CRAZING AND LARGE DEFORMATION BEHAVIOR IN A MODEL SET OF POLYSTYRENE/POLYBUTADIENE DIBLOCK COPOLYMERS

by

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ABSTRACT

The toughening mechanisms were studied in a model set of microphase separated polystyrene/polybutadiene diblock copolymers and blends with homopolymers through isolated craze growth and macroscopic stress-strain experiments. Thin section transmission electron microscopy of the internal craze structure in materials of spherical and cylindrical morphology indicates that the crazes form by cavitation in the rubber domains and subsequent craze fibril formation through drawing in the continuous polystyrene matrix between domains. This mechanism was modelled in the spherical morphology by considering the rate limiting step to be the cavitation in the rubber microsphere. Thermal stresses induced by the thermal expansion coefficient mismatch between polystyrene and polybutadiene accounts for nearly half the stress required for cavitation. This mechanism predicts the isolated craze growth kinetics for materials with a high volume fraction rubber (>11%). At lower rubber contents, the craze growth mechanism switches to the meniscus instability model as observed for craze growth in homopolymers. The relationship between isolated craze growth velocity and overall toughness as measured in stress-strain experiments is developed, allowing various features of the stress-strain behavior, including craze flow stress and elongation to break, to be partially explained. The substantially higher craze growth rates generated by the cavitation mechanism are shown to be important in determining the toughness of the materials, especially at low temperatures.

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I am deeply indebted to my wife who persevered with me through the whole process, but will receive no piece of paper at the end for her efforts.

And finally, MIT and Boston were not easy steps for one accustomed to the sticks of Wisconsin, but the many friends we have made and the enjoyable times we have shared have made these years in Cambridge very memorable, and to all those friends, I am very grateful.
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Chapter 1. INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Toughness is often the deciding factor in materials selection. To that end, considerable effort has been directed towards adding toughness to stiff brittle polymers without sacrificing the desirable properties of rigidity, cost, processibility and weight. Over the years the problem of toughness has typically been attacked via Edisonian techniques of trial and error perpetrating the "black art" status of materials engineering. One of the earliest techniques for toughening polystyrene was achieved by polymerizing styrene with rubber in the simple hopes of combining the beneficial properties of high modulus and high yield strength of polystyrene with the high elongation and toughness of rubber (Ostromislensky 1927). The mechanism of the successful outcome of this process has been clarified only after considerable research. As a result of this, it has become clear that it is essential to develop a fundamental understanding of the relationship between polymer structure and their large deformation properties. With the growing sophistication in analytical techniques, specifically in electron microscopy, characterization of polymer structure is now possible down to the nanometer scale. Developing a fundamental approach to the large deformation behavior of polymers though has only recently begun. Of primary importance is the recognition that the overall toughness of a polymeric material is governed by many separate deformation processes, each of which should be studied independently. Among the prominent toughening processes in glassy polymers is crazing. The systematic study of the mechanisms of toughness has been undertaken by several investigators who
studied the processes of initiation, propagation and termination of crazes in several glassy polymers. This thesis continues along this path by investigating the growth of crazes in block copolymers of styrene and butadiene. Block copolymers are a novel class of materials which often exhibit a microphase separated structure with domain sizes of the order of 100 Å. Most of the morphological features can be controlled independently in block copolymer systems providing excellent knowledge and control of the structure in these materials making it possible to study specific microstructure/property relationships. The property chosen to be investigated is primarily the craze growth rate since it is expected to be strongly influenced by morphological variations and is one of the important variables governing toughness of polymers. In addition, stress-strain data are also obtained and partially explained from the fundamental understanding of the isolated craze growth kinetics.

1.2 Literature Review

Two separate bodies of literature are relevant to this study. The first involves fundamental studies of toughening mechanisms in pure glassy polymers. Most such studies have been conducted by researchers in mechanics or materials, who rarely have access to model materials such as block copolymers. The second group involves very qualitative studies of toughness in block copolymer systems. The latter studies have been typically conducted by chemists or chemical engineers who are skilled at the synthesis techniques necessary for preparing block copolymers but with little knowledge of the mechanics of materials. The interdisciplinary nature of the present work is one of the primary reasons for its originality and success.
Improving fracture toughness is generally achieved by inducing energy absorbing deformation processes such as shear banding, crazing and homogeneous yielding and by inhibiting crack propagation mechanisms. Under tensile loads, the main deformation mechanism in polystyrene is crazing. In an excellent paper published over 30 years ago, Hsiao and Sauer (1950) describe all the salient features of crazing including the effects of environment and the type and magnitude of stress on the initiation and growth of crazes. They documented the load carrying capacity of crazes in contrast to cracks. Through X-ray scattering they determined that crazes are filled with highly oriented material and speculated that this material may be organized into fibrils. Since the pioneering work of Hsiao and Sauer, many subsequent investigators have filled in the picture on crazing in glassy polymers.

The details of the internal structure of crazes have been elucidated through more extensive X-ray scattering (Brown and Kramer 1981, Westbrook et al 1983, LeGrand and Forth 1983), electron diffraction (Brown 1983), and transmission electron microscopy (Kambour 1964, Beahan et al 1971, Lauterwasser and Kramer 1979, Donald and Kramer 1981). Typical crazes in homopolymers were found to be from 0.1 to 1.0 μm thick filled with an open network of oriented polymer fibrils approximately 100 to 500 Å in diameter with a total void fraction of about 0.8. A transmission electron micrograph of a polystyrene craze is shown in fig. 3-5a. Two excellent reviews of crazing in glassy polymers have been published (Kambour 1973, Rabinowitz and Beadmore 1972) with a third soon to be published (Kausch 1983).
The kinetics of craze initiation (Argon and Hannoosh 1977, Fellers and Kee 1974), growth (Argon and Salama 1977, Verheulpen-Heymans 1979) and fracture (Murray and Hull 1969, Chen et al 1981, Doyle 1982) in several glassy polymers have been measured. Many of the above researchers were also successful at modelling their results.

While crazes absorb energy and produce considerable strain, they are also very susceptible to breakdown into catastrophic cracks. Optimum toughness then is achieved when massive craze initiation is followed by stabilization or non-fatal termination of the crazes prior to fracture. Commercially this is accomplished by incorporating a second rubbery phase whose primary role is to provide sites for stress concentration for craze initiation. Whether or not the rubber inclusions can stabilize crazes or also initiate shear bands is still not fully established. Nevertheless, rubber toughened materials are a great commercial success with the principle being applied to polystyrene, polypropylene, Nylon and epoxies.

Because of their commercial importance, High Impact Polystyrene (HIPS) and Acrylonitrile Butadiene Styrene (ABS) have been studied extensively. Much of the current work and understanding in the field has been discussed by Bucknall (1977) and focuses on the details of the rubber inclusion and its relationship to toughness. While there exists a large body of literature on rubber toughened polystyrene, it has little relevance to the present study for the simple reason that the rubber particles in HIPS and ABS are considerably larger than a craze whereas the inverse is true for the rubber containing block copolymers used in this work. Thus while the particles in the former case initiate crazes which grow through the homopo-
polymer between particles, in the later case the crazes initiate at surface flaws (no particles are large enough to nucleate crazes) and grow through the composite material interacting strongly with the rubber phase. Thus previous work has concentrated on the initiation of crazes and, to a lesser extent, the termination of crazes whereas the present work has concentrated on the intervening stage of growth of crazes in a two phase material on a much finer scale than previously investigated.

The second body of literature that needs to be reviewed is on block copolymers. The easiest method for preparing block copolymers is through anionic polymerization which has been used for over 20 years (Szwarc 1983). Anionic polymerization has become a routine method for preparing model polymers for laboratory study and has been applied to several commercial plastics. The first successful commercial block copolymer was a triblock copolymer consisting of a long polybutadiene polymer chain capped on both ends with a short polystyrene chain. This material along with other model rubbery continuous polymers have been the object of considerable work (Estes et al 1970, Shen 1979).

Much of the knowledge gained during this early work has been applied to the present study. Specifically, the synthesis techniques, thermodynamic model foundations, techniques of solvent casting for sample preparation and experience in homopolymer and block copolymer blending have all been utilized in this work.

Block copolymers of styrene and butadiene have been studied for some time so the techniques for preparing monodisperse model polymers of desired molecular weight are well known (Morton 1983).
If the two blocks making up a diblock copolymer are immissible, they will phase separate into domains of approximately molecular chain dimensions. Several thermodynamic theories have been developed which predict the size, shape and interfacial properties of block copolymers as a function of the molecular weight, composition and monomers chosen. Helfand and Wasserman (1982) have recently reviewed these theories. In general, the microdomain shape is primarily a function of the composition and varies from spheres of the minor component in a continuous matrix, to cylinders in a matrix, to alternating layers or lamellae. The characteristic size of these domains is roughly proportional to the square root of the block molecular weight. At very low molecular weights however, the material will become homogeneous.

The above theories predict the equilibrium morphology, but like many phenomena in polymer science, the actual resultant morphology is strongly affected by the kinetic limitations imposed during the intervening processing steps. One reproducible technique well suited for laboratory sample preparation is solvent casting. During this procedure of dissolving a polymer in a solvent and evaporating to dryness, the morphology will set up in dilute solution and be trapped in the resultant film. Thus while no solvent is present in the final sample, the choice of solvent can have a profound effect on the final morphology. A large body of empirical data has been collected on the effect of various solvents on the resultant morphology (e.g. Inoue et al 1969). Understanding the thermodynamics and kinetics of phase separation in the presence of solvents continues to be a very active area of study (e.g. Shibayama et al 1983).
When homopolymers of the same type as the blocks are blended with a block copolymer, they will add to their respective domains and swell their size. The amount of homopolymer which can be solubilized by the block polymers depends on the morphology and molecular weights of all species. Again a large body of relevant empirical data has been collected for this technique.

Using the above techniques of controlled polymer synthesis, homopolymer blending and solvent casting many molecular and morphological features on the scale of 10-1000 Å can be controlled independently. With this powerful capability, the goal of this thesis is to develop a fundamental understanding of the relationship between large deformation behavior and the molecular and morphological features of the material.

Many investigators have studied the large deformation stress-strain behavior of glassy/rubbery block copolymers. While most studied materials with topologically continuous rubbery phases, using or duplicating the commercial thermoplastic elastomers on the market, several researchers considered systems with topologically continuous or co-continuous polystyrene systems with the early work of Matsuo et al (1968, 1969) being very prominent. Using a model set of polystyrene/polybutadiene block copolymers which varied independently in block arrangement and composition, they demonstrated the extremely attractive properties of these materials, some of which were superior to HIPS. They also identified thicker than normal crazes which also proved very important in the present work (Chapter 3). Other investigators who studied similar systems with comparable conclusions are Holden et al (1969), Robinson and White (1970), Akovali et al (1977), Noshay et al (1977), Hashimoto et al (1979), Bajaj and Varshney (1980).
Recently Kawai et al (1980) conducted a similar systematic investigation. In their study stress-strain results were obtained for numerous di and triblock polymers and blends with homopolymers. Correlations between the area under the curve (toughness) to a large number of morphological and molecular parameters were attempted, including domain shape and size, amount of interfacial bonding, interfacial volume percent, overall composition, and block molecular weight. While no relationship between these structural features and toughness was found, several important results can be drawn from this work. First the important phenomena of large plastic deformation of the polystyrene phase between two rubber domains was identified for the case of lamellar morphology. Second the need for a fundamental understanding of the microscopic processes involved in toughening materials was pointed out again by the lack of correlation with properties on the macroscopic scale.

While all of these researchers had excellent control over molecular and morphological structure, they all had difficulty developing correlations with large deformation properties. Systematic independent studies of the individual toughening processes need to be performed on the block copolymer materials similar to those already conducted for the pure homopolymers. For many glassy polymers this involves the initiation, propagation, and termination of crazes. Only two studies to date have been conducted along these lines in block copolymer materials.

Schirrer and Goett (1981) did a phenomenological study of craze growth preceeding a crack in a triblock copolymer of polystyrene and polyisoprene. They were the first to notice the strong effect of the morphological orien-
tation on the craze structure. A more complete study of craze structure and craze growth was conducted on two commercial polystyrene/polybutadiene block copolymers with cylindrical and lamellar rubbery domain morphology by Argon et al (1981). They discovered novel craze structures, apparently formed through the cavitation of the rubber domains and noted the considerably faster craze growth in block copolymers relative to homopolymers. This second feature will be shown to be very important in explaining the tough stress-strain behavior of the block copolymer materials (Chapter 5). This study by Argon et al was the impetus for the present work. Their study pointed out the need for a model set of materials to study the novel craze structures and craze growth kinetics in block copolymers of controlled microstructure.

1.3 Thesis Overview

The thesis is organized as follows:

Chapter 2 documents the material synthesis and procedures used in the rest of the work.

Chapter 3 covers work conducted on cylindrical morphology materials. Stress-strain results are presented and the need for fundamental toughness measurements is again stressed. Considerable evidence for craze growth via cavitation in the rubbery phase is also presented.

Chapter 4 begins by developing a mathematical expression for relating the toughness determined by a stress-strain experiment to the individual processes of initiation, propagation, and termination of crazes. Two models for craze growth in block copolymers are developed; a modified meniscus instability mechanism, (which is observed to occur in
homopolymers), and a new mechanism based on cavitation in the polybutadiene phase and subsequent craze fibril formation from the continuous glassy matrix.

Chapter 5 uses the two models to describe isolated craze growth data obtained for many prepared samples. Differences in the stress-strain behavior for these materials is explained by the variations in the isolated craze growth rates. Low temperature craze growth kinetics and stress-strain results are obtained and explained.

Chapter 6 presents some anomalous behavior observed in some blends containing homopolybutadiene. Several explanations are presented along with the attractive properties of these materials.

Chapter 7 summarizes the work and contains suggestions for future study.
Chapter 2. MATERIALS AND PROCEDURES

2.1 Polymer Synthesis and Characterization

All of the homopolymers and diblock copolymers used in this work were synthesized via homogeneous anionic polymerization. Under ideal reaction conditions, this process yields a nearly monodisperse polymer with the molecular weight directly calculable from the amount of initiator and monomer charged to the reactor (Szwarc 1968). Anionic polymerization also provides one of the most convenient methods of preparing block copolymers. Due to the absence of a natural termination reaction, the "living" polymer can continue propagating with a second monomer after the first monomer has been exhausted. The only significant drawback to this process is that the polymerization can be terminated by any common impurities, which creates the stipulation that the combined impurity levels in all reactants and solvents be very much less than the initiator concentration (Bates and Cohen 1981).

Block copolymers and homopolymers of styrene and butadiene used in this work were synthesized in this laboratory with the exception of two homopolymers, BO and S4, which were purchased from Pressure Chemical Company. All other polymerizations were carried out with about 5% by weight monomer in benzene and using n-butyl lithium enhanced with anisole as initiator. Reaction temperatures were 40°C for styrene polymerizations and 50°C for butadiene polymerizations. Methanol was used to terminate the polymerizations. The overall reaction scheme is shown in Figure 2-1. Polymers were recovered by precipitation in methanol and stored at 0°C in the dark to inhibit possible degradation.
Figure 2-1 Reaction scheme for synthesizing a diblock copolymer of styrene and butadiene
Molecular weights and polydispersities of the synthesized homopolymers and of the polystyrene first block in the diblock synthesis were determined by high pressure size exclusion chromatography (HPSEC) calibrated with nine polystyrene standards. HPSEC chromatographs of the final diblocks were used to find the diblock polydispersity and also to confirm that no more than 10% by weight homopolystyrene was present. The polybutadiene block molecular weight was calculated from the weight fraction of polybutadiene in the polymer, and the amount of and molecular weight of homopolystyrene present. The weight fraction of polybutadiene was determined with quantitative ultraviolet spectroscopy. The polybutadiene microstructure was shown to be 87% 1,4 addition by proton NMR spectroscopy.

A very detailed description of the theory and kinetics of anionic polymerization, all synthesis equipment and procedures used, and the characterization techniques and results can be found in the doctoral thesis of Bates (1982). Table 2-1 lists the polymers used in this work and their characterization results. Polymer designations are the same as those in previous publications (Bates et al 1982, Bates et al 1983a, Bates et al 1983b).

2.2 Film Casting

Polymer films used for testing were prepared using a high temperature, inert atmosphere, solvent spin casting technique (Kaelble 1965). This method is well suited for handling the small (~10 grams) sample sizes, provides a reproducible method for blending polymers (in dilute solution), and as mentioned in Chapter 1, provides additional control over the morphology and domain size through proper choice of casting solvent mixtures.
Table 2-1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn (kg/mol)</th>
<th>Mw/Mn</th>
<th>Wt % PB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S-B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SB1</td>
<td>77-11</td>
<td>1.06</td>
<td>.120</td>
</tr>
<tr>
<td>SB2</td>
<td>77-21</td>
<td>1.06</td>
<td>.217</td>
</tr>
<tr>
<td>SB3</td>
<td>85-45</td>
<td>1.07</td>
<td>.317</td>
</tr>
<tr>
<td>SB4</td>
<td>149-20</td>
<td>1.07</td>
<td>.118</td>
</tr>
<tr>
<td>SB5</td>
<td>126-46</td>
<td>1.06</td>
<td>.242</td>
</tr>
<tr>
<td>SB6</td>
<td>122-66</td>
<td>1.07</td>
<td>.329</td>
</tr>
<tr>
<td>SB7</td>
<td>560-59</td>
<td>1.11</td>
<td>.096</td>
</tr>
<tr>
<td>SB8</td>
<td>400-120</td>
<td>1.10</td>
<td>.230</td>
</tr>
<tr>
<td>SB9</td>
<td>420-230</td>
<td>1.12</td>
<td>.328</td>
</tr>
<tr>
<td>SB10</td>
<td>600-260</td>
<td>1.20</td>
<td>.230</td>
</tr>
<tr>
<td>SBd3</td>
<td>380-46</td>
<td>1.10</td>
<td>.106</td>
</tr>
<tr>
<td>S2</td>
<td>116</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>390</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>S4*</td>
<td>300</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>B0*</td>
<td>3.0</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>20</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>44</td>
<td>1.04</td>
<td></td>
</tr>
</tbody>
</table>

S = polystyrene; B = polybutadiene; Bd = perdeuteropolybutadiene; SB, SBd = diblock copolymer

* Pressure Chemical Co.
The spin casting apparatus is shown in Figure 2-2. Dilute polymer solutions (about 5% by weight) were injected through 10 µm filters into the casting cup which was fitted with a Mylar liner. Nitrogen purging through the caster insured an inert environment and removed the solvent. The casting cup was enclosed in a temperature chamber controlled to 1°C accuracy. Uniform cast films were between 0.5 and 1.0 mm in thickness, depending on the amount of polymer charged to the caster.

The casting rate is a function of the nitrogen purge flow rate, casting temperature, and solvent vapor pressures. Typical casting conditions, optimized by trial and error, are listed below for two solvent systems:

<table>
<thead>
<tr>
<th>Toluene (BP=110°C)</th>
<th>THF (BP=67°C)/MEK (BP=80°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (day)</td>
<td>1 2 3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>65 80 100</td>
</tr>
<tr>
<td>N₂ flowrate (SCFH)</td>
<td>.1 .1 1.0</td>
</tr>
</tbody>
</table>

The cast films were further dried and annealed at 100°C in a vacuum oven, and subsequently stored under vacuum in the absence of light.

2.3 Transmission Electron Microscopy

Morphology of the cast films and internal structure of crazes were observed with transmission electron microscopy. Samples of each cast film along with various heavily crazed specimens were prepared for microscopy by staining in a 1% aqueous solution of osmium tetroxide for several days (Kato 1967). Crazed specimens were stained in a strained state by use of a stainless steel jig. Ultra-thin sections suitable for transmission
Figure 2-2 Solvent spincasting apparatus with a detail of the casting cup.
electron microscopy were cut on a LKB microtome using fresh glass knives. Morphology and domain size were observed in 300-700 Å thick sections cut at room temperature with water as the trough liquid. Internal craze structure was observed in 0.1 to 1.0 μm thick sections cut as above or at low temperature using a LKB cryomicrotome with a 50:50 mixture of DMSO and water as the trough liquid. During low temperature operation, the specimen was maintained at -140°C and the glass knife was kept at -50°C. The orientation of the cutting knife to the crazed sample was chosen to minimize interaction between crazes and microtoming artifacts (see Fig. 2-3). The electron microscope, a Philips EM 200, was operated at 60 KeV and calibrated with a diffraction grating carbon replica (21,600 lines/cm).

2.4 Isolated Craze Growth Experiments

Samples for isolated craze growth experiments were trimmed from the annealed cast films with fresh surgical blades using the mold shown in Fig. 2-4 as a template. The samples were then washed in a dilute aqueous Ivory soap solution to clean the surface and remove any oils which might be crazing agents. After rinsing with copious volumes of distilled water, the samples were hung vertically in a vacuum oven and annealed for 24 hours at 100°C. The samples were slow cooled (20°C/hour) and tested within two days.

Controlled nucleation of crazes was achieved by indenting the sample surface using a Leitz Microhardness Tester (Hawkins 1983). The 25 and 50 gram weights were used, depending on the hardness of the sample, to yield diamond indentations about 0.05 mm across. Indentations were made on the nitrogen side of the cast film. It was discovered that the side which was
Figure 2-3 Illustration showing the orientation between the crazed sample and microtoming knife to minimize artifacts.

Figure 2-4 Isolated craze growth and stress-strain sample template
against the Mylar liner had too many imperfections resulting in a craze density too high for the experiments whereas the nitrogen side was nearly flawless. The few spurious crazes which did nucleate from surface flaws followed the same kinetics as crazes grown from the controlled sites indicating that the indentation procedure to initiate crazes does not affect craze growth.

Crazes were grown under constant stress in a controlled environment. The apparatus (described in detail by Hawkins (1983)) was able to craze samples in any gas at any pressure from atmospheric to \(10^{-7}\) torr and at a wide range of temperatures. Nearly all experiments described in this work were, however, performed in laboratory air or dry nitrogen and at room temperature (20°C) or -20°C.

The growth of crazes was monitored by photographing their length as a function of time through a microscope at 16X magnification. The camera was interfaced with a Hewlett-Packard 1000 microcomputer and fired linearly in time using the computer's real time clock. The time between pictures was systematically varied from 3 seconds to 1 hour allowing over three orders of magnitude change in growth rates to be measured. The craze lengths were measured from enlarged views of the film negatives. Calibration of the film was through photographing a millimeter scale in place of the test sample.

2.5 Tensile Testing

Samples for tensile testing were trimmed from the annealed cast films with fresh surgical blades using the mold shown in Fig. 2-4 as a template.
They were then annealed for 24 hours, slow cooled (20°C/hour) and tested within two days. Load-extension data were obtained on a tabletop Instron (Model 1122) which could be fitted with a controlled temperature chamber cooled with liquid nitrogen. Stress-strain curves were calculated based on a gauge length of 1/4 inch. Actual initial grip separation was 3/4 inch.
Chapter 3 CYLINDRICAL MORPHOLOGY AND CAVITATION IN RUBBER DOMAINS

Through controlled synthesis of materials, polymer blending, and solvent casting many parameters on a molecular and morphological scale can be independently altered in block copolymer materials. The goal of this chapter is to identify the effects of such molecular parameters as block molecular weight, domain shape, size and spacing, interfacial adhesion, cross-linking, etc. on the toughness of polystyrene/polybutadiene diblock copolymers.

Relationships between molecular structure and macroscopic properties such as toughness in commercial rubber toughened polymers (e.g. HIPS, ABS) have been investigated for many years and continue to be an active area of interest (see Chapter 1). These investigations are hampered by the lack of ability to independently control molecular and morphological parameters which are all inter-related via the synthesis procedure. Hence the potential exists for the use of block copolymers and their blends as model rubber toughened polymers to develop fundamental structure-property relationships.

While determining the molecular and morphological structures is fairly routine with standard techniques, defining the toughness of a material is complicated by the many testing procedures available. Most of these tests have been designed to measure a particular form of toughness for a particular application and yield little fundamental information. The test chosen for this study is the stress versus strain curve to failure at constant strain rate with the toughness equal to the area under the curve.
This test can be considered more fundamental than alternative experiments but more importantly, it is both well accepted as a benchmark for measuring toughness and well suited for testing limited quantities of polymer.

3.1 **Pure Diblocks**

Initial experiments were conducted on materials SB2, SB5, SB8, and SB10 which all contain 23 weight % polybutadiene (see Table 2-1). The morphologies for the four materials cast from toluene are shown in Figures 3-1 a-d. As expected (see Chapter 1), the "equilibrium" morphology is in the form of cylindrical domains with the diameter and spacing between cylinders increasing as the block molecular weights increase. The stress-strain behavior of the four materials is shown in Figures 3-2 a-d. The most striking difference is the nearly brittle behavior of SB2 and SB5 whereas SB8 and SB10 both show significant strains to fracture and generally tough behavior.

In an effort to understand which parameters control the toughness in block copolymers, stress-strain results were obtained for a series of materials. Each prepared film is designed to isolate a single molecular or morphological feature to determine its effect on the toughness in block copolymer materials.

3.2 **Effect of Diblock Blending**

A blend consisting of 25% SB3, 50% SB5 and 25% SB7 by weight was prepared to investigate the effect of polystyrene molecular weight on toughness. The polybutadiene block molecular weight of these three polymers is nearly identical and the blend consists of 23% rubber by weight. The
Transmission electron micrographs of cylindrical morphologies (dark regions are polybutadiene stained with OsO₄). Materials cast from toluene: A) SB2, B) SB5, C) SB8, D) SB10. Blends of SB3, SB5, and SB7: E) cast from toluene, F) cast from MEK/THF.
FIGURE 3-2 a,b
STRESS-STRAIN RESULTS FOR THE PURE DIBLOCKS

SB2

STRESS (MPa) vs STRAIN (%) for different strain rates:
- 0.013 sec⁻¹
- 0.00013 sec⁻¹

SB5

STRESS (MPa) vs STRAIN (%) for different strain rates:
- 0.013 sec⁻¹
- 0.00013 sec⁻¹
FIGURE 3-2 c, d
STRESS-STRAIN RESULTS FOR THE PURE DIBLOCKS

SB8

STRAIN RATE

\[ \square 0.013 \text{ SEC}^{-1} \]
\[ \circ 0.00013 \]

SB10

STRAIN RATE

\[ \square 0.013 \text{ SEC}^{-1} \]
\[ \circ 0.00013 \]
polystyrene block molecular weights vary from 85 Kg/mole to 560 Kg/mole. The number average molecular weight of the polystyrene blocks is slightly higher than the polystyrene block in SB5 but the weight average molecular weight is almost twice that weight ($\overline{M}_n = 143$ Kg/mole, $\overline{M}_w = 243$ Kg/mole).

This blend of diblocks cast from a toluene solution, resulted in a very tough material as shown in Fig. 3-3a. Unfortunately this material no longer had the straight cylinder morphology of the pure diblocks cast from toluene (see Fig 3-1 e,f). This effect of polydispersity on block copolymer morphology has been documented by Kraus et al (1979) and used by Phillips Petroleum in K-Resins to achieve lamella morphologies in polystyrene rich materials.

The microstructure can be altered into a straighter cylindrical morphology by casting the diblock blend from a suitable solvent - in this case a mixture of 80% THF, 20% MEK by volume. The resulting film had the desired morphology but was brittle (Fig. 3-3b). Not only does this point out the large sensitivity of toughness to details in the morphology but it also indicates that the polystyrene molecular weight in and of itself is not the limiting parameter in the toughness of the blends. Provided that optimum conditions, such as an interconnected cylindrical morphology, the polystyrene phase is able to deform, form stable crazes and otherwise absorb significant amounts of deformation work before final fracture.

The effect of morphology on physical properties in block copolymers has been studied extensively, especially in the case of systems with continuous or co-continuous rubber phases (Estes, Cooper, and Tobolsky 1970).
FIGURE 3-3 a, b
STRESS-STRAIN RESULTS FOR DIBLOCK BLENDING

STRAIN RATE
□ 0.013 SEC\(^{-1}\)
○ 0.00013

STRAIN RATE
□ 0.026 SEC\(^{-1}\)
○ 0.00026
In general, the large change in properties could be explained in terms of the elasticity of the topologically continuous rubber phase with a hard filler (Shen and Kawai 1978). These concepts do not apply to the present materials because they have topologically continuous polystyrene phases and the dominant large deformation processes are inelastic and involve yielding and crazing of the polystyrene phase. Discovering how these processes are affected by changes in morphology is difficult but several observations are possible. The test specimens viewed through a light microscope show significant differences between the crazing behavior in the interconnected cylinder and a typical straight cylinder morphology (Fig. 3-4 a,b). The dense, uniform crazes in the interconnected morphology appear to be very thin and lie in planes normal to the principal applied stress. In contrast, the crazes in the straight cylinder morphology are nonuniform, thick bands of deformation which do not necessarily lie in planes normal to the applied stress. They have a feathery appearance which seems to be a result of its anisotropic morphology. Whereas both morphologies exhibit isotropic behavior on a macroscopic scale, only the interconnected cylinder microstructure maintains this isotropy down to a scale of typical craze structures (~2000 Å). This anisotropy in the straight cylinder morphology appears to have a strong effect on the growth of crazes and also on the craze structure (see Section 3.5).

3.3 Effect of Crosslinking Polybutadiene Domains

A simple way to alter the polybutadiene molecular weight is to crosslink the prepared films with an electron beam. Crosslinking was accomplished with 3 MeV electrons from a Van de Graaff particle accelerator to dosages of 10 or 40 Mrad.
Figure 3-4  Effect of bulk morphology on the crazing behavior. 
A) straight cylinders (see fig. 3-1c),  
B) interconnected cylinders (see fig. 3-1e).
When specimens prepared from irradiated films of SB2 and SB5 were tested they showed greatly improved toughness (Fig. 3-5 a,b). Since pure polystyrene irradiated has unchanged stress-strain behavior and all microstructural dimensions and morphology are unchanged, the improved properties can be attributed to the crosslinking of the polybutadiene phase. The crosslinking reaction of polybutadiene by irradiation has been studied by Basheer and Dole (1982) but the details of the chemical changes in the polybutadiene domains are still difficult to ascertain. Specifically, the number of crosslinks and hence the average and distribution of molecular weight between crosslinks is unknown due to shielding effects of the polystyrene phase (Samuels and Wilkes 1973). Also the effect of irradiation on the adhesion of the rubber domains to the matrix through grafting reactions at the interface is unknown. The mechanics of the crazing process including stress levels and distributions may be altered due to significant modulus changes in the rubber phase as a result of heavy crosslinking. As shown in Fig. 3-5a, very high dosages are required to achieve improved properties. Nevertheless, the improved toughness can be attributed to changes of some form in the polybutadiene domains.

3.4 Effect of Homopolymer Blending

Homopolymer blending is an additional way of isolating the effects of block molecular weight on toughness. It also can be considered to affect the interfacial adhesion. In a block copolymer system, the only covalent bonding between a domain and the matrix occurs where the covalent bond joining the polymeric blocks together passes through the domain/matrix interface. In the pure diblock systems, every polybutadiene chain in the
FIGURE 3-5 a,b
STRESS-STRAIN RESULTS FOR CROSSLINKING DIBLOCKS

STRESS (MPa)

STRAIN (%)
rubber domains is connected to a polystyrene chain in the matrix. If, for example, homopolybutadiene is blended in to a diblock, it will add to the rubber domains and reduce the fraction of polybutadiene chains covalently connected to the matrix. In this sense, homopolymer blending reduces the domain/matrix adhesion. An alternative way to view the domain/matrix adhesion is to consider the interfacial area associated with each diblock junction bond in the interface. This area/bond can be considered proportional to the adhesion and if all geometrical features remain constant, i.e., domain shape, size and volume fraction, the interfacial area per junction bond will also remain constant for the case of homopolymer blending.

A blend of SBd3 with B0 was prepared to contrast with SB8. Both of these materials have the same block polystyrene molecular weight, volume fraction polybutadiene and straight rod morphology. The film prepared from the blend can be thought of as the result of snipping the polybutadiene chains in the rubber domains of the SB8 film into many shorter chains. The polystyrene is still connected to the rubber domain but with a much shorter polybutadiene block and a substantial amount of rubber in the domains exists as homopolymer.

The homopolymer blended sample is clearly less tough than the pure diblock material, again implying the polybutadiene molecular weight is a significant factor in controlling toughness (Fig. 3-6a). But there are some additional anomalies which cannot be easily explained. For example, the strain rate dependence of the toughness seems to reverse. The pure diblock exhibits a non-regular behavior of high strains to fracture at higher strain rates whereas the blend shows the opposite and more expected behavior of reduced strains to fracture at higher strain rates.
FIGURE 3-6 a, b
STRESS-STRAIN RESULTS FOR HOMOPOLYMER BLENDING
A similar blend using polystyrene homopolymer can be prepared to investigate the effect of lowering the polystyrene molecular weight. Due to limitations imposed by the set of 10 diblocks prepared, the blended sample and the pure diblock used contain 13% polybutadiene instead of the 23% rubber used in all previous comparisons. As seen in Figure 3-6b, the blended sample is weaker than the pure diblock indicating that the lower polystyrene molecular weight of the blend is responsible for the loss of toughness. Unfortunately, it is difficult to apply this result to the pure, 23% rubber, diblock in that the 13% polybutadiene materials have a spherical morphology. As discussed in Section 3.2, the morphology has a profound effect on the toughness, thus it is incorrect to state that the effect of polystyrene molecular weight on toughness is the same in both a spherical and cylindrical morphology.

3.5 Electron Microscopy of Craze Matter

The crazes observed in block copolymer materials with cylindrical morphology are considerably different than typical crazes in homopolymers (see Chap. 1). As shown in Figure 3-7 a,b, the crazes in the diblock materials are over two orders of magnitude thicker and not nearly as planar as homopolymer crazes. As noted in Section 3.2, this is a consequence of the anisotropy of the straight cylindrical morphology. The relative ease of craze growth in block copolymer materials is a function of the polybutadiene cylinder orientation. This results in crazes growing preferentially through regions of desired morphological orientation in contrast to expected craze growth along any arbitrary plane normal to the maximum principal stress. Crazes also apparently thicken to consume the regions of desired orientation.
Figure 3-7  Effect of bulk morphology on the internal craze structure. A) homopolystyrene (from Argon and Salama 1977), B) polystyrene/polybutadiene diblock.
A higher magnification view of the diblock craze matter in Fig. 3-8 shows that craze fibril diameter and void fraction are similar to those in homopolymer crazes. A much more important observation though, is the similarity between the inter-fibril spacing in the "fishnet" craze structure and the inter-cylindrical spacing in the bulk material. Thus the craze matter is apparently formed through the cavitation of the rubber domains and subsequent necking and drawing in the continuous polystyrene matrix. The line drawing in Fig. 3-8 illustrates the result of this process for the idealized case of rubber failure in three rows of a hexagonally packed cylindrical morphology. The phenomenon of craze growth through rubber cavitation has been observed in other diblock systems (Fig. 3-9 a-d) and in the lamella morphology of commercial materials (Argon et al 1981).

While the important ramifications of this discovery will be discussed in the following section, this result again indicates the importance of the rubber domains in controlling the crazing behavior and hence toughness of these block copolymer materials.

3.6 Conclusions

The goal of this investigation was to understand how various molecular parameters affect the toughness of polystyrene/polybutadiene diblock systems. The advantage of the microphase separated block copolymer systems is the ease in controlling many molecular and morphological parameters independently such as block molecular weights, polydispersity, microdomain shape, size, and spacing, etc. Unfortunately, no conclusive correlation could be obtained between the toughness as measured in a stress-strain experiment and any of the molecular parameters that could be independently
Figure 3-8 Details of the cellular cavitation mode of craze matter production. Illustration depicts voiding and craze tuft formation in an idealized cylindrical morphology.
Figure 3-9 Transmission electron microscopy of craze structure formed by cavitation mechanism in several diblocks. A) SB5, B) SB6, C) SB8, and D) SB10.
investigated. Many tests indicated the important role played by the rubber domains: the domain shape, orientation, crosslink density and molecular weight, all of which have a strong effect on the toughness. Nevertheless, no clear picture detailing the role of these molecular parameters in controlling toughness could be developed. The same problem was encountered by Kawai et al (1980).

The inability of investigators to develop a fundamental relationship between molecular parameters and toughness in HIPS and other heterogeneous polymer systems stems from two problems. First, the various molecular and morphological parameters of interest are difficult to control independently due to the synthesis procedures used. This problem is not encountered in the block copolymer systems. Second, a high value of toughness is the successful combination of several mechanisms working in concert. For materials in which the primary energy absorption mode is crazing, optimal toughness will be achieved after massive initiation at a high stress, rapid growth, and termination/stabilization of crazes just prior to breakdown into cracks. An individual molecular parameter can affect each of these processes in various ways leading to conflicting results when only a single effect, toughness, is investigated. Thus not only is control over fundamental molecular and morphological structure necessary, but a more fundamental approach to the question of toughness is needed. In order to fully understand the large deformation behavior of these heterogeneous systems, each step of the toughening process, i.e., initiation, growth, termination and stability of crazes, must be understood independently. It is this second aspect which has made interpretation of the stress-strain behavior of diblock copolymers with cylindrical morphology so difficult.
Nevertheless, many qualitative conclusions can be reached from the data. As mentioned above, the important role of the rubber domains was demonstrated in several tests. This was clearly illustrated in the transmission electron microscopy of craze matter. There are many important ramifications of this observation:

1) The observation suggests a mechanism for craze growth consisting of the cavitation of rubber domains under stress and subsequent necking and drawing in the continuous polystyrene phase. Ideally this mechanism of craze growth could be modelled, but would be severely complicated by the uncharacterized distribution of domain orientations in the straight cylindrical morphology.

2) The role of various polybutadiene molecular and morphological parameters can be better understood in light of a mechanistic view of the crazing process. The mechanism of craze growth suggests the importance of various rubber domain features including: a) ease of polybutadiene cavitation as influenced by free volume considerations and interfacial adhesion, b) alterations in the stress field as influenced by domain orientation and rubber modulus, and c) stability of the rubber phase as influenced by rubber crosslinking and molecular weight. In addition, each molecular parameter, for instance rubber molecular weight, could affect each of these features resulting in a complicated effect just in the craze growth rate itself. A mechanistic view, though, makes the problems more tractable, and quantitative correlations possible.

3) The mechanism of craze growth suggests the ability to control the craze structure on the scale of a few hundred Angstroms. Ideally the craze
fibril diameter and spacing between fibrils could be controlled by fixing the rubber domain size and spacing. These morphological features are easily controlled in block copolymer systems. The possibility exists for finding an optimal craze structure and for preparing a block copolymer system which will craze with that structure. In addition, the potential for producing materials with controlled pore diameter and spacings at the 100-1000A size has many applications such as selective membranes, selective catalyst supports, etc.

The rate of craze growth and the craze matter stability are probably the processes most strongly affected by the microphase separated nature of the block copolymer systems. The rubber domains showed no evidence of either initiating or terminating crazes which is expected due to their very small size. In the following chapters the growth of isolated crazes is studied and modelled as a function of several rubber domain parameters for the case of spherical polybutadiene domains, where a more unique mechanistic connection between morphology and crazing behavior is presented.
Chapter 4 ISOLATED CRAZE GROWTH MODELS

As pointed out qualitatively in the previous chapter, the toughness in crazable polymers is dependent on the separate processes of initiation, propagation, termination, and breakdown of crazes. A mathematical expression relating these fundamental processes to the macroscopic toughness will be developed below following the procedure of Argon et al (1983). The craze growth velocity, which enters directly into the expression, will then be considered separately and two models for craze growth in microphase separated block copolymers will be considered.

4.1 Toughness in Crazable Polymers

The toughness, $W$, as measured in a stress-strain experiment is equal to the area under the curve and is approximately the product of the tensile flow stress, $Y_{cr}$, with the strain to fracture, $\varepsilon_f$, (see Fig. 4-1). The latter is simply the product of the imposed strain rate, $\dot{\varepsilon}$, with the time to failure, $t_f$. Hence

$$W = Y_{cr}\varepsilon_f = Y_{cr}\dot{\varepsilon}t_f$$  \hspace{1cm} 4-1

In polymers where the primary mode of deformation is crazing, the imposed strain rate must be matched by the total dilatational strain rate, $\phi$, created by the crazing process. This dilatational strain rate can be decomposed into three terms:

$$\phi = \rho b u$$  \hspace{1cm} 4-2

where $\rho$ is the total active craze front length per unit volume, $b$ is the typical craze thickness, and $u$ is the velocity of craze growth. Hence the total expression for toughness is

$$W = Y_{cr}\rho b u t_f$$  \hspace{1cm} 4-3
Figure 4-1 Typical stress-strain curve of a polymer exhibiting dilatational (craze) plasticity.
The total active craze front length is the result of a kinetic balance between initiation and inactivation of crazes. This term is expected to be strongly influenced by the density of initiation sites both on free surfaces and internal interfaces, and by the efficiency of these sites as a function of stress and temperature. The term would also be influenced by various non-catastrophic craze termination processes such as intersection of crazes and traverse of crazes through the entire cross-section. This term has received the most attention from material engineers in creating tougher heterogeneous polymers due to the flexibility of controlling the initiation sites.

The craze thickness in many cases is found to be a relatively constant material parameter. While it is known that mature crazes often continue to thicken, principally by drawing fresh polymer into the fibrils (Lauterwasser and Kramer 1979), this rate is quite small for most polymers and most of the strain generated through crazing results from the initial craze tip growth processes.

The time to fracture of a craze is the typical time required before the oldest craze breaks down into a catastrophic crack. This breakdown is envisioned to occur by the breaking of fibrils inside the craze. When enough neighboring fibrils are broken, the load-carrying capacity of the surrounding fibrils will be exceeded leading to catastrophic fibril failure by the outward propagation of the fracture, turning the craze into a crack. This time to failure term and its dependence on stress, temperature, etc. is presently inadequately understood and little data exist for this process. As in all time dependent fracture processes known in
solids, the time to fracture of craze matter is expected to be inversely and non-linearly dependent on the applied stress (Murray and Hull 1970). It is also expected to be strongly influenced by the temperature and details of the craze fibril structure including defects (Murray and Hull 1969).

Using the above mathematical expression the important role of each step in the crazing process is apparent and the need to understand the stress and temperature dependence of each process is clear. The craze growth velocity, \( u \), enters directly into the material toughness expression and will be dealt with extensively both mechanistically and experimentally below.

4.2 Craze Growth via Interface Convolution

Argon and Salama (1976) have proposed that craze matter in glassy homopolymers is produced by the repeated convolution of the craze tip interface as depicted in Fig. 4-2. This mechanism produces the topologically interconnected air passages observed in craze matter and has been observed directly by transmission electron microscopy for polystyrene crazes by Donald and Kramer (1981). Using this meniscus instability idea, Argon and Salama (1977) developed an expression for asymptotic steady-state craze growth velocity

\[
\frac{da}{dt} = \frac{D_1}{\sigma_{\infty}} \exp \left[ \frac{-B}{kT} \left( 1 - \left( \frac{\sigma_{\infty} \lambda'}{\gamma} \right)^{5/6} \right) \right]
\]

The exponential term arises from the inelastic deformation theory of Argon (1973) which is used to describe the polymer drawing process in craze tuft
Figure 4-2 The interface convolution process for producing craze matter in homopolymers (Argon et al 1977).
formation. The values of B, the scale factor of the activation energy for plastic flow, \(\hat{Y}\), the athermal flow stress, and \(\dot{\varepsilon}_0\), the pre-exponential frequency factor (included in \(D_1\)) are all theoretically predicted by the yield theory (Argon and Bessonov 1977). The effective stress in the craze tuft causing the tuft drawing is the applied stress, \(\sigma_{\infty}\), enhanced by a term, \(\lambda'\), which accounts for both the extension ratio, \(\lambda\), in the craze tuft and the orientation hardening of the glassy polymer. Since these effects are difficult to experimentally measure in tension, \(\lambda'\) is used as a fitting parameter. The details of the meniscus instability mechanisms are contained in \(D_1\), which is calculable from several material properties including the polymer surface tension, and the exponent of the phenomenological constitutive expression, \(\sigma = A \dot{\varepsilon}^\eta\), which describes the plastic flow behavior of the polymer.

In the experiments of Argon and Salama (1977), the polystyrene craze growth rate data was fitted using B and \(\lambda'\), with \(D_1\) calculated from the material parameters. The value of B was found to be 26.0 Kcal/mol for two different polystyrene samples, with the predicted value of 25.5 kcal/mole (see Argon et al 1983). The value of \(\lambda'\) varied from 1.85 to 2.48. It is expected to be equal to the craze tuft extension ratio reduced by the percentage increase in the plastic resistance as a result of orientation hardening in the tuft. The craze tuft draw ratio in polystyrene crazes has been recently measured by Lauterwasser and Kramer (1979) and was found to vary from 3.5 to 6.0. Unfortunately, the orientation hardening effect cannot be measured on a macroscopic scale due to the brittle failure of polystyrene in tension experiments. Nevertheless, a doubling in the plastic resistance of polystyrene at the large tuft strains observed is not excessive making the fitted values of \(\lambda'\) reasonable.
In order to apply the meniscus instability model to craze growth in phase separated block copolymers, the same expression is used with the parameters calculated from the composite material properties. In addition, the applied stress in the exponent is normalized by \((1-x)\) where \(x\) is the volume fraction polybutadiene, because only the polystyrene volume fraction is involved in the tuft drawing process. The theoretical value of \(B\) was used along with the value of 1.85 for \(\lambda'\) as found by Argon and Salama, but \(D_1\) was used as a fitting parameter since the calculated value based on model sensitive details of craze tip did not give good agreement.

The value of \(D_1\) used was \(2.0 \times 10^7\) m/sec which is nearly an order of magnitude less than the predicted value of \(1.5 \times 10^8\) m/sec calculated by Argon and Salama. Recent work by Hawkins (1983) has shown that craze growth rates in polystyrene are strongly affected by sample preparation procedures. He found that samples pre-treated by high vacuum annealing at 80°C for 24 hours yielded craze growth over two orders of magnitude slower than reported by Argon and Salama who pre-treated their samples at 110°C for 24 hours at room pressure and slow cooled at 1.2°C/hr. Hawkins attributed this discrepancy primarily to the role of volatiles in the polystyrene on craze growth which were removed in the vacuum pre-treatment. An equally important effect may be physical aging of the samples induced by annealing them slightly below the glass transition temperature. The pre-treatment procedure used for the diblock copolymer materials is intermediate between the procedures of Hawkins and of Salama, with a medium vacuum annealing at 100°C for 24 hours and relatively fast (20°C/hr) oven cool to room temperature. The craze growth rates observed in the low
volume fraction rubber material were intermediate between the data of Hawkins and of Salama and an intermediate value of $D_1$ fit the data well (see Figure 4-5). The effect of thermal pre-treatment on craze growth has also been addressed by Verheulpen-Heymans (1976).

4.3 Craze Growth through Rubber Cavitation

A model for craze growth based on a mechanism of cavitation of the microspherical rubber domains under concentrated stresses and subsequent drawing and fibril formation in the polystyrene matrix will be developed. This process can be visualized in the stress-strain behavior of an idealized cube of material containing a rubber sphere as illustrated in Figure 4-3a. Initially the material is linearly elastic up to a strain of $\varepsilon_m$ where the rubber cavitates under the concentrated stresses in the sphere. These stresses arise from two contributions: the thermal stresses induced by the thermal expansion coefficient mismatch between the phases, and the local stress concentration which exists ahead of the growing craze tip due to its crack-like geometry is concentrated in the spherical inclusions due to the bulk modulus mismatch. While the tensile modulus of polybutadiene is quite low (in comparison to polystyrene), the spherical inclusion can still transmit significant stresses due to its bulk modulus. Once cavitation has occurred, this is no longer the case, resulting in a rise in the effective stress on the polystyrene matrix to the level of plastic flow. The polystyrene contained between cavitated spheres should then yield and deform into a fibril under the elevated stresses. Due to the strain hardening nature of the matrix, it is expected that an equilibrium strain, $\varepsilon_{cr}$, will be reached in the fibrils for a given local stress.
Figure 4-3 The cavitation mechanism for craze growth:
a) idealized stress-strain behavior of a cube of the material with spherical morphology,
b) model of the craze tip processes including the craze tip stress distribution.
The formation of craze fibrils from the polystyrene matrix between rubber domains was seen clearly in the preceding chapter for the cylindrical morphology materials. While not as striking, similar evidence exists that the same process occurs in the spherical morphology materials as shown in Fig. 4-4. Although the craze matter is affected by the microtoming process, several partially voided spheres are observable along with the scalloped craze matter/bulk material interface expected from a sphere cavitation growth mechanism.

The process of straining, cavitation and subsequent fibril drawing is imagined to occur in a craze tip process zone where undeformed bulk material enters the zone and mature craze matter leaves (see Fig. 4-3b). The craze growth rate can be thought of as the process zone length, $\Delta$, divided by the time needed to convert fresh material into mature craze fibrils. This time is also equal to the effective strain rate in the fibrils, $\dot{\varepsilon}_e$, divided by the final craze fibril strain, $\varepsilon_{cr}$. Thus

$$\frac{da}{dt} = \Delta \frac{\dot{\varepsilon}_e(\sigma_e)}{\varepsilon_{cr}}$$  

4-5

The craze tip process zone length is related to the craze tip driving force by linear elastic crack mechanics as,

$$K_I = (\sigma_m - \sigma_{\infty}) \sqrt{\pi \Delta}$$  

4-6

where $K_I$ is the Mode I stress intensity factor, $\sigma_m$ is the maximum traction for which cavitation occurs and $\sigma_{\infty}$ is distant applied stress. This applied stress intensity factor must be balanced by the craze tip process zone resistance, $K_{IC}$. This has been determined by Andersson and Bergkvist.
Figure 4-4 Transmission electron micrographs of craze structure in block copolymer systems of spherical morphology.
(1970) for the case of crack propagation in a degrading material in which they use a similar material traction law as in Figure 4-3a. They determine this fracture toughness to be

$$K_{IC}^2 = \frac{E_C^2 \epsilon_m^2 \delta (1- \frac{1}{\theta})}{(1-\nu_c^2)}$$  \hspace{1cm} 4-7

where $E_C$ is the composite tensile modulus, and hence the slope of the ascending portion of the traction law, $\epsilon_m$ is the strain at which degradation begins and $\theta$ is the ratio of the descending slope to the ascending slope in the material degradation law (see Fig. 4-3a). The terms $\nu_c$ and $\delta$ are the composite Poisson's ratio and degradation zone half-thickness respectively.

Substituting these expressions and again using the general yield theory of Argon as modified for the meniscus model before gives

$$\frac{da}{dt} = D_2 \exp \left[ \frac{-B}{kT} \left( 1 - \left( \frac{\sigma_{\omega} \lambda'}{\nu C(1-\chi)} \right)^{5/6} \right) \right]$$  \hspace{1cm} 4-8

$$D_2 = \frac{E_C^2 \epsilon_m^2 \delta (1- \frac{1}{\theta}) \epsilon_0}{(\sigma_m-\sigma_{\omega})^2 \pi (1-\nu_c^2) \epsilon_{cr}}$$  \hspace{1cm} 4-9

Composite material properties were calculated from the pure component properties using the equations of Chow (1978), and are,

$$\frac{K_C}{K_{PS}} = 1 + \frac{\chi(K_{PB}/K_{PS} - 1)}{1 + \frac{1}{3} (K_{PB}/K_{PS} - 1)(1-\chi)(1+\nu)}$$  \hspace{1cm} 4-10
\[
\frac{E_C}{E_{PS}} = 1 + \frac{\chi \left( \frac{K_{PB}}{K_{PS}} - 1 \right)}{3 + (1-\chi)(1+\nu_{PS})\left( \frac{K_{PB}}{K_{PS}} - 1 \right)} - \frac{2\chi}{3 - (1-\chi)(2\left( \frac{4-5\nu_{PS}}{5} \right) - 1)}
\]

\[
\nu_C = \frac{1}{2} \left( 1 - \frac{E_C}{3K_C} \right)
\]

\[
G_C = \frac{3E_CK_C}{9K_C - E_C}
\]

where \( K, E, \nu, \) and \( G \) represent the bulk modulus, tensile modulus, Poisson's ratio, and shear modulus respectively, the subscripts \( PS, PB, \) and \( C \) denote polystyrene, polybutadiene and composite respectively and \( \chi \) is the volume fraction of polybutadiene. The equations are for spherical rubber domains with \( G_{PB} \ll G_{PS} \). These composite properties are also used in calculating the composite athermal yield stress (Argon and Bessonov 1977)

\[
\hat{\gamma}_C = 0.133 \frac{G_C}{(1-\nu_C)}
\]

The other parameters used in the yield theory, \( B \) and \( \lambda' \), were chosen as before with the identical values used as in the modified meniscus instability model presented in Section 4.2.

The craze zone thickness, \( 2\delta \), is proportional to the polybutadiene sphere size as depicted in Figure 4-3b, and was chosen to be twice the sphere diameter. The value used for the final craze fibril strain, \( \varepsilon_{cr} \), was 5.0 from the previously mentioned work of Lauterwasser and Kramer (1979).

The slope of the descending portion of the degradation law (Fig. 4-3a) can be estimated by assuming that the true stress in the fibril remains
constant and approximately equal to the initial drawing stress, $\sigma_m$. This assumption is valid in the initial unloading portion, and the slope in this region is desired because it counts most heavily in the craze tip process zone stresses. Thus

$$\sigma_m = \frac{\text{force on a fibril}}{\text{fibril cross-sectional area}} = \frac{F}{A} = \text{constant}$$

The fibril volume is also constant so

$$A_0 \varepsilon_0 = A \varepsilon$$

The strain is defined as

$$\varepsilon = \frac{\varepsilon}{\varepsilon_0} - 1$$

and the engineering stress as

$$\sigma_{yy} = \frac{F}{A_0}$$

Substituting yields

$$\frac{\sigma_{yy}}{\sigma_m} = \frac{1}{1 + \varepsilon}$$

Thus the unloading slope is

$$\frac{d\sigma_{yy}}{d\varepsilon} = -\sigma_m \frac{1}{(1 + \varepsilon)^2}$$

which gives an initial value as $\varepsilon \to 0$ of $-\sigma_m$.

Thus

$$\theta = -\frac{\sigma_m}{E_C} = -\varepsilon_m$$

using the relation

$$E_C = \frac{\sigma_m}{\varepsilon_m}$$

This leaves only $\sigma_m$ to be determined, which is found from an analysis of the stresses causing cavitation in the spheres. As mentioned pre-
viously, the stress required to cavitate the polybutadiene in the microspheres comes from two contributions:

\[
\sigma_{ca} = \sigma_{th} + \Omega (\sigma_{\infty} + \sigma_{tip}) \tag{4-22}
\]

where \( \sigma_{th} \) is the thermal stress due to the thermal expansion coefficient mismatch, \( \sigma_{\infty} \) is the applied distant stress, \( \sigma_{tip} \) is the additional concentrated stresses existing ahead of the craze tip and \( \Omega \) is the stress concentration effect in the sphere due to the modulus mismatch.

The three components of the craze tip stresses are calculated from the linear elastic crack tip solutions, and are, for Mode I loading,

\[
\sigma_{rr} = \frac{K_I}{\sqrt{\pi a}} \tag{4-23}
\]

\[
\sigma_{\theta\theta} = \frac{K_I}{\sqrt{\pi a}} + \sigma_{\infty}
\]

\[
\sigma_{zz} = \nu C (\sigma_{rr} + (\sigma_{\theta\theta} - \sigma_{\infty})) = 2 \nu C \frac{K_I}{\sqrt{\pi a}}
\]

Summing these components and noting that

\[
\frac{K_I}{\sqrt{\pi a}} = (\sigma_m - \sigma_{\infty}) \tag{4-6}
\]

yields (Argon et al 1983)

\[
\sigma_{tip} + \sigma_{\infty} = 2(1+\nu C)(\sigma_m - \sigma_{\infty}) + \sigma_{\infty} \tag{4-24}
\]

The negative pressure enhancement induced in the sphere due to distant tension is,

\[
\Omega = \frac{1}{3} \left( 1 + \frac{2(1-4\nu C + \nu C^2)(K_{PB}^{K_C} - 1)}{(1+\nu C)(2(1-\nu C)+1+\nu C)(K_{PB}^{K_C})} \right) \tag{4-25}
\]

The thermal stress are determined by
\[ \sigma_{th} = \frac{(\gamma_{PS} - \gamma_{PB}) K_{PB} \Delta T}{1 + \frac{1}{2(1-x)} \frac{K_{PB}}{K_{PS}} \left( \frac{1+x}{1-2x} \left( \frac{1+\nu_{PS}}{1-2\nu_{PS}} \right) \right)} \]

where \( \gamma_{PS} \) and \( \gamma_{PB} \) are the volumetric thermal expansion coefficients for polystyrene and polybutadiene respectively. Here \( \Delta T \) is the temperature difference between the matrix glass transition temperature \( (T_{gPS} = 95^\circ C) \), below which thermal stress can develop, and the test temperature.

The value of \( \sigma_m \) can be determined from the above expressions substituted into Eq. 4-22 if \( \sigma_{cav} \) is known. While cavitation in rubber has been recognized for some time (Gent and Lindley 1958, Sultan and McGarry 1973, Breuer et al 1977) there are no reported values of an intrinsic cavitation stress. Bates et al (1983b) have shown that the cavitation stress of most of the materials used in this work is greater than 79 MPa at -90°C. Unfortunately neither the actual cavitation stress nor its temperature dependence was determined. Therefore \( \sigma_{cav} \) is used as a fitting parameter with a value of 60 Mpa for tests at room temperature yielding excellent agreement with the craze growth rate data.

The little theoretical work done on rubber cavitation has dealt with the stress required to expand indefinitely a pre-existing flaw (Kaelble 1971, Gent and Tompkins 1969). In typical materials, these flaws are greater than 1.0 \( \mu m \) in size, which is about 2 orders of magnitude larger than the polybutadiene sphere domain sizes, and result in cavitation stresses of \(-25\) MPa. Gent and Tompkins extended their treatment to very small initial hole sizes by including surface energy effects. Using a rubber shear modulus of .1 MPa, the assumed cavitation stress of 60 MPa
would be predicted for an initial hole of around 30 Å radius. This value represents approximately 1% of the volume of the microspheres used in this work. Thus while the cavitation stress for polybutadiene has not been measured, the fitted value of 60 MPa seems reasonable.
Chapter 5 ISOLATED CRAZE GROWTH AND STRESS-STRAIN BEHAVIOR IN SPHERICAL MORPHOLOGIES

The need for a better understanding of the factors influencing the toughness of crazable glassy polymers has lead to the study of the various molecular processes involved. This chapter deals with the measurement and modelling of isolated craze growth in diblock copolymer materials with microspherical inclusions of polybutadiene. The chapter will conclude with some qualitative statements relating the toughness of these materials, as measured through a stress-strain curve, with the fundamental information on the individual craze growth kinetics.

5.1 Craze Growth Kinetics

The samples for which craze growth data were obtained are listed in Table 5-1 along with various molecular and geometric data, the latter obtained from routine transmission electron microscopy of each sample. The data are presented in Figures 5-1 through 5-12 and are fairly well bracketed by the predictions of the two models developed in the previous chapter. It can be seen that the materials containing a high volume fraction of rubber follow the cavitation model and the materials with little rubber are well predicted by the meniscus instability model proposed by Argon and Salama (1977) for craze growth in homopolymers. A region of unpredictable and often intermediate craze growth rates is observed in materials containing between 6 and 11 volume percent polybutadiene. This general picture is intuitively appealing in that a mechanism based on cavitation in the rubber domains would be expected to dominate at high rubber volume fractions but give way to the craze growth mechanism observed in
<table>
<thead>
<tr>
<th>CODE</th>
<th>POLYMER</th>
<th>VOLUME %</th>
<th>CASTING SOLVENT</th>
<th>POLYBUTADIENE MOL.WT.(Kg/mol)</th>
<th>POLYSTYRENE MOL.WT.(Kg/mol)</th>
<th>SPHERE CENTER TO CENTER(A)</th>
<th>SPHERES CENTER TO EDGE(A)</th>
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<tr>
<td>A</td>
<td>SB8</td>
<td>26.</td>
<td>MEK/THF</td>
<td>120</td>
<td>400</td>
<td>320</td>
<td>880</td>
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<tr>
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<td>18.</td>
<td>MEK/THF</td>
<td>230</td>
<td>230</td>
<td>350</td>
<td>1090</td>
</tr>
<tr>
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<td>SB9/S4</td>
<td>18.</td>
<td>MEK/THF</td>
<td>230</td>
<td>230</td>
<td>395</td>
<td>1230</td>
</tr>
<tr>
<td>C</td>
<td>SB8/S3</td>
<td>15.</td>
<td>MEK/THF</td>
<td>120</td>
<td>300</td>
<td>325</td>
<td>1080</td>
</tr>
<tr>
<td>D</td>
<td>SB4</td>
<td>14.</td>
<td>TOLUENE</td>
<td>20</td>
<td>150</td>
<td>140</td>
<td>470</td>
</tr>
<tr>
<td>E</td>
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<td>11.</td>
<td>MEK/THF</td>
<td>230</td>
<td>200</td>
<td>365</td>
<td>1340</td>
</tr>
<tr>
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<td>SB9/S3</td>
<td>11.</td>
<td>MEK/THF</td>
<td>230</td>
<td>240</td>
<td>360</td>
<td>1320</td>
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<tr>
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<td>11.</td>
<td>TOLUENE</td>
<td>59</td>
<td>560</td>
<td>220</td>
<td>810</td>
</tr>
<tr>
<td>FF</td>
<td>SB7</td>
<td>11.</td>
<td>TOLUENE</td>
<td>59</td>
<td>560</td>
<td>280</td>
<td>1030</td>
</tr>
<tr>
<td>G</td>
<td>SB7</td>
<td>11.</td>
<td>MEK/THF</td>
<td>59</td>
<td>560</td>
<td>180</td>
<td>660</td>
</tr>
<tr>
<td>H</td>
<td>SB7/S4</td>
<td>8.7</td>
<td>TOLUENE</td>
<td>59</td>
<td>390</td>
<td>225</td>
<td>890</td>
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<tr>
<td>I</td>
<td>SB8/S3</td>
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<td>MEK/THF</td>
<td>120</td>
<td>250</td>
<td>200</td>
<td>810</td>
</tr>
<tr>
<td>J</td>
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<td>TOLUENE</td>
<td>120</td>
<td>250</td>
<td>310</td>
<td>1260</td>
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<tr>
<td>K</td>
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<td>135</td>
<td>580</td>
</tr>
<tr>
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<td>SB7/S4</td>
<td>5.8</td>
<td>TOLUENE</td>
<td>59</td>
<td>284</td>
<td>250</td>
<td>1140</td>
</tr>
<tr>
<td>M</td>
<td>SB7/S4</td>
<td>5.8</td>
<td>MEK/THF</td>
<td>59</td>
<td>284</td>
<td>200</td>
<td>910</td>
</tr>
<tr>
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<td>5.8</td>
<td>MEK/THF</td>
<td>230</td>
<td>170</td>
<td>400</td>
<td>1820</td>
</tr>
<tr>
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<td>TOLUENE</td>
<td>59</td>
<td>210</td>
<td>250</td>
<td>1430</td>
</tr>
<tr>
<td>X</td>
<td>SB9/S4/B1</td>
<td>11.</td>
<td>MEK/THF</td>
<td>51</td>
<td>180</td>
<td>450</td>
<td>1650</td>
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<tr>
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<td>MEK/THF</td>
<td>4.2</td>
<td>354</td>
<td>265</td>
<td>970</td>
</tr>
</tbody>
</table>

**NOTES:** Sphere sizes corrected from TEM results (Berney et al 1982)  
Block molecular weights based on chain ends  
BCC packing assumed for spacing calculations (Bates et al 1982)
FIGURE 5-1

- CODE A
- CODE D
- CAVITATION MODEL
- MENISCUS MODEL

CRAZE GROWTH RATE (m/sec)

10^-5
10^-6
10^-7
10^-8
10^-9

12.0 14.0 16.0 18.0 20.0 22.0

STRESS (MPa)
FIGURE 5-2

CRAZE GROWTH RATE (m/sec)

STRESS (MPa)

- CODE B 20°C
- CODE BB -20°C
- CAVITATION MODEL
- MENISCUS MODEL
FIGURE 5-3

CRAZE GROWTH RATE (m/sec)

10^{-4}

10^{-5}

10^{-6}

10^{-7}

10^{-8}

10^{-9}

STRESS (MPa)

16.0

18.0

20.0

22.0

24.0

26.0

28.0

- CODE C
- CAVITATION MODEL
- MENISCUS MODEL
FIGURE 5-5

CRAZE GROWTH RATE (m/sec)

10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9}

20.0 22.0 24.0 26.0 28.0 30.0 32.0

STRESS (MPa)

- CODE F
- CODE G
- CAVITATION MODEL
- MENISCUS MODEL


FIGURE 5-6

- CODE H
- CAVITATION MODEL
- MENISCUS MODEL

CRAZE GROWTH RATE (m/sec)

STRESS (MPa)
FIGURE 5-7

- CODE I
- CODE J
- CAVITATION MODEL
- MENISCUS MODEL

CRAZE GROWTH RATE (m/sec)

STRESS (MPa)
FIGURE 5-9

CRAZE GROWTH RATE (m/sec) vs STRESS (MPa)

- CODE L
- CODE M
- CAVITATION MODEL
- MENISCUS MODEL
FIGURE 5-10

CRAZE GROWTH RATE (m/sec)

CODE N
CAVITATION MODEL
MENISCUS MODEL

STRESS (MPa)

10^{-8}
10^{-7}
10^{-6}
10^{-5}
FIGURE 5-11

CRAZE GROWTH RATE (m/sec)

10^-5
10^-7
10^-9

STRESS (MPa)

20.0 22.5 25.0 27.5 30.0 32.5 35.0 37.5

- CODE 0
- CAVITATION MODEL
- MENISCUS MODEL
homopolymers at some low but finite volume fraction rubber. At these low rubber contents, the cavitation mechanism should become inoperative due to large intersphere spacings and/or to the increasing "homogeniety" of the material as seen by the advancing craze tip. Predicting the transition then, between mechanisms would be complicated by the expected sensitivity of the choice of mechanism to the details of the morphology, especially that existing immediately before the growing craze tip.

The sensitivity of the growth rate to morphological perturbations is most apparent for the case of the identical polymer system cast from different solvents yielding different sphere size and spacings. Codes F and G (Fig 5-5) exhibit the two extremes with only a 20% change in the sphere size and spacing. Codes I and J (Fig. 5-7) are a similar but not as striking example.

Two samples exhibited craze growth rates faster than the cavitation model, Codes A and D (Fig 5-1). One explanation for the faster than predicted growth rates for code A may lie in the non-equilibrium morphology. The predicted cylindrical morphology for the 26% polybutadiene (Bates 1983) sample was overridden by using a better solvent for the polystyrene phase (see Chap. 2). The resultant non-equilibrium morphology may manifest itself as a residual energy contribution resulting in easier cavitation of the spherical morphology and hence faster than predicted craze growth. An excellent fit to the data is achieved if the stress required to cavitate the polybutadiene sphere is decreased from 60 MPa to 50 MPa for this particular case, but it is not known, without further information, if this is reasonable.
Sample code D also crazes at a faster rate than predicted by either model. While this material (and all materials other than code A) have a predicted spherical morphology, the rubber spheres in code D are expected to cavitate at a lower stress than normal due to the low polybutadiene molecular weight of 20 Kg/mol. Rubber failure has been observed by Bates et al (1983b) in the low polybutadiene molecular weight material simply as a result of large thermal stresses generated at cryogenic temperatures. Again, an excellent fit with the data in this case is achieved when the cavitation stress is lowered from 60 MPa to 55 MPa. It may also be significant in the case of Code D that the lower molecular weight materials show increased order in packing both in the electron microscope and through neutron scattering (Bates et al 1982). This increased order may also facilitate craze growth.

An interesting observation in some of the low volume percent polybutadiene samples is the occasional jump from craze growth via the meniscus instability model to growth via the cavitation model at high stresses. Code O (Fig. 5-11), Code H (Fig. 5-6), and to a lesser extent, Code N (Fig. 5-10) and Code FF (Fig. 5-12) all show this behavior. Argon and Salama (1977) suggested that craze growth even in homopolymers may switch to a cavitation process involving pore formation preceding the craze tip since that mechanism yields faster growth at very high stresses. The cavitation model for craze growth in block copolymer materials predict a faster growth rate at all stresses investigated but is not always the dominant mechanism. Explaining this transition between mechanisms in the same material is no better understood quantitatively than the transition between mechanisms in
different materials as the rubber volume fraction changes. Nevertheless, the higher stresses would again facilitate sphere cavitation and hence be expected to induce a mechanism shift as was observed.

One final observation is that the choice of homopolystyrene used for blending seems to have no effect on the isolated craze growth behavior, as shown by codes E and EE (Fig. 5-4).

5.2 Low Temperature Craze Growth

Over half the stress required to cavitate the polybutadiene microspheres is induced by the thermal expansion coefficient mismatch between the rubber and matrix in cooling the sample from 95°C (T_g for the polystyrene matrix) to the test temperature (Equation 4-22). If the test is conducted at a lower temperature this thermal stress is larger resulting in easier cavitation of the spheres for a given stress. Hence the craze growth rate is expected to increase at lower temperatures due to this effect. This effect, however, is overpowered by the direct temperature dependence in the exponential of the craze growth expression as a result of the increasing deformation resistance (Equation 4-8). It is also not as strong in that the stress required to cavitate the rubber rises as the temperature drops, although not as fast as the induced thermal stresses rise. Thus, while the value of the pre-exponential D_2 is increasing as the temperature drops, the exponential term controls. This can be contrasted with the temperature dependence prediction for the meniscus instability model in which the pre-exponential D_1 is expected to be temperature independent and only the exponential is temperature sensitive. Thus at lower temperatures the difference between the craze growth rates predicted by the
two models will become larger with the difference exceeding several orders of magnitude at a test temperature of -20°C.

Low temperature craze growth experiments confirm these predictions. Code BB is well predicted by the cavitation model at -20°C (Fig. 5-2). Code FF with 11% volume rubber lies in the transition region where the mechanisms switch. At -20°C this latter material has apparently switched to the meniscus model with craze growth values being three orders of magnitude lower than those predicted by the cavitation model.

5.3 Stress-Strain Results

The difficulty of interpreting stress-strain results without a fundamental understanding of all the processes involved in material toughness has been stressed and repeated throughout this thesis. Nevertheless, stress-strain results for several of the spherical morphology samples will be presented for three reasons: 1) completeness, 2) to demonstrate the considerable and attractive toughness in the "as prepared" thin films, and 3) to show how several features of the stress-strain behavior can be qualitatively explained with an understanding of the isolated craze growth behavior.

The spherical morphology materials exhibit a very attractive mix of three important properties: high modulus, high yield stress, and good elongation to break. The modulus for a material with spherical rubber inclusions is the highest compared to any other morphology for a given volume fraction of rubber (Chow 1978). The high yield stress is no doubt due to the restriction of craze initiation to surface flaws only. Compared
to HIPS, with controlled internal craze initiation sites, the flow stresses are nearly twice as high. Finally, the elongation to break, while not as good as the best HIPS, is still considerable, typically 20%-60%. With controlled initiation sites, these block copolymer materials could easily outperform HIPS, but of course at a higher cost.

Stress-strain results are shown in Fig. 5-13 A-0 and Fig. 5-14. Several general trends are observed. The materials with the highest volume fraction of rubber have the lowest tensile modulus, lowest flow stresses, and highest elongations to fracture. As the volume percent polybutadiene drops, the modulus increases, the flow stress rises and the elongation to fracture decreases. The dependence of the modulus on rubber content is well understood (see eq. 4-11). The changes in flow stresses can be understood from data on isolated craze growth rates.

As explained in Section 4.1, in materials which primarily deform via crazing, the imposed test strain rate is matched by the craze dilational strain rate

\[ \phi = \rho b u \]  

4-2

While the craze thickness, b, is expected to be constant, the active craze front length, \( \rho \), is expected to depend on the flow stress since at higher stress more surface flaws would become effective at initiating crazes. If \( \rho \) is assumed to be relatively constant though, all materials should have the same number of crazes growing at the same rate, \( u \), for a given imposed strain rate. Since the applied stress required to achieve a given craze growth rate is much lower for the materials with higher rubber content, the lower flow stress in these materials is expected.
FIGURE 5-13 A, B

**CODE A**

- STRAIN RATE: 0.026 $\text{sec}^{-1}$
- STRAIN RATE: 0.00026 $\text{sec}^{-1}$

**CODE B**

- STRAIN RATE: 0.026 $\text{sec}^{-1}$
- STRAIN RATE: 0.00026 $\text{sec}^{-1}$
FIGURE 5-13 D, E

CODE D

STRAIN RATE \( \frac{\text{sec}^{-1}}{} \)

- \( 0.026 \frac{\text{sec}^{-1}}{} \)
- \( 0.00026 \frac{\text{sec}^{-1}}{} \)

CODE E

STRAIN RATE \( \frac{\text{sec}^{-1}}{} \)

- \( 0.026 \frac{\text{sec}^{-1}}{} \)
- \( 0.00026 \frac{\text{sec}^{-1}}{} \)
FIGURE 5-13 F, G

**CODE F**

- **STRAIN RATE**
  - □ 0.026 sec⁻¹
  - O 0.00026

**STRESS (MPa)**

**STRAIN (%)**

**CODE G**

- **STRAIN RATE**
  - □ 0.026 sec⁻¹
  - O 0.00026

**STRESS (MPa)**

**STRAIN (%)**
FIGURE 5-14
LOW TEMPERATURE STRESS - STRAIN RESULTS

CODE BB

STRAIN RATE

□ 0.026 sec⁻¹
○ 0.00026

CODE FF

STRAIN RATE

□ 0.026 sec⁻¹
○ 0.00026
Likewise, the higher strain rate tests will have a higher flow stress to induce a higher craze growth rate. The craze growth rate change expected by the imposed strain rate change (factor of 100) does not cause a commensurate change in the flow stresses though. This is because at the higher stresses the craze initiating efficiency of surface flaws is increased, decreasing the need for higher craze growth rates.

This isolated craze growth rate/flow stress relationship explains the different stress-strain behavior in codes F and G (Fig 5-13 F, G). These two materials are chemically identical but morphologically different (Table 5-1). Code F exhibits craze growth via the cavitation mechanism whereas code G has switched to the meniscus instability mechanism which has growth rates over a decade slower (Fig. 5-5). This slower growth rate manifests itself in the higher flow stresses for code G.

The significantly lower craze growth rates at lower temperatures are evidenced in the low temperature stress-strain results (Fig. 5-14). The increase in flow stress for code BB at -20°C is completely explained by the increased stress required to generate the same craze growth rate (Fig. 5-2). Code FF requires a considerably higher stress to maintain a given craze growth rate due to the shift in craze growth mechanisms (Fig. 5-12) resulting in a very high craze flow stress.

The elongation to fracture is expected to be related to the craze flow stress, with craze fibril breakdown occurring quicker at higher stresses (see Section 4.1). Since the flow stresses are related to volume fraction polybutadiene through the craze growth velocities, the elongations to fracture are also expected to relate to the rubber content.
This points to the importance of the cavitation mechanism of craze growth. Since the crazes grow several orders of magnitude faster by this mechanism than by the meniscus instability mechanism, the craze flow stress required to match any imposed strain rate can be significantly lower, resulting in much higher elongations to fracture. This is very clear in the low temperature stress-strain results (fig. 5-14) where the material which crazed via the cavitation mechanism (code BB) maintained its toughness with a lower flow stress and the material which switched to the meniscus instability mechanism (code FF) lost all toughness.
Chapter 6 NON-LINEAR CRAZE GROWTH

The craze growth models developed in Chapter 4 predict constant craze growth velocities for a given stress and temperature. This comes out of the assumption that the stress on the mature craze matter rises up to the applied stress and hence the craze tip stress perturbations simply propagate through the material unchanged at a constant speed.

The craze tip processes are assumed to dominate in both of the above models, but this may not always be the case. Verheulpen-Heymans (1979) modeled craze growth in polycarbonate as dominated by the mature craze fibril drawing processes and predicted the craze growth rate to decay with time under constant stress. On the other hand, Chern and Hsiao (1982) assumed various viscoelastic properties for the craze matter and predicted accelerating craze growth.

In all the materials discussed in the last chapter, the craze length increased linearly with time for a given test condition and were generally well predicted by one of the two models developed in Chapter 4. Two samples though, consisting of blends with low molecular weight polybutadiene homopolymer, occasionally exhibited accelerating craze growth. These samples were prepared to isolate the effect of rubber molecular weight on craze growth. For pure diblock systems the rubber microsphere diameter is dependent on the rubber molecular weight (see Chapter 1), but through polybutadiene blending large microspheres consisting of low molecular weight rubber can be prepared. See Table 5-1 for molecular and morphological information on these two samples labelled codes X and Y.
As seen in Figure 6-1 a,b the craze lengths for code X increase linearly with time for tests conducted at low stresses. But at higher stresses the craze growth rate begins to increase with time (Figure 6-2 a,b). The rubber inclusions in the prepared films were crosslinked by exposing samples to a 10 Mrad dosage of electrons in order to investigate the effect of polybutadiene molecular weight. The crosslinked films exhibited similar behavior (Figure 6-3 a-d) except that the transition to accelerating craze growth seems to have been shifted to a higher stress. When the constant growth velocity data are compared with the model predictions, more scatter than typical is observed but in general the cavitation mechanism models the data well (Figure 6-4). The craze growth rates predicted for the cavitation model at the higher test stresses are included on those craze length versus time plots as a slope (Figure 6-2 a,b and 6-3 c,d). While the craze may grow with the predicted rate initially, the craze growth rate quickly increases to much higher values.

In an effort to understand this anomalous behavior, electron micrographs of the craze matter in these accelerating crazes were obtained (Figure 6-5). The craze matter in code X is considerably different than that for code E (Figure 4-4) which is a very similar material for the exception of the polybutadiene molecular weight (see Table 5-1). Most striking is the thicker craze structure along with the presence of cavitated spheres within the bulk material above and below the craze. The craze growth model developed in Section 4-3 and illustrated in Figure 4-3b assumes that only a single plane of microspheres undergo transformation into craze matter. The thicker crazes observed in code X material could
FIGURE 6-1 a,b

CODE X 12.2 MPa

SLOPE .000082 mm/min
.000074
.000052

CRAZE LENGTH, 2a (mm)

TIME (min)

CRAZE LENGTH, 2a (mm)

TIME (min)
FIGURE 6-2 a, b

- CODE X 17.2 MPa
- CODE X 26.1 MPa

CRAZE LENGTH, 2a (mm)

TIME (min)

CRAZATION MODEL
FIGURE 6-3 a, b

The figure shows two graphs with data points representing craze length, 2a (mm), over time (min).

**Top Graph: CODE X 10 Mrad 16.0 MPa**
- SLOPE: 0.000786, 0.000327, 0.000276

**Bottom Graph: CODE X 10 Mrad 18.5 MPa**
- SLOPE: 0.0101 mm/min
- Additional data points: 0.0100, 0.0105, 0.00975, 0.0101
FIGURE 6-4

CRAZE GROWTH RATE (m/sec)

- CODE X
- CODE X, 10 Mrad
- CODE E

-- CAVITATION MODEL
-- MENISCUS MODEL

STRESS (MPa)
either have grown from a zone thick enough to contain several planes of microspheres, or alternatively, the mature craze could grow in thickness by cavitating the microspheres above and below the craze.

The first explanation could be taken into account in the cavitation model by increasing the degradation zone half-thickness, $\delta$, to a value more representative than a single sphere diameter. Unfortunately, the model would still predict linear growth but at a higher rate. But the models for craze growth developed in Chapter 4 cannot account for significant craze thickening as speculated above, primarily because the assumptions about the stress field for the mature craze body are no longer valid. If the craze continues to thicken, the stress carried by the body of the craze would not completely rise to the applied stress. Due to equilibrium requirements, this difference between the applied stress and the craze body stress would have to be balanced by an increase in the stress concentration at the craze tip. Thus the longer the craze became, the higher the stress developed before the advancing craze tip. These higher tip stresses would be expected to cause faster growth; hence a craze thickening hypothesis would predict accelerating growth (Argon et al 1983).

While this development is appealing, there are several problems with the above simplistic explanation. First, no significant stress concentrations exist in the bulk material near the craze body to induce cavitation. Second, independent of the mechanism, there is no reason to suspect that crazes would accelerate in code X but not in any of the materials tested in Chapter 5. Even though low molecular weight polybutadiene was blended in, the number average rubber molecular weight is still
Figure 6-5  Transmission electron micrograph of a craze in a diblock blend prepared with homopolybutadiene. Note the numerous cavitated spheres in and near the craze.
51 Kg/mole and hence expected to have the same high cavitation stress. Rheovibron results for this material (Drzewinski 1983) showed a shift in the polybutadiene glass transition temperature, indicating a high cavitation stress, following the experiments of Bates et al (1983b). Indeed, the cavitation model predicts the low stress linear growth data well using the same 60 MPa cavitation stress.

Similar experiments were conducted on a blend with SB7, denoted code Y, with the average polybutadiene molecular weight prepared very low at 4.2 Kg/mole. As noted in Section 5.1 and observed by Bates et al (1983b), a lower cavitation stress is seen in materials with a lower rubber molecular weight. In the low stress, linear growth region for this material, the cavitation stress used to fit the data had to be dropped to 41 MPa (Figure 6-6). The model predictions became very sensitive to the cavitation stress at these low values because the sum of the thermal stress and the applied stress concentrated inside the microspheres is nearly equal to the cavitation stress. As seen in Figure 6-6, at an applied load of 20 MPa they become equal and the model predicts homogeneous cavitation/crazing everywhere in the sample as manifest by an infinite craze growth rate. For this material a craze thickening mechanism is reasonable especially at the higher stresses.

Thus while both code X and Y exhibit accelerating craze growth, it is only expected in code Y. The only common feature is the presence of polybutadiene homopolymer which at present does not explain the accelerating growth. Two features of the blended samples would be different than all samples tested in Chapter 5, the interfacial adhesion and the sphere size
FIGURE 6.6

- CODE Y
- CAVITATION MODEL ($\sigma_{cav} = 41$ MPa)
- CODE F
- CAVITATION MODEL ($\sigma_{cav} = 60$ MPa)
- MENISCUS MODEL

CRAZE GROWTH RATE (m/sec)

STRESS (MPa)
distribution. As noted in Section 3.4, homopolymer blending reduces the interfacial adhesion since only a fraction of the polybutadiene chains in the microspherical domains are covalently bonded to the polystyrene matrix. Unfortunately, lightly cross-linked samples exhibited the same accelerating growth. Homopolymer blending has also been shown to disrupt both sphere packing and uniformity of sphere size by Bates et al (1983a). Not only does code X have a much broader sphere size distribution (Figure 6-5 versus Figure 4-4) but the largest spheres seem most susceptible to cavitation. Two possible reasons may exist for this – ease of sphere cavitation may be a function of sphere size or alternatively, the largest spheres could consist predominantly of polybutadiene homopolymers which, due to its lower molecular weight, would be expected to cavitate at a lower stress, as documented above. Considerable understanding is necessary before these ideas can be tested and incorporated into a growth model.

The stress strain behavior for code Y is shown in Figure 6-7 a,b. As explained in section 5.3, the low craze flow stress compared to code F (Figure 5-13 F) is explainable from the high craze growth rate. The low cavitation stress for code Y results in growth rates over an order of magnitude faster than those for code F but seems to have no effect on the strain to fracture.

The low cavitation stress would also make the cavitation mechanism of craze growth more favorable at low temperatures. As shown in Section 5.2, materials with 11 volume percent rubber are in a transition region where the meniscus instability mechanism seems more favored at lower test temperatures (Fig 5-12). While low temperature isolated craze growth data were
FIGURE 6-7
STRESS - STRAIN RESULTS FOR CODE Y

Room Temperature

STRAIN RATE $\text{sec}^{-1}$
- $\square$ 0.026
- $\bigcirc$ 0.00026

-20°C

STRAIN RATE $\text{sec}^{-1}$
- $\square$ 0.026
- $\bigcirc$ 0.00026
not obtained for this material, the tough behavior exhibited in the low
temperature stress-strain experiments indicate that the cavitation mecha-
nism is still controlling (see section 5.3).

Two important ramifications have come out of this part of the work. First, it was discussed in Section 5.3 how the low temperature toughness can be increased by taking advantage of the faster craze growth rates generated by the cavitation growth mechanism. One method of insuring that the cavitation mechanism dominates at low temperatures is to use a high volume percent rubber composition (see Figure 5-2). As shown in this chapter, an alternative method is to add low molecular weight polybutadiene to a lower rubber composition material. This technique has previously been used for improving the low temperature toughness of HIPS and ABS (Kruse 1979) although not through craze growth rate changes.

A second ramification of the novel craze growth kinetics in these polybutadiene blends is the possibility of tailoring impact toughness through control of the craze growth rate instead of the craze initiation rate. As shown in Figure 6-6 the craze growth rate is predicted to rise sharply at 20 MPa while experimentally the crazes are observed to continuously accelerate at these higher stresses. Thus, even with constant craze initiation sites, the amount of energy absorbed through crazing (equation 4-3) would suddenly increase when the applied stress exceeded 20 MPa. With the proper initiation sites, the potential exists for designing a material which would be unaffected at typical service loads but homogeneously craze and deform extensively and at high impact stresses.
Chapter 7 SUMMARY AND FUTURE WORK

The objective of this work was to develop a better understanding of the toughness in heterogeneous block copolymers systems. In this novel class of materials, the molecular and morphological features can be controlled independently making block copolymers ideal for studying model two phase systems.

The study of toughness really involves the study of governing large strain deformation processes, crazing being the dominant mechanism in many glassy polymers. Thus a complete understanding of the toughness would require knowledge of the separate processes of initiation, propagation, and termination of crazes and how these processes are affected by changes in the microphase separated morphology.

7.1 Summary

The foundations of this work lie in the synthesis of a model set of polystyrene/polybutadiene diblock copolymers and corresponding homopolymers. Combining this set of materials with the techniques of homopolymer blending and solvent casting provides excellent control over the microstructural features including the domain shape, size, molecular weight and adhesion to the matrix.

Stress-strain results for a series of materials with cylindrical morphology demonstrated the attractive properties of the block copolymers but yielded little fundamental information on the relationship between toughness and microstructure. Transmission electron microscopy of the craze structure indicated that the crazes form by necking and drawing in
the polystyrene matrix between voiding rubber domains. In order to develop a more fundamental approach to toughness, the isolated craze growth kinetics were investigated in a microspherical morphology. This morphology proved easier to work with both experimentally and mathematically.

Two mechanisms for craze tip advance were modelled: the meniscus instability mechanism which has been shown to govern craze growth in homopolystyrene and a new mechanism based on cavitation in the rubber domains and craze fibril formation from the continuous polystyrene matrix between domains. Each model had one parameter which could not be fixed by independent measurement. The pre-exponential term in the meniscus instability model was used as a fitting parameter since it has been shown to be strongly affected by the sample preparation procedure which although reproducible is difficult to quantify. The intrinsic stress required to cavitate rubber has not been satisfactorily measured and hence is used as a fitting parameter in the cavitation model. The value chosen however, is quite reasonable in light of some theories for rubber cavitation and also rubber cavitation data obtained at cryogenic temperatures.

Craze growth rate data were obtained for 20 samples prepared with widely varying molecular and morphological features. The data were compared with the two model predictions and were generally bracketed by them. The samples with a high volume fraction polybutadiene are well predicted by the cavitation mechanism while the samples with very little rubber follow the predictions of the meniscus instability mechanism. A transition region extends from 6 to 11 volume percent polybutadiene where the choice of mechanism is at present unpredictable. Low temperature isolated craze
growth experiments showed that high rubber volume fractions are necessary to insure crazes growth via the cavitation mechanism in that the transition region apparently moves to higher rubber content at lower temperatures.

Various features of the stress-strain behavior of the microspherical morphology materials including the craze flow stress and the elongation to break can be partially explained from the knowledge on the isolated craze growth kinetics. The substantially higher craze growth rates generated by the cavitation mechanism are shown to be important in determining the toughness of the materials, especially at low temperatures.

Some anomalous craze growth data were presented in the final chapter. Accelerating crazes are observed in blends prepared with polybutadiene homopolymer at higher stresses which cannot be explained by the craze growth models. This novel craze growth behavior yields attractive stress-strain results though, especially at low temperature. Thus, homopolybutadiene blending is an alternative method to preserve toughness at low temperature.

7.2 Future Work

Suggestions for future work fall into two groups - studies to pursue phenomena which could not be explained in this thesis and new investigations into the ramifications of this work. Two observations in this work could not be effectively accounted for. First the switch between craze growth mechanisms for different materials could only be qualitatively explained. Finding the criteria which determine the choice of mechanism would be very helpful in tailoring the toughness of these materials. The
switch from a meniscus instability mode of growth to a cavitation mechanism at higher stress in some materials may also be better understood. Besides requiring more extensive experiments, a mathematical stability analysis of the growth mechanisms may be necessary to answer these questions.

The accelerating craze growth observed in samples with homopolybutadiene blended in could not be adequately explained and deserves further attention. In addition, the effect of rubber blending on the stress required to cause a switch to accelerating growth should be investigated. Preliminary results also indicate that polybutadiene blending lowers the overall volume fraction of rubber required to insure craze growth via the cavitation mechanism which has been shown to be important in the overall toughness.

In addition, the two adjustable parameters used in the two isolated craze growth models could be put on a more theoretical foundation. A fundamental understanding of the intrinsic cavitation process in pure rubbers would be desirable. The phase separated block copolymers are an ideal experimental apparatus for applying tri-axial stress to pure rubbers - what is also needed is a technique for determining when and how much cavitation has occurred. The effect of thermal pre-treatment on craze growth rates in pure polystyrene is being further investigated and similar experiments could be conducted on the block copolymer materials. Techniques for controlled aging are well known and could provide insight into the variability in pre-exponential, $D_1$, of the meniscus instability model.

Other suggestions for further work include studying craze growth in other morphologies. For significant results it would be desirable to
highly orient the morphology and hence isolate its affect. Techniques for orienting block copolymer morphologies have been published (Weil and Pixa 1977, Hadziioannou et al 1979).

One of the ramifications of the cavitation growth mechanism is that the craze fibril diameters and spacings should be directly related to the bulk morphology. The internal craze structure has been measured for many homopolymers using X-ray scattering (see chapter one) and these techniques could be applied to block copolymers. The thin film techniques of Lauterwasser and Kramer (1979) could also be applied to these materials to visualize and quantify the craze structure better. Several potential problems with this technique need to be kept in mind however (Donald et al 1981, Cohen and Reich 1981, Brown 1983), along with the added complications introduced by the heterogeneous block copolymer systems.

Finally the other processes involved in toughening a block copolymer need to be studied. While initiation of crazes is not expected from block copolymer domains, the breakdown of crazes in the block copolymer systems should be a very fruitful area of study. Crazes in block copolymers seem inordinately resistant to failure compared to pure polystyrene, even at high stresses. While the presence of the rubber is obviously important, a mechanistic understanding needs to be developed. The rubber could affect the craze fracture toughness in at least two ways. It could act as a sizing agent protecting the polystyrene fibrils from abrasion and hence early breakdown, or alternatively, the regular array of rubber domains could yield a more regular array of uniform size craze fibrils which would be expected to be more resistant to breakdown. This later idea could be investigated via the small angle scattering suggested earlier.
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>craze fibril cross-sectional area, $A_0$ is initial area</td>
<td>(4-15)</td>
</tr>
<tr>
<td>a</td>
<td>craze length</td>
<td>(4-4)</td>
</tr>
<tr>
<td>B</td>
<td>activation energy for plastic flow of polystyrene</td>
<td>(4-4)</td>
</tr>
<tr>
<td>b</td>
<td>mature craze thickness</td>
<td>(4-2)</td>
</tr>
<tr>
<td>$D_1$</td>
<td>pre exponential term in meniscus instability model</td>
<td>(4-4)</td>
</tr>
<tr>
<td>$D_2$</td>
<td>pre exponential term in cavitation model</td>
<td>(4-9)</td>
</tr>
<tr>
<td>E</td>
<td>Youngs Modulus</td>
<td>(4-7)</td>
</tr>
<tr>
<td>G</td>
<td>Shear Modulus</td>
<td>(4-13)</td>
</tr>
<tr>
<td>K</td>
<td>Bulk Modulus</td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>Mode one stress intensity factor</td>
<td>(4-6)</td>
</tr>
<tr>
<td>KIC</td>
<td>Critical stress intensity factor for craze propagation</td>
<td>(4-7)</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmanns constant</td>
<td></td>
</tr>
<tr>
<td>$\ell$</td>
<td>craze fibril length, $\ell_0$ is initial length</td>
<td>(4-15)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>(4-4)</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>(4-4)</td>
</tr>
<tr>
<td>$t_f$</td>
<td>time to fracture of a mature craze</td>
<td>(4-1)</td>
</tr>
<tr>
<td>W</td>
<td>toughness as defined by the area under a stress-strain curve</td>
<td>(4-1)</td>
</tr>
<tr>
<td>$Y_{cr}$</td>
<td>craze yield stress</td>
<td>(4-1)</td>
</tr>
<tr>
<td>$\hat{Y}$</td>
<td>athermal flow stress</td>
<td>(4-4)</td>
</tr>
</tbody>
</table>
\gamma \quad \text{volumetric thermal expansion coefficient} \quad (\gamma_{ps} = 2.0 \times 10^{-4} \text{ K}^{-1}, \quad \gamma_{ps} = 7.5 \times 10^{-5} \text{ K}^{-1}) \quad (4-27)

\delta \quad \text{degradation zone half thickness} \quad (4-7)

\Delta \quad \text{degradation zone length} \quad (4-5)

\varepsilon \quad \text{strain}

\varepsilon_{cr} \quad \text{mature craze fibril strain} \quad (\varepsilon_{cr} = 4.0) \quad (4-5)

\varepsilon_{f} \quad \text{strain to fracture in stress-strain experiment} \quad (4-1)

\varepsilon_{m} \quad \text{strain at which degradation begins} \quad (4-7)

\dot{\varepsilon} \quad \text{test strain rate} \quad (4-1)

\dot{\varepsilon}_{0} \quad \text{yield theory frequency factor} \quad (\dot{\varepsilon}_{0} = 10^{13} \text{ sec}^{-1}) \quad (4-9)

\zeta \quad \text{natural wavelength of convoluted interphase}

\Theta \quad \text{ratio of descending to ascending slopes of the degradation traction law} \quad (4-7)

\phi \quad \text{craze dilatational strain rate} \quad (4-2)

\chi \quad \text{overall sample volume fraction polybutadiene}

\lambda' \quad \text{craze fibril extension ratio reduced by the effect of orientation hardening} \quad (\lambda' = 1.853) \quad (4-4)

\nu \quad \text{poissons ratio} \quad (4-7)

\rho \quad \text{active craze front length per unit volume} \quad (4-2)

\varphi \quad \text{craze growth velocity} \quad (4-1)

\Omega \quad \text{stress concentration induced in the rubber domains due to an outside applied tensile stress} \quad (4-25)

\sigma \quad \text{stress}

\sigma_{m} \quad \text{stress at which degradation begins} \quad (4-6)

\sigma_{cav} \quad \text{stress at which polybutadiene cavitates} \quad (\sigma_{cav} = 60 \text{ MPa @ 293k, 73 MPa @ 253k}) \quad (4-22)

\sigma_{\infty} \quad \text{distant applied stress} \quad (4-4)
\( \sigma_{th} \) thermal stress induced in rubber domain as a result of thermal expansion coefficient mismatch

\( \sigma_{tip} \) stress concentrations existing before craze tip

\( \sigma_{rr}, \sigma_{\theta\theta}, \sigma_{zz}, \sigma_{yy} \) components of the stress tensor

subscripts

c composite
cr craze
cav cavitation
ps polystyrene
pb polybutadiene
References


Kambour, R.P. (1964) Structure and properties of crazes in polycarbonate and other glassy polymers, Polymer, 5, 143.


