous step is transferred to another dilute suspension. The process is repeated until a limit is reached. The Differential Method is a combination of several models and this sequence of models might lead to a result which is very different than a single model involving very tightly packed spheres. R.M. Christensen [138] compared these three models over the full volume fraction range without any approximation and showed that full range results are consistent with the asymptotic results. His comparative results are given in Fig.B.1 and Fig. B.2 for the cases of $\nu_m = 0.2$ and $\nu_m = 0.5$ respectively. As seen in Fig. B.1, bulk modulus calculations using the Generalized SCM and the Mori-Tanaka Method give identical results while results are very close to each other for shear modulus calculations. On the contrary, the Differential Method predictions are drastically different from both of them. For the incompressible matrix material case, (Fig. B.2) all three methods give different predictions while the biggest difference is between the Generalized SCM and the Mori-Tanaka Method. In Fig. B.2, some experimental data which are presented by Thomas [142] are also included.



Ref.: R.M. Christensen, and K.H. Lo, "A Critical Evaluation for a Class of Micromechanics Models,"
J. Mech. Phys. Solids, Vol. 38, 3, pp. 379-404 (1990)

Figure B.1: Comparison of Micromechanics Models for Compressible Matrix Material Case ($v_m = 0.2$) Through Full Range of Volume Fraction, c



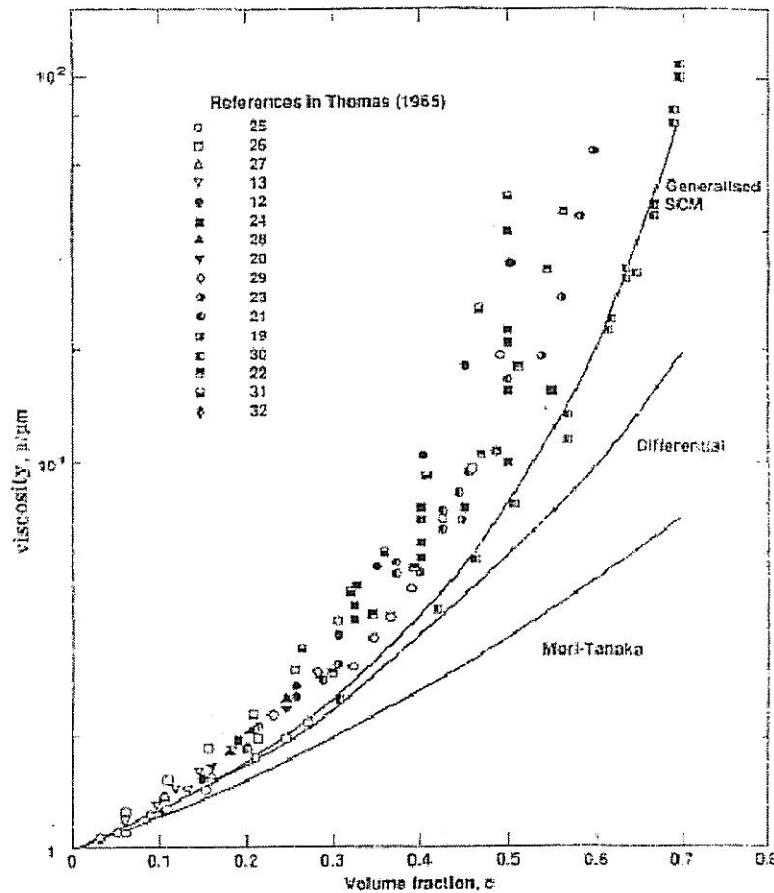
Ref.: R.M. Christensen, and K.H. Lo, "A Critical Evaluation for a Class of Micromechanics Models,"
J. Mech. Phys. Solids, Vol. 38, 3, pp. 379-404 (1990)

Figure B.2: Comparison of Micromechanics Models for Incompressible Matrix Material Case ($v_m = 0.5$) Through Full Range of Volume Fraction, c

In Fig. B.3, which is taken from R.M. Christensen paper, [138] the three methods are compared with different experimental results. In the figure, effective viscosity instead of shear modulus change with volume fraction is plotted. However, difference is merely notational [138]. The lowest data set is considered as a comparison criterion in the sense

that for a fixed value of c , higher viscosity values correspond to the mono-disperse inclusion suspensions while lower viscosity values correspond to the poly-disperse inclusion suspensions which is more suitable for $c \rightarrow 1$ cases. The chosen set of data from Eilers [143] belongs to a polydisperse emulsion of solid spherical droplets with diameters from 1.6 to 4.7 μm .

The Generalized SCM fits experimental data (Fig. B.3) the best. From Fig. B.2, it is revealed that, in linear scale, both the Differential Method and the Mori-Tanaka Method deviate drastically from the experimental data.



Ref.: R.M. Christensen, and K.H. Lo, "A Critical Evaluation for a Class of Micromechanics Models,"
J. Mech. Phys. Solids, Vol. 38, 3, pp. 379-404 (1990)

Figure B.3: Comparison of Micromechanics Models for Incompressible Matrix Material Case ($\nu_m = 0.5$) Through Full Range of Volume Fraction, c .

APPENDIX C: Continuum Damage Mechanics Variables

C.1 Geometrical Definition of Craze Damage

A representation of craze damage in a glassy polymer under uniaxial loading (damaged solid and representative volume element (RVE)) is given in Fig. C.1. If δS is a cross sectional area of the RVE at local coordinates, and $\delta \hat{S}$ is an effective cross sectional area which excludes the domain cut through the craze. As expected, $\delta S \geq \delta \hat{S}$, and the difference of the areas give the area of damage traces δS_D :

$$\delta S_D = \delta S - \delta \hat{S}. \quad (C.1)$$

The measure of a local craze damage D_n at point K in the direction n can be defined as

$$D_n(K, n, \xi) = \frac{\delta S_D}{\delta S}. \quad (C.2)$$

Based on this definition, one has the following:

$$\begin{aligned} D_n &= 0 && \text{(virgin state)} \\ D_n &= 1 && \text{(fracture state)} \\ 0 < D_n < 1 && \text{(any craze damage state).} \end{aligned} \quad (C.3)$$

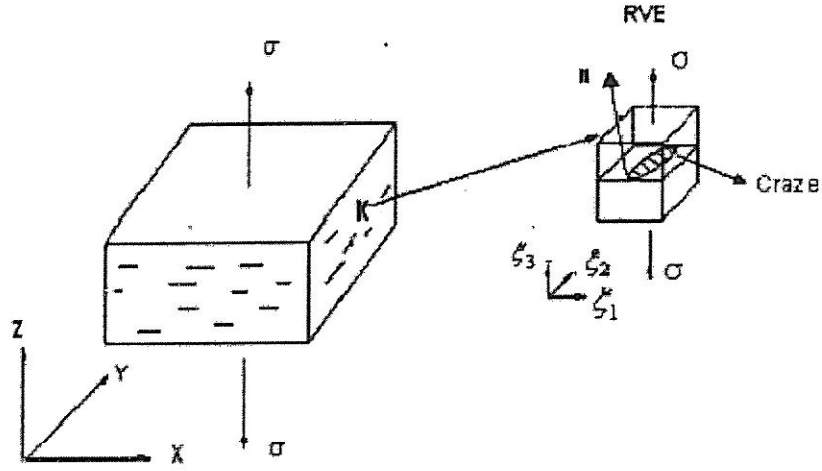


Figure C.1: Craze Damage and Its Damage Mechanics Representation.

If the craze damage is homogeneous (Fig. C.1) and if the maximum D_n is selected for representation then

$$D(X, n) = \text{Max}|D_n(K, n, \xi)|, \quad (\text{C.4})$$

where ξ_i are local coordinates. In the case of multiaxial isotropic damage, D does not depend on the orientation of the normal n .

An effective stress is the stress calculated over the section which effectively resists the forces. Based on the effective stress concept, the total stress may be defined without considering the space that the crazes take. In a uniaxial loading case, if the applied load is F on a representative volume element, then the stress is

$$\sigma = \frac{F}{A}. \quad (\text{C.5})$$

An effective area, $\delta\hat{S}$, by definition is

$$\delta\hat{S} = \delta S - \delta S_D = \delta S(1 - D). \quad (\text{C.6})$$

Using Eqs. (C.5 and C.6), an effective stress may be represented as

$$\tilde{\sigma} = \frac{\sigma \delta S}{\delta \hat{S}}$$

or (C.7)

$$\tilde{\sigma} = \frac{\sigma}{(1-D)}.$$

Evidently, $\tilde{\sigma} \geq \sigma$ and $\tilde{\sigma} = \sigma$ for a virgin material, and $\tilde{\sigma} \rightarrow \infty$ for a fractured material. In the case of uniaxial stress, for example, a linear elastic constitutive law of a damaged polymer is

$$\varepsilon_e = \frac{\tilde{\sigma}}{E} = \frac{\sigma}{(1-D)E}. \quad (C.8)$$

C.2 Thermodynamic Driving Force Of Crazes In Glassy Polymers

Thermodynamic driving force, $-Y$, is the associated variable for craze damage parameter, D . It has been shown [74] to relate to the elastic energy release rate during craze damage growth. The $-Y$ may be derived from the Helmholtz free energy, $\psi = \psi(\varepsilon, T; D)$. Consider a glassy polymer with craze damage. One may express ψ as

$$\rho\psi = \frac{1}{2}(1-D)C_{ijkl}\varepsilon_{ij}\varepsilon_{kl}, \quad (C.9)$$

where the C_{ijkl} is the stiffness matrix of the polymer. Then, constitutive equations for the polymer with craze damage become

$$\sigma_{ij} = \rho \left(\frac{\partial \psi}{\partial \varepsilon_{ij}} \right)_T = (1-D)C_{ijkl}\varepsilon_{kl}. \quad (C.10)$$

The associated variable $-Y$ (damage driving force) for D is defined as

$$-Y = -\rho \left(\frac{\partial \psi}{\partial D} \right)_T = \frac{1}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl}, \quad (\text{C.11})$$

The strain energy density function for the craze damaged polymer may be written as

$$W_e = \int_0^{\varepsilon_{ij}} C_{ijkl} (1-D) \varepsilon_{ij} d\varepsilon_{kl} \quad (\text{C.12})$$

or

$$W_e = \frac{1}{2} C_{ijkl} (1-D) \varepsilon_{ij} \varepsilon_{kl}. \quad (\text{C.13})$$

Comparing Eq.(C.11) with (C.13), one has

$$-Y = \frac{W_e}{1-D}. \quad (\text{C.14})$$

The $-Y$ is positive definite and takes the unit of strain energy.

C.2 Craze Damage Evolution

Damage evolution can be studied with irreversible thermodynamics based on the second principle. In fact, the second principle of thermodynamics is used for formulating a mathematical description of craze damage evolution. However, some assumptions need to be made for suitable application of the second principle. The first one assumes that entropy is a state function, valid for both reversible and irreversible processes. The second is that the second principle of thermodynamics is extendable locally to the entire system. Based on these, the second principle of thermodynamics (total entropy change) is

$$dS = d_e S + d_i S, \quad (\text{C.15})$$

where $d_e S$ is the external (surrounding) entropy, shows the interaction of a system with surrounding and $d_i S$ is the intrinsic (system) entropy, stands for the internal changes of the system.

The second principle of thermodynamics requires that intrinsic entropy to be positive. For an isothermal case, intrinsic entropy change can be written as

$$\sigma \dot{\varepsilon}^p - Y \dot{D} - A_k \dot{V}_k \geq 0, \quad (\text{C.16})$$

where $\dot{\varepsilon}^p$ is the plastic strain rate tensor, A_k is the k^{th} thermodynamic driving force associated with the k^{th} internal (flux) variable $\dot{V}_k$. In addition to isothermal case, one can have damage with insignificant plastic deformation then,

$$-Y \dot{D} \geq 0. \quad (\text{C.17})$$

To construct the evolution law(s), dissipation potential(s), which is the representation for the change of state of a system, needs to be derived using existing energy potential(s). It is suggested [74] that taking dissipation potential, φ , as a positive and quadratic function of flux variables would be the simplest form, i.e., for an isothermal case

$$\varphi \equiv \varphi(\dot{\varepsilon}^p, \dot{V}_k, \dot{D}) \quad \text{with} \quad A_k = \frac{\partial \varphi}{\partial \dot{V}_k}. \quad (\text{C.18})$$

It is also stated that a dissipation potential, φ_i , exists for each irreversible process, expressed in terms of flux variables [74]. For example, intrinsic dissipation, which is mechanical and microstructural induced dissipation, is

$$\varphi_1 = \sigma : \dot{\varepsilon}^p - A_k \dot{V}_k \geq 0 \quad (\text{C.19})$$

and for example, craze damage dissipation is

$$\varphi_2 = -Y \dot{D} \geq 0. \quad (\text{C.20})$$

Eqs. (C.19 and C.20) imply that total dissipation potential can be written as

$$\varphi = \varphi_1 + \varphi_2. \quad (\text{C.21})$$

For a damaged polymer, assuming that the matrix is elastic all the time and inelastic deformation results from crazing is taken in to consideration by the damage variable, D , dissipation function (for isothermal case) may be constructed as

$$\varphi = -Y \dot{D} \geq 0. \quad (\text{C.22})$$

Using Legendre-Fenchel transformation, complementary dissipation function, φ^* , can be constructed so that $\dot{D}$ is expressed in terms of D and $-Y$ as

$$\varphi^* \equiv \varphi^*(Y, D) \quad (\text{C.23})$$

and a kinetics law for a crazed damaged polymer may be stated with the help of generalized normality conditions as

$$\dot{D} = -\frac{\partial \varphi^*}{\partial Y}. \quad (\text{C.24})$$

APPENDIX D: Inelastic Deformation of Rubber-Toughened Polymers

Mechanical behaviors of polymers are difficult to be characterized because of their loading-rate and temperature dependency. Their mechanical properties are also dependent on the conditions of testing [144, 145]. Glassy polymers can show all the characteristics of thermoelastic, viscoelastic, rubbery state and rubbery flow behavior of solids depending on the temperature and time scale of measurements.

At a temperature below ($T_g - 50^\circ\text{C}$) solid polymers tend to exhibit elastic behavior at small strains. When they are strained to higher levels, the relationship between stress and strain is non-Hookean [4, 5]. Inelastic deformation, such as yielding, starts at the stress level above which irreversible deformations appear. Yield stress is the minimum stress at which irreversible strain generates when applied stress is removed.

Yielding in the polymers may be interpreted differently from plastic deformation in metals. Two different yielding modes, namely crazing and shear yielding, occur in polymers. Both the normal stress yielding (crazing) and the shear yielding are dependent on dilatational and deviatoric components of the stress tensor [6]. A study by Sternstein and Myers [10] show that depending on the stress state, a glassy polymer may exhibit four different yielding responses (Fig. D.1):

- a. No crazing and no shear yielding
- b. Crazing only
- c. Shear yielding only
- d. Simultaneous crazing and shear yielding

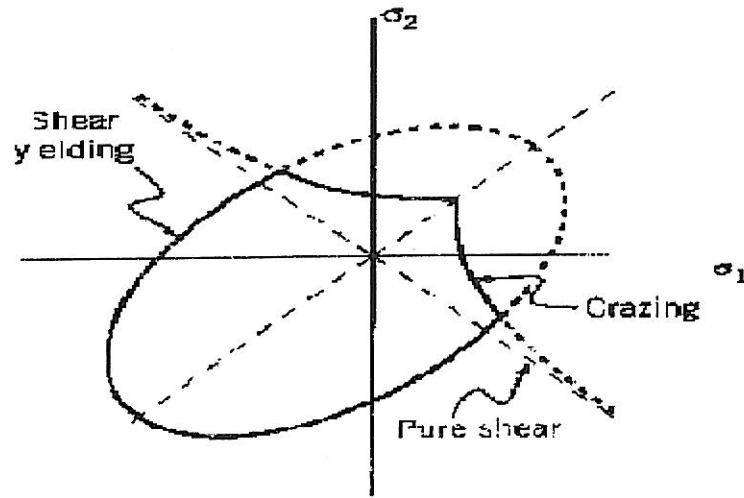


Figure D.1: Biaxial Stress Yielding of a Glassy Polymer.

D.1 Shear Yielding

S.S. Sternstein, L. Ongchin [6] propose that shear yielding in a glassy polymer is governed by

$$\tau_{OCT} = \tau_0 - \mu \sigma_m, \quad (D.1)$$

where

$$\tau_{OCT} = \frac{1}{3} \sqrt{(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2} \quad (D.2)$$

is the octahedral shear stress, and

$$\sigma_m = \frac{1}{3} (\sigma_1 + \sigma_2 + \sigma_3) \quad (D.3)$$

is the mean normal stress. The μ and τ_0 are material constants, which have temperature and rate dependency, respectively. Equation (D.1) is a modified von Mises' criterion, including the hydrostatic stress, σ_m . When $\mu=0$, it becomes the von Mises yield criterion.

D.2 Tensile Yielding

S.S. Sternstein, L. Ongchin, propose [6] the following necessary and sufficient conditions for craze formation in a glassy polymer:

$$|\sigma_1 - \sigma_2| \geq A(T) + \frac{B(T)}{I_1} \quad \sigma_1 \neq \sigma_2 \quad (D.4)$$

where $I_1 = \sigma_1 + \sigma_2 + \sigma_3 > 0$; σ_1 and σ_2 are the non-zero principal stresses; $A(T)$ and $B(T)$ are temperature dependent material parameters.

D.3 HIPS Yielding

Yielding criteria given above are for homopolymers, i.e., Eqs. (D.1) and (D.4) are good for single-phase polymers. They need to be modified for multiphase rubber polymers such as HIPS. Yielding of a HIPS polymer usually depends on dilatational stress components. Moreover, even under a uniaxial stress state, stress field at the second-phase particle and the matrix interface will be triaxial. Therefore, a yield function including effective stress and dilatational stress components is needed. The following form of a yield function may be used for HIPS polymer

$$f(\bar{\sigma}, I_1) - k = 0 \quad (D.5)$$

In the equation, $\bar{\sigma}$ is the effective (or average effective stress) related with global HIPS system (effective HIPS properties) and may be defined by

$$\bar{\sigma} = \left(\frac{3}{2} \langle \sigma'_{ij} \rangle \langle \sigma'_{ij} \rangle \right)^{1/2},$$

where $\langle \sigma'_{ij} \rangle$ is effective deviatoric stress for the HIPS polymer and the first stress invariant, I_1 , is also given in terms of average stress components (average HIPS hydrostatic stress) and might be written as

$$I_1 = \langle \sigma_{ii} \rangle = 3 \langle \sigma_h \rangle.$$

The k is a material constant and equal to HIPS yield stress in this case. One can modify Eqn. D.1 and write it in the following form

$$\frac{\sqrt{2}}{3} \bar{\sigma} + \mu \frac{I_1}{3} = \tau_0 = k = \text{constant.} \quad (\text{D.6})$$

In Eqn. (D.5), the μ and τ_0 are material constants, which have temperature and rate dependency, respectively. For the calculation of $\bar{\sigma}$ and I_1 , local stress field averaging over the entire HIPS volume is needed. Corresponding relationship may be given as

$$\langle \sigma_{ij} \rangle = \langle \sigma'_{ij} \rangle + \langle \sigma_h \rangle \delta_{ij}$$

with

$$\langle \sigma_{ij} \rangle = \frac{1}{V} \int_V \sigma_{ij} dv$$

where σ_{ij} represents the local stress field.

APPENDIX E: A case study: Plane Stress-strain comparison

A case study is done so that a comparison of analyses conducted in plane stress and plane strain can be made. The same micromechanics model given in Section 9.7 to study particle volume fraction effect is considered. In other words, the same problem is formulated assuming plane strain condition (using plane strain elements for meshing). A limiting case, polystyrene with holes, is considered for comparison and the stress concentrations at the equator of a hole are reported for both plane stress-strain conditions at different volume fraction (Fig. E.1). Obtained values are given in Table E.1.

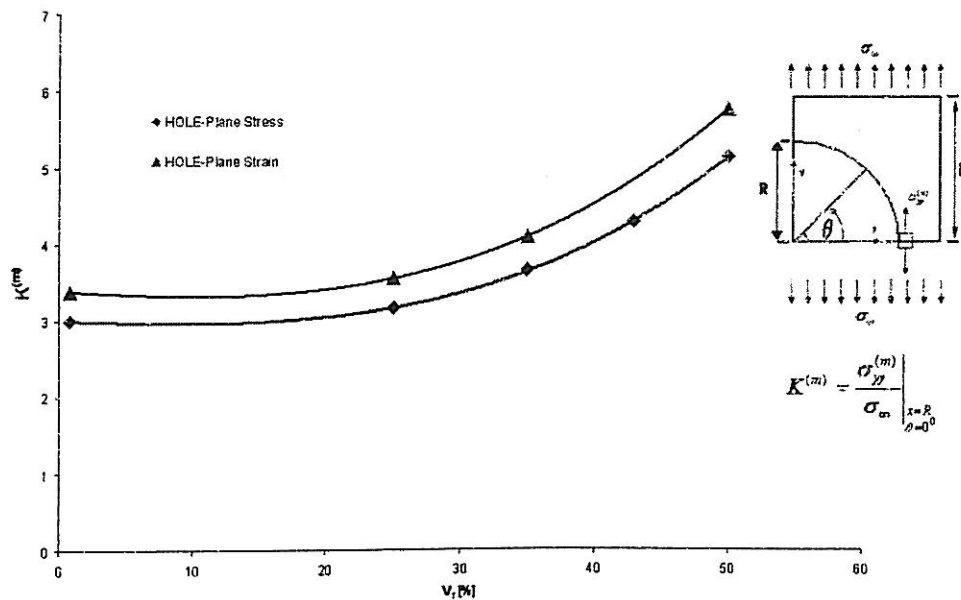


Figure E.1: Plane Stress-Strain Comparison: Stress Concentrations at the Equator of a Hole in HIPS with Different Volume Fractions.

Table E.1: Stress Concentrations under Plane Stress-strain Cases.

Volume Fraction [%]	K^m (Plane Strain)	K^m (Plane Stress)
0.8	3.382	2.995
25	3.559	3.171
35	4.103	3.656
50	5.754	5.127