Toughening and Fracture Mechanisms of Rubber Modified Polyamides

by

Orhun Kamil Muratoğlu

Submitted to the Department of Material Science and Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Materials Science and Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

The crystalline morphology and the orientation in thin films of polyamide 6 crystallized on polystyrene or ethylene-propylene-diene rubber coated silicon substrates were analyzed by TEM, x-ray and electron diffraction. Bright field TEM imaging of thin films demonstrated that lamellae organize into disc-shaped crystals, or ‘discoids’, when the film thickness is below 0.5 μm. A model is presented for the organization of lamellae and the polyamide 6 chains in the lamellae of the discoids. In the inter-discoid regions, the films are semi-crystalline and the lamellae fill the space randomly. Orientation studies by means of electron diffraction and wide angle x-ray scattering showed that in relatively thin films (< 0.5 μm) the (002) hydrogen bonded planes are parallel to the surface of the film. This orientation gradually diminishes as the film thickness increases. The change in orientation affects the mechanical properties: Under uniaxial tension, the modulus and the flow stress of the films increase with decreasing thickness, hence with increasing orientation.

Rubber modified polyamides were probed using various analytical techniques: TEM studies showed that in tough samples the crystalline orientation in the interparticle region is of distinctly different character. The lamellae are organized perpendicular to the rubber/matrix interface, while the hydrogen bonded planes of low slip resistance are aligned parallel to these interfaces. Based on this observation a model is proposed to elucidate the deformation and toughening mechanisms of these materials.

The microstructural processes of fracture in rubber-modified polyamides were studied in blends of polyamide 66/ethylene propylene diene rubber (PA66/EPDR) in Izod bending impact experiments. Izod tests were performed at various temperatures to determine the ductile-brittle transition as a function of temperature, rubber weight fraction, and particle size. Subsequent analysis of the fracture surfaces by scanning electron microscopy revealed unique morphologies for various regions of toughness: in the brittle region, the fracture surface is patchy; in the transition region, there are occasional striations present on the fracture surface, along with the brittle fracture morphology; in the tough region, the fracture surface is fully covered by striations.
which penetrate only \( \sim 2 \, \mu m \) beneath the surface in the form of shallow cracks perpendicular to the surface. The striations lie parallel to the main crack front and are a signature of the effective toughening of the polyamide through the incorporation of rubber particles. This drastic change in the fracture surface morphology and formation of striations at the ductile-brittle transition point is the result of elastic-plastic buckling of previously highly stretched material layers on the crack flank as they undergo a constrained accommodation. Morphological studies in the process zone, mainly below the crack flanks, has confirmed this hypothesis of buckling of surface layers. The spacing between the striations observed on the fracture surface of tough specimens varied with rubber content, particle size, temperature, and strain rate. These effects are discussed in terms of local adiabatic heating and variations in the plastic resistance of the matrix material. A model for striation formation based on plastic buckling of a thin surface layer on a porous elastic foundation is provided that serves as a scaling relation accounting well for the temperature dependent changes in striation spacing.

The process of massive cavitations of deformation in an ethylene/propylene diene grafted maleic-anhydride modified polyamide 66, initiated from cavitation rubber particles, has been studied in the region ahead of the crack front by scanning electron microscopy associated with stable crack propagation in compact tension and Izod impact experiments. The very tough stable ductile tearing behavior of the material was manifested by steady state crack opening angles of 60° and large stress whitened zones. The process zone ahead of the advancing crack comprised of two regions with distinct morphologies: a) within a radius of 30 \( \mu m \) in an 'intense' deformation zone in front of the crack the cavities are elongated to large draw ratios (\( \sim 10 \)); b) and in the remaining 'weak' zone cavities were found to be substantially equiaxed. The material with the elongated cavities of the crack front is parted by the propagating crack and immediately sheared by about 60° and left lying parallel to the crack flank surfaces. The very tough behavior of the material has been analyzed by the well known mechanics of fracture of tough structural materials and the calculated tearing moduli were found to be quite comparable with the toughest structural steels.

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Chapter 1

Overview: Polyamides and Toughening

1.1 Elements of Toughening

Polyamides are strong engineering thermoplastics used in a variety of applications. However, under high strain rates and/or low temperatures their mechanical properties deteriorate, leading to the embrittlement of the material. It is known that their low resistance to crack propagation causes this ductile to brittle transition in the presence of a notch that provokes high strain rates. Plasticization with a diluent or modification with rubber particles prevents the embrittlement and improves the impact properties. Incorporation of diluents, such as water, lowers the glass transition temperature which, in turn, reduces the the stiffness and the flow stress of the material and enhances the toughness. Generally, rubber modification is preferred over plasticization because of unacceptable compromises in the level of modulus and/or heat distortion temperature in the latter case; also associated with plasticization are migration and heterogeneous distribution of the diluent that create problems. Rubber modification has been successfully utilized in preventing the embrittlement of polyamides. The governing parameters in this method are the morphology of the blend, local orientation of crystallites in the matrix, particle size, rubber concentration, interparticle distance, strength of the interface, and physical properties and chemical
structure of the rubber. By varying processing conditions and the functionality of
the rubber it is possible to exert some control over these parameters. The influence
of these parameters on the toughening efficiency has been extensively studied; sev-
eral models have been proposed to explain the mechanism by which rubber particles
enhance the toughness of polyamides. These aspects are discussed in the following
sections.

The main processes that absorb energy during impact in rubber modified poly-
amides are the cavitation of the particles in conjunction with the shearing of the
matrix to large strains. The second mechanism accounts for the major source of
toughness. Unlike amorphous matrices where crazing is the main mode of energy
absorption, semi-crystalline polymers do not craze. To avoid premature cavitation
the matrix/rubber interface should be strong enough to prevent debonding and the
particle size distribution should be favorable. It is only below a critical interparticle
distance that the matrix gains an ability for large strain deformation. Unless these
conditions are met, catastrophic failure with consequent embrittlement is inevitable.
There is still need to understand the causes of catastrophic failure and why certain
conditions help the material avoid it.

In the following overview, critical parameters affecting the toughening of poly-
amides are discussed and previous work is assessed. Section 1.3 outlines the crystal
structures and physical properties of the polyamides (namely, polyamide 6 and 66)
used in this study. In Chapter 2, the effect of the rubber particle interface on the adja-
cent crystalline morphology of the polyamide matrix is demonstrated. Based on the
results of Chapter 2, Chapter 3 discusses a mechanism of toughening in conjunction
with the critical interparticle distance concept. The micromechanical mechanisms
that are involved in the fracture of toughened polyamides are disclosed in Chapter 4,
while Chapter 5 proposes a new method of studying the crack propagation in mater-
ials with large scale yielding and large crack opening angles. Appendix A describes
the image analysis algorithm developed to measure the inter-striation distance on
fracture surfaces. Appendix C summarizes the diffusion experiments of the staining
agent (for TEM) into polyamide 6 films.
1.2 Critical Parameters in Toughening

1.2.1 Water Content

Polyamides are susceptible to water absorption because a large proportion of the hydrophilic sites in the amorphous regions cannot find a hydrophobic site to form H-bonds. Therefore, water molecules penetrate polyamides to cluster around the amide groups with unsatisfied H-bonds [8]. LeHuy and Rault [8] have shown that at 100 % relative humidity a high concentration of water molecules are present in the polymer; and about three water molecules cluster around each amide group. The number of molecules per cluster does not change with the level of relative humidity. Due to strong H-bonding involved between the water molecules and polyamide chains, complete removal of moisture is often not possible. At high water concentrations all of the amide groups are surrounded by clusters of three water molecules leaving the rest of the moisture loosely bound which is easily removed by heating. On the other hand, in the low concentration regime, water molecules have to diffuse from one amide site to another and also within the cluster. This is a fairly tortuous path for diffusion associated with high activation energies giving rise to tightly bound water that cannot be removed simply by heating.

Increasing the moisture content in homo-polyamides may reduce the glass transition temperature from above to below room temperature. Consequently, moisture alters the mechanical properties considerably: at high levels of relative humidity, the modulus and the yield stress decrease and the strain to fracture increases [9]. Absorption of water influences the mechanical properties of rubber modified polyamides in an identical manner [10].

1.2.2 Particulate Inclusions

Polyamides are readily toughened by the incorporation of particles of various types of rubber, polyethylene (PE) [11], and poly(phenylene ether) [12]. Besides rubbers such as isobutylene-co-p-methylstyrene [13], methyl metacrylate-butadiene-styrene [14],
and styrene-(ethylene-co-butylene)-styrene (SEBS) [15, 16], the most commonly utilized rubber is the random copolymer of ethylene-co-propylene (EPR). The toughening efficiency of various rubbery inclusions were studied by Borggreve et al. [17] as a function of the elastic modulus of the rubber particles. In the order of decreasing modulus, the modifiers they used were PE, a partially cross-linked thermoplastic elastomer, EPR, and ethylene-co-propylene-co-diene rubber (EPDR). Impact properties gradually improved with decreasing modulus of the rubbery component, leaving EPDR as the best choice for a modifier.

1.2.3 Particle Size and Interfacial Strength

The size distribution of inclusions in a polyamide matrix can be altered by controlling the interfacial tension and/or rheology during blending. For instance by varying the extrusion temperature Borggreve and co-workers were able to alter the viscosity of the rubbery phase relative to that of the matrix, and change the particle size more than three fold [18]. This method of varying rheological parameters also affects the shear stresses in the extruder resulting in variations of local crystalline texture in the matrix. A better control over the particle size is obtained by altering the interfacial strength. Maleic anhydride (MA) functionality has been successfully used in improving the interfacial strength and controlling the particle size of modified polyamides. At high temperatures of blending, maleic anhydride reacts with the amine end groups and amide linkages of polyamides. Rubbers functionalized with MA graft randomly onto polyamide molecules. This grafting then increases the interfacial strength and reduces the particle size. Since, the particle size and interfacial tension are strongly interrelated, it is difficult to determine individually their effects on the toughening efficiency.

At a constant rubber concentration, toughness of a modified polyamide will increase with decreasing particle size. Borggreve et al. [18] have shown that a ductile to brittle transition is induced in a polyamide 6/EPDR blend by increasing the MA functionality of the rubbery phase, hence reducing the particle size. Other systems also exhibit identical response to the reduction in the particle size such as e.g., poly-
amide 66/natural rubber [19] and polyamide 6/SEBS [15] blends. The critical particle size where the transition in toughness occurs increases with increasing rubber concentration or increasing temperature. However, there is a lower bound for the particle size distribution in achieving effective toughening. In polyamide 6 systems, this minimum is reported to be around 0.1 - 0.2 μm [15]. Polyamide 66 systems appear to have no minimum limit on particle size [16].

Increasing the level of interfacial strength not only decreases the particle size, but it also prevents premature debonding of the particles from the matrix. In most cases, debonding is not desirable, in that it generates local instabilities that could lead to catastrophic fracture.

1.2.4 Rubber Content

Similar to the particle size effect, increasing the rubber concentration induces a brittle to ductile transition in polyamide matrices. The critical concentration level where the transition occurs increases with increasing particle size and decreasing temperature. Borggreve [18] and Wu [20] have documented this effect on polyamide 6/EPDR and polyamide 66/natural rubber blends, respectively.

1.2.5 Interparticle Distance

Wu [21] examined the variations in toughness with interparticle distance and concluded that independent of particle size and rubber content there exists a critical interparticle distance (ligament thickness) $ID_c$, value below which the blend experiences a drastic increase in toughness. In the polyamide 66/natural rubber blends that Wu studied, the critical transition occurred at an $ID_c$ of 0.3 μm. Borggreve et al. [18] have observed the same effect in polyamide 6/EPDR system at an $ID_c$ of around 0.2 - 0.3 μm. They also demonstrated the effect of temperature on $ID_c$. The $ID_c$ increases only slightly from 0.2 - 0.3 μm to 0.4 μm upon increasing the temperature from room temperature to 60 °C.
1.2.6 Proposed Mechanisms for Toughening

Hobbs [22] proposed a mechanism where the extensive shear banding of the matrix leads to toughening of the blends via the overlap of the shear stress fields around the particles. Following the proposal of this model Wu [19] demonstrated the critical interparticle distance effect in the toughening of polyamides, and claimed that the overlap of the stress fields would reach a critical limit with decreasing interparticle distance. In this slight modification to the model of Hobbs, Wu also considered the percolation of such regions with large local stress field overlap [23-25]. In another attempt, Wu [20] proposed a model where the stress triaxiality in the interparticle region diminishes as the density of particles increase, leaving these regions under plane stress, hence toughening the blend. However, if the rubber content is kept constant these models become independent of particle size: both the triaxiality of the stress state and the stress field overlap in the interparticle region are constant at a given rubber volume fraction regardless of the particle size. Therefore, the increase in toughness by the reduction in particle size at a constant rubber concentration cannot be accounted for by these models. The real mechanism should be related to the local properties of the matrix itself where most of the deformation takes place. Chapter 3 of this thesis outlines a micromechanical mechanism that associates the critical interparticle distance effect to the changes in the local crystalline texture of the polyamide matrix.

1.3 Physical Properties: Polyamide 6 and Polyamide 66

The identification of polyamides with integers such as 6, 66, 610, 46 ... depends on the type of monomer used in the synthesis process. When polyamide is synthesized from a single monomer (e.g. polyamide 6), the number of carbon atoms in the monomer is used for identification. Whereas, two numbers are used when two monomers are the constituents of the polymerization (e.g. polyamide 66). In the case
of two monomer synthesis route, the first number indicates the number of methylene units in the diamine and the second number indicates the number of carbon atoms in the diacyl [26]. Polyamide 6 is polymerized via the opening of cyclic monomer lactam, while the synthesis route to polyamide 66 is the condensation polymerization of hexamethylene diamine and adipic acid [27]. The difference in the synthesis leads to a variation in the chemical structure and packing of the chains in a crystal. Figure 1-1 (a) and (b) show the schematic of the chemical structure and structure of hydrogen bonded sheets for polyamide 6 and 66, respectively. Within the crystal,

![Schematic of hydrogen bonded sheets in α polyamide 6](image)

Figure 1-1: (a) Schematic of hydrogen bonded sheets in α polyamide 6. Redrawn from [1]

the hydrogen bonded sheets are stacked up with weak Van der Waals forces. This sheet-like superstructure of crystals lead to extensive anisotropy in elastic and plastic properties [28].

Polyamide 6 can be found in two crystal forms: the α form is the thermodynamically stable one at room temperature [1]; and the γ form can be obtained by iodine treatment [29-33] or by shearing [31, 34-36]. Several intermediate crystal forms (γ*, β*, ...) have also been obtained by quenching from the melt [4, 37, 38]. In fact, hydrogen bonds (H-bonds) randomly form in the melt, and fast quenching leads to a crystalline
Figure 1-1: (b) Schematic of hydrogen bonded sheets in $\alpha_1$ polyamide 66. Redrawn from [1]

state where the H-bonds are formed between both the parallel and antiparallel chains leading to these intermediate structures. Parker and Lindenmeyer [4] have reviewed various crystal forms of polyamide 6. The unit cell data are summarized in Table 1.1 from which the following quantities can be obtained: the distance between the hydrogen bonded chains ($= a/2$); chain repeat distance ($= b$); and distance between hydrogen bonded sheets ($= c \sin(\beta)$). In the $\alpha$ form $\beta > 60^\circ$ and $b > 17 \text{ Å}$, while

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Angle $\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>monoclinic, $\alpha$</td>
<td>9.45-9.66</td>
<td>17.00-17.20</td>
<td>8.01-8.32</td>
<td>65-68°</td>
</tr>
<tr>
<td>hexagonal, $\beta^*$</td>
<td>9.60</td>
<td>17.20</td>
<td>9.60</td>
<td>60°</td>
</tr>
</tbody>
</table>

in the $\gamma$ form $\beta < 60^\circ$ and $b < 17 \text{ Å}$. The H-bonds of the $\alpha$ phase are between the antiparallel chains (Figure 1-1 (a)) which are in the extended conformation. In the $\gamma$ form, the chains are twisted at the amide linkages shortening the chain length, $b$,
and creating H-bonds between parallel chains. The H-bonds of α polyamide 6 are contained within the (001) crystallographic planes, and those of γ form lie in the (100) planes.

Polyamide 66 is a polymorphic polymer as well. The unit cell data for the corresponding crystal forms are reported in Table 1.2. The triclinic, α₁, is the stable crystal form at room temperature. The H-bonds in α₁ are contained in the (010) crystallographic planes (c = chain direction). An increase in the temperature causes a phase change in polyamide 66 at around 160 °C where the triclinic α₁ phase transforms into pseudo-hexagonal α₂ phase. This transition was first reported by Brill [39]. Below the Brill transition the H-bonds are in the (010) planes. At the transition the amide groups tilt and force some of the H-bonds to break and reform in a direction perpendicular to (010) planes.

Brill transition occurs only in polyamide 66 and 46 because the packing of the chains in the low temperature crystal form allow the slight tilting of amide linkages to form new H-bonds between the previously H-bonded sheets. These polyamides also have higher melting temperatures \( (T_{m_{PAA6}} = 290° \text{ and } T_{m_{PAA6}} = 265°) \) compared to polyamide 6 \( (T_{m_{PAA6}} = 215°) \) which does not exhibit a Brill transition. This drastic difference in the melting point is related to the so called ‘Brill’ transition. The melting points of polyamides strongly depend on the linear density of H-bonds. However, both polyamide 6 and polyamide 66 have the same linear density of H-bonds and very similar crystal structures. Yet, the latter melts at 50°C higher than the former. In fact, close to the Brill transition the unit cell dimensions of the α₁ phase of polyamide 66 increase gradually, increasing the unit cell volume \( V_{α₁} = 302.5 \text{ Å}^3 \).
$V_{\alpha_2} = 351.0 \text{ Å}^3$). The amide linkages tilt about the chain axis to preserve the H-bonds. However, some bonds are broken in the process of cell expansion. The unsatisfied bonds rearrange and reform establishing H-bonds across hydrogen bonded sheets and forming a 3-dimensional H-bonded network that melts at a higher temperature. In polyamide 6 the packing of the chains does not favor the formation of new H-bonds across the H-bonded sheets with the expansion of the unit cell at higher temperatures. Consequently, polyamide 6 melts at a lower temperature.
Chapter 2

Crystalline Morphology of Polyamide 6 Near Planar Surfaces

2.1 Introduction

Polyamides are known to be high strength engineering thermoplastics. Although they are ductile at room temperature, they become brittle under severe conditions such as high strain rates and/or low temperatures [40]. This is due to low crack propagation resistance of polyamides in general [41]. Several methods are effective in modifying these materials: For instance, rubber particles within a range of particle size and rubber concentration enhance the toughness by as much as 50 fold [19, 18]. Similarly, the presence of glass fibers can improve both the toughness and the fatigue and creep resistances [42, 43]. Composites of polyamide 6 with poly(p-phenylene terephthalamide) (PPTA) fibers have proven to have excellent mechanical properties [44]. The presence of a modifying inclusion influences the crystallization behavior of the matrix. Second phase particles that are crystalline at the crystallization temperature of the matrix often act as heterogeneous nucleation sites resulting in epitaxial growth of the polyamide matrix. For instance, polyamide 6 crystallizes epitaxially at a PPTA fiber interface with the chain direction almost perpendicular (inclined 84°) to the fiber axis [45]. In a polyamide 6-clay hybrid, epitaxy results in the preferred orientation of the γ-(020) hydrogen bonded planes parallel to the montmorillonite inclusion
interface [46].

In most cases, the influence of the interface vanishes when the substrate is amorphous. However, interface effects have been observed in several systems where an amorphous substrate induces an artificial epitaxy in the crystallizing matrix [47-51]. For instance, Andrews [49] demonstrated that cis-polyisoprene thin films on a water substrate crystallize with a preferred orientation of chain axis perpendicular to the film plane. The films displayed no preferred azimuthal orientation. When the same films are crystallized under uniaxial strain, the chain axis acquires a new orientation parallel to the film plane [48]. Similarly, Keller [50] and Scott [51] studied the orientation in thin films of polyamide 66 and 610 prepared by shearing a solution on a hot glass plate. The films were not annealed following the evaporation of the solvent, hence they carried along the orientation induced by shearing. Both studies showed that crystallization in polyamide thin films result in the orientation of the hydrogen bonded planes parallel to the film plane. The present paper investigates the effect of film thickness on the orientation and crystalline morphology in thin films of polyamide 6 melt-crystallized on a rubbery substrate. The results of this orientation study on thin films are consistent with the findings of Keller [50] and Scott [51]. In thicker films the orientation approaches a random texture. In thin films the preferred orientation arises from the overlapping effect of the interfaces.

2.2 Experimental

2.2.1 Thin Films

Thin films of polyamide 6 were prepared by spin coating on a silicon substrate. The spinning rate and the concentration of the solutions, given in Table 2.1, were chosen to obtain films with thicknesses ranging from 0.15 \( \mu m \) to 2.25 \( \mu m \). Figure 2-1 shows a schematic rendering of the multilayer films made in the spin coating process. The substrate was a silicon wafer on top of which a layer of polystyrene (PS) or ethylene-propylene-diene rubber (EPDR) was deposited from a solution of toluene or hot xylene
respectively. The polyamide 6 film was spin coated from a trifluoroethanol (TFEtOH) solution as a second layer. Finally, a top layer of PS or EPDM rubber was added to sandwich the thin film of polyamide. A profilometer, DEKTAK 8000, was used to measure the thickness of each layer. The thickness of the polyamide 6 layer did not depend on whether it was spin coated on EPDR or PS.

After the thin film preparation, each sample was subjected to a thermal treatment to remove the orientation induced through the spinning process by melting and recrystallizing the polyamide 6 layer. A brass vacuum chamber in an oil bath was used to melt the films at 225°C for 20 minutes. Following the melting process, the vacuum chamber was rapidly immersed in a second oil bath which was kept at various annealing temperatures (170°C - 210°C). The films were subjected to such isothermal crystallization excursions for 20 minutes.

PS and EPDR were used interchangeably as the contact surface for polyamide films. During the thermal treatment, the temperature was always above the glass transition temperature of PS. Therefore, the substrate for polyamide was always in a rubbery state during the crystallization of the polyamide 6 film.

2.2.2 Transmission Electron Microscopy

For electron microscopy studies the films had to be placed on a copper grid; however, after the thermal treatment, the films strongly adhere to the substrate and it is impossible to remove the polyamide layer. Therefore, it was necessary to dissolve the PS or EPDM-rubber film. Since the former is readily soluble in toluene, polyamide films sandwiched between polystyrene layers were preferred for microscopy. These films were soaked in toluene to dissolve the polystyrene layers after the thermal treatment. Subsequently, the free standing polyamide 6 films were transferred to copper grids which were further exposed to toluene vapors to dissolve any remaining polystyrene. No staining was necessary to view the crystals; mass thickness contrast induced by radiation damage provided the contrast for bright field imaging at an accelerating voltage of 200 kV with a Joel 200CX transmission electron microscope. The orientation and the crystal structure of the films were qualitatively determined by electron
diffraction at an accelerating voltage of 100 kV under normal incidence (sample perpendicular to electron beam) and at various tilt angles. The electron diffraction patterns were internally calibrated with a standard of cubic thallous chloride (TlCl) of known d spacings.

2.2.3 X-Ray Diffraction

The crystalline orientation in the thin films was qualitatively determined from 2θ/θ scans and partial pole figure measurements. These experiments were performed on a horizontal goniometer and a pole figure attachment using a Rigaku RU200 rotating anode x-ray generator (Cu Kα radiation) with a point source. An accelerating voltage of 50 kV and an intensity of 60 mA was used. Following thermal treatment, the thin films were spun at 3000 RPM and washed with toluene to remove the top PS layer. When the polyamide film was sandwiched between EPDR films, the top layer was spin-dissolved by washing with hot xylene (90°C). After the films were spin-dried, x-ray measurements in reflection mode were performed while the films were still lying flat on the silicon substrate. For transmission mode, free standing films were prepared by selectively dissolving the PS layers in toluene.

The films were too thin (0.15 - 5.00 µm) and had a signal to noise ratio that was too low for a reliable x-ray analysis in the transmission mode. Diffraction peaks that were hardly discernible above the background noise in reflection mode, could not be resolved in transmission mode. Consequently, a conventional pole figure measurement was incapable of furnishing information on the orientation of the crystals. Therefore, partial pole figure measurements were used, where 2θ/θ scans at various δ angles were recorded (see Figure 2-2) to calculate the integrated intensity of the strong (002) diffraction peak from the hydrogen bonded sheets. The thin film was mounted on a pole figure goniometer which can rotate independently around 3 mutually orthogonal axes. For this method, only δ rotations around the vertical axis were used to determine the crystalline orientation. Standard 2θ/θ scans from 22° to 26° were performed at small steps (5 - 10°) of δ, which was varied from 0° to 75°, the upper limit of the pole figure attachment. For these measurements the slit system was chosen to provide a
0.3° divergent incident beam.

2.2.4 Mechanical Testing

The thin films were subjected to uniaxial tension in an Instron 4200 Testing Machine using a special load cell with a maximum capacity of only 2.5 N. For these experiments thin films of uniform thickness were prepared by spin coating, followed by a procedure of detaching them from substrates after the thermal treatment. The films were spin coated on a square silicon wafer (3×3 cm²). Following the thermal treatment, the films and substrate were placed in liquid nitrogen and rectangular pieces were cryofractured from the center region of uniform thickness. The cryofracturing is rather simple, as cracks follow straight paths along the cleavage planes of the single crystal wafer of the chosen orientation and results in perfectly uniform rectangular shaped samples.

Since the films are very fragile and adhere strongly to the substrate after annealing, it is impossible to remove them directly from the silicon wafer. The first PS layer was very useful in helping to detach the polyamide 6 film from the substrate following the thermal treatment. Figure 2-3 shows schematically the sample preparation method for the uniaxial tensile test: The annealed films are directly immersed in a toluene bath to dissolve the PS layers. After 10 minutes the film, still lying on top of the wafer, is taken out of the bath and two pieces of scotch tape are attached to two opposing edges. By slowly lifting the scotch tapes, the films are separated from the substrate. Subsequently, the films are mounted on cardboard frames and subjected to toluene vapors to remove any remaining PS. For the uniaxial tensile test, the cardboard frames were mounted on the Instron machine. Before applying the load, the frames were cut and the films were strained at room temperature. A cross-head speed of 5 mm/min was used which, for the range of gauge-lengths of specimens tested, corresponded to an initial strain rate ranging from $6 \times 10^{-3}$ to $9 \times 10^{-3}$ sec$^{-1}$. 

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2.3 Results

Thin films of polyamide 6 are transparent to electrons in TEM in the thickness range of 0.10 μm to 2.00 μm. Figures 2-4 and 2-5 are two electron micrographs from an unstrained thin film of 0.15 μm thickness. During TEM exposure, the crystallites first appear as unresolved black shadows. In 3-4 seconds, however, the shadows develop into the images seen in Figures 2-4 and 2-5. In these images the dark figures define the crystalline lamellae, in disc shaped aggregates to be called 'discoids.' Besides these discoids of crystallites (Figure 2-4), the remaining morphology is comprised of randomly oriented individual lamellae embedded in amorphous material (Figure 2-5). These features will be discussed in more detail below.

The electron transparent films were also used to determine the crystal structure and the orientation of the crystals. Figure 2-6 (a) is the diffraction pattern obtained with normal incidence of the electron beam of approximately 20 μm diameter sampling a number of discoids in a 0.15 μm thick film. Table 2.2 summarizes the indexing of the sharp rings to the corresponding d spacings and crystalline planes. Other than the absence of (002) diffraction, the pattern matches that of the α form of polyamide 6. Figure 2-6 (b) is the diffraction pattern from the same sample with a tilt of 45°. The rings of Figure 2-6 (a) turn into arcs and a new set of arcs appears after tilting. The rings are formed by the diffraction from the (002) planes of α-polyamide 6. The absence of (002) diffraction with normal incidence and formation of arcs after tilting are indications of a preferred orientation in this thin film.

A more detailed information on the crystallographic orientation in the films was obtained from x-ray diffraction measurements. Figure 2-7 is an example of a series of 2θ/θ scans for the 1 μm thick film, obtained at various δ angles as described in Section 2.2. Figure 2-8 shows these same scans in a corrected and shifted form. The correction is necessary to account for changes in the scattering volume and absorption in the thin films as the tilt angle δ is varied from 0° to 75°. In organic materials such as polyamides, x-ray absorption is very low and can be neglected; however, the scattering volume changes considerably with tilt angle. To account for this change
the background signal of each curve was normalized to the background level of the ununtilted film. In Figure 2-7, the background can be identified to lie in the range of $2\theta$ from $22^\circ$ to $23^\circ$ and from $25.2^\circ$ to $26^\circ$ for all $\delta$ angle values. The weighted average of the normalization factors for all data points in these ranges of $2\theta$ background was used to shift each curve to a common background level. The result of this shift is depicted in Figure 2-8 where the backgrounds are matched and the peak intensities are slightly changed relative to Figure 2-7.

To determine the relative orientation of these (002) poles, the integral of the corrected x-ray intensity with respect to $2\theta$ from $22^\circ$ to $26^\circ$ was calculated. The background was determined by least squares fitting of a line through the points in the $2\theta$ range of 22-23$^\circ$ and 25.2-26$^\circ$. The integral of the background curve was then subtracted from the integrated x-ray intensity of the original curves. The resulting integrated intensities of the peaks were normalized with respect to that of the curve at $\delta = 0^\circ$. Figure 2-9 is a collective representation of these curves for films of polyamide 6 with different thicknesses. In this figure the curves represent the normalized diffracted intensity of (002) planes making an angle of $\delta$ with the surface. The crystalline orientation should be axi-symmetric in the plane of the film due to the 2-dimensional constraint imposed by the thin film geometry. In fact, the Debye-Scherrer rings present in the electron diffraction of Figure 2-6 (a) from a thin film suggest an axisymmetric orientation about the film normal. Therefore, curves identical to those shown in Figure 2-9 are expected for every azimuthal $\beta$ angle and full pole figures of (002) planes can be constructed based on this axial symmetry. Figure 2-8 (a) to (e) show such constructed pole figures for various thin films of polyamide 6. These sombrero shaped surfaces are three dimensional representations of the (002) pole densities, where the z-axis is the intensity of the pole at a specific set of Euler angles $\delta$ and $\beta$.

The results of the uniaxial tensile tests at a strain rate of around $10^{-2}$ sec$^{-1}$ are displayed in Figure 2-9. The flow stress and the apparent Young's modulus obtained from the linear initial portions of the stress-strain curves decrease with increasing thickness. Table 2.3 summarizes these apparent Young's moduli and flow stresses
of various thin films. The fracture strains are not clearly defined in these samples, since they tend to tear gradually after the onset of flow. Once tearing initiates, the cross-sectional area decreases and the load drops. Stress and strain plots (load-extension) have little meaning after tearing. Thus, the curves are shown only up to the point where tearing begins. Only the sample of 1.00 μm thickness went to very large uniform strains without tearing.

2.4 Discussion

2.4.1 Crystallites in Thin Films: TEM Study

Grubb [52] has reviewed the effect of radiation on polymers under electron beam irradiation (TEM), demonstrating that the contrast in thin films of semi-crystalline polymers appears after some radiation damage has occurred. This phenomenon was encountered in the polyamide 6 thin films and is the source of the contrast shown in Figures 2-4 and 2-5. Thus, the morphological features were visible without staining. The crystals first appear as black shadows under the beam. In 3 to 4 seconds, the radiation damage destroys the crystalline phase and induces a gradient of mass thickness between the lamellae and the amorphous regions. The destruction of the crystals can be ascertained from the electron diffraction pattern which transforms itself from a collection of sharp rings to a diffuse pattern during the same time-frame as the contrast build-up occurs. According to Grubb [52], the crystalline regions distort upon radiation damage; this, in turn, results in an undulated thin film with increasing surface relief where the destroyed crystals are thicker and the amorphous regions are now thinner. This mass thickness variation throughout the film is thought to provide the contrast.

Studies on the crystalline morphology of bulk semi-crystalline polymers have shown that lamellae organize themselves into a spherulitic structure [53]. It is also known that under certain geometric constraints, semi-crystalline polymers are not capable of growing three dimensional spherulites [48-51, 54-57]. For instance, Phillips
and Vatansever [56] have prepared solution cast thin films of cis-polyisoprene to study the crystallization regime transitions. Their films crystallized in a spherulitic structure with an in-plane diameter (2.5 μm) ~3 times larger than the film thickness (800 Å) suggesting two dimensional crystalline aggregates. Similarly theoretical calculations have shown that in thin films, the lamellae are arranged in rather disc-shaped crystalline aggregates [55]. The TEM results of the present study support such constraint effects. Figure 2-4 shows a TEM micrograph of a polyamide 6 thin film crystallized between two layers of PS. The film is 0.15 μm thick while the average lateral dimension of a crystal aggregate is around 1.25 μm. Considering the thickness of the film and the diameter of the crystal aggregate it is reasonable to conclude that these crystal aggregates have a ‘discoid’ structure. Based on such TEM observations the following model, illustrated in Figure 2-10, is proposed for the organization of the lamellae in the polyamide 6 thin film: The growth of the lamellae is constrained by the confined film geometry and is only free in the plane of the film. Consequently, lamellae nucleated from the same point, eventually organize into a disc-shaped crystal. Figure 2-10 has been drawn with chain axis, b, in the plane of the film for reasons that will be explained below.

Another interesting aspect of this morphology lies in the interdiscoid region: Unlike bulk spherulitic morphologies, in which spherulite impingement occurs, many of the discoids did not impinge on each other in the thin films. These inter-discoid regions are also semi-crystalline with well defined lamellae which are, however, organized randomly. Although the radiation damage is advantageous in sharpening the contrast, it is not so in recording the electron diffraction patterns. Before the crystals are destroyed, the diffraction pattern is composed of sharp rings which become diffuse as the radiation damage progresses. However, one can tilt the sample and observe arcs in the diffraction pattern for a few seconds before radiation damage occurs. In order to carry out a detailed analysis of these rings to determine the crystal structure and orientation, the TEM was operated at a lower accelerating voltage of 100 kV. This provided enough time to record the diffraction pattern on a photographic plate before the radiation damage occurred. Figure 2-6 (a) is the diffraction pattern of a
0.15 μm film with normal incidence of the electron beam. The rings represent various d spacings of the direct lattice. By using an internal TiCl standard of known d spacing, the d spacings for each ring of Figure 2-6 (a) were calculated (see Table 2.2). These d spacings correspond to the α crystal form of polyamide 6 and are identical for films of various thicknesses indicating no influence of film thickness on crystal structure. The α form of polyamide 6 is monoclinic and belongs to the P2₁ space group for which the diffraction is absent for \( l = 2n + 1 \) for the family of (0l0) planes. The chain direction and the screw axis 2₁ are parallel to the b axis. The lattice parameters are \( a = 9.56 \) Å, \( b = 17.24 \) Å, and \( c = 8.01 \) Å with \( \beta = 67.5^° \). There are 8 monomer units per unit cell. The diffraction pattern of Figure 2-6 (a) represents the reciprocal lattice: the inner ring is from the (200) planes and the outer ring is from the (0 14 0) planes. The absence of diffraction spots or arcs in Figure 2-6 (a) suggest a random orientation of the crystals in the plane of observation; however, the (002) ring representing the hydrogen bonded planes is absent. This is due to a preferred orientation of (002) planes such that the diffraction condition from these planes is not satisfied [50]. One way of determining the existence of preferred orientation is to tilt the sample about an axis and examine the changes in the diffraction pattern. Figure 2-6 (b) is recorded after a tilt of 45°. The existing rings transform into arcs after tilting and a new diffraction appears from a spacing of 3.70 Å which corresponds to hydrogen bonded sheets in the (002) planes. This indicates a preferred orientation of the hydrogen bonded planes parallel to the surface of the thin film: That is the reciprocal lattice vector \( c^* \) which is normal to (002) planes is also normal to the film surface, while direct lattice vectors \( a \) and \( b \) assume random directions in the plane of the film. It is rather difficult to quantify this orientation using electron diffraction due to rapid radiation damage and low transmission of electrons through thick films. Therefore, x-ray pole figure measurements were conducted to determine the orientation as a function of film thickness in a more quantitative measure.
2.4.2 Influence of Thickness on Crystalline Orientation: X-Ray Study

As explained above, the crystalline orientation could not be determined from electron diffraction experiments due to rapid radiation damage. Instead, x-ray diffraction was used to study changes in the orientation of the polyamide 6 crystals as the film thickness was varied from 0.10 μm to 4.60 μm. The films were mounted on a pole figure attachment and a series of 2θ/θ scans were performed at various tilt angles δ. A 2θ/θ scan detects only the planes that are parallel to the surface of the film. When the sample is tilted by δ, only the diffraction from the planes that are inclined at an angle δ to the surface are detected. After correcting for changes in the scattering volume, one can obtain a ‘partial’ pole figure, representative of the texture in the film. Figure 2-9 summarizes these results. The y-axis represents the density of (002) poles and the x-axis is the tilt angle between the normal of the thin film and the (002) plane normal, i.e. reciprocal lattice vector \(c^\ast\). For the 0.10 μm film, most of the (002) planes are either parallel to the surface or are tilted up to 25°; whereas, the 4.60 μm film has (002) planes in every orientation with a decrease in intensity as the tilt angle increases to 75°.

A clearer way of presenting the data of Figure 2-9 is to construct full pole figures. The orientation of the crystalline planes is axisymmetric in the plane of the films, as confirmed by the rings of the electron diffraction pattern in Figure 2-6. Consequently, the curves in Figure 2-9, which are measured at the Euler angle \(\beta = 0^\circ\), are identical for every \(\beta\) angle. Therefore, full pole figures can be constructed by rotating the curves of Figure 2-9 around the y axis. The results are illustrated in Figure 2-8 (a)-(e) where the z-axis is the density of the (002) poles. These 3-D orientation distributions indicate that the sharp peak of the 0.10 μm film reflects a clustering of (002) planes parallel to the surface of the film. For the slightly thicker 0.20 μm film, the sharp peak is still present; however, a new family of planes starts to emerge. The intensity of this new family of planes increases with increasing thickness until the sharp peak disappears in the film of 2.37 μm thickness. For thicker films the density of poles
increases and a cone shaped surface is formed. Eventually, for a perfectly random sample the surface would assume a cylindrical shape indicating a uniform distribution of (002) pole density.

This orientation study reveals that in thin films of polyamide 6, (002) planes are preferentially oriented parallel to the initial rubber interface (the subsequent free surfaces) with a random azimuthal orientation. For thicker films, the orientation distribution approaches that of bulk polyamide 6. The preferred orientation of hydrogen bonded sheets parallel to the film plane arise in other polyamides as well. Keller [50] and Scott [51] have independently shown that thin films of polyamide 66 experience a similar orientation in which the (010) crystallographic planes containing hydrogen bonded sheets remain in the plane of the film. Polyamide 610 assumes a similar orientation in thin film geometries [50].

The high anisotropy of polyamide crystals can account for the orientation of hydrogen bonded in the plane of thin films: In a polyamide crystal, chains are attached with strong hydrogen bonds that arrange in sheets which interact with relatively weak Van der Walls forces. The relative difference between the energies of these secondary forces results in a high anisotropy in terms of surface energies of the crystal. It is therefore very likely for polyamides to preferentially align the low energy hydrogen bonded planes parallel to the rubber or glass interfaces to minimize the interfacial free energy. Such a phenomenon has been observed in other systems: For instance, a thin film of tin on a PS film assumes a perfect orientation of (001) planes parallel to the interface [47]. Similarly, in thin films of lamellar block copolymers (P(S-b-MMA)) an alternating assembly of PS and PMMA blocks forms upon annealing with the lamellae oriented parallel to the interface [58]. The effect of the interface on these systems seems to decline in thicker films. In both the Sn/PS and block copolymer systems the preferred orientation comes about from the minimization of the interfacial free energy by creating low energy contacts with the substrate.

As shown above the preferred orientation in thin films of polyamide 6 degenerates as the film thickness increases, i.e., as the two rubber/polyamide interfaces move apart. In fact, an oriented skin layer should always be present near the interface.
When the film is thin, the interfaces are close to each other and the skin layers overlap leaving the whole film with a preferred orientation. As the film thickness increases and the interfaces move apart at a critical film thickness (~0.07 \( \mu \text{m} \)), the skin layers cease to overlap. This results in the appearance of increasing thicknesses of randomly oriented material in the bulk of the film. It is important to note that, in polyamide 6 the (002) planes are parallel to the chain axis [020]. This indicates that the chain axis is parallel to the surface of the film. That is, during crystallization, a chain segment prefers to lie parallel to the film surface near the interface. The outcome of the orientation measurements supports the sketch of Figure 2-8 where the chain direction, \( \mathbf{b} \), is drawn in the plane of the film.

2.4.3 Mechanical Properties of Thin Films: Instron Study

Semicrystalline polymers are composites which, when in organized form, consist of the alternating organization of crystalline and amorphous layers. The mechanical properties of these building blocks define the macroscopic behavior of the polymer under various states of stress. While amorphous regions have more or less isotropic properties, the crystalline regions are strongly anisotropic. Therefore, the overall crystalline orientation affects the mechanical properties of the polymer. Slip, the main mode of inelastic deformation in the crystalline component of the semi-crystalline polymers, encounters various levels of resistance depending upon the type of slip plane and its geometrical relation relative to the applied stress axis. Lin and Argon [28] have shown that three slip systems can be activated in polyamide 6, namely the (001)[010] and (100)[010] chain slip systems and the (001)[100] transverse slip system. The corresponding critical resolved shear stresses (CRSS) are reported to be 16.24 MPa, 23.23 MPa, and 23.18 MPa respectively at room temperature. The (001)[010] chain slip is easier to activate than the other slip systems. As determined above, in the thin films of polyamide 6, the crystallite orientation relative to the film surfaces depends strongly on film thickness. Therefore, the mechanical properties should also depend on the thickness. Figure 2-9 clearly demonstrates this effect – the flow stress and the apparent modulus decrease with increasing film thickness. For the 0.15 \( \mu \text{m} \) thick
film, the (002) planes are observed to be parallel to the surface of the film. At this orientation the resolved shear stress on these (002) planes is nearly zero and slip initially occurs on the other high resistance slip systems. This increases the flow stress considerably and the film yields at 108 MPa. In comparison, the 2.15 μm thick film consists of both oriented skin layers and a substantial amount of randomly oriented core region. In this case, the resolved shear stress on most of the (002) planes is finite. This in turn leads to a decrease in the macroscopic flow stress; as the thickest film yields at 48 MPa. The changes in the apparent modulus are also due to changes in the orientation distribution. These effects can be quantitatively modeled by means of polycrystal plasticity models of the type described by Lee et al. [59], and modified for use with polyamide 6 by Ahzi et al. [60]. These models are presently being used to elucidate different mechanical behavior of these films; and the results will be published in due time.

2.4.4 Local Orientation in the Proximity of Second Phase Particles in a Filled Polyamide 6

The present study lends strong support to the view that in a rubber/polyamide 6 blend, the (002) planes of polyamide 6 are preferentially aligned parallel to the interfaces. Therefore, in a rubber modified polyamide 6 the local crystalline orientation of the matrix in the proximity of a rubber particle could be altered, resulting in a locally oriented skin layer around the interface. If the interparticle distance is small, the skin layers would overlap, resulting in a locally oriented interparticle region. For a sparse distribution of the particles, the overlap will be minimal. Under these conditions, the orientation of the matrix would be randomized.

In a rubber modified polyamide where the particles are closely spaced, the locally oriented interparticle regions would possess a high degree of anisotropy. As a result, the local flow stress will vary depending on the relative direction of the applied stress. When the resolved shear stress on the (002) planes of the oriented interparticle region is high, the flow stress in these regions will be reduced markedly. As long as such
regions percolate through the specimen, the overall flow stress will be reduced. As a consequence, early precipitation of fracture processes will be avoided and the specimen will have a high strain to fracture; hence the blend would be tough. Since the overlap of the skin layers would occur at a critical interparticle distance, the above mechanism of toughening is consistent with Wu's observation of a critical interparticle distance for a brittle to tough transition [21]. Preliminary studies in our laboratory on ethylene-propylene-diene rubber modified polyamide 66 support these assertions. The results of these studies will be the subject of a forthcoming paper.

2.5 Conclusions

Crystallization of polyamide 6 in the form of thin films on a PS or EPDM rubber coated silicon substrate produces lamellae organized into a disc-shaped crystal aggregate, namely a 'discoid.' The transition from discoids to spherulites occurs at a film thickness of about 2 \( \mu \text{m} \). Below this critical limit the diameters of the crystal aggregates are larger than the thickness of the film; and above 2 \( \mu \text{m} \) thickness the crystal aggregate size is smaller than the film thickness. From the electron and x-ray diffraction studies it follows that polyamide 6 prefers to have its low energy (002) hydrogen bonded planes lie parallel to a rubber interface. This gives rise to a preferred orientation within a skin layer of 0.07 \( \mu \text{m} \) in thin polyamide films. For film thicknesses below 0.15 \( \mu \text{m} \), these oriented skin regions overlap and the film has a preferred orientation as a whole. Thicker films lead to a random orientation of crystals since the influence of the interface cannot penetrate more than 0.05 - 0.07 \( \mu \text{m} \). The dependence of the orientation of (002) planes on thickness affects the mechanical properties of thin films: the Young's modulus and flow stress both drop with increasing thickness. This observation is in accord with the crystallographic texture of the films and the known slip resistances of the polyamide 6 crystal. Finally, the morphology-property relations observed for these thin films of polyamide 6 are thought to have relevance to the mechanism of modification of polyamide 6 via second phase particles.
Table 2.1: Thickness of Polyamide 6 Thin Films.

<table>
<thead>
<tr>
<th>Concentration (wt. %)</th>
<th>Substrate Spinning Rate (rpm)</th>
<th>Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4000</td>
<td>0.15±5.0%</td>
</tr>
<tr>
<td>3</td>
<td>3000</td>
<td>0.20±6.0%</td>
</tr>
<tr>
<td>5</td>
<td>3000</td>
<td>0.60±10%</td>
</tr>
<tr>
<td>7</td>
<td>3000</td>
<td>1.00±6.0%</td>
</tr>
<tr>
<td>10</td>
<td>3000</td>
<td>2.25±7.0%</td>
</tr>
</tbody>
</table>

Table 2.2: Crystallographic Interplanar Spacings of α-Polyamide 6.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>d(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0140</td>
<td>1.23</td>
</tr>
<tr>
<td>002</td>
<td>3.70</td>
</tr>
<tr>
<td>200</td>
<td>4.42</td>
</tr>
</tbody>
</table>

Table 2.3: Mechanical Properties of Thin Films of Polyamide 6.

<table>
<thead>
<tr>
<th>Film Thickness (μm)</th>
<th>Flow Stress (MPa)</th>
<th>Apparent Young's Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15±5.0%</td>
<td>112.5±8.0%</td>
<td>377±7.0%</td>
</tr>
<tr>
<td>0.20±6.0%</td>
<td>96.1±3.0%</td>
<td>326±4.0%</td>
</tr>
<tr>
<td>1.00±6.0%</td>
<td>63.1±6.0%</td>
<td>133±7.0%</td>
</tr>
<tr>
<td>2.15±5.0%</td>
<td>53.4±5.0%</td>
<td>180±10%</td>
</tr>
</tbody>
</table>
Figure 2-1: Schematic of the spin coated layers of rubber and polyamide 6 on a silicon wafer. The top and bottom rubber layers are coated from a solution of hot xylene and the sandwiched polyamide 6 layer is spin coated from a solution of trifluoroethanol. \( n \) is normal to the film plane.
Figure 2-2: Schematic of the partial pole figure measurement where the sample is mounted on a goniometer and 2 $\theta/\theta$ scans are carried out at various values of tilt angle $\delta$. $\sigma_{002}$ represents the reciprocal lattice vector that would be normal to (002) planes, $S_0$ and $S$ are the incident and diffracted beam vectors.
Figure 2-3: Detaching the polyamide 6 film from the substrate after the thermal treatment: The films are shown schematically on the silicon wafer. The polystyrene layers are dissolved in a toluene bath and the polyamide 6 film is removed by means of a pair of scotch tape strips. The free-standing film is then mounted on a cardboard frame.
Figure 2-4: TEM micrograph of discoids in a 0.15 μm thick film crystallized between two polystyrene layers at 180°C for 1 hour, following a melting treatment at 225°C for 1 hour. The film is not stained; and the electron beam destroys the crystals giving a mass thickness contrast.
Figure 2-5: TEM micrograph of an inter-discoid region in a thin film of 0.15 μm polyamide 6 crystallized between two polystyrene layers at 180°C for 1 hour, following a melting treatment at 225°C for 1 hour.
Figure 2-6: Electron diffraction patterns of a 0.15 µm polyamide 6 film: (a) with normal incidence of the electron beam to the film surface, (b) after a 45° tilt: a and b are direct lattice vectors while c* is the reciprocal lattice vector.
Figure 2-7: $2\theta/\theta$ scans of a 2.37 $\mu$m thick polyamide 6 thin film at various values of the tilt angle $\delta$. The curves are overlaid to show the variations in the background intensity at various $\delta$ angles. In order of decreasing peak intensity, the curves correspond to $\delta$ angles of 0 $^\circ$ C, 10 $^\circ$ C, 20 $^\circ$ C, 30 $^\circ$ C, 50 $^\circ$ C, 60 $^\circ$ C, and 75 $^\circ$ C.
Figure 2-8: The 2θ/θ scans shown in Figure 2-7 are shown after being shifted by the normalization of the backgrounds to the background of the curve at δ = 0°, i.e. the untilted film. In order of decreasing peak intensity, the curves correspond to δ angles of 0 °C, 10 °C, 20 °C, 30 °C, 50 °C, 60 °C, and 75 °C.
Figure 2-9: The normalized intensity of the (002) peak in various thin films of polyamide as a function of tilt angle $\delta$. 
Figure 2-8: Pole figures of (a) 0.10 μm, (b) 0.20 μm, (c) 1.00 μm, (d) 2.37 μm, and (e) 4.60 μm thick films. The z-axis is the density of the poles.
Figure 2-9: The engineering stress vs. engineering strain of freestanding thin films of polyamide 6 crystallized between polystyrene layers. The strain rate for these samples was in the range of $10^{-2}$ sec$^{-1}$. 
Figure 2-10: The proposed model showing the organization of crystals in the form of thin ribbons in a very thin film of polyamide 6. The disc-shape of the crystal is justified by TEM observations. The x-ray results showed that the chain axis is parallel to the interface.
Chapter 3

Toughening Mechanism of Rubber Modified Polyamides

3.1 Introduction

Polyamides are known to be notch sensitive engineering thermoplastics arising from a significantly lower resistance to crack propagation than crack initiation. As a consequence, polyamides are brittle at high strain rates and/or low temperatures. Modification of these semi-crystalline polymers with thermoplastic elastomers or rubbers is a commonly employed practice to counteract such embrittlement. For instance, the addition of 20 wt % ethylene propylene diene rubber in polyamide 6 increases the notched Izod toughness 20 fold when the rubber particle size is kept below 1.0 \( \mu \text{m} \) [18]. Previously, several studies have documented the effect of various parameters such as rubber particle size [18, 23], rubber concentration [18], and interparticle distance [21] on the toughening efficiency of such rubber modifiers. From these studies it has been established that for the blend to be tough, the particles should be smaller than a critical size that depends on the rubber concentration. Similarly, the rubber concentration should be above a critical level which is a function of the particle size. Wu [21] considered these two inter-dependent parameters in combination in the form of a single parameter, namely, the interparticle distance (ID). Based on the assumption of a lattice-like packing of uniform sized particles, Wu has calculated the
interparticle distance using the following relation:

\[ ID = d \left( \left( \frac{\pi}{\phi_r} \right)^{\frac{1}{3}} - 1 \right) \]  

(3.1)

where \( \phi_r \) is the rubber concentration and \( d \) is the rubber particle diameter. This relation provides a rough estimate for \( ID \), in that variations through which the spatial and size distributions of the particles, and possible occlusions of polyamide inside the particles, affect the assumptions involving lattice-like packing of uniform sized particles.

Wu's observations on a rubber modified polyamide 66 demonstrated that regardless of particle size and rubber concentration, the blends are toughened if the interparticle distance is less than 0.3 \( \mu m \). Several attempts have been made to identify the mechanism behind this critical transition phenomenon [21, 19], and some models [21, 19, 41, 61, 22, 62] have been proposed.

Thus, Wu proposed first, that strong overlap of the stress fields around the particles induces shear yielding and crazing of the matrix, thereby toughening the polyamide 66/rubber blends [19]. In later work however, Wu recognized the inadequacy of this model in explaining the particle size effect on toughening [21], since the local stress level in an inclusion filled matrix is only a function of the ratio of the center to center distance (L) to the diameter of the particle (d). This ratio remains constant at a given volume fraction of particles regardless of their size. Therefore, according to the stress field overlap model, toughening should be unaffected by the presence of large particles at any given L/d ratio. This is contradictory to the experimental results which show clearly that smaller particles are more effective in toughening [18].

In another attempt to offer an explanation of this effect, Wu proposed a second model which is based on the stress-state transition at the critical interparticle distance [21]. In this model, it is stated that as the particle density increases and the interparticle distance goes through the critical value, the material in this region transforms from a state of plane strain to plane stress. As a consequence, the deformation resistance of these regions decreases and the blend becomes tough. However, a dif-
ferentiation of local stress state between plane stress or plane strain has no meaning in this context. The model indirectly attributes the embrittlement to the presence of high triaxial stresses. Once again, the presence or the absence of triaxial stresses in local regions between particles can be affected only by changes in geometrical ratios, which remain constant at a given volume fraction and geometrical dispersion of particles regardless of their size. Thus, such an argument is unacceptable, leaving the explanation at a true size dependent material property rather than stress state, or any other characteristic of a deformation field.

Currently available explanations of the toughening effect of rubbery inclusions in polyamide matrices are ambiguous and require clarification. The present study takes a new approach to explore this toughening mechanism by examining the changes in the matrix morphology (crystallographic texture) induced by the second phase particles. This is based on detailed examinations by the present authors of the crystalline texture in thin films of polyamide 6 which established that the (001) (presumably lowest energy) planes of polyamide 6 containing the hydrogen bonds preferentially align parallel to a rubber/polyamide interface [63]. Based on this observation, the rubber-matrix interface in a toughened polyamide is believed to similarly influence the crystallization behavior of the matrix. In the present study we discuss these morphological changes in a similar matrix (polyamide 6) using our observations on polyamides modified with ethylene propylene diene rubber grafted with maleic anhydride (PA 66/EPDR-g-MA). We also relate these crystallographic textures in the polyamide to the morphologies observed after the deformation of these blends. Since the (001)[010] system in polyamide 6 is known to have by far the lowest slip resistance [28], a definite material-specific explanation of the toughness transition becomes possible.
3.2 Experimental

3.2.1 Sample Preparation

The blends of polyamide 66 and ethylene/propylene anhydride-functionalized rubber were prepared in a 28 mm Werner & Pfleiderer extruder. The rubber weight fractions and functionality levels were independently varied. The resulting pellets were molded in a 6 oz., 150 ton Van Dorn injection molding machine into dog-bone tensile bars (gauge length = 100 mm, width = 12.5 mm, thickness = 3.2 mm) and flexural test bars (127 mm long, width = 12.5 mm, thickness = 3.2 mm). The flexural bars were then divided into two 63.5 mm long pieces, one close to the gate, the other far from the gate. Notches were cut into each part with a TMI Notching Cutter according to the specifications of ASTM D256.

3.2.2 Particle Size Determination

The particle sizes of the PA 66/EPDR-g-MA have been determined using two complementary techniques: microscopy and scattering. The experimental procedure for particle size determination using electron microscopy is explained below in Section 3.2.5. Small angle X-ray scattering (SAXS) is particularly useful for accurately determining rubber particle sizes in molded parts because of the large electron density difference between the polyamide and the rubber. In addition, SAXS scans about $10^{12}$ particles vs. about 102 particles in TEM. Here, an ultra high resolution diffractometer (Bonse-Hart) was used to allow resolution of particles less than about 800 nm in diameter. To obtain size information, the scattering results were modeled with a log-normal distribution of independent spherical particles. Analysis of the invariant (the intensity times the square of the scattering angle) leads to a size distribution characterized by its median and a breadth factor [64]. Because the method gives a weight average particle size, its values are generally slightly higher than those obtained from TEM images.
3.2.3 Transmission Electron Microscopy

The PA 6/EPDR-g-MA samples of various particle size and rubber concentration were dissolved in trifluoroethanol to prepare 2 wt. % solutions. Thin films of 0.5-1.0 μm thickness were spin coated from these solutions on a polystyrene (PS) coated polished silicon substrate. The PS layer was then dissolved in a toluene bath to transfer the polyamide films onto copper TEM grids. The samples were annealed in a brass vacuum chamber immersed in an oil bath at 230°C for 4 hours, in order to remove the orientation, induced through the spinning process. Following the method of Martinez-Salazar [65], an aqueous solution of 2 vol. % phosphotungstic acid (PTA) and 2 vol. % benzyl alcohol was prepared to stain the thin films to reveal the lamellar microstructure. Staining was carried out at room temperature by immersing the films in the PTA solution for 15 minutes. The samples were then washed in distilled water. A Jeol 200CX transmission electron microscope was operated at 100 kV accelerating voltage to record the morphology in the bright field mode.

3.2.4 Mechanical Testing

Dog-bone tensile specimens of PA 66/EPDR-g-MA prepared as described in Section 3.2.1, were tested in an Instron 4200 testing machine at an initial strain rate of 1 sec⁻¹. The Izod tests were conducted on dry-as-molded samples according to ASTM D256. The results in Table 3.1 are the averages of tests from the "far" end of the bars. The samples were not conditioned prior to testing to remove the water and eliminate its effect on mechanical properties. Rather, all samples were handled according to exactly the same procedures prior to testing to ensure that they all contained essentially the same concentration of water. Immediately after injection molding, the samples had been put in air tight bags under dry nitrogen and kept in a dessicator until they were tested. It is known from earlier experiments [66] that complete removal of water from thick polyamide specimens is virtually impossible, nor is this desirable since it results in a very brittle and irrelevant material. Through a comparison of the results of the present study with that of Galeski et al. [67], we
estimate the water content of our material to be around 1.0 wt %.

3.2.5 Scanning Electron Microscopy

Scanning electron microscopy was performed on an Electrosan environmental scanning electron microscope (ESEM) with a cerium hexaboride filament. This microscope operates under an adjustable vapor pressure in the range of 0.1 - 10 torr. This moist environment can prevent electron charging on insulating surfaces. Although charging of the sample was not an issue, a very thin discontinuous coating of Au or Au/Pd was applied to improve the resolution of the microscope.

To measure the particle size, undeformed rubber modified polyamide 66 tension specimens were cryofractured perpendicular to the flow direction in the mold. These surfaces were then gold coated and micrographs were recorded in the ESEM. The cavitation in the bulk of the deformed samples was also studied. This was done by cryofracturing the broken tensile bars and Izod flex bars along different directions. Figure 3-1 shows a schematic illustration of the cryofracturing process for both the Izod bar and tensile specimens: IZOD1 and IZOD2 type cryofracturing exposed the internal structure of the cavities in the intensely deformed regions near the crack flanks in planes parallel and perpendicular to the line of the crack tip, respectively, while TENS1 direction provided surfaces with a lateral view of the cavities formed during deformation. The tensile bars were fractured only along the tensile axis because the orientation induced during testing does not permit successful cryofracturing perpendicular to the loading direction. The cryofracturing is performed as follows: A notch is introduced along a desired direction and the sample is left in liquid nitrogen for 20 minutes. A wedge is then driven into the notch to cleave the specimen while it is still at liquid nitrogen temperature. The exposed internal surfaces were then gold-coated and examined under ESEM at an accelerating voltage of 15 kV.
3.3 Results and Discussion

Our recent study [63] of thin films of polyamide 6 sandwiched between EPDR layers, demonstrated that upon melt crystallization, the (001) crystallographic planes containing the hydrogen bonds preferentially align themselves parallel to the rubber-polyamide interface. This orientation is prevalent in films thinner than 0.15 μm. The reciprocal lattice vector $c^*$ is normal to the film plane and the direct lattice vectors $a$ and $b$ are randomly oriented in the plane of the film. In relatively thicker films, the average preferred orientation degrades and approaches a random texture, while a thin oriented surface layer of a sub-micron thickness always remains. It was postulated that the preferred orientation of low energy hydrogen bonded planes parallel to the interface serves to minimize the interfacial energy and that this effect has a penetration depth of the order of 100 nm. In thin films of a thickness in the range of 0.1 - 0.2 μm, the influence of the top and bottom interfaces overlaps and the film assumes a preferred orientation throughout. In thicker films, the two interfaces move apart; and the overlap is not possible, while other random lamellar orientation fill-in between the two interface layers, leaving the film as a whole approaching a random orientation.

3.3.1 Matrix Morphology in the Interparticle Region

The above mentioned discovery of preferred orientation of hydrogen bonded planes near rubber/polyamide interfaces led to the present investigation of the matrix morphology in rubber modified polyamides. Unlike the earlier study where the interface is planar [63], in a rubber modified polyamide system the particles are spherical in shape and the interface has a finite curvature. To determine the local orientation of the polyamide crystals near the interface, transmission electron microscopy was utilized. The crystalline texture had to be preserved during sample preparation. Therefore, microtoming methods were not used since these can induce very large orientational changes during the microtoming process where shear strains of the order of 200 - 300 % can destroy the crystalline texture. Instead, thin films of 0.1 - 0.2 μm thickness were di-
rectly prepared via spin coating as explained in the Section 3.2. Figure 3-2 depicts the morphologies observed in thin films of polyamide 6 modified with EPDR-g-MA. The contrast is achieved by staining the films with phosphotungstic acid (PTA). When the thin films are immersed in the aqueous solution of PTA/BzOH, benzyl alcohol penetrates and swells the amorphous regions, locally enhancing the diffusion of WO\textsubscript{3} which we have determined is the penetrating species in PTA staining (Appendix C). Therefore, the dark zones are the amorphous regions and the bright lines represent the crystalline lamellae. The stain does not penetrate the rubbery phase leaving these regions on the bright side of the contrast.

As Figure 3-2 depicts, the lamellae are randomly oriented in the bulk of the matrix. Around some of the particles the morphology of the matrix appears at first sight to be unaffected. A closer perusal, however, shows a prevalence of lamellae impinging particle interfaces along radial directions. In particular the interparticle regions of closely spaced particles exhibit a different morphology. That is, the lamellae are organized parallel to each other and perpendicular to the rubber-matrix interface. One possible path of reaching this morphology could be through the nucleation of the lamellae near the particle/matrix interface. Assuming that this nucleation process has come about, the hydrogen bonded planes should become oriented parallel to the interface for energetic reasons which should also govern the free energy of formation of crystal nuclei: The crystallization of polyamides occurs by the formation of one hydrogen bonded sheet at a time [50] which implies that the normals to these planes constitute the direction of rapid growth. Once nucleation of the oriented lamellae occurs near the particles, the growing face of the lamellae, i. e. the H-bonded planes, should remain parallel to the interface. This hypothesis is consistent with our previous observations which closely demonstrated that the hydrogen bonded planes of polyamide 6 align parallel to a planar rubber/polyamide interface [63]. The proposed orientation of the crystalline planes with respect to the interface can be confirmed through selected area electron diffraction. Unfortunately, the crystalline state in the films degrades too rapidly under the electron beam to permit the examination of the short lived diffraction patterns.
It is not clear from TEM micrographs whether or not the crystallization of the lamellae starts from the interface. Around most of the closely spaced particles, the morphology suggests a near interface nucleation process. However, some of the particles are surrounded by randomly oriented lamellae and most exhibit the preferred orientation in certain regions around the interface. The interpretation of these ambiguities are beyond the scope of this study and will not be discussed here. Yet we use the observed morphology, and based on the preferred organization of lamellae in the interparticle regions of tough samples, we propose the following model to elucidate the local plastic deformation and toughening mechanisms of rubber modified polyamides.

3.3.2 Toughening and Deformation Mechanisms

The deformation behavior of semi-crystalline polymers is strongly dependent on the crystalline orientation [28, 68]. Consequently, tough specimens where interparticle regions retain local preferred orientation would possess a strong local mechanical anisotropy. With these findings, it is possible to construct a unique model of deformation in rubber modified polyamides. We propose a local anisotropy model where the blended system is considered to be made up of three distinct regions: i) low modulus rubber particles, ii) oriented interparticle region, and iii) bulk matrix. Figure 3-3 illustrates a schematic rendering of the morphology and the proposed model with parallel lines indicating the oriented lamellae. For clarity, the randomly oriented lamellae of the bulk are not shown in the schematic illustration. The interparticle region is the distinctive feature between brittle and tough specimens: for the former, the region between the particles would maintain a substantially random orientation of the crystals, while the latter would have a preferred orientation of hydrogen bonded planes parallel to the rubber-matrix interface. The bulk matrix, away from the fringing layer around the particles, on the other hand, has a randomly oriented crystalline morphology; therefore, it can be treated as an isotropic material. Lin and Argon [28] showed that the hydrogen bonded planes of polyamides have the lowest slip resistance. As a consequence, in tough samples the local deformation around the particles
would strongly depend on the resolved shear stress on these planes. For instance, Figure 3-4 (a) shows 7 rubber particles reinforcing a matrix in an idealized packing. The parallel lines represent the intersection of the lamellae with the plane of the paper. The hydrogen bonded planes are perpendicular to the lamellae. Therefore, in the polar extremes of the particle, with reference to the direction of the applied load, the resolved shear stress on these planes is zero; and slip preferentially occurs in other high resistance slip systems resulting in small or no deformation. On the other hand, the resolved shear stress on the meridional H-bonded planes is finite and slip is likely to occur on these low resistance planes. Figure 3-4 (b) shows the expected shape change of this simple model upon application of a uniaxial tensile stress: the rubber particles cavitate in response to the deformation induced build-up of negative pressure in them, and the surrounding aligned crystalline regions shear to result in the pattern shown in Figure 3-4 (b). Upon cavitation, the rubber withdraws towards the matrix to which it is strongly adhered; and coats the inside surface of the cavity. The interparticle regions deform mostly by crystalline slip and some required deformations in the amorphous component. At the same time the crystals undergo lattice rotation. The insert of Figure 3-4 (b) shows the expected crystalline morphology in the ligaments where the parallel lines represent the intersection of H-bonded planes with the plane of the paper.

According to this model, the yield stress should be lowered in regions of easy shear. This local softening phenomenon should then reduce the overall flow stress of the material allowing it to deform to large strains without initiating any critical fracture process, thus enhancing its toughness. Wu's observation of a critical interparticle distance in rubber modified polyamides [21] can also be rationalized by this model. When the effective interparticle distance is below the critical value, the entire sample would behave tough through the percolation of the favorably oriented interparticle regions through the specimen. On the other hand, percolation of the readily deformable material would not be achieved in brittle samples where the particles are sparsely distributed-with much of the background matrix being randomly oriented, having a high deformation resistance.
3.3.3 Stress Whitening and Morphological Features

To provide a test of the above proposed model, tensile dog bone specimens and Izod bars with various particle size and rubber concentration were prepared. Table 3.1 summarizes the sample characteristics as well as various mechanical properties of different blends used in the tensile and notched Izod tests. Figure 3-5 (a) depicts the tensile test results at constant rubber concentration of 19 wt % and varying particle size. Similarly, Figure 3-5 (b) represents the stress-strain behavior of samples at constant particle size of 250 nm at varying rubber concentrations. The strain to failure increases while the yield stress decreases with increasing rubber concentration and decreasing particle size.

The deformation induced during the tensile and Izod tests creates stress whitened regions in the samples. The tensile bars start to whiten once the stress in the gauge section of the specimen reaches the yield point. The samples that are tough at high strain rates (Izod) form a stable neck and undergo cold drawing under the low strain rate tensile test. Within the neck zone, the whitening becomes more intense. The neck travels along the gauge length of the sample and eventually fracture occurs as a critical size imperfection is acquired by the widening neck region. In like manner, tough Izod bars whiten around the fracture surface, while the brittle ones do not exhibit any whitening. In the super-tough region, the Izod specimen does not break. The crack in the sample propagates with a substantial plastic process zone at its tip as the sample bends sufficiently to permit the pendulum to swing by.

To explore the evolution of the stretch induced morphology change in these blends during deformation the samples were cryofractured in various modes as explained in the experimental section above. Figures 3-6 (a) and (b) shows the stress whitened TENS1 view of an unmodified (no rubber) tensile bar after fracture outside and inside the neck zone, respectively. Figure 3-7 is recorded from the TENS1 view of sample 98-2 to capture the cavitation of the rubber particles that were well bonded to the matrix by a grafting agent. In contrast, the debonding process in sample 98-1 with no grafting agent is depicted in Figure 3-8. The widespread cavitation of particles in the
stress whitened region of sample 98-4 are shown in Figures 3-9(a) and (b) recorded from the TENS1 view outside and inside the neck zone, respectively. The series of micrographs shown in Figure 3-10 are recorded from the IZOD1 view of sample 98-5. Figure 4-15 shows the IZOD2 view of the same sample. The above micrographs are mostly recorded from the stress whitened regions of ductile or semi-ductile (within the brittle-ductile transition region) specimens. The brittle samples did not show any stress whitening around the fracture surface resulting in featureless micrographs in IZOD1 and IZOD2 views. Therefore, the micrographs of brittle samples are not included in this communication.

Figure 3-6 indicates that the stress whitening in homo polyamide 66 is due to bulk cavitation from intrinsic plastic inhomogeneities, with the cavity size ranging from 5 to 10 μm outside the neck zone. In the same sample, the cavities inside the neck region are narrower with an average width of 1 μm and are far more elongated. Upon rubber modification the cavitation process changes entirely. In this case cavitation occurs almost exclusively in and around the rubber particles while the matrix stays intact. The fracture of samples that are in the brittle-ductile transition region occurs at the early stages of cavitation process. Therefore, cavitating particles could only be captured in these samples (e.g. 98-2) within the stress whitened region. Figure 3-7 is an example of cavitation in rubber particles of sample 98-2 where the particles were well adhered to the matrix. The morphology of the particle plays an important role in this process. Ban and co-workers [69] showed that the particles formed in these blends are composite in nature, containing as much as 40 vol. % trapped polyamide occlusions. These occlusions in the rubber particles are the most likely sites of initiation of cavities. In fact, the fibrils seen inside the cavity shown in Figure 3-7 are likely to have arisen from the rubber surrounding the polyamide occlusions.

The cavitation of the rubber particle is only possible if the interface between the rubber and polyamide matrix is strong enough. Otherwise, the blend is brittle and debonding of the interface occurs at low strains, where any one of the larger rubber particles can act as the fracture initiating flaw. The strength of the interface that governs the particle size effect in toughening depends on the amount of grafting between
the rubber and polyamide [70]. Figure 3-8 demonstrates the extensive debonding of the rubber-matrix interface in a brittle sample (98-1) with no grafting agent (maleic anhydride). The average particle size is around 28 μm and no internal cavitation of the rubber particles is discernible in the morphology, suggesting also an absence of occluded polyamide particles inside the larger rubber particles.

In tough samples where the interface is strong enough the cavitation process is abundant and occurs in almost all particles resolved in the SEM. Figure 3-9 (a) shows an example of cavitation in a sample (98-4) containing 19 wt. % rubber. This micrograph is the TENS1 view outside the neck zone of a fractured tensile specimen. The cavities are uniformly distributed throughout the polyamide matrix. Unlike the spherical cavities nucleated in this region, Figure 3-9 (b) shows elongated cavities in the neck zone. Although the average width of the cavities remains the same after necking, the cavities elongate to an average aspect ratio of 8. Hence the deformation of the cavity proceeds in such a way as to produce strain only in the direction of the applied tensile stress. Simultaneously, the matrix undergoes large strains (800 %) by forming thin ligaments between the elongated cavities. Under similar conditions homo-polyamide 66 failed at a strain level of 22.4 % (see Figure 3-5 (a)). Exhibiting such dissimilar responses to deformation, the mechanical properties of the matrix in the interparticle region of a tough specimen should be entirely different than that of the bulk polyamide 66. In fact, as mentioned above, the interparticle region preserves an altogether different morphology that imparts distinct mechanical properties to this region. Therefore, our observation of elongated cavities supports the prediction from the model shown in Figures 3-4(a) and (b).

The stress whitening around the fractured notch of tough Izod bars was also examined through cryofracturing in different directions as explained above in the experimental section. Figure 3-10 (a) - (d) represents the IZOD1 view while Figure 4-15 (a) - (d) shows the IZOD2 view of sample 98-4. In both Figures 3-10 and 4-15, the micrographs have been recorded to capture the evolution of cavities at different depths in the stress whitened zone away from the crack flanks. Figure 3-10 (e) shows approximate locations of the micrographs with respect to the fracture surface. To
demonstrate the significant changes in cavity size, all micrographs have been recorded at the same magnification level.

The initial particle size in the sample depicted in Figures 3-10 and 4-15 was around 250 nm. Near the fracture surface, the particles cavitated and grew to an average diameter of 1500 nm, with actual aspect ratios achieving levels of 6-8, indicating that the matrix had to undergo a strain of 600-800% before failure. This supports our model which allows the matrix to deform to large strains by locally lowering the flow stress through the initial preferred orientation of the easy shear planes around the particles in the matrix ligaments. The shape of the cavities in Izod samples are similar to that of the tensile bars. The lateral view (IZOD2-Figure 4-15) of cavities in the Izod bar and the elongated cavities of the tensile bar shown in Figure 3-9 (b) both suggest a cylindrical shaped cavity. In both samples, the axis of the cylinders are aligned parallel to the principle strain direction. Another aspect of the elongated cavities in the stress whitened regions of both the tensile and Izod specimens is that the width of the cavities do not vary during elongation. That is the mean particle size of the specimens is almost the same as the mean width of the elongated cavities after deformation. While the cavities and the matrix ligaments elongate up to 800% strains, little or no deformation occurs in the polar regions of the cavities. The matrix in these regions undergoes almost no deformation. This observation is consistent with our model and the schematic illustration of the deformation shown in Figures 3-4 (a) and (b). It is important to emphasize the different nature of sampling the deformed material in the whitened zone by the IZOD1 and IZOD2 modes of sectioning. As Figures 4-15 (a) - (d) show there are fundamental rotations of the principal axes of stretch of the cavitated microstructure as a crack progresses through it. The principal axes of stretch near the fracture surface are aligned much more nearly parallel to the crack flank. This is revealed fully in IZOD2 section while the IZOD1 section takes an oblique cut through these elongated and rotated cavities. These important features of how the cavitated material is strained by a propagating crack will be the subject of a future separate communication.

From the above observations one can summarize the deformation behavior of
rubber modified tough polyamides (with interparticle ligament thickness less than 0.3 - 0.5 μm) as shown in Figure 3-11:

Initially, the response of the material is elastic. In a tensile test, the sample starts to cavitate inside the rubber particles around the yield point. In the post yield region of extensive plastic stretch the matrix undergoes large deformations and the cavities elongate in the direction of the applied stress (also directions of principal stretch). Thin ligaments form between the cavities as the deformation progresses resulting in fine fibrillation of the matrix. Eventually, the fibrils reach the ultimate draw ratio and fail from some inhomogeneity. Similarly, in an Izod test, the crack propagation incorporates undeformed material into the process zone, each time repeating the stages shown in Figure 3-11. Failure of the fibrils in this case represents an intrinsic property of the cavitated and stretched microstructure. Each fibril breaks upon reaching the limiting draw ratio of the matrix material. This fracture mechanism is currently under investigation. In the brittle samples with interparticle ligament thicknesses well above the critical threshold of c.a. 0.3 - 0.5μm, the overall deformation resistance remains high and fracture is precipitated prematurely from a non-characteristic impurity particle or structural flow before much overall plastic stretch can take place.

3.4 Conclusions

Rubber modified polyamides go through a brittle to tough transition at a critical interparticle distance [18, 23, 21, 19]. This phenomenon is related to the changes in the matrix morphology induced by the rubber-matrix interface as the interparticle distance is varied. Brittle samples have a sparse distribution of the rubber particles with large interparticle spacings (well above 0.3 - 0.5 μm.). Therefore, the influence of the interfaces do not overlap and the matrix morphology is substantially random. On the other hand, in a tough sample where the particles are closer to each other, there is overlap of the interface-induced orientation of the crystalline morphology. This results in a substantial fraction of material with preferred orientation of hydrogen bonded planes parallel to the rubber-matrix interface in the interparticle zone, as indicated by
clearly discernible perpendicular alignment of lamellae around the particles in TEM studies. The low slip resistance of these planes and their preferred orientation has been related to the toughening mechanism and a model has been proposed. The principal element in the proposed model is the local reduction of the flow stress that results in the hindrance of premature fracture from inevitable entrapped inorganic impurities. The morphological features observed in the stress whitened zones of various blends are in support of this model. The chart presented in Figure 3-11 summarizes phases of the deformation behavior in rubber modified polyamides.
Table 3.1: Mechanical Properties of the PA 66/EPDR-g-MA Samples used in Tensile and Notched Izod Tests.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>EPDR-g-MA Concentration [wt. %]</th>
<th>SEM Particle Size $^a$ (nm)</th>
<th>SAXS Particle Size $^b$ (nm)</th>
<th>Notched Izod (J/m)</th>
<th>Yield Stress (MPa)</th>
<th>Strain to Failure (%)</th>
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<tr>
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<td>-</td>
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<td>&gt;800</td>
<td>69</td>
<td>-</td>
<td>1.96</td>
</tr>
<tr>
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<td>1500</td>
<td>&gt;800</td>
<td>213</td>
<td>50</td>
<td>14.70</td>
</tr>
<tr>
<td>98-3</td>
<td>19</td>
<td>1420</td>
<td>&gt;800</td>
<td>752</td>
<td>50</td>
<td>32.50</td>
</tr>
<tr>
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<td>720</td>
<td>715</td>
<td>876</td>
<td>50</td>
<td>50.00</td>
</tr>
<tr>
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<td>349</td>
<td>1099</td>
<td>50</td>
<td>67.10</td>
</tr>
<tr>
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<td>250</td>
<td>252</td>
<td>1191</td>
<td>45</td>
<td>97.40</td>
</tr>
</tbody>
</table>

**Constant Rubber Concentration**

**Constant Particle Size**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>EPDR-g-MA Concentration [wt. %]</th>
<th>SEM Particle Size $^a$ (nm)</th>
<th>SAXS Particle Size $^b$ (nm)</th>
<th>Notched Izod (J/m)</th>
<th>Yield Stress (MPa)</th>
<th>Strain to Failure (%)</th>
</tr>
</thead>
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<tr>
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<td>240</td>
<td>232</td>
<td>75</td>
<td>76</td>
<td>28.62</td>
</tr>
<tr>
<td>98-8</td>
<td>10</td>
<td>250</td>
<td>255</td>
<td>224</td>
<td>65</td>
<td>34.15</td>
</tr>
<tr>
<td>98-9</td>
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<td>248</td>
<td>966</td>
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</tr>
<tr>
<td>98-10</td>
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<td>254</td>
<td>939</td>
<td>57</td>
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</tr>
<tr>
<td>98-6</td>
<td>19</td>
<td>250</td>
<td>252</td>
<td>1191</td>
<td>45</td>
<td>97.40</td>
</tr>
</tbody>
</table>

$^a$ Number Average Particle Size

$^b$ Weight Average Particle Size
Figure 3-1: The cryofracturing of the deformed samples. The shaded surfaces were exposed for microscopy by cryofracturing along the indicated notch: (a) IZOD1 view, (b) IZOD2 view, and (c) TENS1 view.
Figure 3-2: TEM micrographs of different regions in a polyamide 6 modified with EPDR-g-MA: (a) and (b) are taken at low magnification and (c) at high magnification. The sample was negatively stained with phosphotungstic acid; therefore, the dark lines are the amorphous regions and white lines are the lamellae. The rubber particles are not stained and appear white. The micron-bars represent 200 nm in (a) and (b) and 100 nm in (c).
(c) 200 nm
Figure 3-3: The schematic of the proposed model and the idealized morphology of the rubber modified polyamide system. The parallel lines between the particles are the lamellae. The randomly oriented lamellae of the matrix is left out for clarity.
Figure 3-4: Schematic for the deformation mechanism of an idealized morphology under uniaxial tensile test: (a) is before and (b) is after deformation. In (a) the parallel lines represent the intersection of lamellae with the plane of the paper while in (b) the lines in the enlarged region represent that of the hydrogen bonded planes.
Figure 3-5: Tensile test results of rubber modified polyamide 66 at (a) constant rubber concentration with particle size decreasing from left to right as 28, 1.5 1.42, 0.72, 0.35, 0.25 μm and at (b) constant particle size with rubber concentration increasing from left to right as 0, 6, 10, 12, 14, 19 wt. %. The curves are shifted for clarity.
Figure 3-6: TENS1 view of homo-polyamide 66 after uniaxial tensile test: (a) was recorded from the stress whitened zone outside the neck region and (b) was recorded from the stress whitened zone inside the neck region. Both micron-bars represent 10 μm.
Figure 3-7: Cavitation of two rubber particles in a rubber modified polyamide 66 recorded from the stress whitened zone of TENS1 view of sample 98-2 after uniaxial tensile test. The micron-bar represents 2 μm.
Figure 3-8: Debonding of rubber particles from the polyamide 66 matrix in sample 98-1 with no grafting agent. Note the large particle size and large inter-particle spacing. Such a morphology has a relatively minor amount of the interfacially oriented nylon crystals and as a result displays relatively poor toughness. The micron-bar represents 50 \( \mu \text{m} \).
Figure 3-9: TENS1 view of polyamide 66 modified with 19 wt. % rubber after uniaxial tensile test of sample 98-4: (a) was recorded from the stress whitened zone outside the neck region and (b) was recorded from the stress whitened zone inside the neck region. The micron-bars represent 5 \( \mu \text{m} \).
Figure 3-10: IZOD1 view of sample 98-4 taken inside the stress whitened zone near the fracture surface. The location of each micrograph with respect to the fracture surface is indicated in (e) where the shaded area is the stress whitened region. The micron-bars represent 5 μm.
Figure 3-11: Summary of the deformation mechanism in rubber modified polyamides.
Chapter 4

Microstructural Processes of Fracture of Rubber-Modified Polyamides

4.1 Introduction

PolyAmides are strong engineering polymers. They exhibit high resistance to crack initiation which imparts high toughness to unnotched material. However, their low resistance to crack propagation [41] leads to embrittlement in the presence of a notch that results in high local strain rates. Upon modification with rubbery inclusions, the resistance to crack propagation increases, leading to super-tough materials. This toughening procedure by the incorporation of submicron sized rubber particles has been extensively studied [22, 21, 70, 15, 71, 72]. The effects of rubber concentration [18], particle size [18, 19], and interparticle distance [21] on the toughening process are well documented: increasing the concentration of rubber particles, decreasing the particle size, or decreasing the interparticle distance all improve the toughness. Wu showed that at a critical interparticle ligament thickness, independent of rubber concentration and particle size, there exists an abrupt transition from ductile to brittle behavior with increasing ligament size [21]. This transition is reported to occur
around a ligament thickness of 0.3 \( \mu m \) in rubber-modified polyamide 66 [21].

Several mechanisms have been proposed to explain this abrupt transition. Recently, Muratoğlu et al. [63] have demonstrated that the rubber/polyamide interface significantly alters the morphology of the crystallization process that has important consequences on the toughness transition. The hydrogen bonded crystallographic planes of the matrix preferentially align parallel to this interface creating an oriented skin layer around the rubber particles. This preferred orientation had been observed in polyamide 6 [63], polyamide 66 [50, 51], and polyamide 610 [50]. When the interparticle distance in a rubber modified polyamide is decreased sufficiently, the skin layers overlap, and a critical fraction of the matrix assumes a preferred orientation of hydrogen bonded planes parallel to the rubber/matrix interfaces [3]. Lin and Argon [28] have shown that the hydrogen bonded planes of polyamides possess the lowest resistance to slip. Therefore, the oriented crystalline regions exhibit varying flow stresses depending on the direction of the applied load relative to the hydrogen bonded planes. In some regions of ligaments where the skin layers overlap, the plastic resistance is significantly reduced. As long as regions with such orientation percolate through the material, early fracture processes are avoided and the material is tough; this 'catastrophe avoidance' approach to toughening of polyamides has been described in detail elsewhere [3].

The above-mentioned approach to toughening does not directly address the intrinsic fracture process. Nevertheless, the rubber modification and its attendant local preferred orientation imparts to polyamides a high resistance to crack propagation and enhanced toughness. While much has been learned from such previous studies, ultimately it is important to study the crack propagation to understand the underlying mechanism in action which is responsible for the increase in the resistance to crack propagation. Dijkstra et al. [73], have studied the effect of strain rate and temperature on the crack initiation and propagation of rubber-modified polyamide 6. Based on measurements of fracture energy during crack propagation in a singly notched tensile specimen, they have concluded that the resistance to crack propagation in rubber-toughened polyamide 6 was due to localized melting in the process zone that resulted
in the thermal blunting of the crack tip. In the present study, we have investigated the local fracture process in notched Izod flexural bars. The detailed analysis of the fracture surface and the zone of intense plastic deformation of the crack flanks has provided a new level of understanding of the operating microstructural processes that occur during crack propagation in rubber-toughened polyamide 66.

4.2 Experimental

4.2.1 Sample Preparation and Characterization

A 28 mm Werner & Pfleiderer extruder was used to blend polyamide 66 with maleic anhydride functionalized ethylene/propylene diene rubber. The functionality levels were varied to obtain a range of particle sizes. The resulting blends were pelletized and then molded in a 6 oz., 150 ton Van Dorn injection molding machine into flexural test bars (length = 127 mm, width = 12.5 mm, thickness = 3.2 mm). The Izod bars were cut from the middle part of the flexural bars. Notches were introduced into each part with a TMI Notching Cutter according to the specifications of ASTM D256. Following the injection molding and notching process, the samples were placed in airtight bags and stored in a dessicator to prevent the absorption of water. To determine the particle size of rubber inclusions, small angle x-ray scattering (SAXS) [64] and scanning electron microscopy (SEM) techniques were used. Table 4.1 summarizes the sample characteristics.

4.2.2 Izod Impact Test

The Izod impact tests were conducted at various temperatures on dry, as-molded samples. Prior to testing, flexural bars were conditioned in a sealed chamber immersed in a heating or a cooling bath to achieve the desired sample temperature. The samples were heated or cooled under a flow of dry argon gas to avoid further absorption of water. All samples were handled according to exactly the same procedures in an effort to ensure that they all contained essentially the same concentration of water. Izod
values reported in this study are the energy to break normalized with the specimen thickness and the average of five tests.

4.2.3 Single-Notch Tensile Test

The notched Izod flexural bars of Sample 8 were also tested in uniaxial tension in an Instron 4200 universal testing machine. The crosshead speeds used were 1, 10, 100, and 500 mm/min. Figure 4-1 shows the corresponding load-displacement curves. While the load in the specimen increases, a crack initiates at the tip of the notch. This is followed by the propagation of a crack that starts when the load reaches the maximum level beyond which the crack travels at a constant velocity governed by the crosshead speed. The relation between the average crack velocity, $v_c$, the nominal displacement required for full fracture, $d_p$, and cross-head speed $v_{ch}$ is as follows:

$$v_c = \frac{r}{d_p/v_{ch}}$$  \hspace{1cm} (4.1)

where $r$ is the distance traveled by the crack. In this case $r$ is simply the distance, $t$, from the tip of the notch to the edge of the sample since the experiment is carried out to total fracture. Using the above equation, the corresponding crack velocities attained in cross-head speeds of 1, 10, 100, and 500 mm/min are calculated to be 0.005, 0.1, 1, and 5 cm/sec, respectively. Thus, the progressive fracture, or separation of the sample shows no instability, and reflects the behavior of a very tough material with a very high tearing resistance.

4.2.4 Scanning Electron Microscopy

Following the Izod and single-notch tensile tests, the samples were examined in an SEM to determine the fracture surface features and changes in the morphology of the cavities within the process zone; the parameters of the study were temperature, rubber concentration, and particle size for the Izod tests and crack propagation velocity for the single-notch tensile tests. To view the morphology of cavities in the stress-whitened zone below the crack flanks, the samples were cryo-fractured along a median
plane from a notch cut perpendicular to the original Izod notch as shown in Figure 3-1. A similar method to examine the internal cavitation in rubber modified polyamide 6 has been used by Speroni et al. [74]. Primary fracture surfaces and the cryofractured surfaces of specimens were coated with a thin layer of Au and examined in an Elektroscan environmental scanning electron microscope (ESEM). The instrument used a cesium hexaboride filament operated at an accelerating voltage of 15 kV.

4.2.5 Image Analysis

The distribution of striation spacing on the primary fracture surface of tough specimens was determined by taking the fast Fourier transforms (FFT) of the fracture surface micrographs. The method used for the FFTs consisted of: scanning the micrographs at a scan resolution of 300 dots per inch (dpi) and rotating the scanned images such that the striations are vertical as shown in Figure 4-2 (a). Scanning divides the image into pixels and assigns them integers between 0 and 255 depending on the level of gray where 0 is white and 255 is black. Figure 4-2 (b) shows the intensity profile along one horizontal line – the top border of the scanned image shown in Figure 4-2 (a). The striations in the image give rise to fluctuations in the intensity profile of the scan. Along each line splines are fitted to smooth the image as shown in Figure 4-3 (a). The intensity profile of the top line after smoothing is plotted in Figure 4-3 (b) along with the raw profile. The FFT of each line was then taken and Fourier coefficients were plotted as a function of Fourier frequencies. As an example, Figure 4-4 shows the transform of the fracture surface of Sample 9 tested at 60 °C. The peak is taken to be the mean frequency of the striations on the fracture surface. The frequency-distance conversion is established using the following equation:

\[ S_d = C \frac{n \nu}{(dpi) M} \]  \hspace{1cm} (4.2)

where \( S_d \) is the striation spacing in \( \mu \text{m} \), \( n \) is the number of pixels along one line, \( dpi \) is the scanning resolution in dots per inch, \( M \) is the magnification of the scanned micrograph, \( \nu \) is the Fourier frequency, and \( C(= 2.54 \times 10^4) \) converts from inches
to $\mu$m.

4.3 Results and Discussion

The central purpose of the present research was to study the microstructural processes involved in the fracture of rubber-modified polyamide 66 via morphological analyses of the fracture surfaces and process zones. During the deformation of these rubber-toughened polymers, the particles cavitate at a critical stress and cause the observed whitening in the deformation zone. Several studies [74, 3] have already shown that under various straining modes, the cavities elongate in the principal direction of extension while the interparticle regions of the matrix deform to draw ratios of about 8 and form microfibrils. Only the tensile specimens that are able to form a stable neck exhibit the desirable microfibrillation of the matrix which is found to be an indication of effective toughening [3]. The analysis of the fracture process in Izod impact specimens subsequent to this cavitation and microfibrillation is reported below.

4.3.1 Izod Impact Test Results

The results of Izod impact tests performed on various samples at different temperatures are reported in Table 4.2. Some samples were not tested at certain temperatures where their toughness values were below the lower or above the upper (brittle or ductile) bounds. The results are plotted in Figures 4-5 and 4-6. As seen in Figure 4-5, toughness increases as the rubber concentration increases or as the particle size decreases. In both cases there exists a ductile-brittle transition. Previous studies have shown that the location of this transition is a function of temperature [18]. Figures 4-6(a) and 4-6(b) show the effect of temperature when the other two parameters are held constant. The ductile-brittle transition temperature decreases as the particle size decreases at a constant rubber fraction of 20 wt. % (Figure 4-6 (a)); whereas it increases as the rubber fraction decreases at a constant particle size of around 0.17 $\mu$m (Figure 4-6 (b)). These results are in accord with findings reported in the literature [18, 19], and consistent with the concept of percolation of preferentially
oriented material in interparticle ligaments [3].

4.3.2 Fracture Surface Morphology

To gain a better understanding of how the microstructural failure processes interact with a growing crack, the fracture surface morphology of the Izod samples were examined in an ESEM. Three distinctive features, a) a patchy surface, b) striations and c) a combination of a) and b), were found dominant on the fracture surfaces. Figure 4-7 summarizes these different forms in the fracture surface features and identifies them in relation to the observed levels of toughness. In the brittle region, the fracture surface exhibits a macroscopically smooth surface with irregular features which are typical to brittle failure [75] (see Figure 4-7 (b)). The fracture surfaces of all the ductile specimens are fully covered with striations (Figure 4-7 (d)), while the specimens in the transition region (Figure 4-7 (c)) show a combination of the irregular-patchy brittle fracture surface and striations. In the micrographs included in Figure 4-7, the direction of crack propagation is from left to right. The variable on the abscissa of inserted schematic graph of the toughness level (Figure 4-7 (a)) could be alternatively the rubber weight fraction, or the inverse particle size. In all cases, the evolution of fracture surface morphology with toughness is identical. That is, the type of fracture surface morphology generated by the propagating crack depends only on the level of toughness of the sample and not explicitly on the particle size, rubber fraction, or temperature of fracture, while these factors, of course, establish the appropriate level of toughness. Therefore, the drastic transition from a fracture surface with irregular features to a fracture surface with regularly spaced striations is solely due to the variations in the toughness level. To gain more insight in understanding the toughening of these materials, it is necessary to relate the evolution of the fracture process to the formation of the striations in tough samples to establish a mechanistic connection.
4.3.3 Striations in Impact and Fatigue Fracture

The type of brittle fracture surfaces encountered in this study have been widely reported for other materials with 'granular' microstructure under brittle modes of failure. Striations have also been observed in ductile impact fracture of polyamides. The fracture surface micrographs reported in references [41] and [19] show striations that were not mentioned by the authors. For instance, Figure 12 of reference [41] depicts the impact fracture surface of a toughened polyamide exhibiting striations that are \( \sim 6 \mu m \) apart. Similarly, Figure 4 (a) of reference [19] shows an impact fracture surface micrograph of a rubber-toughened polyamide 66 where the striations are discernible. Recently, Speroni et al. [74] showed that striations parallel to the crack front coexist with 'fish-bone' shear bands on impact fracture surfaces of water conditioned homo-polyamide 6. They also observed that rubber modification suppresses the formation of 'fish-bone' shear bands and the fracture surfaces are fully covered by striations. Upon examining the substrate morphology of the flanks they noted that the elongated cavities are inclined at an angle of 20° to the fracture surface and intersect the direction of cavitation fronts at an angle of \( \sim 76° \); hence they proposed that the striations are formed as a consequence interaction of shear bands with the crack surface. However, the micrograph (Figure 15 (f) of reference [74]) shows that the substrate morphology of the flanks, must have resulted from extensive buckling of the elongated cavities near the crack flank, suggesting deformation of a thin layer on the fracture surface undergoing an instability.

The striations have often been associated with fatigue fracture surfaces where they indicate the intermittent, cyclic propagation of the fatigue crack. In some instances, the distance between these arrest lines is not the same as the average cyclic crack-growth increments [76-78]. If the incremental advancement of the crack occurs after several cycles, the spacing of the fracture lineage will be larger than the macroscopic crack growth increments [79]. Particular semi-crystalline [80] as well as glassy polymers [79] exhibit this so-called discontinuous crack growth. Conversely, some polymers display regular lines on fatigue fracture surfaces with spacings smaller than
the cyclic crack-growth increments.

For instance, in fatigue crack propagation experiments on polyamide 66 and its rubber toughened grades, Hahn et al. [77] observed both a patchy fracture surface and a 'rumpled' one depending on the level of the stress intensity factor. The former corresponds to the brittle fracture surface type observed in this study, while the latter is identical to the regularly spaced striations shown in Figure 4-7 (d). They found that the transition from the patchy surface to the 'rumpled' one occurs with increasing water content, rubber concentration, and test frequency; the spacing between the ripples varied with water content and rubber concentration at a constant test frequency. This observation implies that the 'rumples' are not formed by the intermittent cyclic crack growth but by another mechanism. Hahn et al. [77] proposed a model where secondary cracks in the form of fissures perpendicular to the main crack plane, form ahead of the propagating crack tip due to the delamination of highly stretched material. As fracture proceeds the oriented material between the fissures fractures and gives rise to the 'rumpled' fracture surface. However, the authors did not provide any direct evidence of fissure formation in front of the crack tip.

In another study, White and Teh [78] have examined fatigue fracture surfaces of low density polyethylene (LDPE); and found that the expected 8 μm/cycle growth increments are much larger than the average 'micro-striation' spacing of 0.5 μm (at room temperature). Under a higher amplitude tensile strain cyclic loading the fracture surface consisted of macro-striations with spacings corresponding to cyclic crack-growth increments and micro-striations lying between macro-striations. White and Teh proposed a mechanism for the formation of micro-striations; where the crystalline lamellae are oriented parallel to the crack front and perpendicular to the crack flank; so that when the crack propagates, the previously oriented lamellae fracture and leave features on the fracture surface that are identified as micro-striations. However, the spacing of the observed micro-striations (∼ 0.5 μm) is much larger than the average lamellar thickness of polyethylene (∼ 10 nm) [76] leaving this model of questionable validity. In Section 4.3.6 a hypothesis is presented, based on morphological observations, for the formation of similar striations (also observed by Speroni et al. [74] on
impact fracture surfaces) formed upon impact fracture in rubber modified polyamides.

4.3.4 Morphology of Striations in Impact Fracture

The striations on the fracture surface of ductile specimens have the distinct appearance of shallow grooves perpendicular to the surface of the crack flank and lie parallel to the crack front. Figure 4-8 gives a schematic view of striations on a fracture surface where they are depicted as a square wave of amplitude \( a \) and wavelength \( S_d \). Figure 4-9 depicts the typical striations formed at temperatures of 20 and 50°C, respectively, during the Izod impact test of specimens of Sample 8. In these micrographs, recorded under conditions of high contrast, the striations appear to penetrate deep into the fracture surface. To obtain a better view of the actual depth of penetration, the samples were cryo-fractured following the method described in Section 4.2 and depicted in Figure 3-1. A representative micrograph is displayed in Figure 4-10 from which it is quite clear that the striations are surface folds that do not penetrate deeply into the sample. The approximate depth of penetration as measured from such micrograph is around 2 \( \mu \)m.

The striations are not only created by the propagation of the main crack. They were also associated with secondary cracks which initiate from separate fracture nuclei and propagate radially outwards, within the main crack plane. Figure 4-11 gives a clear example of such nucleation of a secondary crack and its radial outward propagation, where the striations indicate the direction of the radial crack propagation. Eventually, the secondary crack meets the main crack and the fracture process proceeds with the opening of the former. Such secondary nuclei are well known in the fracture surfaces of glassy [81-83] and semi-crystalline polymers [78] where they give rise to the ubiquitous parabola, studied by many investigators.

4.3.5 The Parameters Affecting the Inter-striation Distance

Fracture surface analysis of various samples revealed that while the depth of penetration of the striations remains unchanged, the striation spacing, \( S_d \), varies with
the rubber content, particle size, temperature, and deformation rate. The $S_d$ values measured by the image analysis technique described in Section 4.2.5 are listed in Table 4.3 for samples exhibiting tough behavior (hence striations) within the temperature range covered in this study. Figure 4-12, a plot of $S_d$ versus the rubber content, demonstrates that the striation spacing increases in samples with higher rubber concentrations. The values of striation spacing measured from the series of samples with a constant rubber content and varying particle size are plotted in Figure 4-13. In this case, the spacing between striations increases with increasing temperature and the curves are shifted up for samples with larger rubber particles. The shape of curves of constant particle size suggests an effect of transition in the formation of the striations at around 30 - 50 °C. The effect of deformation rate on the striation spacing could not be ascertained from Izod tests. Therefore, single-notch tensile tests were carried out on specimens of Sample 8 at various cross-head speeds of 1, 10, 100, and 500 mm/min that resulted in crack velocities of 0.005, 0.1, 1, and 5 cm/sec. Figure 4-14 displays the fracture surface morphologies of these specimens. The distance between the striations increases with decreasing crack velocity. When the velocity of the crack is around 0.005 cm/sec the striations are not even discernible on the fracture surface. The variations in the striation spacing with temperature and deformation rate are a consequence of localized adiabatic heating during deformation and its attendant effects on local plastic resistance of the matrix, which will be discussed in Section 4.3.7.

4.3.6 Hypothesis for The Formation of Striations

The characteristics of the observed fracture surface striations in rubber-toughened polyamide 66 have been described but the mechanism that produces them requires clarification. One possibility is that they are the result of the dynamic effects of impact testing investigated in detail by Williams [84], who demonstrated clearly that oscillations of a fracturing, relatively compliant, specimen struck by the pendulum could produce intermittent crack advance and could lead to totally non-representative behavior in an impact test. If such oscillations are produced in the Izod test, the crack could propagate intermittently, generating arrest lines on the fracture surface. In the
Williams phenomenon the oscillations are damped out and full contact is achieved soon after the beginning of the fracture process. Thus, if such oscillations were the cause of the striations, amplitude of the folds, as seen in Figure 4-10 should diminish and the striations should become less distinct as the crack proceeds in its growth over the fracture surface. In the present case, the striation spacings measured on various specimens remained constant throughout the fracture surface, ruling out the possibility of transient oscillations.

A more consistent explanation for the formation of the striations is the regular elastic-plastic buckling of a thin and stretched surface layer as a process of accommodation involving also a certain amount of strain retraction, after the main crack front has passed. The deformation field in front of a crack tip and on the crack flanks has been extensively studied and modeled for cases of relatively low strains to local fracture as is characteristic for metals (for references see Shih and Xia '85]). The crack tip deformation fields, including residual strains in the crack flanks for very large local fracture strains are not well known. Qualitative considerations for large strain flow fields of advancing cracks, with substantial opening angles, would lead to the very large residual stretching strains that have been observed in the present study. Thus, in the process of accommodation of these stretched layers on the crack flanks it is reasonable to expect that these layers will be required to shorten. While this can, in part, involve some strain retraction, the major form of accommodation is apparently accomplished by the formation of the shallow periodic folding patterns. Then the principal wavelength of these patterns ($S_d$) and their amplitude ($a$) of fold heights must depend on the thickness of the stretched layer and the residual stretches in it. Clearly, the accommodation is aided by a significant out-of-surface compliance of the aligned porous microstructure which we present below.

In an effort to provide support for the hypothesis of surface folding the stretched porous microstructure was studied in some detail to assess the level of the actual stretching strains ($\lambda$) and their principal directions ($S$) beneath the crack flanks. To this end the Izod tested specimens were cryo-fractured following the method described in Section 4.2.4 and examined under the scanning electron microscope. The morphol-
ogy of the stretched material at and below the crack flanks could be readily resolved to determine the magnitudes and principal directions of the residual strain field and its variation with distance away from the crack flanks. The micrographs shown in Figure 4-15 give a clear representation of the local strain field below the crack flanks. The location of each micrograph with respect to the crack flank is clarified on the left margin of Figure 4-15, and the actual depth is given in Figure 4-17. The gradual change in the orientation of the elongated cavities relative to the crack flank, as shown in Figure 4-15, have also been observed by Speroni et al. [74] in rubber modified polyamide 6 as well as in other materials [86]. In an attempt to identify the toughening mechanisms in polyamide/poly(phenylene oxide) (PA/PPO) alloys, Sue and Yee [86] examined the sub-fracture surface morphology of various types of impact specimens. In their system, the modifying phase (PPO) is rigid and does not undergo cavitation. As a result, the particles deform to small strains and eventually debond from the matrix. The orientation of the deformed and debonded particles relative to the flank depicted on their representative micrographs are similar to the detailed morphology shown in Figure 4-15.

The cavities, which serve as convenient markers of the deformation field in these micrographs, are known to originate from the cavitation of the rubbery inclusions; this cavitation produces the observed stress whitening in the deformation zone. These cavities elongate in the direction of the local principal stretch [3]. Figure 4-15 (a) is recorded right below the crack flank and shows that the cavities are elongated and aligned almost parallel to the fracture surface. The micrographs in Figure 4-15 (b) - (f) clarify the monotonic rotation of the principal stretch axis of the cavities from the interior of the whitened zone to the crack flank. This demonstrates that the direction of the principal stretch axis is nearly parallel to the fracture surface right below the crack flank and undergoes a progressive rotation of nearly 90 degrees going into depth away from the flanks. Clearly, an anisotropic porous material of this constitution at the crack flanks will have a high out-of-surface compliance that should have a low resistance to the periodic folding of the stretched surface layer undergoing the required accommodation.
The variations in the principal residual stretching strain ($\lambda$) and rotation of the orientation of the principal stretch direction ($\psi$) (measured away from the normal toward the crack flank into the direction of crack propagation) was obtained directly from a series of micrographs recorded below the crack flank in the region between the white strips indicated in Figure 4-16, that shows an overall view of the side cross section below the crack flank. This series was recorded at a magnification of 3200, generating 45 micrographs which formed a continuous strip of 3 meter length representing an actual area of 40 $\mu$m $\times$ 1 mm. The strain induced rotation angle $\psi$ of the principal stretch axis was measured as indicated above, and the associated local residual stretch, $\lambda$, was determined by measuring the aspect ratio of the stretched cavities. The results are summarized in Figure 4-17 which also identifies the locations of the micrographs of Figure 4-15 (a) - (f)\textsuperscript{1}. A similar plot was also presented by Speroni et al. [74] showing only the variations of the length of the elongated cavities as a function of distance away from the fracture surface. The direction of the local principal deformation was not included in their plot. Such information is important in understanding how the intense deformations and the associated cavities arrive at the crack flanks and how the accommodation of such stretched material might result in deformation instabilities that would produce the striations.

According to Figure 4-17 where both $\lambda$ and $S$ are plotted as a function of depth away from the crack flank, the major axis of the elongated cavities rotates by $\sim 80^\circ$ in a layer of 1 mm thickness under the crack flank. Within the first 30 $\mu$m depth below the flank, the rotation is approximately 30$^\circ$ which amounts to around 35 % of the total rotation. Similarly, the aspect ratio of the cavities which represents the local residual stretch diminishes from 10 to 1 within the same 1 mm thickness of flank surface layer. The decrease of stretch within the first 30 $\mu$m is around 5 which is about 50 % of the total change in the whole stress whitened zone. Therefore, a thin surface layer (in this case of 30 $\mu$m thickness), the 'intense process' zone, below the crack flank is

\textsuperscript{1}The waviness in the stretch distribution is real and appears to be due to layer-like localization of cavity elongation. The cause of this is not clear. An adiabatic deformation localization is a possible explanation
subject to a large rotation of principal stretch axis and large local residual stretch. Figure 4-18 is a schematic of the morphology of the cavities below the crack flank depicting the ‘intense process’ zone of thickness $h$ and the stress whitened zone of thickness $L$. The ratio $h/L$ was found to be typically of the order of 0.03 (as measured in Sample 8). That is, effectively 3% of the stress whitened zone undergoes local residual stretches of the order of 10 parallel to the crack flank. Figure 4-19 (a) shows a hypothetical reconstruction of the processes associated with the passage of intense deformation zone of the crack tip material elements that are then left behind along the crack flanks. If the intensely stretched material layer were unconstrained it would be much longer than the length of the crack flanks. The constraint of the stiffer substrate material, however, forces the stretched layer to shorten. This is accomplished, in part, by some strain retraction, but, apparently in a more major way by periodic folding of this thin and stretched surface layer. A certain amount of delamination might be expected below the crack flank under such compressive forces and buckling. However, this is apparently unnecessary because of the rather low ‘plucking resistance’ of the substrate permitted by the elongated cavities that provide enough flexibility in the direction normal to the crack flank (see Figure 4-19 (b)).

Section 4.3.3 summarizes the prominent models that have been proposed for the formation of linear fracture features that are not due to cyclic crack growth on the surface of fatigue fractured semicrystalline polymers. These purely hypothetical models, lack supporting evidence [77, 78]. The buckling of a thin and intensely stretched surface layer on the fracture surface of impact tested rubber modified polyamides may also give more insight into the formation of linear features on fatigue fracture surfaces. Although in a fatigue test the specimen is under continuous cyclic loading and the crack opening angle fluctuates, the deformation induced in the material at every incremental crack propagation step is similar to that in impact testing, at least during the ‘opening part’ of the cycle. Therefore, at each cycle during fatigue crack propagation through a tough solid a highly stretched thin region should form, along the crack flank which should have a tendency to buckle and fold during the ‘closing part’ of the cycle. Thus, this could give rise to ‘micro-striations’ on the fatigue frac-
ture surfaces, at least in material where out-of-surface compliance is large, as in the present case.

4.3.7 Dependence of Striation Spacing on Crack Velocity and Temperature

The plastic deformation resistance of polymers rise in a predictable manner with increasing strain rate and decreasing temperatures. These effects have been studied experimentally in considerable detail both in glassy polymers [87], in semicrystalline HDPE [88], and in polyamide 6 [89], in the light of molecular level mechanisms. Moreover, most polymers have rather poor thermal diffusivity which can result in a substantial temperature rise at high strain rate deformation and adiabatic strain localization due to the concomitant deformation-induced decrease of plastic resistance. On the other hand in experiments carried out at different temperatures a sharp decrease in toughness is observed as the temperature is decreased below a certain level where the material undergoes brittle behavior as is clear from the observations related to Figure 4-7. In the light of these responses it was of interest to perform tensile fracture experiments on singly notched specimens at different extension rates and different temperatures to note the effect of these on the striation spacing.

High Speed Tensile Fracture Experiments

Examination of the fracture surfaces of the singly notched tension experiments carried out at room temperature showed a decrease in the striation spacing with increasing average crack velocity. To relate this observation to the morphology and orientation of the stretched cavities the cryo-fractured surfaces of the median plane of specimens fractured at various rates were examined. Figure 4-20 shows the side view of these singly notched tensile bars of Sample 8 where all micrographs were recorded at the same level of magnification for direct comparison. The morphology immediately below the flank changes drastically as the crack growth rate increases from 0.005 to 5 cm/sec. The draw ratios, as measured from the aspect ratio of the elongated
cavities that are nearly parallel to the crack flank in the ‘intense deformation’ zone, increase with increasing crack growth rate. However, at higher deformation rates induced by higher crack velocities, the plastic resistance of the material in the ‘intense deformation’ zone should increase, if isothermal conditions could be maintained, and result in lower draw ratios. Because of the poor thermal diffusivity of polymers, however, isothermal conditions cannot be maintained and deformation becomes adiabatic instead, resulting in a deformation induced temperature rise and accounting for the increase in the local draw ratio. Thermal effects in the fracture of rubber modified polyamides have indeed been encountered by Dijkstra et al. [73] who have shown that the rise in temperature within the process zone of a crack tip can become quite high, and possibly even approach the melting point of the matrix. Their samples consisted of rubber modified polyamide 6 with a melting point around 215°C. From the morphology below the crack flank they were able to observe a thin layer with healed cavities (no cavitation) which they attributed to a local melting process during crack propagation (or more likely due to a rapid healing in the adiabatically heated zone). In the present experiments, such local melting and softening effects below the crack flanks were not observed, probably because of the higher melting point of polyamide 66 (∼ 250°C). However, any local increase of temperature in the crack tip zone would lower the local plastic resistance and localize the deformation there. As a result, the amount of residual stretch should increase while the lightly deformed substrate material encounters a more modest temperature rise. Thus, when the ‘intense process’ zone accommodates itself to the stiffer substrate it should undergo folding with a smaller wavelength in the samples with higher crack growth rates. The corresponding fracture surface micrographs of these samples are shown in Figure 4-14 where the observed decrease in striation spacings and other evolving features with increasing crack growth rates are consistent with a higher local rise in temperature in the ‘intense process’ zone.
Experiments at Higher Temperatures

The increase in the striation spacing with deformation at higher temperatures must be a consequence of the less localized nature of the deformation as more of the substrate also deforms during crack propagation. Thus, the final draw ratios in the 'intense process' zone are lower and the surface layer folding process does not produce as many striations as it does at lower temperatures. While quantitative confirmation of these explanations are lacking, the observed effects of increasing crack velocity and temperature are in broad agreement with the hypothesis for striation formation advanced above.

4.3.8 A Model for Striation Formation

As presented in Section 4.3.6 above we view the formation of the striations parallel to the crack front, left behind on the fracture surfaces, as a surface layer buckling process occurring during compressive accommodation of the previously stretched crack front material. We view this as a plastic buckling process where the surface layer with thickness $h$ undergoes a periodic cycloidal buckling under a compressive force $P$ exerted on the layer by the less deformed substrate as depicted in Figure B-1. The forces that oppose this buckling are: first the plastic bending resistance of the surface layer which we will treat as if it were an elastic solid with an effective Young's modulus $E$, and second, the substrate plucking resistance $k$ which is governed by the regularly cavitated microstructure depicted in Figure B-2, which we will estimate separately. We offer the analysis, fashioned as a classical plastic plate on an elastic foundation, only as a means of obtaining a potentially useful scaling law—recognizing that the actual problem will no doubt be considerably more complex.

We state the buckling condition of the thin plate on the substrate under the compressive surface load per unit length $P$ by the usual energy method widely used in obtaining an upper bound solution (see den Hartog [90]). For the characteristic length $l$ of the surface layer undergoing buckling the elastic strain energy of bending,
\( U_b \) per unit length, is,
\[
U_b = \frac{1}{2} \int_0^l EI \left( \frac{d^2 y}{dx^2} \right)^2 dx
\]  \hspace{1cm} (4.3)

while the elastic strain energy of plucking the substrate, \( U_p \) per unit length, by the buckling surface layer as it attempts to partially raise the substrate and partially indent it, is,
\[
U_p = \frac{1}{2} k \int_0^l y^2(x) dx.
\]  \hspace{1cm} (4.4)

Where \( k \) is the foundation elastic spring constant, familiar in problems of beams and plates on elastic foundations (see again den Hartog [90]). Finally the work done, \( W \) per unit length, by the compressive load \( P \) during the impending development of the buckling shape is,
\[
W = \frac{P}{2} \int_0^l \left( \frac{dy}{dx} \right)^2 dx.
\]  \hspace{1cm} (4.5)

In all of the above the displacement \( y(x) \), normal to the surface is measured from the initially flat neutral plane of the surface plate as depicted in Figure B-1. We note moreover, that since there are no net out-of-surface tractions applied to the plate,
\[
k \int_0^l y(x) dx = 0.
\]  \hspace{1cm} (4.6)

By the principle of virtual work, the work done by the compressive load must equal the sum of the two other forms of energy, i.e.
\[
W = U_b + U_p.
\]  \hspace{1cm} (4.7)

In the spirit of seeking a workable upper bound solution we take the buckled shape of the plate as a simple second order parabola as
\[
y = A + Bx + Cx^2,
\]  \hspace{1cm} (4.8)

and impose the condition of symmetry as \( y = y_0 \) at \( x = 0 \), and \( x = l \) together with
the condition of no net traction given by Equation 4.6 above to obtain

\[ y = C \left[ \frac{l^2}{6} - lx + x^2 \right]. \tag{4.9} \]

Substitution of Equation 4.9 into Equations 4.3 - 4.5, and use of Equation 4.7, with some simplifications, gives the second order simple differential equation relating \( l^2 \) to \( P \), as:

\[ kL^2 - 60PL + 720E'I = 0 \quad (L = l^2) \tag{4.10} \]

In Equation 4.10 we have replaced \( E \) with \( E' \) which we now interpret as the strain hardening rate \( E' = dY/de \) as is usually done for problems involving plastic buckling.

In normal practice equation 4.10 would be used to solve for the buckling load in a given geometrically defined system. Here we will invert the problem. We assume that buckling sets in while the surface layer is in a state of reverse plastic deformation and that \( P \) is the plastic yield load. We then use Equation 4.10 to solve for \( L \). To proceed, further we need to relate the substrate plucking resistance to the substrate porous microstructure and relate \( E'I \) to the microstructure of the surface layer.

These relations can be readily obtained from elementary beam theory and are developed with the help of Figures B-2 and B-3 in the Appendix B. The result is:

\[ k = \frac{E}{4\lambda^4d} \left( \frac{\pi}{4\lambda} \frac{1-c}{c} \right)^3 \tag{4.11} \]

\[ E'I = \frac{(dY/de)h^3}{12 \left( 1 + \frac{4\lambda}{\pi} \frac{c}{1-c} \right)^4}, \tag{4.12} \]

where \( c \) is the volume fraction of the initially spherical rubber particles of diameter \( d \), which are considered to have cavitated while reaching the crack tip, leading to the elongated parallel cavities of Figures B-2 and B-3, having been stretched out to a principal extension ratio of \( \lambda \) which also becomes nearly parallel to the crack flank surfaces, as the stretched material is left behind on the crack flanks.
The two roots of Equation 4.10 are

\[ L_{1,2} = 30 \frac{P}{k} \left[ 1 \pm \sqrt{1 - \frac{720 \frac{E'}{k}}{rac{900}{P^2}}} \right], \quad (4.13) \]

where

\[
\frac{P}{k} = \frac{4Yhd\lambda^4}{E\beta} \quad (4.14) \\
\frac{E'I}{k} = \frac{h^3d\lambda^4(dY/\delta)}{3\beta E} \quad (4.15) \\
\beta = \left(1 + \frac{4\lambda}{\pi (1-c)} \right) \left(\frac{\pi (1-c)}{4\lambda c} \right)^3. \quad (4.16)
\]

We now note that for a typical case of \(c = 0.1, \lambda = 8\), with \((dY/\delta)/E = O(1/\delta) = O(0.04), d/h = O(0.2)\), giving \(\beta = 1.47\), the second term under the radical in Equation 4.13 is very much smaller than unity. This permits obtaining two positive solutions for the wave length of the striation spacing as:

\[
l_1 = 2h \sqrt{\frac{(dY/\delta)}{Y}}, \quad (4.17) \\
l_2 = \lambda^2h \sqrt{120 \left(\frac{Yd}{Eh\beta} \right)}. \quad (4.18)
\]

Of these two solutions the first is for the range of properties where the substrate plucking resistance dominates and the plastic bending resistance is negligible while the second is for the complementary one where the plastic bending resistance of the surface layer dominates and the substrate plucking resistance is negligible.

For the typical case properties given above with \((dY/\delta)/Y \approx O(1.0)\) we obtain

\[
l_1 = 2h, \quad (4.19) \\
l_2 = 51.7h. \quad (4.20)
\]

While our idealization of the problem has been severe, we find the second predicted wave length far too long to be meaningful and conclude that our problem is governed
primarily by the substrate plucking resistance leading to the first predicted wave length for which the geometrical effects of the microstructure do not enter; but the important result is established that reduction of the plastic resistance $Y'$, by whatever cause, will increase the striation spacing—noting that the strain hardening rate $dY'/de$ should be primarily temperature and strain rate independent. This is of course what has been observed.

4.4 Conclusions

To investigate the fracture process in rubber-modified polyamide 66, Izod flexural bars with varying particle size and rubber content were tested at different temperatures. The fractured samples were examined in an SEM to reveal the morphology of the fracture surfaces and process zone below the crack flanks. The features detected on the fracture surfaces of the samples varied significantly, depending on the level of toughness. These features consisted of a patchy but generally smooth surface on brittle samples, striations on ductile ones and a combination of the two on samples in the transition zone. The microstructural processes of fracture involved in crack growth of these toughened polyamides consists of: cavitation of rubber particles within the process zone; stretching and rotation of cavities in the direction of the local major principal strain axis; and formation of striations via folding of the stretched fracture surface by plastic buckling. The spacing between the striations increased with increasing temperature, particle size, rubber content, and deformation rate. These variations were attributed to temperature and rate dependence of the viscoplastic properties of the matrix material and the anticipated adiabatic localization of deformation for high crack velocities. A model for striation formation was developed based on plastic buckling of a thin plate on an elastic foundation which is in reasonable agreement with observations—particularly the effect of temperature on the striation spacing. The proposed model of buckling of thin surface layers to explain the formation of striations on the fracture surface can also be a possible explanation for the formation of the well known fatigue striations that cannot be associated with
cyclic crack growth ('micro-striations').
Table 4.1: Sample Characteristics

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Rubber Concentration (wt. %)</th>
<th>Particle Diameter (μm)</th>
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<tr>
<td>1</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.19&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.17&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>0.17&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>12.00&lt;sup&gt;b&lt;/sup&gt;</td>
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</tr>
<tr>
<td>9</td>
<td>20</td>
<td>0.17&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>SAXS Values  
<sup>b</sup>ESEM Values

Table 4.2: Izod Toughness Values<sup>a</sup> (J/m) at Various Temperatures(°C)

<table>
<thead>
<tr>
<th>Sample ID</th>
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<th>20</th>
<th>30</th>
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<tr>
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<td>990</td>
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</table>

<sup>a</sup> Average of 5 tests at each temperature
Table 4.3: Striation Spacings on Fracture Surfaces of Izod Impact Samples.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Striation Spacing (μm)(^a) of Samples</th>
</tr>
</thead>
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<td></td>
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<tr>
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<td>0.86</td>
</tr>
<tr>
<td>80</td>
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</tbody>
</table>

\(^a\)Error bars are typically ± 1%, based on the breadth of distribution of the Fourier frequencies (transformed to real space) discussed in Section 4.2.5
Figure 4-1: Nominal stress-elongation curves of singly notched tensile tests of Sample 8 (total length of specimen is 127 mm) at crosshead speeds of: a) 500, b) 100, c) 10, and d) 1 mm/min, corresponding to crack velocities of 5, 1, 0.1, and 0.005 cm/sec
Figure 4-2: The scanning step of the image analysis procedure: (a) is the scanned image of the fracture surface micrograph of Sample 9 tested at 60°C; (b) is the gray level profile of the top horizontal border of the figure.
Figure 4-3: The smoothing step of the image analysis technique: (a) is the smoothed image of Figure 4-2 (a), resulting from the smoothing of all line scans in the manner described in the text; (b) is the smoothed (solid curve) and as-scanned (dashed curve) profiles of the top horizontal border of the figure.
Figure 4-4: The fast Fourier transform of the smoothed fracture surface micrograph (Figure 4-3 (a)) of Sample 9 tested at 60°C. The transform is the average of individual transforms of ~ 600 horizontal lines constituting the image.
Figure 4-5: The effect of: (a) rubber concentration, and (b) particle size on Izod toughness, determined at room temperature.
Figure 4-6: The effect of temperature on Izod toughness at: (a) constant rubber concentration of 20 wt % with a particle size of (o) 0.32 μm, (+) 0.63 μm, (⋆) 1.12 μm, (x) 12 μm; and (b) at constant particle size of ~ 0.17 μm with a rubber content of (x) 20, (⋆) 15, (+) 10, and (o) 5 wt %.
Figure 4-7: The evolution of fracture surface morphology, related to levels of Izod toughness: (a) is the schematic variation of the toughness level with temperature, (b), (c) and (d) are representative fracture surface morphologies of samples from regions of toughness as indicated in (a).
Figure 4-8: Schematic of striations left on the fracture surface of a tough specimen during fracture. The striations are parallel to the propagating crack front.
Figure 4-9: Fracture surface of Sample 8 tested at: (a) 20 and (b) 50 °C. The direction of crack propagation is from left to right.
Figure 4-10: The side view of a crack flank showing a set of striations. The direction of crack propagation is from left to right.
Figure 4-11: Striations on the fracture surface of Sample 9; showing an example of a secondary crack in the plane of the main cracking event
Figure 4-12: The variation of striation spacing with rubber concentration measured on the fracture surface of specimens, fractured at 60 °C via the image analysis technique described in Section 4.2.5 (rubber particle size is constant at \( \sim 0.17 \) \( \mu \)m).
Figure 4-13: The variation of striation spacing with temperature as measured on the fracture surface of specimens of: Sample 7 (+), 8 (○), and 9 (★), via the image analysis technique described in Section 4.2.5: All samples had the same rubber content (20 wt %) and the particle size varied as follows: 0.63 μm (+), 0.32 μm (○), 0.17 μm (★). The error bars are left out of this plot, because they are of the same size as the plot symbols.
Figure 4-14: Fracture surface micrographs of specimens of Sample 8 after the single notch tensile tests at crack velocities of: (a) 0.005, (b) 0.1, (c) 1, and (d) 5 cm/sec. The direction of crack propagation is from left to right.
Figure 4-15: Morphology of the cavities seen from a side view below the crack flank after an Izod test. The inserts next to the micrographs indicate their locations relative to the crack flank. The direction relative to the crack flank in which the micrographs were recorded is schematically shown in Figure 3-1. The direction of crack propagation is from left to right.
Figure 4-16: The view of Sample 8 observed in an ESEM as depicted in Figure 3-1. The indicated rectangular region (between the white strips) was photographed at a magnification of 3200 to determine the data summarized in Figure 4-17 (See the text for details). The direction of crack propagation is from left to right.
Figure 4-17: Distribution of magnitudes of draw ratio, $\lambda$ (+), and angle of rotation of, $\psi$ (×), of the major principal stretch direction, away from the plane of the crack flank. The locations of the micrographs of Figure 4-15 (a) - (f) are indicated as A - F.
Figure 4-18: Schematic rendering of the morphology of cavities below the crack flank from the viewpoint described in Figure 3-1. $L$ indicates the extent of the stress whitened region, while $h$ indicates the 'intense process' zone. The shaded circles represent uncavitated rubber particles. The undulation on the top edge represents the side view of striations on the fracture surface.
Figure 4-19: The schematic view in the direction depicted in Figure 3-1 of Izod impact samples after fracture: (a) is the expected hypothetical sample shape that accommodates high local stretches without interacting with the rest of the sample, while (b) is the actual shape where the high local stretches are accommodated by the buckling of the 'intense process' layer.
Figure 4-20: The side view below the crack flank of the single-notched tensile bars of Sample 8 tested under uniaxial tensile loading with corresponding crack growth rates of: (a) 0.005, (b) 1, and (c) 5 cm/sec.
Chapter 5

Microstructural Fracture Processes Accompanying Growing Cracks in Tough Rubber Modified Polyamides

5.1 Introduction

The processes of crack initiation and growth in fracture of moderately tough materials have been extensively studied and a number of mathematical models have been proposed (for an overview see Hutchinson [91]). The initiation stage is well understood and successful quantitative models have been developed for cases in which the material is only moderately tough so that the crack growth instability can be satisfactorily described by the so-called small scale yielding approximations. Modelling the processes associated with a growing crack is far more complex. In very tough materials where crack growth is often stable in finite size parts, the crack advance conditions can best be viewed as a finite and relatively large crack opening angle. For such materials where extending the crack requires a continued--albeit decreasing rate of increase of the crack driving force $J$. The toughness of the material is often de-
scribed by a so-called tearing modulus, $T$, defined as $(E/\sigma_0^2)(dJ/da)_i$ where $E$ and $\sigma_0$ are the Young's modulus and the plastic shear resistance in tension, respectively, and $(dJ/da)_i$ is the initial rate of increase of the crack tip driving force $J$ with crack length, to initiate crack advance (for succinct definitions of crack driving forces, particularly the so-called $J$ integral see Hutchinson [91]). A very useful and clear model of the complex mechanics of this process is described by Rice and Sorensen [7]. The rubber modified polyamide blends (Nylon 6 or 66) are very tough materials and furnish excellent examples for stable crack advance with very substantial crack opening angles [2].

The model material used in the present study is a rubber toughened polyamide. The effect of various parameters in this toughening process such as that of particle size, rubber concentration, temperature, and interparticle distance have been studied extensively [22, 21, 70, 15, 71, 72, 18, 19]. Recently, Muratoğlu et al. have proposed a mechanism of toughening of such semi-crystalline polymers based on the lowering of the local plastic shear resistance in the interparticle ligament regions by the preferred orientation of the low slip resistance hydrogen bonded sheets ((001) for polyamide 6 and (010) for polyamide 66) parallel to the rubber/matrix interface [3]. The reduction of the local flow stress prevents premature catastrophic failure and large local deformations are accommodated in the matrix before fracture occurs. Morphological studies in the stress whitened zone of the tough blends showed that the rubber particles cavitate and elongate to large draw ratios ($\sim 12$) in the direction of the local principal stretch axis [92, 74]. The evolution of the cavities and their spatial distribution have been examined by Muratoğlu et al. in considerable detail from the crack flanks in to the interior region of an Izod impact tested tough PA66/EPDR blend. Using the stretched out cavities as built-in strain gauges, the local draw ratio and the orientation of the principal stretch axis were measured as a function of depth away from the crack flank [92].
5.2 Experimental

5.2.1 Sample Preparation and Characterization

A 28 mm Werner & Pfleiderer extruder was used to blend polyamide 66 with maleic anhydride functionalized ethylene/propylene diene rubber (PA66/EPDR) at a rubber concentration of 20 wt %. The particle size was kept constant at around 0.32 μm by choosing the right maleic anhydride functionality level in the rubbery component of the blend [92]. The resulting blends were pelletized and then molded in a 6 oz., 150 ton Van Dorn injection molding machine into flexural test bars (length = 127 mm, width = 12.5 mm, thickness = 3.2 mm) and 0.64 cm thick sheets. The Izod bars were cut from the middle part of the flexural bars. Notches were introduced into each Izod bar with a TMI Notching Cutter according to the specifications of ASTM D256.

The compact tension specimens were machined out of the 0.64 cm thick injection molded sheets in the form schematically shown in Figure 5-1. Two grooves on both sides and a chevron notch were machined in the specimens to prevent the deviation of the crack plane from the plane of symmetry of the specimen, and to achieve reproducible initiation of crack growth. The side grooves were machined in the form of 0.5 mm deep 90° V notches. The details of the chevron notch are shown in Figure 5-2, while Figure 5-3 summarizes the dimensions of the specimen which, as can be seen, was made longer than usual to achieve a good approximation to steady growth. Following the injection molding, notching, and machining processes, the samples were placed in air-tight bags and stored in a dessicator to prevent further absorption of water and to achieve uniformity in response of all specimens [28].

5.2.2 Izod Impact Experiments

The Izod impact tests were carried out following ASTM D256 standards. The procedure to view the crack front morphology is schematically summarized in Figure 5-4. In the Izod impact test, a pendulum hits and breaks the specimen. However, since the material used for this study is of very high toughness the fracture is incomplete.
That is, as a result of the large rotations of the sample arms accompanying the large crack opening angles the Izod bar bends and the pendulum swings by. As shown in Figure 5-4 the partially broken samples are taken out of the Izod tester; the opened crack is filled with a low shrinkage, low viscosity epoxy (Epofix resin purchased from Struers); the specimen is left overnight to achieve complete cure of the epoxy filling; a small section of the specimen containing the crack tip is cut out; and four notches are introduced around the cut section as shown in Figure 5-4 (d). After 20 minutes soaking in liquid nitrogen a wedge is driven through one of the notches to expose the lightly shaded area of Figure 5-4 (e) for microscopy.

5.2.3 Compact Tension Experiments

The machined compact tension specimens were tested in an Instron 4200 universal testing machine at a cross-head speed of 500 mm/min. Figure 5-5 schematically represents the procedure that was followed to propagate the crack in the specimen quasi-statically. The specimen is progressively torn apart in the Instron machine until a total pin to pin displacement of \( \sim 20 \) mm is reached. A typical load-pin displacement curve is shown in Figure 5-6. The progressive decline of the tearing load is a result of the decreasing length of untorn specimen. Without removing the load, the opened crack was then framed from two sides by two strips of scotch tape and filled with the low shrinkage, low viscosity epoxy (Epofix resin). The specimen was then held under load for 12 hours to ensure total curing of the epoxy filling. Once the epoxy was hardened, the specimen was unloaded and a small section around the crack tip was cut (see Figure 5-5 (c) and (d)). To examine the internal morphology of the cavities in SEM, four notches were introduced around the piece as shown in Figure 5-5 (d) and a wedge was driven through one of the notches after the specimen was left in liquid nitrogen for over 20 minutes.

The exposed internal surface of both the compact tension and Izod bars were then coated with Au and the morphology of the cavities were examined in an Elektroscan environmental scanning electron microscope (ESEM). The microscope used a lanthanum hexaboride (LaB\(_6\)) filament and was operated at an accelerating voltage
of 15 kV.

5.3 Results and Discussion

5.3.1 Method of Examination of Deformation Gradients around the Crack

The model material used in the present study was a rubber toughened polyamide 66 modified with 20 wt % rubber particles of 0.34 μm diameter (PA66/EPDR). Early studies have shown that under various stress states, the rubber particles cavitate [3, 61, 62] and the cavity elongates in the direction of the principal stretch axis, S, to large draw ratios [3, 92, 74, 93]. Matrix ligaments can withstand such large stretches (draw ratios of ~ 10) because the initially built-in local preferred orientation of the low slip resistance hydrogen bonded planes parallel to the rubber/matrix interface facilitates large deformations by undergoing lamellar shear followed by textural alignment [3]. During elongation, the width of the cavities does not change significantly for reasons described in the earlier study [3]; hence the aspect ratio of the elongated cavities provide an estimate of the level of local draw ratio, λ, in the material. If the morphology of the cavities in a deformed material can be examined; the aspect ratio and direction of the major axis of the ellipsoidal cross-sections of the cavities on the micrographs can be used to determine the actual local draw ratio and direction of the principal stretch axis, respectively. Following are two methods used in this study to determine the morphology of the cavities around a propagating crack front which clearly reveal the variations of the local parameters (S, λ) around the crack tip for material elements flowing towards the crack front, separating and being deposited along the crack flank.

5.3.2 Crack Closure in Izod Impact Samples

The microscopy of the crack tip of Izod impact tested specimens showed that a substantial decrease of crack opening angle occurs due to the springback of the Izod
bar after the pendulum swings by. The maximum crack opening angle during the Izod test is calculated to be around $60^\circ$ based on the geometry of the pendulum swing and the angle where the pendulum loses contact with the specimen. After the test, the crack angle decreases to a residual opening of approximately $20^\circ$ as measured from Figure 5-7. The reversal of the crack angle is not readily obvious from this micrograph. However, Figures 5-8 (a) and (b) showing the crack tip at higher magnifications reveal the extensive buckling of the crack front as a result of the crack closure. The folding of the elongated cavities and the undulations in a surface layer of thickness 15 - 20 μm are clearly discernible on these micrographs. Therefore, the morphology of the cavities are altered by the closure process and this method cannot be used in determining the crack tip morphologies in rubber-modified polyamides. The following section discusses the second method where the crack in a quasi-statically deformed compact tension specimen is filled with epoxy while it is held under load preventing the springback of the sample. Hence no crack closure takes place and the cavity microstructure around the crack tip is substantially unaltered.

5.3.3 Crack Tip Microstructural Alterations in Compact Tension Specimens

The compact tension experiments were performed in an Instron machine and the final shape of the advanced crack was preserved by infiltrating the large crack opening with a low viscosity, low shrinkage epoxy as described above. As Figure 5-5 summarizes, the morphology of the cavities around the crack front were examined in an SEM on a cryofractured surface containing the crack tip. Figure 5-9 shows typical micrographs from various parts of the crack front. The bright filling inside the crack is epoxy. Microscopically, the opening angle is measured to be $\sim 60^\circ$ which is consistent with the macroscopic crack opening angle ($\sim 60^\circ$) measured from the final opening of the crack while it was held under load in the Instron machine. Such large opening angles have been reported for rubber modified polyamides by Huang [2] in in situ studies of crack propagation in rubber toughened polyamide 66 in a field emission
scanning electron microscope. The microscopic observations of Huang also revealed that the crack tip is blunted before growth is initiated. When the stable crack growth conditions were reached, the profile of the tip resembled the schematic shapes shown in Figure 5-10. The top sketch is the side view of the crack front before initiation with a sharp tip. First, blunting occurs at the crack tip in the initial stages of deformation. When the critical crack opening displacement is reached the crack propagation initiates. Eventually steady state growth will be reached and the flanks will curve towards the crack tip. The latter stage of the crack propagation evolution demonstrated by Huang, is in agreement with our light microscope examination of the epoxy filled crack tip.

There is no indication of crack closure in epoxy infiltrated compact tension specimens. The morphology at the crack tip recorded at high magnifications does not show any large scale buckling of the cavities and folding of the fracture surface (see Figures 5-9 (a)-(d)). Therefore, the morphology of the cavities are not altered; and this method can be used to determine the variations in the local draw ratios around the crack front.

The uniform macroscopic stress whitening around the propagating crack defines the boundaries of the process zone where the whitening is due to the cavitation of the rubber particles. However, on a microscopic scale, the morphology of the process zone varies significantly. There are two distinct morphologies as shown in Figure 5-9 (b) representing the area within a radius of 30 μm ahead of the crack front, and Figure 5-9 (d) recorded from the far field ahead of the crack front. The former region would be referred to as the ‘intense’ process zone, while the latter as ‘weak’ process zone in the remainder of this communication. In the ‘intense’ process zone cavities are elongated to large draw ratios of around 10, whereas the ‘weak’ process zone consists of equiaxed, spherical cavities. As the crack propagates, the material immediately ahead of the crack front starts to come apart, probably when the matrix ligaments reach their ultimate draw ratio. The elongated cavities of this region then undergo a rotation of ~ 60° about the crack front. Hence, the morphology of the cavities immediately beneath the fracture surface is comprised of a thin layer of elongated cavities aligned
parallel to the crack flanks (see Figure 5-9 (c)). Figure 5-11 schematically represents the morphology of the cavities in the process zone. The lightly shaded region is where the cavitation is homogeneous with a spherical pore structure. The darkly shaded region in front of the crack tip is where the cavities are extended to large draw ratios. This region is then divided in two, and is left on the surface of the crack flanks as the crack propagates. The highly stretched cavities on and under the parting surfaces undergo a rotation of about 60°. As the micrograph of a flank region of Figure 5-12 indicates, the thickness of the zone of elongated cavities that were rotated by the crack advance is about 30 µm which is very close to the radius of the ‘intense’ process zone, namely 30 µm before it parts. Thus, the elongated cavities of the flank surface region originate from the ‘intense’ process zone and are simply rotated and translated to their final positions at the crack flanks, immediately behind the crack tip. The cartoon of Figure 5-13 summarizes the cavitated material flow with shear and rotation around the propagating crack front with a large opening angle. The flanks curve smoothly towards the crack front where they join in on the blunt tip. The principal axes of the cavities within the ‘intense’ process zone at the blunt tip are placed parallel to the flank surfaces as the rupturing crack tip material parts in two. Thus, the cavities beneath the freshly formed fracture surface suffer a substantial rigid body rotation, resulting from the shear of the parting material.

The evolution of the morphology around the propagating crack front could also be visualized alternatively as the relative flow of the rubber particles from right to left by an observer traveling with the blunted crack tip. As the particles approach the crack, they start to feel its intensifying stress field. Cavitation of the rubber and elongation of the surrounding matrix perpendicular to the crack plane intensifies as the particles get closer to the front. Upon division of the material flow in two and passage of the parts by the front, the cavities near the flanks rotate with the intense final shear of the parted material. Further away from the plane of the crack and the flanks, the rotation will be less severe due to the much lower concentration of shear strain in this region as is depicted in the schematic view of Figure 5-13. The sub-flank morphology of the cavities with the distribution of the level of cavitational strain and
its principal stretch directions below the fracture surface have been described in detail elsewhere [92].

Two distinctive zones ahead of the advancing crack front and below the crack flank have also been observed by Sue and Yee [86] in polyamide/poly(phenylene oxide) (PA/PPO) blends. Their modifying phase (PPO) is a rigid polymer. Therefore, the samples exhibit smaller crack opening angles and the modifying rigid particles do not cavitate. Large deformations are accommodated by some elongation of the particles followed by their debonding at the interfaces and elongation of the surrounding cavities. Morphological analysis of the crack front showed that the process zone incorporated widespread cavitation but contained a central region of more intense shear in the cavitated zone. Below the crack flank, the authors observed a thin sheared layer near the fracture surface in the previously cavitated material. Similar morphological observations were made by the authors as reported in the present study. From the micrographs of Sue and Yee [86] showing the processed morphology, the angle between the flank and elongated cavities underneath the fracture surface can be estimated to be 60° which is much larger than that (≈ 10°, nearly parallel to the flank) encountered in this study. In fact, the rotation imposed by the advancing crack on the elongated cavities is ≈ 60° for both the PA/PPO (as measured from the micrographs of reference [86]) and the present PA66/EPDR blends. Yet, the crack opening angle in our blends is much larger then theirs. This is why the orientation of the elongated cavities below the flank surfaces are different.

5.3.4 Distribution of Local Deformation

To determine the local draw ratios 25 micrographs were recorded from a thin strip ahead of the crack front. When connected together, they represent an area of 30 μm × 0.5 mm. The local draw ratios were estimated by measuring the aspect ratios of the cavities at various distances from the crack tip. Figure 5-14 is a plot of the draw ratio as a function of distance away from the crack front. Within the 'intense' process zone the local draw ratio is constant at 10 but rapidly drops to 1 within a distance of 30 μm beyond which it remains constant for the remainder of the
process zone of roughly 1 cm length. Figure 5-14 is similar to Figure 18 of our previous study [92] and Figure 13 of reference [74] where respectively, the variations of the local draw ratio and the length of the elongated cavities are plotted as a function of depth away from the crack flank. In the present study, the rate of deformation in the CT (compact tension) specimen was much lower in comparison with that of the Izod impact experiments of references [92] and [74]. Still, the thickness of the ‘intense’ process zone in all samples was around 30 μm and it appears to be independent of the deformation rate. On the other hand, the maximum draw ratio observed in the CT specimens (low strain rate) is around 10 while that value was above 12 for Izod impact specimens (high strain rate). This could be due to high rate deformation induced adiabatic heating and temperature rise in the process zone that would in turn lower the flow stress of the material and allow it to deform to larger draw ratios.

5.3.5 Toughness of Rubber Modified Polyamide

The experiments reported above indicate that the rubber modified polyamides are remarkably tough materials. Therefore, it is of interest to evaluate their behavior in a quantitative framework to permit more meaningful comparison with other tough materials.

Materials which do not exhibit fracture instabilities in the usual laboratory experiments, such as the special compact tension specimen used in the present study, require special considerations to evaluate their toughness levels. It is customary to present the specific fracture work of such materials by means of the J integral that represents the driving force for the fracture process of materials undergoing large strain plasticity. In such tough materials the J integral will rise monotonically with crack extension until a steady state value \( J_{ss} \) of the J integral is reached for the local process of separation. This type of behavior giving the required rise of \( J \) with increasing crack length is known as a fracture resistance (R-curve) curve. Depending on the specimen or part geometry and the mode of loading, an eventual fracture instability is usually encountered before a steady state \( J_{ss} \) is reached. In the present experiments with specimens of progressively increasing compliance such instabilities were
not reached. The characteristic load-pin displacement curve of Figure 5-6 constitutes stable behavior.

To obtain a measure of the material fracture toughness we nevertheless use the information provided in Figure 5-6 to determine a crack driving force $J$ which we will interpret to be close to the steady state $J_{ss}$.

The $J$ integral, crack driving force for a compact tension specimen of the type shown in Figure 5-3 is [94]

$$J = \alpha \varepsilon_0 \sigma_0 (1 - \phi) c \ h_1 \left( \frac{a}{b}, n \right) \left( \frac{P}{P_0} \right)^n$$

(5.1)

where $a$, $b$, $c$, $\phi$, $\alpha$, $\varepsilon_0$, $\sigma_0$, $n$, $P_0$, $h_1(a/b, n)$ are in order the following:

$\begin{align*}
    a &= \text{crack length measured from pin-line} \\
    b &= \text{distance from pin-line to free end of specimen} \\
    c &= b - a \\
    \phi &= \text{volume fraction of rubber} \\
    P_0 &= 1.455 \ \eta \sigma_0 (1 - \phi) \\
    \eta &= ((2a/c)^2 + 2(2a/c) + 2)^{1/2} - (2a/c + 1) \\
    \varepsilon_e &= \alpha \varepsilon_0 (\sigma_e/\sigma_0)^n
\end{align*}$

where $\varepsilon_e$ is the power-law fit, strain hardening expression, relating the stress $\sigma_e$ and $\varepsilon_e$ (equivalent quantities for 3-D behavior), where $\alpha \varepsilon_0$ and $\sigma_0$ are fitting constants. It is customary to consider $\sigma_0$ to be the yield stress of the material. The parameter $h_1(a/b, n)$, which is a tabulated function of $a/b$ and $n$, is obtained from numerical solutions of the crack tip field [94]; $P$ is the pin-load per unit specimen thickness $t_s$. In the present study the following magnitudes for the above quantities are appropriate for the geometrical parameters:

$\begin{align*}
    a &= 5 \times 10^{-3} \text{m} \\
    b &= 6.73 \times 10^{-2} \text{m}
\end{align*}$
\[ c = 6.23 \times 10^{-2} \text{m} \]
\[ t_s = 5.4 \times 10^{-3} \text{ m} \text{ (taking account of side grooves)}, \]
\[ \eta = 0.371 \]

all determined from the Compact Tension Specimen (CTS) shape given in Figure 5-3. For the material parameters, determined from data given by Lin and Argon [89], we have,

\[ \alpha \varepsilon_0 = 3.95 \times 10^{-2} \]
\[ \sigma_0 = 31.6 \text{ MPa} \]
\[ n = 2.70 \]
\[ E_0 = 1300 \text{ MPa, Young’s modulus} \]
\[ \mu_0 = 500 \text{ MPa, Shear modulus} \]
\[ \phi_0 = 0.2 \text{ (given in Section 5.2.1) (taken here as equal to the wt fraction).} \]

The numerical parameter \( h_1(a/b,n) = 1.64 \) was determined by interpolation and extrapolation of tabulated information for the CTS for the material parameters given above, for a plane stress problem.

From the peak load in Figure 5-6 and \( t_s \) above we determine

\[ P = 333 \text{ kN/m}. \]

Moreover, the information above gives

\[ P_0 = 870 \text{ kN/m}. \]

With these values for the relevant parameters we determine the peak crack tip driving force \( J \) from Equation 5.1, and interpret it as a good measure of the steady-state driving force \( J_{ss} \) as:

\[ J_{ss} = 754 \text{ J/m}^2. \]  \hspace{1cm} (5.2)
The corresponding steady-state damage zone radius is \([7]\),

\[ R_{ss} = \lambda \frac{E}{\sigma_0^2} J_{ss} \approx 0.2 \text{ mm. } \quad (\lambda = 0.16 \ [7].) \quad (5.3) \]

The comparison of the toughness of materials of this type is customarily facilitated by a so-called tearing modulus \(T\) defined as \([7]\):

\[ T = \frac{E}{\sigma_0^2} \left( \frac{dJ}{da} \right)_{in} = \frac{\beta}{\alpha} \ln \left( \frac{J_{ss}}{J_{1c}} \right) \quad (5.4) \]

Where \((dJ/da)_{in}\) is the required initial rate of increase of the crack driving force with initiation of crack growth, and \(J_{ss}/J_{1c}\) is the ratio of the steady state driving force to \(J_{1c}\), the driving force to initiate crack growth. A model for the latter ratio has been given by Rice and Sorensen \([7]\) as:

\[ \frac{J_{ss}}{J_{1c}} = \frac{\alpha \sigma_0}{\lambda e E} \exp \left( \frac{E}{\sigma_0} \frac{1}{\beta \rho} \right) \quad (5.5) \]

where \(\alpha, \lambda, \beta\) are theoretically determined constants, \(e = 2.72\) is the basis of the natural logarithm, and \(\theta^p\) is the steady state plastic crack opening angle for the propagating crack. Rice and Sorensen \([7]\) recommend the following magnitudes, based on crack tip numerical models,

\[ \alpha = 0.50 \]
\[ \lambda = 0.160 \]
\[ \beta = 4(2 - \nu)/\sqrt{3} = 3.9 \quad (\nu = 0.3). \]

In the present experiments of fracture of the CTS, a steady state total crack opening angle of 60° was determined under load. To determine the plastic crack opening angle we need to determine the elastic springback. A good measure of this can be readily obtained from the load displacement curve of Figure 5-6 by noting the pin displacement rate based on the initial slope of the curve and calculating the elastic pin displacement for the peak load. This for an initial crack length \(a = 5 \text{ mm gives} \]
an elastic rebound angle $\theta^c = 0.231$ rad, which gives for $\theta^p = 0.819$ rad. Thus, we obtain from Equations 5.5 and 5.4

$$\frac{J_{ss}}{J_{ic}} = 158$$ (5.6)

$$T = 39.5$$ (5.7)

respectively. It is worth noting that in the evaluation of Equation 5.5, $\sigma_0/E$ appear as a ratio. Thus, the fact that the crack tip zone material is cavitated has no specific effect on the answer in Equation 5.5, since the cavitation should effect $\sigma_0$ and $E$ in the same way and the net effect should cancel. Therefore, we have used $\sigma_0/E$ for the intrinsic polyamide.

Moreover, from Equations 5.2 and 5.6 we obtain a value for the initial crack driving force $J_{ic}$ to start crack growth as.

$$J_{ic} = 4.77 \text{ J/m}^2.$$ (5.8)

Considering the possible substantial errors that can be made in the evaluation of Equation 5.5 due to the uncertainty of the numerical constants we consider this value as a low estimate.

### 5.3.6 Comparison with other Tough Materials

We note that the analysis of the toughness of the rubber modified polyamide, given in the section above is quite approximate since the crack tip material in the damage zone undergoes very substantial cavitation and develops very significant plastic anisotropies arising from the alignment of the stretched-out cavities. How these important effects modify the crack tip field and the model of Rice and Sorensen which we have used as a guide is unknown, and must be determined from a more specific numerical analysis which is planned. The great attraction of the rubber modified polyamide with its quasi-regularly cavitating microstructure is that it can serve as an ideal model material to develop a quantitative understanding of the mechanics of
fracture and tearing of very tough materials, which has not been possible with the more irregular microstructures of tough structural alloys.

Here a comparison of the rubber modified polyamides with tough structural steels is also enlightening. For this purpose we reproduce a comparative table assembled by Rice and Sorensen [7] of the performance of some of the toughest structural steels (see Table 5.1). We note that with a steady state plastic crack opening angle of \( \theta_p = 0.819 \) rad the rubber modified polyamides lie above the best structural steels on a relative comparison. Admittedly some of these steels have larger \( J_{ss}/J_{1c} \) ratios and much higher tearing moduli than the rubber modified polyamides. This is a direct result of their substantially smaller \( \sigma_0/E \) ratios which tend to amplify the tearing modulus. Even on this basis, however, the rubber modified polyamides have relative behavior commensurate with some of the best structural steels.

5.4 Conclusions

To study the interaction of a growing crack with the cavitating microstructure of the very tough rubber modified polyamides, Izod impact experiments and fracture of compact tension specimens were carried out. The former resulted in the forced closure of the crack due to the dynamic springback of the specimen after the pendulum swung by, therefore, significantly altering the morphology of cavities by widespread buckling of ligaments. On the other hand, the compact tension specimens were deformed under stable crack growth conditions, with steady state crack opening angles of 60°. The tearing process was studied in detail by ‘freezing’ the crack in its open condition by infiltrating the specimen with epoxy while it was held under load. SEM examinations of the propagating crack revealed the evolution of the morphology of the cavities in and around the crack front: in the far field the rubber particles cavitate forming spherical voids; near the crack front these are elongated to draw ratios of around 10; past the crack front and below the crack flank, the elongated cavities are rotated by shear about 60° and become aligned parallel to the crack flank. Two distinct regions within the process zone can be distinguished: i) an ‘intense’ process zone
with elongated cavities and, ii) a 'weak' process zone with spherical cavities. The former is translated to the flank region upon the separation of the material at the crack tip as it advances.

The 'intense' and 'weak' process zones were observed only in tough blends of rubber modified polyamides. The brittle blends are not endowed with the local preferred orientations of low resistance slip planes parallel to the rubber/matrix interface [3]; hence elongation of the cavities and crack tip blunting does not occur, leading to brittle failure.

The toughness of the rubber modified polyamides were evaluated by the well known mechanics of fracture of very tough materials. The plastic crack opening angles and tearing moduli were found to compare very favorably with some of the toughest structural alloys on a relative basis.
Table 5.1: Crack growth parameters for specific pressure vessel steels compared with EPDR reinforced polyamide 66 (steel parameters based on data of Clark et al. [6], arranged by Rice and Sorensen [7])

<table>
<thead>
<tr>
<th>Material</th>
<th>$\delta_{lc}$ (mm)</th>
<th>$\theta_0$ (rad)</th>
<th>$\sigma_0/E$</th>
<th>$J_{ss}/J_{lc}$</th>
<th>$T_{init.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A533B (1 hr 670 °C, 36 hr 620 °C)</td>
<td>0.19</td>
<td>0.74</td>
<td>0.0024</td>
<td>$8 \times 10^{30}$</td>
<td>555</td>
</tr>
<tr>
<td>A533B (4 hr 650 °C)</td>
<td>0.18</td>
<td>0.20</td>
<td>0.0028</td>
<td>$2 \times 10^5$</td>
<td>94.5</td>
</tr>
<tr>
<td>HY-80 (5 hr 650 °C)</td>
<td>0.125</td>
<td>0.39</td>
<td>0.0035</td>
<td>$5 \times 10^{9}$</td>
<td>174</td>
</tr>
<tr>
<td>(average) (average)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HY-80 (20% prestrain)</td>
<td>0.045</td>
<td>0.12</td>
<td>0.0046</td>
<td>3.6</td>
<td>10.0</td>
</tr>
<tr>
<td>HY-130 (2 hr, 610 °C)</td>
<td>0.06</td>
<td>0.13</td>
<td>0.0045</td>
<td>7.1</td>
<td>15.3</td>
</tr>
<tr>
<td>Weld deposit L</td>
<td>0.03</td>
<td>0.02</td>
<td>0.0035</td>
<td>0.02</td>
<td>†</td>
</tr>
<tr>
<td>(HY-80 MMA 4-pass)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weld deposit N</td>
<td>0.03</td>
<td>0.06</td>
<td>0.0037</td>
<td>0.02</td>
<td>†</td>
</tr>
<tr>
<td>(HY-100 MMA 4-pass)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA66/EPDR Blend</td>
<td>*</td>
<td>0.82</td>
<td>0.0243</td>
<td>158</td>
<td>39.5</td>
</tr>
</tbody>
</table>

* Available information is too unreliable to determine initial critical opening displacement
† Spontaneous fracture
Figure 5-1: Sketch of the compact tension specimen with a chevron notch. Side grooves are machined in on both sides of the specimen to ensure planar crack propagation.
Figure 5-2: Sketch showing the geometry of the chevron notch machined in the compact tension specimens
Figure 5-3: The dimensions of the compact tension specimen machined from the injection molded sheets. The thickness of the specimen is 0.64 cm and contains side grooves each 0.5 mm deep.
Figure 5-4: The fracture and preparation for microscopy of Izod impact specimens: (a) and (b) depict the Izod impact test where the specimen does not break and the pendulum swings by; (c) the opened crack is filled with epoxy; (d) a small section is cut from the crack front region and four notches are introduced around the cut piece; (e) a wedge is driven in to one of the four notches at liquid nitrogen temperature to expose the lightly shaded internal surface for microscopy.
Figure 5-5: The testing of the compact tension specimen: (a) the specimen is pulled in an Instron machine at a cross-head speed of 500 mm/min to a nominal displacement of $\sim 20$ mm, (b)-(c) the opened crack is filled with epoxy while the specimen is kept under load, (d) upon hardening of the epoxy the load is removed and the indicated square region is cut out of the specimen, notches are introduced on all four sides of the cut piece, and (f) a wedge is driven through one of the notches at liquid nitrogen temperature to expose the lightly shaded internal surface for microscopy.
Figure 5-6: Load-pin displacement curve of the compact tension specimen tested at a cross-head speed of 500 mm/min, net specimen thickness is 5.4 mm
Figure 5-7: The SEM micrograph of the stopped crack front in the Izod impact test, showing evidence of reverse deformation by touching of rebounding crack flanks

Figure 5-8: The SEM micrograph of the stopped crack front in an Izod impact test recorded from the side view as shown in Figure 5-5. Extensive folding of the flank surface layer and buckling of the elongated cavities are readily discernible
Figure 5-9: The SEM micrographs showing the variations in the morphology of the cavities within the process zone. The location of each micrograph with respect to the crack is also indicated in the schematic of Figure 5-11: (a) the crack environment, (b) the crack tip region of 'intense' deformation, (c) below the crack flank (d) far field ahead of the crack front. Figure 5-5 shows the method followed to expose the cavity morphology around the advancing crack tip.
Figure 5-10: The profile of the advancing crack front in rubber modified polyamide 66 proposed by Huang [2]
Figure 5-11: The schematic representation of the process zone around a crack propagating at steady state. The dark shaded area is the 'intense' process zone which is translated to crack flank surface by the shear and rotation of the cavities upon parting of the material at the crack front. The magnified sketches of the cavity shapes shown in frames b,c,d, correspond to micrographs b,c,d in Figure 5-9.
Figure 5-12: The morphology of the cavities above the upper crack flank. The thickness of highly deformed layer on the flank surfaces with the distinct morphology of rotated and elongated cavities is around 30 μm thick.
Figure 5-13: Schematic rendering of a traveling crack processing the morphology of the cavities in the material 'flowing-by' the propagating crack.
Figure 5-14: The distribution of the local draw ratios in the region ahead of the crack front in the plane of the crack
Chapter 6

Conclusions and Future Work

6.1 Conclusions

The toughening and fracture mechanisms of rubber modified polyamides have been studied in terms of the matrix morphology and the microstructural processes governing the crack growth. To determine the morphological variations in the structure of the matrix, thin films of polyamide 6 sandwiched between rubber films were used as model constructions the interparticle region of rubber modified polyamides. X-ray texture analysis and mechanical testing of films with various thicknesses showed that the hydrogen bonded sheets align parallel to the rubber/polyamide interface in films with thicknesses < 0.15 μm [63].

Based on the thin film observations, a toughening mechanism is proposed based on the local reduction of the flow stress in the interparticle regions where the low slip resistance hydrogen bonded sheets are aligned parallel to the rubber/matrix interface. This local softening is a function of the principal stretch direction relative to the normal to the hydrogen bonded planes of the oriented interparticle regions. In an attempt to provide evidence for such local orientation phenomena, thin films of rubber modified polyamides were examined under TEM. In tough samples, where the particles are closely spaced, the interparticle regions consisted predominantly of lamellae oriented normal to the rubber/matrix interface, bridging particle pairs; while in brittle samples (sparse distribution of particles) such preferentially oriented lamellae
next to the particles constituted only a small portion of lamellae in the interparticle ligament. The local preferred orientation is a consequence of nucleation of the hydrogen bonded sheets near the interface and their rapid growth in a direction normal to them. Thus, for closely spaced particles, the final matrix morphology is dominated by the near interface nucleated lamellae; while for sparse distribution of particles other nucleation sites in the matrix contribute to the crystallization, resulting in a predominantly, randomly oriented matrix in the interparticle ligaments.

Morphological analysis within the stress whitened zone of various tensile dogbone, Izod impact, compact tension, and single notch tension specimens revealed the evolution of the cavitation processes. Stress whitening in brittle blends is mainly due to the debonding of the rubber particles from the matrix. However in tough blends, rubber particles cavitate and form spherical voids under low strains. In the large strain range, the cavities elongate in the direction of the local principal stretch axis while the changes in the width of the cavities remain negligible. Therefore, the rubber particles act as built-in strain gauges indicating the local draw ratio (aspect ratio of the cavities) and direction of the principal stretch axis (direction of the major axis of the cavities). The elongation of the cavities to draw ratios as high as 12 without fracture of the matrix ligaments is facilitated by the initial matrix morphology, namely the preferred orientation of the low slip resistance hydrogen bonded planes parallel to the interface.

The morphology of the cavities within the process zone of deformed compact tension specimens revealed an accurate map of local draw ratios and local direction of the principal stretch axes around an advancing crack. Ahead of the crack front, in the far field, the cavities are spherical; whereas, within a small region around the crack tip they are elongated to draw ratios near ten. Below the crack flanks, the elongated cavities are rotated by $\sim 40^\circ$. Hence, they are aligned nearly parallel to the fracture surface. With depth away from the flanks, the cavities become less elongated and more normal to the distant fracture surface. As a consequence of the rotation of the elongated cavities, contained within the first $\sim 30 \, \mu\text{m}$ beneath the crack flank, the fracture surface undergoes an elastic-plastic buckling process to accommodate the
extra surface generated by the rotation induced at the crack tip. The buckling results in the formation of striations on the fracture surface of tough specimens. In fact, the striations are an indication of the toughening efficiency of a specific blend; only in blends with closely spaced particles (interparticle distance < 3.0 μm, i.e. tough), the initial matrix morphology in the interparticle region facilitates large deformations and the elongation of the cavities by locally lowering the flow stress; upon rotation of these elongated cavities the fracture surface is is required to shorten by compression; hence buckling and the formation of striations follow. Brittle blends do not allow large local deformations, hence no striations are formed on their fracture surfaces.

6.2 Suggested Future Work

Although the local preferred orientation in the interparticle region of tough blends is shown to be affected by the close spacing of particles, a mathematical model is still needed to determine the effect of local softening on the global mechanical properties of the blend. This model would also predict if the elongation of cavities to large draw ratios could be facilitated solely by the initial preferred orientation of the interparticle regions.

Another mechanical model should be constructed to calculate the local draw ratios and the direction of local principal stretch axes around an advancing crack front. This would also help in understanding how the rotation of the elongated cavities take place at the propagating crack front and provide more insight in to the understanding of crack advance in materials with large crack opening angles.

Further experimental work is needed to obtain more accurate measurements of the local draw ratios and direction of principal stretch axes around the advancing crack front. The cryofracturing technique used in this study generates rough surfaces due to the grossly brittle nature of the fracture. Therefore, the cross-section of the cavities are rather irregular and the measured aspect ratios are rough estimates. A cryo-sledge microtome can be used to create flatter surfaces to examine the internal cavities under SEM. A special image analysis technique should provide more accurate
measurements of the aspect ratios of the elongated cavities and the direction of their major axes. Other parameters, such as temperature, strain rate, particle size, and rubber content should also be considered in mapping the distribution of the local draw ratios and direction of principal deformation axes. These data could be used to test the second model mentioned above.

Since the size of the cavities are within the micron range, polarized light can be used to detect the morphology of the cavities. Thin cryotomed slices of the stress whitened zone, containing the crack tip, could be examined under polarized light in transmission mode and the cryo-sledge microtomed surface in reflection mode. The birefringence of the cavities will depend on their relative orientation to the incident polarized light. Hence, color pictures generated by this method would be of use in detecting the variation in the direction of the elongated cavities.

The heat generation ahead of the crack tip discussed in Section 4.3.7 could be verified with an in situ measurement of the temperature at the tip of an advancing crack. Radiation temperature measurements have been used successfully by Weichert and Schönert [95] to detect the heat generation due to adiabatic heating ahead of the crack tip in brittle materials. Similar experimental set-ups should be used to determine the increase in temperature in the process zone of rubber modified polyamides and its functionality with particle size and rubber content. This would be an important aspect of the crack growth process, especially for the development of the model mentioned above.
Appendix A

Image Analysis of Fracture Surface Micrographs

A.1 Image Smoothing

The fracture surface micrographs were scanned in an AppleOne scanner at a resolution of 300 dpi (dots per inches). Scanning converts an image file into a series of integers. Each integer corresponds to one pixel (one dot) in the image. The black color is assigned the integer 255 and the white is assigned the value 0. For the smoothing step, the scanned micrograph is divided into horizontal lines which were smoothed individually. An example of smoothing is shown in Section 4. The following is the fortran code developed to smooth the image.

```
PROGRAM filter

integer i, ii, j, k, temp(17), temp2(3000), x(3000)
integer spiked(3000)
integer smoothed(3000), temp3(3000)
integer xpixels, ypixels, maximum, limit, extrapixels
integer totalpixels, lines, linepixels, begin, end
character filename*7, file11*12, file12*12, file13*12
character file14*12, str*1
```

177
real gfit(3000),gcall(3000),ft(3000)

write(*,*)'Enter filename?:'
read(*,')filename

open(10,file=filename,status='old')
file?1=filename//' .cut'
file12=filename//' .lns'
file13=filename//' .smt'
file14=filename//' .raw'
open(11,file=file11)
open(12,file=file12)
open(13,file=file13)
open(14,file=file14)

ii=0
read(10,*)
str='#'
100 if (str .eq. '#') then
   read(10,')str
   ii=ii+1
   go to 100
end if
rewind(10)
do j=1,ii
   read(10,*)
end do
read(10,*) xpixels,ypixels
read(10,*) maximum

***Write the header of the files

do i=11,14
   write(i,')P2'
   write(i,')# CREATOR: XV Version 3.01 Rev:
   & 3/30/93'
write(i,*), xpixels,ypixels-3
write(i,*), maximum
end do

totalpixels=xpixels*ypixels
lines=((totalpixels)/17)
linepixels=(lines*17)
extrapixels=totalpixels-lines*17

do i=1,lines
   read(10,*)(temp(k), k=1,17)
   if (mod(i,500).eq.0) then
      write(*,*),'Reading now',i,lines
   end if
   do k=1,17
      write(14,'(13)')temp(k)
   end do
end do

read(10,*)(temp(k), k=1,extrapixels)
do i=1,extrapixels
   write(14,'(13)')temp(i)
end do

rewind(14)
do j=1,ii
   read(14,*)
end do
read(14,*)
read(14,*)
do i=1,ypixels-1
   write(*,*),'Calculating now',i,ypixels-1
   do j=1,xpixels
      read(14,*)temp(j)
   end do
   call lsfit(gfit,temp,fit,xpixels,x)
* Get the cut file and save it
  do j=1,xpixels
    if (gfit(j).lt.0) then
      write(11,'(I1)')0
      gfit(j)=0
    else
      gfit(j)=255
      write(11,'(I3)')255
    endif
  end do
* Get the ins file and save it
  call halfspike(gfit,spiked,xpixels)
  call smoothspike(gfit,smoothed,xpixels)
* Get the smt file and save it
  do j=1,xpixels
    if (smoothed(j) .lt. 0) then
      smoothed(j)=0
    else if (smoothed(j) .gt. 255) then
      smoothed(j)=255
    end if
    write(12,*),spiked(j)
    write(13,'(I3) '),smoothed(j)
  end do
  end do

  close(10)
close(11)
close(12)
close(13)
end

SUBROUTINE halfspike(temp2,spiked,xpixels)

integer temp2(*), spiked(*), xpixels
integer indexin, indexout, i, x, zeros, firstzero
do i=1,xpixels
    spiked(i)=255
end do
indexin=1
k=1
102 if (k .lt. (xpixels)) then
   write(*,*)k,xpixels
   call findzero(temp2,xpixels,indexin,indexout,
   &       firstzero)
   call countzeros(temp2,xpixels,zeros,firstzero)
   indexin=indexout+zeros
   do i=firstzero,firstzero+zeros
      spiked(i)=255
   end do
   spiked(firstzero+int(zeros/2.))=0
   k=firstzero+zeros
   go to 102
end if
end

$JBROUTINE findzero(temp2,xpixels,
&       indexin,indexout,firstzero)

integer temp2(*), firstzero, i, indexin, indexout,
&       xpixels

* write(*,*)'In findzero'
i=indexin
100 if(temp2(i) .ne. 0 .and. i .lt. xpixels) then
    i=i+1
    go to 100
end if
firstzero=i
indexout=i
end

SUBROUTINE countzeros(temp2,xpixels, zeros, & firstzero)

integer temp2(*), zeros, firstzero, i, xpixels

* write(*,'%AIn countzeros')
i = firstzero
zeros = 0
101 if(temp2(i).eq. 0 .and. i.lt.xpixels) then
    zeros = zeros + 1
    i = i + 1
    go to 101
end if

end

SUBROUTINE smoothspike(temp2,smoothed,xpixels)

integer temp2(*), smoothed(*), xpixels
integer indexin, indexout, i, k, zeros, firstzero
integer prevzero, prevzeros, pmidblack, pmidwhite
integer midblack, midwhite

indexin = 1
k = 1
prevzero = 0
zeros = 0
pmidblack = 0
pmidwhite = 0

102 if (k .lt. xpixels) then
* write(*, '%Ai induct, totalpixels', indexin, totalpixels)
call findzero(temp2, xpixels, indexin, indexout, & firstzero)
call countzeros(temp2, xpixels, zeros, firstzero)
indexin = indexout + zeros
call smooth(temp2,smoothed,firstzero,zeros,prevzero,
& prevzeros,pmidblack,pmidwhite,midblack,midwhite)
pmidblack=midblack
pmidwhite=midwhite
prevzero=firstzero
prevzeros=zeros
k=indexin
go to ?:02
end if
end

SUBROUTINE smooth(temp2,smoothed,firstzero,zeros,
& prevzero,prevzeros,pmidblack,pmidwhite,midblack,
& midwhite)

integer temp2(*),smoothed(*)
integer firstzero,zeros,prevzero,prevzeros
integer i, j, midblack, midwhite
real slope, pslope, ordone, pordone
integer pmidblack, pmidwhite

midwhite=int((firstzero+prevzero+prevzeros)/2.)
midblack=firstzero+int(zeros/2.)
slope=255./(midwhite-midblack)
pslope=255./(midwhite-pmidblack)
ordone=255.-slope*midwhite
pordone=255.-pslope*midwhite

do i=pmidblack,midwhite
   smoothed(i)=int(pslope*i+pordone)
end do
do i=midwhite,midblack
   smoothed(i)=int(slope*i+ordone)
end do
end

* Least square fit

SUBROUTINE lsfit(gfit,gcall,fit,n,x)

integer i,n
real gcall(*), fit(*), gfit(*), numerator
real denominator, xbar, gbar,D,xsum,gsum
integer x(*),limit,fittotal

xsum=0.
gsum=0.
numerator=0.
denominator=0.
do i=1,n
   x(i)=i
end do
do i=1,n
   xsum=xsum+x(i)
gsum=gsum+gcall(i)
end do
xbar=real(xsum/n)
gbar=real(gsum/n)
do i=1,n
   numerator=numerator+(x(i)−xbar)*gcall(i)
denominator=denominator+((x(i)−xbar)**2)
end do

D=numerator/denominator

do i=1,n
   fit(i)=gbar+D*(x(i)−xbar)
end do
do i=1,n
gfit(i) = gcalls(i) - fit(i)
end do

A.2 Fast Fourier Transforms

Fast Fourier transforms on the scanned and smoothed fracture surface micrographs were applied in order to determine the distribution of the interstriaion distances. The following is the FORTRAN code used to perform the FFTs. Each line constituting the micrographs was transformed separately. The average of the FFTs from each line was then taken to obtain the distribution of striation frequency on the micrographs.

PROGRAM imagefft

integer i, j, n, p, n4, k, xpix, ypix
integer tpxix, mag, size, pinit, n4init, step, total
character answer*1, fname*11
parameter(pinit=12, size=2**pinit, n4init=size/4)
*** size=4096, n4=2048
integer m(pinit+1), x(size)
real r(size), rsum(size/2), ravg(size/2), im(size),
& f(size), c(n4init), s(n4init), realavg(size),
& imavg(size), imsum(size), d(size), gavg(size),
& g(size), gfit(size), gcalls(size), rimavg(size),
& fit(size)
real allg(6000000)

call getfile(mag, dpi, xpix, ypix, tpxix, allg, fname)
call getn(size, pinit, n4init, p, n, n4)
call init(rsum, imsum, x, n)

call tfft(xpix, ypix, x, mag, dpi, allg, n, n4, p,
& g, gcalls, gfit, f, s, c, m, r, im, rsum,
& imsum, ravg, rimavg, imavg, d, fname, fit)
call init(rsum, imsum, x, n)

write(*,*)'Do you want to shift the ffts? y/n?:'
read(*, '(a') answer
if (answer.eq. 'y') then
   call sfft(tpix, step, x, gfit, g, allg, r, im,
   & f, s, c, m, n, n4, p, rsum, imsum, ravg,
   & rimavg, imavg, d,
   & dpi, mag, fname, fit)
end if

close(10)
close(11)
end

SUBROUTINE init(rsum, imsum, x, n)

integer i, n, size
real rsum(*), imsum(*)
integer x(*)

do i=1, n/2
   rsum(i)=0.
   imsum(i)=0.
end do
do i=1, n
   x(i)=i
end do
end

SUBROUTINE getn(size, pinit, n4init, p, n, n4)

integer size, pinit, n4init, i, p, n, n4
character answer*1
real pp
n = size
p = pinit
n4 = n4init

write(*,*) 'HELLO, WAKE UP PLEASE!!!!!!'
write(*,*) 'The value of n is currently set at: ', size
write(*,*) 'Would you like to change it? yes/no:'
read(*, '(a)') answer
100 if (answer .eq. 'y') then
    write(*,*) 'Enter the value of n?'
    read(*,*) i
    pp = (log(real(i))/log(2.))
    if ( real(pp - int(pp)) .gt. 0. ) then
        write(*,*) 'The value of n you entered is invalid!'
        go to 100
    end if
    p = int(log(real(i))/log(2.))
    n = i
    n4 = n/4
end if
end

SUBROUTINE getfile(mag, dpi, xpix, ypix, tpix, allg, fname)

character fname*11, str*1
integer mag, dpi, xpix, ypix, tpix
real allg(*)

str = 'n'
do while(str .eq. 'n')
    write(*,*) 'Enter filename?'
    read(*, '(a)') fname
    write(*,*) 'Enter the magnification'
    read(*,*) mag
    write(*,*) 'Enter the scanning resolution in dpi'
    read(*,*) dpi
write(*,*)'THE VALUES YOU ENTERED ARE AS FOLLOWS:'
write(*,*)'Magnification:',mag,' and Dpi:',dpi
write(*,*)'Accept and continue?? y/n?'
read(*,')(a)'str
end do

open(10,file=fname)
i=0
read(10,*)
str='#
300 if (str.eq. '##') then
   read(10,’(a)’)str
   i=i+1
   go to 300
end if
rewind(10)
do j=1,i
   read(10,*)
end do

read(10,*) xpix,ypix
read(10,*)

tpix=xpix*(ypix-1)
write(*,*)'Reading the image file. Be patient...'
do i=1,tpix
   read(10,*)allg(i)
end do
close(10)
end

SUBROUTINE tfft(xpix,ypix,x,mag,dpi,allg,n,n4,p,
& g,gcall,gfit,f,s,c,m,r,im,rsum,
& imsum,ravg,rimavg,imavg,d,fname,fit)
real f(*), r(*), im(*), s(*), c(*), rsum(*)
real d(*), meand
real imsum(*), allg(*), ravg(*), imavg(*), rimavg(*)
integer m(*), x(*), steps
integer xpix, ypix, size
real g(*), gcall(*), gfit(*), slope, fit(*)
integer i, j, ii, iii, jj, n, n4, p, dpi, mag
character str*80, fname*7

steps=0

do j=1, ypix-1
    write(5,*) 'No shifting', j, (ypix-1)
do i=1, xpix
    g(i)=allg(i+(j-1)*xpix)
end do

do i=1, int(xpix/n)
do ii=(n*(i-1)+1), (n*i)
    gcall(ii-(n*(i-1)+2))=g(ii)
end do

call lsfit(gfit, gcall, fit, n, x, slope)
if(j .eq. 1) then
    open(17, file='profile')
do iii=1, n
    write(17,*) iii, gcall(iii), gfit(iii)
end do
    close(17)
end if

call subaverage(g, gavg, n)
call fft(gfit, r, im, f, s, c, m, n, n4, p)
steps=steps+1

do jj=1, n/2
    rsum(jj)=rsum(jj)+r(jj)
    imsum(jj)=imsum(jj)+im(jj)
end do
end do
end do

call getavg(steps, ravg, rsum, imavg, imsum,
& rimavg,n)
str='noshift'
call writer1(d,n,mag,dpi,str,ravg,imavg,rimavg,fname)
call findmax(rimavg,d,n,x,meand)
call writer2(fname,xpix,ypix,mag,dpi,step,str,
& steps,meand,n)
end

SUBROUTINE sft(tpix,step,x,gfit,g,allg,r,im,
& f,s,c,m,n,n4,p,rsum,imsum,ravg,
& rimavg,imavg,d,dpi,mag,fname,fit)

integer i1,i2,tpix,steps,step,j,n,n4
integer p, j, dpi, mag
integer x(*), m(*)
real g(*), allg(*), gfit(*), r(*), im(*), f(*)
real s(*), c(*), rsum(*), imsum(*), ravg(*), imavg(*)
real rimavg(*), d(*), slope, meand, fit(*)
character str*80, fname*8

write(*,*)'Enter the step size:'
read(*,*)step
i1=0
i2=0
steps=0
200 if (i1 .lt. tpix) then
   steps=steps+1
   i1=i1+step
   i2=i2+1
write(*,*)'Shifting',steps,i1,tpix
   do j=1,n
      g(j)=allg(j+step*(i2-1))
   end do
   call lsfit(gfit,g,fit,n,x,slope)
   call fft(gfit,r,im,f,s,c,m,n,n4,p)
   do jj=1,n/2

170
180
190
200
rsum(jj)=rsum(jj)+r(jj)
imsum(jj)=imsum(jj)+im(jj)
end do
go to 200
end if
write(*,*)rsum(2)
call getavg(steps,ravg,rsum,imavg,imsum,
& rimavg,n)
write(*,*)ravg(2)
str='shift'
call writer1(d,n,mag,dpi,str,ravg,imavg,rimavg,fname)
call findmax(rimavg,d,n,x,meand)
call writer2(fname,xpix,ypix,mag,dpi,step,str,
& steps,meand,n)
end

SUBROUTINE writer1(d,n,mag,dpi,str,ravg,imavg,
& rimavg,fname)

integer i, n, dpi, mag
real d(*), ravg(*), imavg(*), rimavg(*)
character str*80, fname*11, sfx*9, temp*16

if (str(1:2) .eq. 'sh') then
   sfx='shift'
else
   sfx='noshift'
end if
temp=fname(1:7)//sfx
open(12,file=temp)
do i=1,n/2
d(i)=real(2.54/dpi)*n*real(i-1)**(-1)*10000/mag
end do
do i=1,n/2
   write(12,*),i,d(i),ravg(i),imavg(i),rimavg(i)
end do
close(12)
end

SUBROUTINE writer2(fname,xpix,ypix,mag,dpi,step,str,
& steps,meand,n)

integer xpix,ypix,mag,dpi,step,steps,n
real meand
character sfx*5, fname*11, temp*12, str*80

sfx=' .dat'
temp=fname(1:7)//sfx
open(13,file=temp)
if (str(1:2).eq. 'sh') then
  write(13,'(a,f12.10)'), 'SHIFTED THE DATA AT STEP SIZE:', step
  write(13,'(a)'),
  write(13,'(a)'), 'NO. OF LINES AVERAGED (SHIFT):', steps
  write(13,'(a)'),
  write(13,'(a)'), 'MEAN SPACING (SHIFT):', meand
else
  write(13,'(a)'), fname
  write(13,'(a)'),
  write(13,'(a)'),
  write(13,'(a)'), 'XPXELS', xpix
  write(13,'(a)'),
  write(13,'(a)'), 'YPXELS', ypix
  write(13,'(a)'),
  write(13,'(a)'), 'MAGNIFICATION:', mag
  write(13,'(a)'),
  write(13,'(a)'), 'SCANNING DPI:', dpi
  write(13,'(a)'),
  write(13,'(a)'), 'THE VALUE OF N WAS:', n
  write(13,'(a)'),
  write(13,'(a)'), 'NO OF LINES AVERAGED (NO-SHIFT):', steps
  write(13,'(a)'),
  write(13,'(a)'), 'MEAN SPACING (NO-SHIFT):', meand

240
250
260
270
write(13,*)

end if

end

SUBROUTINE lsfit(gfit, gcall, fit, n, x, D)

integer i, n
real gcall(*), fit(*), gfit(*), numerator,
& denominator, xbar, gbar, D, xsum, gsum
integer x(*)

xsum=0.
gsum=0.
numerator=0.
denominator=0.

do i=1, n
   xsum=xsum+x(i)
   gsum=gsum+gcall(i)
end do
xbar=real(xsum/n)
gbar=real(gsum/n)
do i=1, n
   numerator=numerator+(x(i)-xbar)*gcall(i)
   denominator=denominator+((x(i)-xbar)**2)
end do

D=numerator/denominator

do i=1, n
   fit(i)=gbar+D*(x(i)-xbar)
end do

do i=1, n
gfit(i)=gcall(i)−fit(i)
end do

end

SUBROUTINE getavg(total,ravg,rsum,imavg,
& imsum,rimavg,n)

integer i,total,n
real ravg(*),rsum(*),imavg(*),imsum(*),rimavg(*)

do i=1,n/2
  ravg(i)=rsum(i)/total
  imavg(i)=imsum(i)/total
  rimavg(i)=sqrt(ravg(i)**2+imavg(i)**2)/total
end do
end

SUBROUTINE subaverage(g,gavg,n)

integer n,i
real g(*), gavg(*), sum, avg

sum=0.

do i=1,n
  sum=sum+g(i)
end do
avg=real(sum/n)

do i=1,n
  gavg(i)=g(i)−avg
end do
end

SUBROUTINE findmax(rimavg,d,n,x,meand)
real rimavg(*), d(*), fit(4096), slope, fitted(4096)
real totint, inti(4096), temp(4096), tempfit(4096)
integer i, max, x(*), n, m, ni
real meand

write(*,*)'Where do you want to start the fitting?:'
read(*,*)m
totint=0.
doi=m,n/2
  temp(i-(m-1))=rimavg(i)
  x(i-(m-1))=i
end do

ni=int(n/2+1-m)
call lsfit(tempfit,temp,fit,ni,x,slope)
doi=m,n/2
  fitted(i)=fit(i-m+1)
end do

coorigin=fitted(m+1)-slope*(m+1)
do i=1,n
  tempfit(i)=rimavg(i)-(slope*i+coorigin)
end do


doi=1,m-1
  totint=totint+(tempfit(i+1)+tempfit(i))*0.5
  inti(i)=totint
end do

i=1
do 100 while(inti(i) .lt. (0.5*totint))
  max=i
  i=i+1
100 continue

meand=d(i)
end

SUBROUTINE fft(g,r,im,f,s,c,m,n,n4,p)
integer n,n4,p

real f(*), g(*), r(*), im(*)
real s(*), c(*), pi, w, a, y, z, b, b1
integer m(*)
integer d, e, i, j, k, l
integer p0, p7, q, s1, s0, s2, u

p7=p-1
do i=1,n
   f(i)=g(i)
c   f(i)=real(i)
end do

*** Get powers of 2
m(1)=1
m(2)=2
do i=2,p
   m(i+1)=m(i)+m(i)
end do

*** Get sin(x) and cos(x)
pi=3.14159265
w=2.*pi/u
a=0.
do i=1,n4
   a=a+w
   s(i)=sin(a)
   c(i)=cos(a)
end do

*** Permute
j=0
i=0
20  i=i+1
p0=p+1
30  p0=p0-1
   j=j-m(p0)
   if (j.ge.0) goto 30
   j=j+m(p0+1)
   if (i.le.j) goto 20
   a=f(i+1)
   f(i+1)=f(j+1)
   f(j+1)=a
   if (i.lt.n-2) goto 20

*** Get 2-element DHTs
   do i=1,n-1,2
      a=f(i)+f(i+1)
      w=f(i)-f(i+1)
      f(i)=a
      f(i+1)=w
   end do
   if (p.eq.1) goto 40

*** Get 4-element DHTs
   do i=1,n-3,4
      a=f(i)+f(i+2)
      w=f(i+1)+f(i+3)
      y=f(i)-f(i+2)
      z=f(i+1)-f(i+3)
      f(i)=a
      f(i+1)=w
      f(i+2)=y
      f(i+3)=z
   end do
   if (p.eq.2) goto 40

*** Stages 3, 4, ...
   u=p7
   s1=4
\[
\text{do } l=2, p7 \\
s2=s1+s1 \\
u=u-1 \\
s0=m(u) \\
\text{do } q=1, n, s2 \\
i=q \\
d=i+s1 \\
a=f(i)+f(d) \\
w=f(i)-f(d) \\
f(i)=a \\
f(d)=w \\
k=d-1 \\
\text{do } j=s0, n4, s0 \\
i=i+1 \\
d=i+s1 \\
e=k+s1 \\
y=f(d)*c(j)+f(e)*s(j) \\
z=f(d)*s(j)-f(e)*c(j) \\
a=f(i)+y \\
w=f(i)-y \\
b=f(k)+z \\
b1=f(k)-z \\
f(i)=a \\
f(d)=w \\
f(k)=b \\
f(e)=b1 \\
k=k-1 \\
\text{end do} \\
e=k+s2 \\
\text{end do} \\
s1=s2 \\
\text{end do} \\
u=\text{real}(n) \\
r(1)=f(1)+f(1)/(2.*u) \\
\text{im}(1)=0.
\]
do i=2,n
    b=f(n-i+2)
    r(i)=(f(i)+b)/u
    im(i)=(f(i)-b)/u
end do
40   continue

end
Appendix B

Geometrical Properties of the Buckling Surface Layer, and the Substrate Plucking Stiffness

To determine the properties related to the microstructure we first idealize the microstructure in two dimensional form as a hexagonally arranged set of cylindrical rubber rods of diameter $d$, and that the large strain extension is in plane strain resulting in a local principal extension ratio of $\lambda$, elongating the surrounding of a cavitated rubber rod as a slot of thickness $d$ and length $b = \lambda d$ as depicted in Figure B-2. In this figure for geometrical clarity we show the rubber particles intact and the cavity having been formed by debonding. The fact that the cavity will upon stretching retain its initial thickness is established from direct observation and relates to the crystallite morphology of the matrix around the particle which we have discussed in detail earlier (see Muratoğlu et al. [3]).

Noting that the initial volume fraction of the rubbery component is

$$c = \frac{\sqrt{3}\pi}{6} \left( \frac{d}{a} \right)^2,$$  \hspace{1cm} (B.1)

we obtain by simple geometrical considerations of conservation of matrix volume the
thickness $t$ of the matrix ligaments depicted in Figure B-2 as.

$$t = \frac{\pi d (1 - c)}{4 \lambda \frac{c}{c}}$$  \hspace{1cm} (B.2)

Then, the required substrate plucking resistance $k$, (foundation stiffness) can be obtained with the help of Figure B-3 with similar ease from simple beam theory as:

$$k = \frac{(2q/\lambda d)}{2\delta}$$  \hspace{1cm} (B.3)

$$\delta = \frac{4q}{E} \left( \frac{\lambda d}{t} \right)^3$$  \hspace{1cm} (B.4)

where the numerator of Equation B.4 is the average plucking stress and $2\delta$ the corresponding plucking displacement as shown in Figure B-3. This gives immediately.

$$k = \frac{E}{4\lambda^4 d} \left( \frac{\pi}{4\lambda} \frac{(1 - c)}{c} \right)^3$$  \hspace{1cm} (B.5)

The effective in-plane Young's modulus $E'$ or more appropriately the tensile or compressive strain hardening rate $(dY/de)'$ are by a direct rule of mixtures, appropriate for the in-plane direction

$$E' = c'E \quad \Rightarrow \quad (dY/de)' = c'(dY/de)$$  \hspace{1cm} (B.6)

where, $c'$ the material volume fraction in the stretched state, that can be given as,

$$c' = \frac{2t}{a'} = \frac{1}{1 + \frac{4\lambda}{\pi} \frac{c}{(1 - c)}},$$  \hspace{1cm} (B.7)

giving

$$E' = \frac{E}{1 + \frac{4\lambda}{\pi} \frac{c}{(1 - c)}} \quad \Rightarrow \quad (dY/de)' = \frac{(dY/de)}{1 + \frac{4\lambda}{\pi} \frac{c}{(1 - c)}}.$$  \hspace{1cm} (B.8)

Moreover, by similar arguments the in-plane effective plastic resistance load $P$ (per
unit thickness) is obtained as

\[ P = Yc'h = \frac{hY}{1 + \frac{4\lambda}{\pi} \frac{c}{(1-c)}}. \]  

(B.9)
Figure B-1: Schematic of the buckling of the surface layer of thickness $h$ that results in the fracture surface striations. The variables used in the model are denoted in the figure.
Figure B-2: Schematic of six particles hexagonally packed before and after large strain deformation below the crack flank. The elongated cavities would be aligned nearly parallel to the fracture surface. The rubber particles are drawn in the deformed morphology as uncavitated to indicate that the change in the width of the specimen is negligible as explained in Reference [3].
Figure B-3: The matrix ligaments around the elongated cavities shown at the top of this schematic were treated as an elastic beam to estimate the plucking resistance of the porous substrate.
Appendix C

Diffusion of Staining Agent in Polyamide: Forward Recoil Experiments

To determine the diffusion behavior and compositional distribution of the staining agent, phosphotungstic acid (PTA), in polyamides (PA), thin films of PA6 on a silicon substrate were prepared via the spin coating method described in Section 2.2.1. The films were annealed in a vacuum chamber immersed in an oil bath at 225 °C for 4 hours and 180 °C for 2 hours to eliminate the spin-induced morphology of the crystals. The annealed films were then immersed in an aqueous solution of 2% benzyl alcohol (BzOH) and 2% PTA. The BzOH swells the PA films and accelerates the diffusion [65]. The diffusion time was varied from 1-40 minutes. Forward Recoil Energy spectroscopy (FRES) experiments were carried at Harvard RBS Laboratory to determine the concentration profile of the staining agent.

Figure C-1 represents the concentration profile of the diffusant in the polyamide film. The horizontal axis, channel, corresponds to the thickness of the film, while the vertical axis, yield, is directly proportional to the amount of diffusant. Although the diffusant (staining agent) was phosphotungstic acid, no phosphorus peak was noted in the overall profile. Only the tungsten, peak as shown in Figure C-1, was present indicating that the diffusant in the PTA staining of polyamides is WO₃.
As the concentration profile of the tungsten oxide indicates (see Figure C-1), initially the diffusion is either very rapid or a thin deposit of the WO₃ forms on the surface. This could be due to the crystallization of an oxide layer. If this is the case, the surface crystals can be detected in a TEM. Figure C-2 shows a micrograph of a thin film left in the staining agent for 24 hours. The surface crystals are readily discernible. However, after 10 minutes in the staining solution these crystals are not present on the surface of the film (see Figure 3-2). Hence, the surface peak that develops in short times is a result of fast diffusion. As seen in Figure C-1 the diffusant reaches the other end of the thin film after 5 minutes in the staining solution. Eventually, if the film is allowed enough time in the staining solution, the concentration will become uniform. However, long exposures of the film to the staining solution results in the formation of surface crystals that are not desirable for microscopy.

Uniform distribution of the stain throughout the film is crucial for microscopy; otherwise, the morphological information recorded in a TEM will be more representative of the surface and not the bulk of the film. We carried out a set of experiments to see if the surface peak could somehow be eliminated. To this end, we placed the stained films (after 30 minutes in the staining solution) in an aqueous solution of 2 vol. % BzOH (without PTA) for 40 minutes to leach out the high concentration surface layer. Figure C-3 shows the profiles before and after the BzOH solution. In 30 minutes the stain penetrated the film forming the surface peak. After 40 minutes in the BzOH solution the surface peak is clearly removed.
Figure C-1: Concentration profile of WO$_3$ diffused in 1 $\mu$m thick polyamide thin film at 30 °C. The diffusion time from the bottom curve to the top is 1, 5, 10, and 20 minutes.
Figure C-2: The micrograph of a rubber modified PA6 stained with PTA for 24 hours. The hexagonal structures are $\text{WO}_3$ crystals deposited on the surface of the film.
Figure C-3: Concentration profile of WO₃ diffused in 1 μm thick polyamide thin film at room temperature. The solid curve represents the WO₃ profile after 30 minutes in the staining solution. The dashed curve is the WO₃ profile of the thin film that was soaked in the staining solution for 30 minutes followed by 40 minutes in 2 vol. % BzOH (to leach out the surface peak)
Bibliography


