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The mechanical behavior and deformation morphology of rubber-modified polypropylene.

Thomas David Juska

University of Massachusetts Amherst

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THE MECHANICAL BEHAVIOR AND DEFORMATION MORPHOLOGY OF RUBBER-MODIFIED POLYPROPYLENE

A Thesis Presented
By
Thomas David Juska

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

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Department of Polymer Science and Engineering
THE MECHANICAL BEHAVIOR AND DEFORMATION
MORPHOLOGY OF RUBBER-MODIFIED POLYPROPYLENE

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CHAPTER I

INTRODUCTION

Industry has found practical application of most inexpensive bulk homopolymers. As new polymers were developed, new uses were found. However, it has become apparent that few new and potentially useful polymers will be synthesized, save for polymers with speciality application, because the range of possibilities has already largely been explored. Since the demand for new and improved properties remains, new techniques for achieving them must be developed.

A widely-used and successful technique for obtaining new and useful properties from existing polymers is to form a heterogeneous mixture of two or more materials (1). The properties of the composite will reflect the properties of the components. Necessarily, some of the composite properties will be worse than those of the homopolymer matrix, but advantageous consequences of the system heterogeneity often result.

One of the first commercially successful polymer composites resulted from the need to improve the impact characteristics of glassy polymers. High impact polystyrene (HIPS) was accomplished by incorporating rubber domains with the glassy polystyrene matrix (2). It was believed that the dispersed rubber phase would absorb strain energy through elastic deformation, and
allow larger strains at break by intercepting growing cracks. Tensile-impact tests on HIPS confirmed that it could absorb more energy and reach larger strains before fracture than unmodified polystyrene. However, after the development of the osmium staining technique allowed microscopists to image the rubber domains in the polystyrene matrix, it was concluded that most of the absorbed energy and increased strain occurred in the matrix phase (2). The rubber domains were found to serve as stress concentration sites which initiated crazes in the matrix. The nucleation and growth of numerous crazes was then recognized as the source of the improvement in impact characteristics (2).

Methods of increasing the impact resistance of brittle polymers have been applied to other systems, and as a result there now exist commercial grades of impact resistant polyvinyl chloride, polymethylmethacrylate, polycarbonate, polysulfone, polyphenylene oxide, and polypropylene (2).

Polymeric glasses such as polystyrene are brittle at all strain rates and use temperatures. The semicrystalline polymer isotactic polypropylene is not. However, polypropylene is brittle at high strain rates and at temperatures below its 0°C glass transition. Impact resistant polypropylene would be advantageous for these use conditions.

This investigation concerns the mechanical properties and deformation morphology of rubber-modified polypropylene. The systems tested include externally compounded blends of poly-
propylene with Exxon ethylene/propylene rubber (EPR), and in situ blends of polypropylene with propylene-ethylene comonomer. Samples were supplied by Hercules Incorporated in the form of injection-molded ASTM tensile bars. The system parameters which were varied include rubber concentration, ethylene content of the EPR used in the blend samples, and the molecular weight of the polypropylene used as the matrix in the blends. A description of the systems studied appeared in Table 1.

I.1. Deformation Mechanisms in Polypropylene

The deformation mechanisms which occur in rubber-modified polypropylene, excluding elastic deformation of the rubber, are those of homopolymer polypropylene. In order to understand the effect of the rubber inclusions, the deformation behavior of the homopolymer matrix must be understood.

Some excellent work has been done in this area, especially in a series of papers by Peterlin and Balta-Calleja \((3-6)\). A brief summary of their conclusions relevant to this study will be reviewed here (i.e., the observed morphological changes which occur in polypropylene during uniaxial tensile deformation at a constant elongation rate.)

Since the crystalline phase of polypropylene forms a nearly continuous substructure, the initial elongation of polypropylene must deform this substructure, and the behavior at very small
A description of the polypropylene systems studied. The blends have different vistalons as the rubber component, but it will be shown that characteristics of the deformation are relatively insensitive to the rubber phase chemistry.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Description</th>
<th>Melt Flow Rate (g/10 min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(L)</td>
<td>Low MW homopolymer polypropylene</td>
<td>12</td>
</tr>
<tr>
<td>PP(M)</td>
<td>Medium MW homopolymer polypropylene</td>
<td>4</td>
</tr>
<tr>
<td>PP(H)</td>
<td>High MW homopolymer polypropylene</td>
<td>0.8</td>
</tr>
<tr>
<td>C/12</td>
<td>In situ Copolymer (12% E/P)</td>
<td></td>
</tr>
<tr>
<td>C/35</td>
<td>In situ Copolymer (35% E/P)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PP-EPR (Vistalon) Blend Compositions (%)</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(L)</td>
<td>PP(H)</td>
</tr>
<tr>
<td>B-1</td>
<td>12</td>
</tr>
<tr>
<td>B-2</td>
<td>24</td>
</tr>
<tr>
<td>B-3</td>
<td>24</td>
</tr>
<tr>
<td>B-4</td>
<td>12</td>
</tr>
<tr>
<td>B-5</td>
<td>24</td>
</tr>
<tr>
<td>B-6</td>
<td>12</td>
</tr>
<tr>
<td>B-7</td>
<td>12</td>
</tr>
<tr>
<td>B-8</td>
<td>24</td>
</tr>
</tbody>
</table>
strains (<1%) can be described as elastic. At strains greater than about 1%, the composite (amorphous plus crystalline) modulus decreases, and a sudden load drop occurs if the cross-head motion is stopped. This behavior suggests a viscous contribution to the load during deformation, even at very small strains. This (pre-yield) deformation is recoverable at no loss of properties, so it can be described as viscoelastic. The most important contribution to viscoelastic strain appears to be motion of the lamellae. The viscous forces probably result when folded-chain lamellae are displaced through resisting amorphous interlayers.

Three types of lamellae motion are observed. Those lamellae oriented perpendicularly to the draw axis increase their separation. Evidence for lamellae separation is the increase in observed long spacing of these lamellae during elongation, as measured by SAXS (6). Peterlin and Balta-Calleja note that this deformation behavior must increase the volume of the sample (6). However, since only a small fraction of the lamellae will be oriented perpendicularly to the axis of draw, this volume increase will be small, and is therefore neglected in subsequent interpretation of the volume strain behavior of polypropylene systems.

The lamellae oriented parallel to the draw direction show a decrease in long period with elongation, indicating that they move closer together with the lateral strain resulting in cross-sectional area reduction. Lamellae oriented diagonally to the
draw axis rotate toward the draw direction with no change in long spacing. This behavior was concluded from SAXS studies, where the intensity maxima from these lamellae move towards the equator (6), and is supported by birefringence studies (7), where the average birefringence decreases initially with elongation. Figure 1 shows a schematic of the several types of lamellar displacement.

When the tensile stress (or the shear component of the tensile stress) is sufficient, plastic strain occurs. The exact mechanism of plastic strain is not known, but it apparently involves fracture of the lamellae into folded-chain (mosaic) blocks, accompanied by chain unfolding and microfibril formation (6). Localized plastic zones take the form of crazes (see figure 2) or shear zones (2). The formation of crazes results in large local volume strains, while plastic deformation in shear zones does not cavitate the matrix. The transformation to the fibrous state results in considerable plastic strain; an average value of 5 or more is reasonable (see section VI.1).
Figure 1. Schematic diagram of the pre-yield deformation of stacked parallel lamellae with three different orientations. Changes in fold period (L) from the undeformed value ($L_0$) are indicated. After Peterlin (6).
Figure 2. Crazes (labeled C) in homopolymer polypropylene matrix (M). This is a view away from the neck. Crazes are propagating normal to the draw direction, which is vertical. The bar is 1 μm.
CHAPTER II

EXPERIMENTAL PROCEDURE

II.1. Morphological Characterization

Morphological characterization employed an ETEC Scanning Electron Microscope. Scanning electron microscopy, SEM, is a useful tool for investigating the initial and deformation morphologies of filled plastics.

Characterization of the initial morphology of the polypropylene systems consists of an approximate measurement of the average rubber particle radius and an estimate of the distribution of size within each system. This argument assumes that the polypropylene phase has identical properties in all systems. Thus the mechanical properties of the blend systems are expected to be determined by the characteristics of the dispersed rubber phase.

Treating the polypropylene phase as equivalent in all systems is a simplifying assumption which should be justified. Polypropylene is reported to crystallize into folded chain lamellae, which grow radially from a central nucleus until impingement with other growth surfaces occurs (forming spherulite boundaries). Stacks of lamellae exist at all orientations with respect to an arbitrary direction such as the draw axis. Optical microscopy was used to image thin films
of the homopolymer. When viewed through crossed polars, the spherulitic morphology was evident, as well as curved spherulite boundaries indicating homogeneous nucleation. Optical micrographs of the two in situ copolymers, samples C/12 and C/35, did not show spherulites. If crystallization of the polypropylene phase is nucleated at rubber domain surfaces, the crystalline regions would not have spherical symmetry about a central nucleus, thus spherulites would not be imaged through crossed polars. However, essential building blocks should still be present. One would expect stacks of lamellae at all orientations, and impingement fronts of growing crystalline regions. A DSC study revealed that the degree of crystallinity of the polypropylene phase (\( \chi \) in Table 2) was about 50 weight percent in each system.

It will be demonstrated that the blends have widely varying properties. The differences will be interpreted as due to differences in the rubber phase characteristics (particle size and size distribution). The assumption that the polypropylene matrix has equivalent properties should at least be true of the blend series, yet the properties of the blends vary. It is the characteristics of the dispersed rubber phase which determine the properties of impact modified polypropylene.

In light of this, characteristics of the dispersed rubber phase must be determined. Rubber particle sizes were measured from micrographs of fracture surfaces of previously undeformed
TABLE 2

The data obtained on rubber-modified PP. The last column is the yield strain, $\varepsilon_y$, measured at a strain rate of .01 (sec)$^{-1}$. The values for B-2, B-4, B-6, and B-8 are approximate, because yielding is not a sudden process in these systems.

<table>
<thead>
<tr>
<th>System</th>
<th>$&lt;r&gt;$ (µm)</th>
<th>Distribution</th>
<th>$N/V$(µm)$^{-3}$</th>
<th>$\chi$</th>
<th>$d/d\varepsilon(\Delta V/V_0)$</th>
<th>$\varepsilon_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP(M)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>.48</td>
<td>.70</td>
<td>.09</td>
</tr>
<tr>
<td>C/12</td>
<td>0.5</td>
<td>broad</td>
<td>0.23</td>
<td>.49</td>
<td>.58</td>
<td>.10</td>
</tr>
<tr>
<td>C/35</td>
<td>0.9</td>
<td>broad</td>
<td>0.11</td>
<td>.50</td>
<td>.74</td>
<td>0.07</td>
</tr>
<tr>
<td>B-1</td>
<td>0.6</td>
<td>broad</td>
<td>0.13</td>
<td>.64</td>
<td>.09</td>
<td></td>
</tr>
<tr>
<td>B-2</td>
<td>0.3</td>
<td>narrow</td>
<td>2.12</td>
<td>.10</td>
<td>~0.25</td>
<td></td>
</tr>
<tr>
<td>B-3</td>
<td>0.6</td>
<td>broad</td>
<td>0.26</td>
<td>.42</td>
<td>.10</td>
<td></td>
</tr>
<tr>
<td>B-4</td>
<td>0.3</td>
<td>narrow</td>
<td>1.06</td>
<td>.20</td>
<td>~0.20</td>
<td></td>
</tr>
<tr>
<td>B-5</td>
<td>0.6</td>
<td>broad</td>
<td>0.26</td>
<td>.60</td>
<td>.09</td>
<td></td>
</tr>
<tr>
<td>B-6</td>
<td>0.3</td>
<td>narrow</td>
<td>1.06</td>
<td>.14</td>
<td>~0.20</td>
<td></td>
</tr>
<tr>
<td>B-7</td>
<td>0.6</td>
<td>broad</td>
<td>0.13</td>
<td>.66</td>
<td>.09</td>
<td></td>
</tr>
<tr>
<td>B-8</td>
<td>0.3</td>
<td>narrow</td>
<td>2.12</td>
<td>.10</td>
<td>~0.25</td>
<td></td>
</tr>
</tbody>
</table>
material. The samples were notched, cooled in liquid nitrogen, and broken quickly in flexure. Brittle fracture with minimal plastic damage was accomplished in this manner.

Rubber particles in the blend systems are apparently not well anchored to the matrix, as the majority of the included domains debond during fracture, leaving a pit-like vacancy. The vacancies are consistently smaller than remaining protruding domains, so these vacancies were not used in a domain size measurement. The sizes were measured from the few domains appearing on each micrograph which did not debond during fracture. The values from several micrographs were averaged, to arrive at \( <r > \).

Other problems occurred in rubber particle size measurement. Sometimes rubber particles are clearly not spherical, and do not have circular cross-sections. It is not known if an embedded particle is revealing its largest diameter. Also, it is not known if particle debonding during fracture is a random process or if it is size dependent. For these reasons, the rubber particle size determined for each system is necessarily approximate.

Deformation morphologies of polypropylene and rubber modified systems were also investigated with SEM. As-received samples were elongated until a neck formed and propagated. A region of sample at the transition between the necked zone (fibrous morphology) and the undeformed zone (folded-chain lamellae) was removed. Fracture was accomplished as before
to minimize morphological changes occurring during fracture.

The fracture surface obtained was parallel to the draw direction, so that changes in the morphology could be observed as they occurred during the transformation from folded-chain lamellae to oriented fibrils. Figure 3 illustrates this technique of deformation morphology characterization, and Figure 4 shows a low magnification view of the transition zone in polypropylene. With this technique, deformation morphology as a function of strain (as a function of position in the transition zone) can be investigated for a given rubber modified system with the observation of only one sample.

II.2. **Volume Change Measurement**

A characteristic of crazes is their high void content, as clearly shown in Figure 13. Volume increase measurements can assess the importance of the craze formation and growth process to the overall plastic strain. Measurement of the volume increase of the systems studied was accomplished with a gas dilatometer (8).

The gas dilatometer was designed for simultaneous and continuous measurement of the volume change (craze content) and the stress-strain behavior of materials in tensile bar form. The instrument has an aluminum body with two cavities, a test cavity and a reference cavity at constant pressure. A hinged plexiglass door with an O-ring seal and swivel locks provides
Figure 3. A schematic of the technique for achieving fracture surfaces parallel to the draw direction, useful in craze and transition zone imaging. (a) A section is cut out of a necked sample, containing undeformed material, the transition zone, and part of the neck. (b) The section is razor notched along the draw axis, and (c) clamped in a vise and cooled to liquid $N_2$ temperatures. Tapping the exposed half of the section results in brittle fracture, shown in (d).
Figure 4. The transition zone in homopolymer polypropylene. The fibrous morphology is evident at F, where the neck begins, while regions M are much less drawn. The draw direction is vertical. The bar is 10 μm.
access to the test cavity, where the sample is fitted into upper and lower specimen grips. The grips are mounted on precision machined rods which pass out of the body through a bushing and seal. The upper rod is connected to a force transducer. The lower rod is connected to an Instron crosshead. As the lower rod leaves the test cavity to elongate the specimen, an identical rod is introduced into the test cavity to maintain the volume. The instrument is frequently tested without a sample to insure that the measured volume change is only the volume change of the sample. The test cavity is separated from the reference cavity by a pressure transducer. A change in volume of the sample during elongation is reflected in an equal but opposite change in air volume in the test chamber, resulting in a pressure difference between the test and reference cavities. The measured pressure difference is related to volume change with a piston micrometer, which changes the volume of the test cavity a known amount and causes a corresponding pressure difference.

Use of the dilatometer to measure volume increase has some drawbacks. Since volume change is related to a pressure difference, any effect which changes the air pressure will affect the measurement. For example, heat is evolved during plastic deformation. The evolved heat increases the temperature, thus the pressure, of the air in the test cavity. Also, systems which cavitate extensively can become open-celled. The air in
the test cavity fills the interconnected voids and reduces the measured pressure. These effects can be reduced by coating the samples with a layer of vacuum grease. The grease slows down heat conduction from the sample to the air in the test cavity, and prevents the gas from filling vacuoles.

A limitation of our gas dilatometer is that samples in standard tensile bar form can only be elongated to 35-40% strain.

II.3. Mechanical Testing

The stress-strain behavior of the polypropylene systems was measured at strain rates of $10^{-3}$, $10^{-2}$, $10^{-1}$, $10^0$, and $10^1$ (sec)$^{-1}$ with an Instron servohydraulic materials tester equipped with an X-Y chart recorder. Data taken at strain rates of $10^0$ and $10^1$ (sec)$^{-1}$ were too rapid to record on the chart recorder, so the load response was measured with an oscilloscope by photographing the output with high speed film.

The as-received (injection molded) tensile bars developed a neck shortly after yielding, in all cases, at the same end of the tensile specimen, notable because of the location of the inlet molding gate. To eliminate the effect of this processing inhomogeneity, all samples were annealed at 150°C for one hour prior to testing. In annealed samples, a macroscopic neck did not form after yielding, as the plastic deformation zones nucleated and propagated in random locations throughout the sample.
The mechanical response of annealed tensile specimens was used to measure the yield strain of each material, where yield strain is defined here as the strain at which load drop occurs. However, some samples did not exhibit a load drop at yield. The values of yield strain ($\varepsilon_y$) in Table 2 indicate the strain at which the slope of the stress-strain curve stops decreasing (see section V.2). Yielding is associated with the formation and propagation of plastic deformation zones, which occurs in the polypropylene systems whether accompanied by a load drop or not.
CHAPTER III

MICROSCOPY RESULTS

III.1. Rubber Domain Size

The rubber domain sizes varied significantly in the modified polypropylene systems. There is a distribution of size within each system, but a reasonable estimation of the average particle radius, \( <r> \), was made for each system. The values are recorded in Table 2.

In the blend systems, the average particle size and size distribution depended on the molecular weight of the polypropylene used as the matrix. More viscous polypropylene with high molecular weight produced small rubber domains, about 0.3 \( \mu m \). The average particle size in blends with low molecular weight polypropylene as the matrix was about twice as large.

Comparison of Figure 5 with Figure 6, depicting rubber particles in blend samples with 24% rubber in different molecular weight polypropylene, clearly shows the difference in particle size. Also evident is a difference in the distribution of sizes. Particle size appears narrowly dispersed in blends of high molecular weight polypropylene, whereas a broad distribution of size occurred in blends with the low molecular weight polypropylene. Examination of many fracture surfaces of polypropylene/rubber blends shows that the average particle size
Figure 5. Rubber particles (R) in sample B-5, a blend with 24% rubber in the low MW PP. The average particle size is approximately 0.6 \( \mu \text{m} \), but the size distribution is clearly broad. The bar is 1 \( \mu \text{m} \).
Figure 6. Rubber particles (R) in sample B-2. The average particle radius is approximately 0.3 μm, with a relatively narrow size distribution. The bar is 1 μm.
and particle size distribution is consistently determined by the molecular weight of the polypropylene used as the matrix.

From knowledge of the volume fraction of rubber in the composite, \( v_f \), and the average particle radius in each system, an estimation of the number of particles per unit volume, \( N/V \), can be made:

\[
\frac{N}{V} = \frac{v_f}{\frac{4}{3} \pi \langle r \rangle^3}.
\]

The number of particles per unit volume and a description of the distribution of size (either broad or narrow) serves to characterize the initial morphology of the rubber-modified polypropylene systems. The mechanical properties and deformation morphologies of the blends and copolymers change in trend with the initial morphology.

### III.2 Deformation Morphology

Since the expected effect of included rubber domains is to produce stress concentrations in the polypropylene matrix, the expected consequence is local plastic deformation nucleated by the rubber particles. One type of plastic deformation easily imaged by SEM is crazing. Inspection of surfaces fractured parallel to the draw axis as described in Figure 3 clearly shows that crazes are nucleated at the rubber particles, as in Figure 7.

Imaging parallel fracture surfaces of deformed samples allows direct observation of the voids which form during elongation.
Figure 7. Crazes (C) nucleated by rubber domains (R) in sample B-6. Voids (V) surrounding the rubber domains are evident. The draw direction is vertical, and the bar has length 1 µm.
The size and shape of these voids depends on the average value of strain in the cross-section of sample in which the voids exist. In regions of the sample away from the necked region, the average strain is low, but some plastic deformation has occurred. Crazes are clearly defined in this region. The voids appear to surround the rubber domains, as shown in Figure 8. In the region of transition between predominantly undeformed material (away from the neck) to the highly drawn material in the neck, the voids no longer surround the rubber domains. They become ellipsoids of revolution, with the major axis coincident with the draw axis (Figure 9). The voids in the necked region (Figure 10) are also ellipsoids of revolution, but with larger major axes than those in the transition zone. The minor axes of the ellipsoids are equal to the particle diameter.

The formation of elliptically shaped voids probably occurs when the matrix material near a particle plastically deforms. While under tension during draw, the fibrils in the plastic zones cannot pack above and below the particle along the axis of draw. Upon release of the load, recovery of matrix material of low average draw ratio (away from the neck) results in void surrounding the particles in these locations. In the transition zone, the average strain varies with position, but this region is predominantly composed of microfibrils. Length recovery upon release of the load is small, so the voids remain ellipsoids with the rubber domain in the center. In the neck region, the
Figure 8. Crazes shown away from the neck ("undeformed" region) in sample B-6. Crazes appear to nucleate at the rubber domains, and voids seem to surround the rubber domains. The draw direction is vertical, and the bar represents 1 \( \mu \text{m} \).
Figure 9. A view in the transition zone (see Fig. 4) of sample B-6. Crazes are not evident in the transition zone, as lateral merging of the microfibrils squeezes out the voids which formed between microfibrils during craze propagation. The voids remain elongated in the draw direction (vertical). The bar is 1 μm.
Figure 10. A view in the neck of sample B-6. Voids are very elongated in the draw direction, and limited in width by the rubber particle diameter. The elongated voids are a result of the fibrous morphology in necked regions. The bar is 1 μm.
morphology is largely oriented fibrils, so almost no length recovery accompanies release of the load. The high draw ratio in the neck results in voids with a large major axis.

Inspection of the neck region of sample C/35 in Figure 11 shows the high void content of a material which plastically deforms almost exclusively by multiple crazing. The shape of the voids in sample C/35 depend on the local average draw ratio as they did in sample B-6, Figures 8-10. The obvious difference in void content in the neck between the two samples occurs because sample B-6 plastically deforms by a mechanism other than crazing (see section IV.1).

Examination of crazes in polypropylene (Figure 12) and in rubber-modified samples (Figures 13-14) reveals that they appear to be essentially identical. The important parameter of a craze, assuming that it forms and grows without reduction in sample cross-sectional area, is the average draw ratio of the fibrils bridging the gap between "undeformed" material which define the craze boundaries. If crazes in high and low molecular weight polypropylene have about the same void content, then the fibrils in the craze have about the same average draw ratio.
Figure 11. A view in the neck of sample C/35. The neck has a large void content, due to the large rubber particle diameter. The elongated voids are a result of the fibrous morphology in necked regions. The bar is 1 μm.
Figure 12. A high magnification view of a craze in homopolymer polypropylene, in a region away from the neck. The draw direction is along the craze fibril direction, and the bar length is only 0.1 μm. Notice the sharp boundary between the craze and undeformed matrix (M).
Figure 13. A high magnification view of a craze in sample B-7. The bar is 1 \( \mu \text{m} \).
Figure 14. A craze in B-6. The bar is 0.1 μm. This craze was apparently nucleated at the rubber domain indicated. Comparison of Figures 13-15 shows no difference between crazes in modified or unmodified PP, or between crazes in different MW PP. The void content of crazes is determined by the draw ratio of the craze fibrils, but only in crazes away from the neck.
CHAPTER IV

VOLUME CHANGE BEHAVIOR

VI.1. Quantitative Estimation of Craze Content

Rubber-modified plastics owe their increased strain and energy absorbing capacity to local failure, that is, plastic damage initiated by the rubber domains. There are apparently two dominant mechanisms of plastic strain (microfibril formation), crazing and shear zone formation. Both mechanisms result in large plastic strain, but while crazes result in matrix cavitation, shear zones form at constant volume (2).

The volume change plots have three regions of behavior, shown schematically in Figure 15. Initial deformation occurs at near constant volume. As the yield strain is approached, an increase in volume results as crazes form and cavitate the matrix. After the yield strain, the rate of volume increase becomes constant.

The limiting rates of volume strain with nominal strain,

\[
\frac{\frac{d(V)}{V_0}}{d\varepsilon_T},
\]

were measured with the gas dilatometer. The values appear in Table 2, taken from data in Figures 16-25.
Figure 15. A schematic of the volume increase behavior typical of polypropylene systems, showing the three regions. In region 1, the deformation occurs at constant volume. In region 2, the sample yields, crazes nucleate and grow, and the volume increases. Region 3 is characterized by a constant rate of crazing evidenced by a constant rate of volume increase.
Figure 16. Continuous stress/strain/volume strain plots obtained for homopolymer polypropylene PP(M) with the gas dilatometer. Notice that yielding of the load response occurs during region 2 of the volume strain curve, indicating that craze (and shear zone) formation is responsible for yielding.
Figure 17. $\sigma/\varepsilon/\Delta V/V_0$ curves for sample C/12, a copolymer. The limiting rate of volume strain is about 0.58.
Figure 18. $\sigma/\varepsilon/\Delta V/V_0$ plots of C/35. This copolymer had the highest rate of volume strain of any polypropylene system tested, about 0.74. This system also had the coarsest rubber domains, with a large distribution of particle radius (see Fig. 11).
Figure 19. $\sigma/\varepsilon/\frac{\Delta V}{V_0}$ curves for sample B-1. The rate of volume strain is about 0.64.
Figure 20. $\sigma/\epsilon_{\epsilon}/\Delta V/V_0$ curves for sample B-2. The limiting rate of volume strain is not distinct, nor is the yield point. This system develops a clear neck, further evidence that conditions for crazing do not exist. Yet, large draw ratios are obtainable. This system had the most rubber domains, with narrowly dispersed size.
Figure 21. $\sigma/\varepsilon/\frac{\Delta V}{V_0}$ curves for sample B-3. The rate of volume increase is moderate, at about 0.42.
Figure 22. $\sigma/\varepsilon/\Delta V/V_0$ curves for sample B-4. The rate of volume strain is low, at about 0.20. Crazing is not as important to the plastic deformation as the (proposed) mechanism of shear zone formation, a constant volume process.
Figure 23. $\sigma/e/\Delta V/V_0$ plots of sample B-5. Crazing is important to post-yield deformation of this system, which exhibits a rate of volume strain of 0.60.
Figure 24. $\sigma/\epsilon/\frac{\Delta V}{V_0}$ curves of sample B-7. The rate of volume strain is 0.66.
Figure 25. $\sigma/\varepsilon/V_0$ curves of sample B-8. This blend has the same properties as B-2, differing only in the vistalon used in the blend. The rate of volume strain is only 0.10. The volume increase may have a contribution from void formation at rubber domains (see Fig. 8).
Measurement of the limiting rate of volume increase of a sample during elongation allows calculation of the contribution to the plastic strain from craze formation and growth. In order to simplify, one must assume that the average value of plastic strain in crazes and shear zones is the same (see section VI.1), and that the only source of matrix cavitation (volume increase) is craze formation and growth.

The measured value of strain, $\varepsilon_T$, is the average value of all the contributions from elastic deformation of the crystalline phase of the matrix, elastic deformation of the rubber, viscoelastic displacement of lamellae, and plastic strain in crazes and shear zones. The total measured strain can be expressed as follows:

\[
\varepsilon_T = f_E \langle \varepsilon_E \rangle + f_R \langle \varepsilon_R \rangle + f_V \langle \varepsilon_V \rangle + f_P \langle \varepsilon_P \rangle
\]

where $f_E + f_R + f_V + f_P = 1$

\begin{align*}
f_E & = \text{volume fraction of crystalline matrix deformed elastically} \\
\langle \varepsilon_E \rangle & = \text{average value of elastic strain in crystalline polypropylene} \\
f_R & = \text{volume fraction of rubber} \\
\langle \varepsilon_R \rangle & = \text{average value of strain in the rubber} \\
f_V & = \text{fraction of matrix material deformed viscoelastically} \\
\langle \varepsilon_V \rangle & = \text{average value of viscoelastic strain} \\
f_P & = \text{fraction of material deformed plastically} \\
\langle \varepsilon_P \rangle & = \text{average value of plastic strain}
\end{align*}
Beyond the yield strain, the rate of volume strain becomes constant. Thus the volume strain is proportional to the nominal strain, and the relation can be expressed:

\[
\frac{\Delta V}{V_o} = a[f_E <\varepsilon_E> + f_R <\varepsilon_R> + f_V <\varepsilon_V> + f_p <\varepsilon_p>] + b
\]

where "a" is the limiting rate of volume strain,

\[
\frac{d(\frac{\Delta V}{V_o})}{d \varepsilon_T}.
\]

With the condition that the only source of volume strain is plastic deformation, \(\Delta V/V_o = 0\) when \(f_p = 0\). Equation 2 becomes:

\[
\frac{\Delta V}{V_o} = a f_p <\varepsilon_p>
\]

Equation 3 states that the accumulated volume strain is proportional to the fraction of material strained plastically. The average value of plastic strain, \(<\varepsilon_p>\), is assumed to be constant. The proportionality constant, \(a\), is determined by the relative contribution to the plastic strain made by craze and shear zone formation.

The total plastic strain, \(f_p <\varepsilon_p>\), can be written as a sum of contributions from the two mechanisms of plastic strain:

\[
f_p <\varepsilon_p> = f_p^c <\varepsilon_p> + f_p^s <\varepsilon_p>
\]

where \(f_p = f_p^c + f_p^s\)

\(f_p^c\) = fraction of material in crazes

\(f_p^s\) = fraction of material in shear zones
The quantity $f_p \langle \varepsilon_p \rangle$ equals the total volume strain, $\Delta V/V_0$.

The quantity $f_p \langle \varepsilon_p \rangle$ equals by equation 3) $\frac{1}{a} \frac{\Delta V}{V_0}$. Thus the fraction of plastically deformed material due to crazing,

$$\frac{f_p \langle \varepsilon_p \rangle}{f_p \langle \varepsilon_p \rangle},$$

equals the limiting slope of the volume change plot, a. If a sample forms only crazes, then "a" = 1 since $f_p \langle \varepsilon_p \rangle = f_p$. If the sample forms only shear zones, then "a" = 0 since $f_p \langle \varepsilon_p \rangle = 0$.

Homopolymer polypropylene has a limiting rate of volume strain of .69. Crazing is responsible for about 70% of the plastic strain, i.e., about 70% of the fibrils in the neck. Rubber-modified polypropylenes exhibit rates of volume strain both greater and less than the rate of volume strain of the homopolymer. Note that all three molecular weight homopolymers had the same rate of volume strain.

Blends with large particles of broadly dispersed size had high rates of volume increase. Sample B-1 has the fewest rubber domains and the highest rate of volume strain in the blend series. Sample B-3 has about twice as many rubber particles, since the rubber concentration was doubled at constant particle size and polydispersity (same molecular weight matrix).

Increasing the number of rubber domains decreased the rate of volume strain. Samples B-1 and B-3 whiten after the yield strain, as do the homopolymers.
Systems with smaller particles of more narrowly dispersed size had significantly lower rates of volume change. Sample B-4 whitens slightly after yielding. Sample B-2, with the most rubber domains per unit volume, had the lowest rate of volume strain. This sample does not whiten at strain rates less than $10^0 \text{(sec)}^{-1}$.

Sample C/35, a copolymer, has the largest sizes and fewest number of rubber particles. The distribution of size is broad (from inspection of figure 11), and it has the highest rate of volume strain. Sample C/12, another copolymer, has about the same number of particles as sample B-5, and a comparable rate of volume strain.

Considering systems which deform exclusively by multiple crazing, when the sample is completely converted to a micro-fibrous morphology, the value of volume strain equals the value of plastic strain.

$$\frac{\Delta V}{V_o} \approx \langle \varepsilon_p \rangle \approx \varepsilon_T$$

since $a = \frac{f_p}{\varepsilon_T} = 1 = \frac{\partial (\frac{\Delta V}{V_o})}{\partial \varepsilon_T}$

The result—that the volume strain in a craze equals the value of plastic strain in a craze—occurs because crazes form without reduction in sample cross-sectional area. However, one should not expect to find that the volume strain in a necked region, which is completely converted to a fibrous morphology, would equal the value of nominal strain in the neck. When the fraction of plastically strained material is sufficiently large,
merging of the crazes occurs and cross-sectional area reduction results. The value of volume strain equals the value of nominal strain only in isolated crazes.

Differentiating equation 3 with respect to time yields:

\[
\frac{d(\frac{\Delta V}{V_0})}{dt} = \frac{df_p}{dt} a <\epsilon_p>
\]

If the competing rates of craze formation and shear zone formation do not change during the course of the test, then all terms on the right hand side of equation 5 are constants, and the rate of volume strain must also be constant. Assuming that the sample is deforming only by plastic deformation mechanisms (i.e. \(f_p\) is constant), then the converse is true. As long as the rate of volume strain is constant, the competing rates of the plastic deformation mechanisms do not change (i.e. "a" is constant). Of course, the rate of volume change may decrease at large strains when craze merging occurs.

The composite HIPS reportedly deforms exclusively by multiple craze formation (2). HIPS tested with the gas dilatometer confirms this belief, because the limiting rate of volume strain equals unity (see figure 26). Recall that for a rate of volume strain, a, to equal unity, no cross-sectional area reduction can occur with deformation. Thus it is reasonable to assume that craze formation occurs at constant cross-sectional area.
Figure 26. $\frac{\Delta V}{V_0}/\epsilon$ curve obtained with the gas dilatometer on HIPS. The slope is about unity, indicating that crazing is solely responsible for post-yield deformation. The load behavior is indicated by a dashed line.
IV.2. Speculation of the Criteria for Shear Zone Formation

The nature of shear zones and the criteria for their formation have not been sufficiently elucidated, so it is difficult to determine precisely why increasing the number of stress concentration sites in the matrix, and obtaining narrowly dispersed domain sizes, should be conducive to shear zone formation. Shear zones are usually associated with plastic deformation of a glassy matrix in a compressive stress field (10). Plastic strain by shear deformation of a material in compression is understandable because an increase in volume via cavitation is difficult under pressure, so craze formation is suppressed. That a glassy matrix (i.e. polycarbonate) should be particularly susceptible to shear zone formation may suggest conditions under which they may form.

Most glassy polymers are relatively isotropic, so they have equivalent properties in all directions and at all locations. The behavior of a region of material will depend on the stresses in the planes the region occupies and the orientations of these planes with respect to the draw axis. Shear failure is common in materials and can be expected to occur in planes at angles near 45° from the draw direction, where the shear stress is largest. Conditions for shear zone formation probably include a homogeneous stress field. One would not expect shear slip over a large planar region unless the shear stress inducing slip is
large over the entire region. Crazes are described as planar deformation zones as well, but they initiate at a point in the matrix, such as a surface flaw or an included rubber domain, and propagate rapidly in the lateral direction achieving a thin plate geometry perpendicular to the draw axis.

Homopolymer polypropylene has a high rate of volume strain, indicating that plastic deformation occurs predominantly by multiple craze formation and growth. This suggests that either the stress state in the material is too inhomogeneous to produce deformation over a broad region, or that weak points in the matrix are yielding before the majority of matrix material. The weak points may be growth front boundaries (spherulite boundaries in the homopolymer), lamellae carrying more than the average share of load such as those oriented parallel to the draw axis, lamellae oriented with a large shear stress on a weak crystal plane, or regions with residual stress or orientation, unrelaxed after processing.

Rubber-modified plastics with large rubber domains (thus few rubber domains) and broad size distributions may produce isolated high stress regions, especially if the stress concentration factor increases with particle size. The stress near a large particle may be sufficient to induce plastic damage while the majority of matrix material is relatively undeformed. The plastic deformation initiated at the rubber particles would occur at points local to the coarsest particles, thus taking the form
of crazes.

Decreasing the particle size of the rubber phase by a factor of two increases their number by a factor of eight, at constant volume fraction of rubber. In blends with a large number of relatively narrowly dispersed small particles, the resulting stress fields due to the particles may be sufficiently homogeneous to produce plastic deformation over a broad region of matrix.
CHAPTER V
MECHANICAL BEHAVIOR

V.1. Yield Strain

The stress-strain behavior of rubber-modified polypropylene depends on the initial morphology, that is, on the average particle size and size distribution in the system. Mechanical response, characterized by a value of yield strain and by the load behavior following yield, is determined largely by the nature of the stress fields caused by the rubber domains. If crazing occurs, the system usually exhibits a small yield strain, a load drop at yield, and post-yield deformation at constant or decreasing load. Systems which do not craze extensively have larger yield strains, yielding is not accompanied by a load drop, and post-yield deformation proceeds with increasing load.

Although mechanical response varied from system to system, differences in properties cannot be attributed to different molecular weight polypropylenes used as the matrix. The three different molecular weight homopolymers had essentially identical mechanical behavior and volume change characteristics (see Figure 27).

The value of yield strain (Table 2) increased with increasing numbers of particles in the system. It was argued that increasing the number of narrowly dispersed rubber domains caused
Figure 27. The mechanical behavior of the three homopolymer polypropylenes, which differ in molecular weight, used as the matrix in rubber modified systems. The volume change behaviors are also essentially identical. Differences in properties cannot be attributed to the matrix molecular weight.
a more homogeneous stress field in the matrix, enabling plastic deformation to occur over a broad planar region of material. The values of yield strain provide evidence for this argument.

Comparison of the data in Figure 33, the mechanical responses of blends with 24% rubber but with different numbers of particles in the system, clearly illustrates the difference in yield strain. Although the slope of the stress-strain curve decreases faster in the system with a large number of 0.3 μm particles, the initial average composite stiffness characteristics should be about the same. Probably, the homogeneous stress field (assumed to exist) in the system with a large number of narrowly dispersed particles affects more matrix material, at any given load, than the system with isolated stress concentration sites due to the broad particle size distribution. The more matrix material involved in the pre-yield strain, the lower the local strain rate. In systems with large particles and broad size distributions, the deformation will be largest where the stress is largest, near the coarse particles. With fewer deforming sites, the local strain-rate at these locations must be large for the average strain rate to equal the applied strain rate. The load response to viscoelastic strain is strain rate sensitive; more rapid deformation requires larger loads. Thus the load increases faster in the system with large particles and broad size distributions.

In the homopolymer, the value of viscoelastic strain at yield does not reflect the materials capacity of pre-yield
strain. More could be achieved, but when the stress is large enough in regions of the matrix to cause plastic strain, the load ceases to increase and the plastic deformation mechanism (crazing) dominates the strain.

Rubber-modified systems with small ($<.3$ μm) narrowly dispersed particles have relatively homogeneous stress fields in the matrix during deformation, which involve more matrix material in the viscoelastic strain, and at lower local strain rates, than the homopolymer. Important high stress regions in the homopolymer may be, for example, isolated stacks of lamellae oriented parallel to the draw axis. The important high stress regions in rubber-modified systems are controlled by the inclusions.

In systems with large particles and broad size distributions, the high stress regions appear to be isolated. Although pre-yield viscoelastic strain may be large near the coarse particles, the stress is small in the majority of the material, thus the strain is small. When the stress is large enough to produce plastic draw, it will only be large enough local to coarse particles, so crazes will form. Interestingly, the system with the most rubber (35%) had the lowest yield strain. This system had the fewest number of particles per unit volume, the size distribution was broad (see figure 11), and it had the largest rate of volume strain (crazed most).

Further evidence for the increasing amount of viscoelastic strain attained in systems with increasing numbers of particles
is found by observing the strain rate sensitivity of the load behavior of the materials. Inspection of Figure 28, the stress-strain behavior at two strain rates of blends with 24% rubber but with different numbers of particles, shows that the system with the large yield strain is more strain rate sensitive. The rate dependence of the mechanical response is due to the viscous contribution to the load during lamellae displacement. The stress causing the large pre-yield strain attained by the system with a large number of narrowly dispersed particles is clearly more strain rate dependent, so the deformation responsible for the large pre-yield strain is not that of the rubber.

Important to the assumption about the homogeneity of the stress fields is a decrease in the stress concentration factor with decreasing particle radius (11). Two effects may cause this departure from the rules of continuum mechanics. First, the matrix material surrounding the rubber domains must be a homogeneous continuum for the stress concentration factor to be independent of inclusion size. The continuum hypothesis falters when the particle radius is reduced, because the region of matrix affected by the inclusion decreases in volume and becomes less homogeneous (11). Second, a third phase may exist at the particle/matrix boundary due to diffusion and mixing of the molecules of the two phases. If such a third phase exists, it will affect the properties of blends with the smallest particles due to the large boundary area in these systems (11).
Figure 28. The dependence of strain-rate on the mechanical response of systems B-5 and B-8. Both have 24% rubber, but B-5 craze extensively while B-8 does not. The pre-yield deformation of sample B-8 is more strain-rate sensitive than that of sample B-5.
V.2. Post-Yield Mechanical Response

The transition from few rubber particles to many changes the mechanism of plastic strain following yield, and this behavior is reflected in the mechanical response. Comparison of the load behavior in Figures 29-33 shows that the samples deforming plastically by craze formation and growth exhibit a load drop following yield, whereas samples which deform predominantly by shear zone formation do not. All samples in Figures 29-33 were annealed prior to testing, and did not develop a neck after yielding.

It was demonstrated in section IV.1 that the rate of volume strain would be constant if plastic strain was the only mechanism of post-yield deformation. There is a range of strain where the rate of volume change is increasing (see figures 16-25). During this curvature region, viscoelastic strain of lamellae displacement and plastic strain are occurring simultaneously (9). As the rate of viscoelastic strain decreases with increasing deformation, the rate of plastic strain by crazing increases and eventually reaches a constant value.

The region of curvature, when both mechanisms of strain are occurring, is narrow in systems which craze extensively. In the systems which do not craze extensively, the two mechanisms of deformation occur simultaneously over a broader range of strain. Inspection of Figures 20 and 25, the volume strain data of blends which craze the least, shows that the rate of volume strain had
Figure 29. The mechanical response of homopolymer PP(M), and copolymers C/12 and C/35. The yield stress decreases with increasing rubber content. However, the shapes of the stress-strain curves are similar, due to the same mechanism of post-yield deformation (crazing) exhibited by these systems.
Figure 30. Mechanical response of samples B-1 and B-4. Both have 12% rubber. Sample B-1 crazes extensively, while B-4 does not.
Figure 31. Mechanical response of systems B-2 and B-3. Both have 24% rubber. B-2 crazes very little, while B-3 has a moderate contribution from crazing.
Figure 32. Mechanical response of systems B-6 and B-7. B-6 crazes little, while B-7 crazes extensively. This behavior is reflected in the shape of the $\sigma/\varepsilon$ curve. Both systems have 12% rubber.
Figure 33. Mechanical response of B-8 and B-5, systems with 24% rubber. As in all the mechanical responses recorded, when crazing is important to post-yield deformation (B-5), yielding is clearly defined. When crazing is suppressed, the load increases throughout the deformation.
not yet reached its limiting value.

Apparently, crazes are easily propagated. Once formed, plastic deformation continues at decreasing load. Viscoelastic displacement of lamellae ceases when the load becomes approximately constant, shortly after the yield strain.

When crazes do not form, plastic deformation occurs at constant volume. It was assumed that microfibrils form in these systems as shear zones propagate through the matrix (see section IV.1.). There is a softening of materials which do not craze extensively at yield, but this is much less dramatic as yielding by craze formation. There is no load drop, and deformation proceeds with increasing load. The increasing load might be responsible for the broad curvature regions on the volume strain plots, where lamellae displacement continues as long as the load keeps increasing. (One should be concerned with the true stress in the material. However, the nominal stress should be a reasonable approximation in the range of strain considered, from 0-35%.)

V.3. Optimum Impact Resistant Polypropylene

The usefulness of characterization and analysis of the deformation morphology and mechanical behavior of polypropylene and its rubber-modified composites is that it enables one to "tailor-make" a material best suited for a given application. The requirements of the material may not be known specifically
enough to design a single test which separates superior blends from poor ones. A ranking of the materials from good to bad may change with test conditions.

The composites of polypropylene and rubber with the best overall properties are those in which the rubber is dispersed into small (<.3 μm) narrowly dispersed domains. The stress fields produce shear zones during deformation. There are several reasons why plastic deformation by shear zone formation is preferable to crazing.

It has been reported in the literature that shear zones act as barriers to craze propagation (2). Large crazes eventually open into cracks which result in fracture (2). Also, the conditions under which shear zones form—a large number of small rubber domains—limit craze size because rubber domains terminate growing crazes as well (2).

The mechanical behavior of the materials which form predominantly shear zones has advantages in use over the behavior of materials which craze extensively. For the reasons discussed, materials which form shear zones have large yield strains. Since the yield strain is associated with the formation and propagation of plastic deformation zones, a large yield strain is preferable. Although local plastic deformation zones postpone fracture, they provide gradual failure mechanisms which weaken the material.

It was noted in section V.2 that when crazing is the dominant form of plastic deformation, the yield strain is
coincident with a load drop (without neck formation), and further deformation continues at constant or decreasing load. When crazing does not occur as the dominant form of microfibril formation, yielding is not accompanied by a load drop. Whether a sample exhibits a load drop or not may have practical significance. If the mechanism which allows deformation to proceed (without fracture) is shear zone formation, then the load must always increase or the rate of deformation will decrease. This is not the case for samples elongating by multiple craze formation, where deformation can proceed at constant load. A material which deforms by shear zone formation may resist fracture longer, under certain loading conditions, than a sample deforming by craze growth.
CHAPTER VI
SUMMARY AND FUTURE WORK

VI.1 Deformation Morphology Characterization

The plastic deformation mechanisms of polypropylene composites must be investigated further. Volume change measurements made on these systems indicate that different amounts of crazing occur, dependent upon the number of rubber domains and their size distribution. Crazing is the most important mechanism of plastic deformation in homopolymer polypropylene and in rubber-modified composites with large particles and broad size distributions. However, it is not certain what deformation mechanism is responsible for the large plastic strain capable by systems which craze little. It has been suggested that the formation of shear zones, local plastic deformation regions confined to planes at angles near 45° from the draw axis, would result in large plastic strain without volume increase.

The value of plastic strain in the shear zones is comparable to the value of plastic strain in crazes. The draw ratio in the neck of sample B-2, which crazes little, was measured at about 4.5, thus having a value of plastic strain of 3.5. Correcting for the fraction of matrix material in the blend, the average
value of strain in the polypropylene phase would be 4.6. The value of plastic strain in a neck region of homopolymer polypropylene, which crazes extensively, was measured at about 5.0.

If such shear zones are occurring during elongation, then a technique must be developed to image them. SEM can be used to image crazes because of the contrast supplied by the voids surrounding the microfibrils in a craze. Since shear zones do not cavitate the matrix, they have the same appearance as the matrix in secondary electron imaging. However, Transmission Electron Microscopy, TEM, is capable of much higher resolution. It is possible to resolve individual lamellae, so it might be possible to recognize the transformation from folded-chain lamellae to oriented microfibrils which would occur in a shear zone.

VI.2. Volume Change Characteristics

The rate of volume strain can be used to determine the importance of crazing to the plastic deformation of polypropylene composites. In this survey, the rates of volume strain were measured at one strain rate and at room temperature. Dilation studies at high strain rates and at low temperatures would provide information about the strain rate and temperature dependence of craze formation. Suppression of crazing may
suggest an increase in the conditions for shear zone formation. This effect can possibly be produced by performing tensile experiments under conditions of hydrostatic pressure.

VI.3. Mechanical Response

Homopolymer polypropylene is tough at moderate strain rates and above its 0°C glass transition temperature. High rate or low temperature use conditions require a tougher material. Rubber-modified polypropylene is tough under some conditions where the homopolymer is brittle. It was demonstrated in this survey that the properties of rubber-modified polypropylene vary significantly, and depend on the characteristics of the dispersed rubber phase.

Analysis of the mechanical response of polypropylene/rubber composites indicates that craze formation should be avoided. When narrowly dispersed rubber domains (with \( \leq 0.3 \) \( \mu \)m radius) are incorporated into the matrix, plastic deformation will occur at constant volume, perhaps by the formation of shear zones. However, the optimum blend parameters (particle size and volume fraction of rubber) were not determined in this survey.

The optimum blend parameters depend on use conditions, but a logical criterion to maximize is energy absorbed before fracture. High rate tensile tests performed as a function of temperature on
systems with varying particle size, size distribution, and volume fraction of rubber would be useful in a determination of the parameters for optimizing the impact characteristics of rubber-modified polypropylene.

Preliminary experiments of this nature have been made. High-rate tensile tests were performed on the materials at room temperature. Although the data should not be extrapolated to lower temperatures, information on room temperature durability is provided. The strain rate was 10 (sec)$^{-1}$, and samples were elongated to 100% strain or until fracture. The typical mechanical responses of homopolymer polypropylene and four blends with varying rubber concentration and particle size are recorded in Figure 34.

If the criterion for the best material is strain at break, then the best materials are those with the largest volume fraction of rubber. The samples with 24% rubber attained 100% strain without fracture. Considering the breaking strain of materials with equal rubber contents, the best materials are those which do not whiten extensively, i.e., those which plastically deform predominantly by a constant volume mechanism.

Although volume change measurements were made at only one strain rate (.005 (sec)$^{-1}$), it appears that an increase in strain rate results in an increase in the conditions for crazing. Sample B-2 does not whiten at moderate strain rates (say .005 (sec)$^{-1}$), but some whitening occurred at a strain rate of
Figure 34. High-rate mechanical response of homopolymer PP(M), and blends B-1, B-2, B-3, and B-4. Systems with 24% rubber, B-2 and B-3, resisted fracture when deformed to 100% nominal strain. At constant fraction rubber, suppression of crazing (B-2 and B-4) results in a higher yield stress and a larger strain at break. The strain rate was 10 (sec)⁻¹.
10 (sec)\(^{-1}\). The mechanical response of this system, Figure 34e, is similar to the mechanical response of systems where crazing is an important deformation mechanism. The value of yield strain is reduced, there is a slight load drop at yield, and post-yield deformation proceeds at approximately constant load. Recall that if the yield strain is reduced, then less matrix material is involved in pre-yield deformation, a condition which results from isolated high stress regions. With increasing strain rate, the stress distribution apparently becomes less homogeneous. Volume change measurement can quantify the increasing rate of craze formation.

From analysis of the mechanical response, volume change behavior, and deformation morphology, we conclude that composite materials of polypropylene and rubber achieve the best properties when the rubber phase is dispersed into domains having an average radius of about 0.3 \(\mu\)m. Blends of varying rubber particle radius were manufactured for this work by blending with varying molecular weight (melt viscosity) homopolymer. Particle size could probably also be varied by blending for different times. Hopefully, longer blending times would reduce the size distribution as well as the average particle size.

The properties of composites with an average particle size less than 0.3 \(\mu\)m have not been investigated. Such systems might prove to be superior. If increasing the number of particles per unit volume further increases the homogeneity of the stress fields
during deformation, then crazes may form less readily at high rates of strain than they do in samples B-2 and B-8, which we presently consider the best rubber-modified polypropylene.
REFERENCES


11) R. J. Farris, private communication.