Triptycene Side Unit Effects on Compressive Yield Strength in Polycarbonates
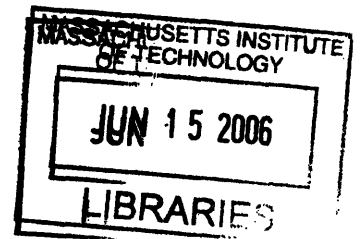
by

Douglas Fraser

SUBMITTED TO THE DEPARTMENT OF MATERIALS SCIENCE AND
ENGINEERING IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF

BACHELOR OF SCIENCE
AT THE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

JUNE 2006

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Signature of Author:＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿
Department of Materials Science and Engineering
May 16, 2006

Certified by:＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿
Edwin L. Thomas
Morris Cohen Professor and Department Head of Materials Science and Engineering
Thesis Supervisor

Accepted by:＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿
Caroline A. Ross
Professor of Materials Science and Engineering
Chair, Departmental Undergraduate Committee

Triptycene Side Unit Effects on Compressive Yield Strength in Polycarbonates

by

Douglas Fraser

Submitted to the Department of Materials Science and Engineering
on May 16th, 2006 in partial fulfillment of the
requirements for the Degree of Bachelor of Science in
Materials Science and Engineering

ABSTRACT

Polycarbonates have long been studied for their excellent mechanical toughness. Adding side units to polycarbonate could increase physical properties of the polymer. The role of triptycene in polycarbonate was studied by adding a low concentration of triptycene-containing polymer chains, and using compression testing. The triptycene polycarbonate was a blend created from two separate products. Differential Scanning Calorimetry was used to determine if the samples had phase separated. Thermal degradation of the samples was checked for using Thermogravimetric Analysis.

Results indicated that triptycene-containing polycarbonates had higher compressive yield strengths than non-triptycene polycarbonates. The polymers were stronger due to the interlocking mechanism and the steric hindrance of the triptycene units. The design of strengthening polymers by adding triptycene units could prove useful to improve high performing polymers, or to give low molecular weight polymers more stability.

Acknowledgements

I would like to thank Professor Thomas for giving me the opportunity to work on this project and for his support throughout the year.

Nicholas Tsui for answering my endless questions, advising me on my research, and helping me with all aspects of this project. I could not have done it without him.

To everyone in the Institute for Soldier Nanotechnologies that helped me along the way.

I dedicate the work that has gone into this thesis to my family and friends who have always supported me in my endeavors.

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1 Introduction

This research focuses on determining if the compressive yield modulus of the ductile amorphous polymer polycarbonate can be increased through the addition of a triptycene side unit. Triptycene has been studied previously as a low molar mass single molecule, but little research has been done with triptycene incorporated as a side unit on high molecular weight polymers. The little amount of work that has been done with triptycene units as side chains in polymers clearly shows an increase in properties with the addition of the side units.[1] However, this work has only been done with tension measurements and only with polyesters. This research focuses on using triptycene side units in a polycarbonate polymer under a compressive state.

1.1 Energy Absorption in Polymers

Polymers have many valuable functions, including energy absorption of ballistic impacts. The mass of the ballistic impact resistant material can be significantly reduced by increasing the energy a given polymer can absorb before yielding. The benefits of a lighter, stronger armor are immense in an occupation where safety is invaluable, such as a soldier or public defender.

Energy is absorbed in a material through two driving forces; ductility and the modulus-strength of a material. The amount of energy absorbed by a material is equal to the amount of work performed by the system. [Figure 1] The work of the system is equal to the integral of the stress with respect to the strain of the substance[2]. Therefore, by increasing either the ductility or the modulus-strength of a substance without decreasing the opposite driving force, the amount of energy absorbed by the polymer before failure will increase. Figure 1 clearly illustrates this point. Kevlar has a much higher modulus and strength than polycarbonate, but it has a lower failure strain. At 60% strain polycarbonate has absorbed as much energy as Kevlar, and it continues to absorb more. Polycarbonate optimizes the ductility aspect in absorbing energy compared to the high modulus aspect that Kevlar optimizes.

Figure 1: Energy absorbed in work versus strain. Kevlar has a higher modulus than polycarbonate but a lower strain to failure. [3]
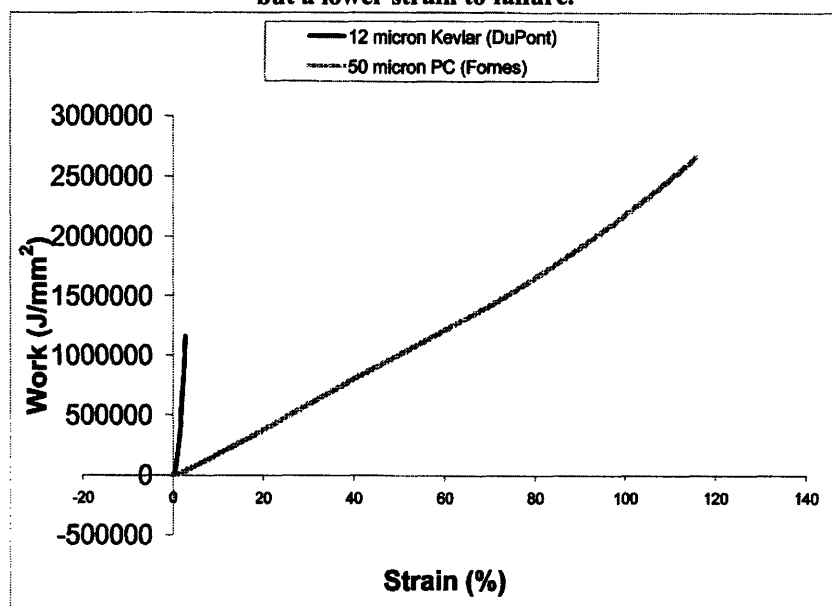
All polymers can be segregated into two groups; semi-crystalline and amorphous. There are two subsets of amorphous polymers. Brittle amorphous polymers have a larger modulus, but do not have a very high failure strain. An example of a brittle amorphous polymer is polystyrene, which has an elastic modulus of 3 GPa[4]. Ductile amorphous polymers usually have a lower modulus, but can withstand a substantial amount of strain. An example of a ductile amorphous polymer is polycarbonate which has an elastic modulus of 2.3 GPa, strength of 700 J m^{-1} and strain to failure of 100 percent[5].

1.2 Polycarbonate

Polycarbonate exhibits a unique property that makes it more favorable for ballistic impact materials than other polymers. Some polymers have two molecular motion transitions referred to as the alpha and beta transitions. The alpha transition, also referred to as the glass transition temperature, occurs when 20-50 units along the backbone of the polymer chain are free to move about. This causes a sudden change in the properties of the polymer. The beta transition occurs when local side segments are able to mobilize. This transition occurs at a lower temperature than the alpha transition. Polycarbonate has a beta transition around -100 degrees Celsius[6]. At ballistic strain rates around 10,000

Hz, the beta transition of polycarbonate translates upward to around room temperature
Celsius according to Time Temperature Superposition. The beta transition of
polycarbonate increases the amount of energy absorbed at this strain rate and
temperature. Polycarbonate is a very favorable polymer to use in ballistic impact
resistant materials because of this increase in energy absorption in ballistic rates.

Figure 2: Polycarbonate molecular motion transitions. Notice the two spikes at 150 and -100 degrees Celsius. These points are the Tg (alpha) and Beta transitions respectively.[3]
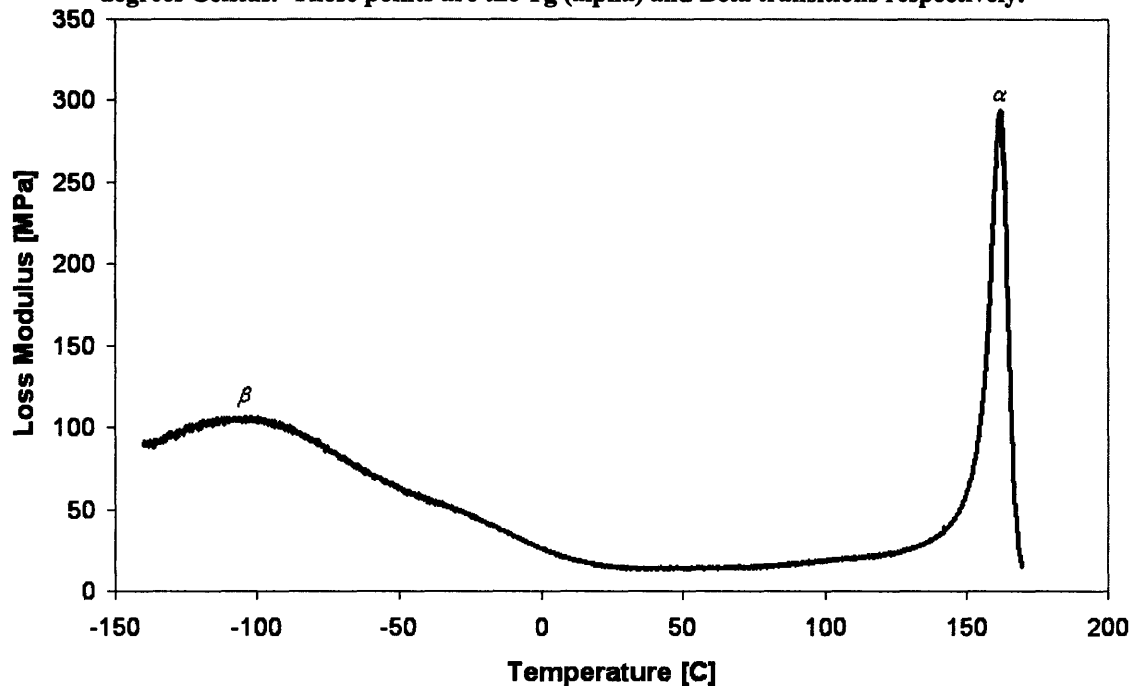
1.3 Tension vs. Compression

In tension the internal molecular free volume (IMFV) in the triptycene side unit is
occupied by a segment of the polymer chain. [Figure 3] This results in an interaction
between the two chains, essentially one chain is "threaded" through the triptycene unit of
the other chain. During tension this interaction increases the modulus and strength of the
polymer. [Figure 4] The triptycene units can be envisioned as barbs along a wire creating
in essence, "molecular barbed wire".

Figure 3: Triptycene Units. One of the three protrusions of the triptycene unit attach to the polymer chain. IMFV stands for Intermolecular Free Volume.[3]

$$IMFV = 3A \cdot t$$
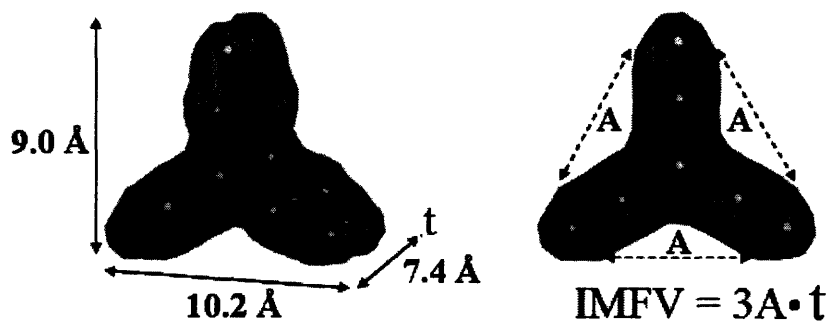
Figure 4: Triptycene Unit Interlocking

no strain
(threading)

Low Tensile Strains
(threading)

High Tensile Strains
(interlocking)
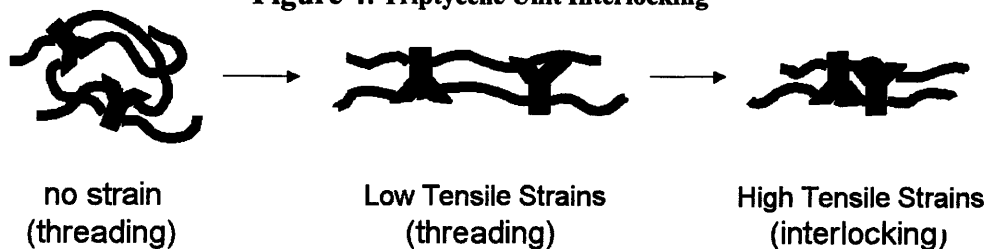
The mechanics of compression of deformation are very different however. Chains do not move past one another as they do in uniaxial tension. During uniaxial compression a material is compressed in the $\hat{k}$ direction, creating an equal expansion in the $\hat{i}$ and $\hat{j}$ directions. The material will flow radially away from the center of the sample. This is shown in Figure 5. The uniaxial compressive stress creates a biaxial stress state. It is not clear if the interlocking mechanism that triptycene side units have been shown to exhibit in tension is also present in a compressive state.

Figure 5: Radial flow of material during compression. The uncompressed sample is on the left and the compressed sample is on the right.
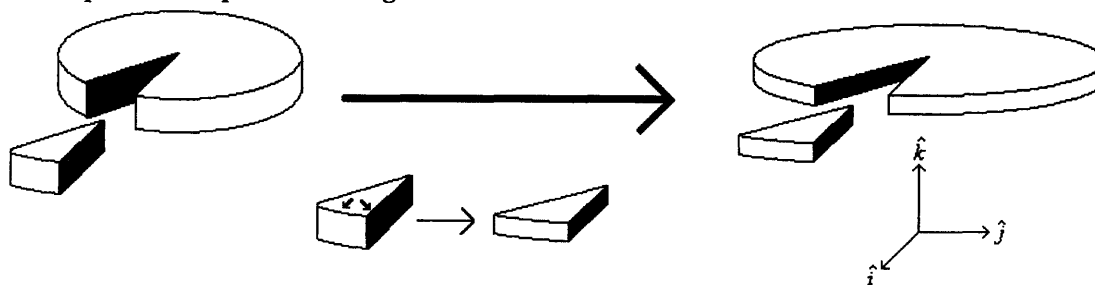
1.4 True Strain vs. Engineering Strain

It is easier to measure Engineering Stress, but True Stress is usually more useful in analysis. Engineering Stress is the amount of force applied to the sample divided by the original area of the sample. However, as the sample is either compressed or pulled in tension the cross-sectional area of the sample changes. True Stress is the amount of force applied to the sample divided by the current cross-sectional area of a sample. Engineering Strain and True Strain are similar in relation. Engineering Strain is the change in the cross-sectional area of a sample divided by the original sample cross-sectional area. True Strain is the natural logarithm of the ratio of the current cross-sectional area divided by the original cross-sectional area.[7] Converting Engineering Stress and Engineering Strain to True Stress and Strain is important because the Engineering terms are much easier to collect data from, but the True values are much more valuable for analysis.

2 Materials

The samples that were used in this experiment were from two separate manufacturers. Iupilon™, from Mitsubishi Corp., was used in powder form. Iupilon™ is a widely available commercial-grade polycarbonate with a numerical molecular weight of 31,700 and a polydispersity index (PDI) of 2.6. Triton Systems Inc. created two samples for use in this experiment. The first powder created was called FX™ and shall be referred to as FX™ Control from here on. This powder was designed as a polycarbonate, but the carbonate group was replaced completely with a phosphorus group that was intended to increase flame retardant properties. The powder was a combination of Biphenyl A and a flame retardant phosphorus group. [Figure 6] The numerical molecular weight of this sample was ~4.0 Kg/mol with a PDI of 8.1. Triton Systems Inc. also created a powder of FX™ that contained 15% triptycene by weight. It should be noted that the triptycene units were not uniformly placed along each polymer chain, but randomly dispersed. The number average molecular weight of the FX™ Triptycene powder was ~6.4 Kg/mol with a PDI of 5.8.

Figure 6: Chemical Formulae for base materials.

Iupilon
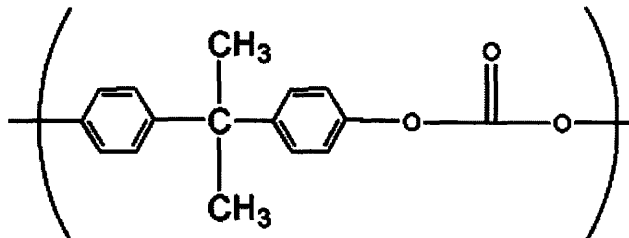
FX Control

FX Triptycene

$$\frac{X}{Y} = \frac{85}{15}$$
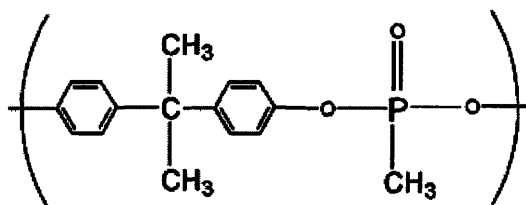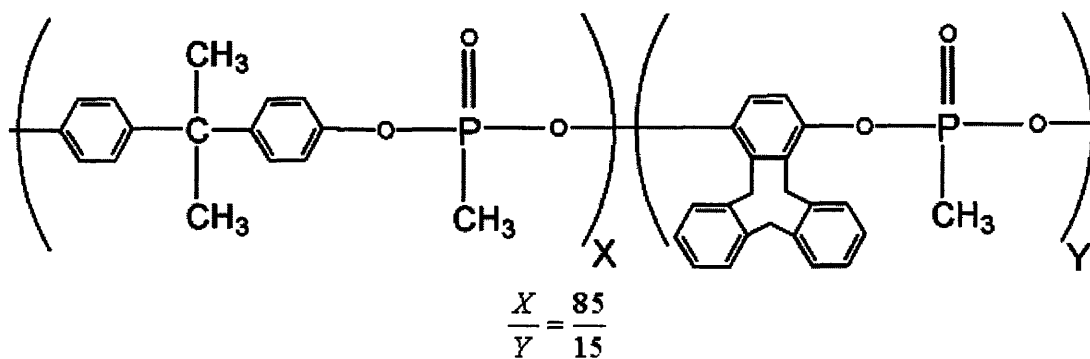
It should be noted that the molecular weights of both FX™ samples are very low compared to the commercial-grade Iupilon™ from Mitsubishi Corp. The number average molecular weight numbers for the FX™ Control and FX™ Triptycene samples are also thought to be inflated due to molecular branching in each of the powders. This could have been caused by manufacturing processes that Triton Systems may have implemented to increase the molecular weight of the powders. A polymer looses entanglement below certain molecular weights and behaves very differently under deformation. To counteract this effect both FX™ samples were blended with Iupilon™ to increase their effective sample molecular weights. The blends contained 10% weight FX™ (Control or Triptycene) and 90% Iupilon™. The amount of polymer chains with triptycene units in the FX™ Triptycene blend is 1.5%.

It should also be noted that blends were also created using 25% weight FX™ (Control or Triptycene) with 75% Iupilon™, as well as 50% FX™ (Control or Triptycene) with 50% Iupilon™. These blends were not used in testing due to a lack of quality. The poor quality of these samples was most likely due to a combination of errors in processing and the low quality of the FX™ base material. Many of these samples were not fully melted during melt pressing, and some had already turned a dark brown color most probably due to thermal degradation.

3 Sample Preparation

The polymer blends of Iupilon™ and FX™ samples were created through a solvent casting process and a melt process. First, the appropriate amount of each powder was weighed out and combined with dichloromethane to form a solution, and then uniformly combined with the FX™ (Control or Triptycene) and Iupilon™. After dissolving, the solution was cast in Teflon boxes and let sit for at least 48 hours. The dried substrate was then powderized using a pestle and mortar and dried in a vacuum oven at 60 degrees Celsius for twelve hours. The powder sample was then melt pressed in a steel ring at 285 degrees Celsius at 7,500 psi for ten minutes. The sample disk was cooled quickly by using chilled water that ran through the plates.

This procedure was repeated three times for the FX™ Control blend and three times for the FX™ Triptycene blend. Three disks of pure Iupilon™ were also created through melt processing at 285 degrees Celsius at 7,500 psi for ten minutes. The Iupilon™ disks were not created through solvent casting. Two of the three solid disks from each of the three blends were shaved to remove surface defects, and then carved into smaller disks. The smaller disks had identical ratios of height to diameter for compression testing purposes. The smaller disks did not necessarily have the same ratio of height to diameter as the larger disk. The larger disks had diameters of roughly six centimeters. All samples were transparent. The clarity of the samples was examined for yellowing and for bubbles trapped in the sample from melt processing. If any visible bubbles existed in the solid disk when it was removed from the iron ring, the disk was

then pressed at 200 degrees Celsius at 15,000 psi for two minutes. For most of the samples bubbles were observed in the blended disks.

4 Testing

4.1 Compression

      To test the hypothesis that triptycene units increase the compressive yield modulus of polycarbonate a static rate compression test was performed. This test was performed using a Zwick/Roell Z010 uniaxial compression tester. The small disks were identical in their height/diameter ratio. Before testing on the Zwick/Roell, the samples were dried in a vacuum oven at 60 degrees Celsius for two days. A lubricant, WD-40, was applied on the compressive plates to avoid any cohesion of the samples to the apparatus. The samples were placed on a Teflon sheet inside the apparatus with another Teflon sheet resting on top to prevent any cohesion of the sample to the testing apparatus. [Figure 7] The compression tests began without contacting the samples. Once the sample was engaged the test continued through 60% engineering strain.

Figure 7: Zwick/Roell Z010 Materials Tester.
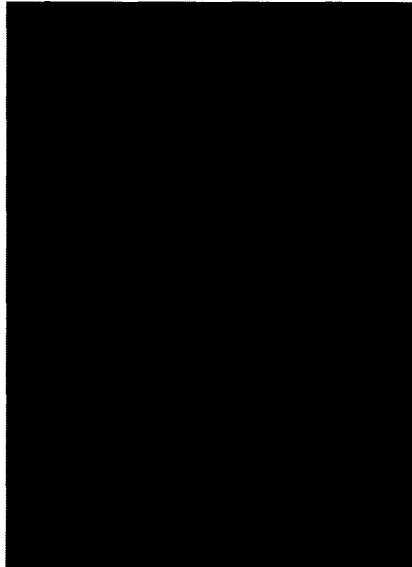
Two of the different blends, FX™ Triptycene and Pure Iupilon™, were tested three times, each at three different strain rates. These strain rates were 0.001, 0.01, and 0.1 strain % per second. FX™ Control was tested five times at 0.001 strain % per second, three times at 0.01 strain % per second, and four times at 0.1 strain % per second. The extra samples were tested for FX™ Control because initial results were not as consistent as for the other two blends, and thus more data points were gathered to remove any anomalies.

4.2 DSC

Differential Scanning Calorimetry (DSC) was used to determine if the sample blends were phase separated. Differential Scanning Calorimetry determines how much heat is needed to increase the temperature of a given sample. It is adept at detecting localized molecular motion transitions through the addition of heat. If a sample is at its glass transition temperature it requires more energy to increase the temperature because some of the energy that is being applied to the system goes into the transition change from glassy to non-glassy. DSC was used to determine where the glass transitions of the original Iupilon™, FX™ Control, and FX™ Triptycene powders lay. DSC was also used to determine if more than one glass transition was present in any of the blended samples. If more than one glass transition temperature was present, it would mean that the blend had phase separated.

Each sample tested using DSC was first cooled to zero degrees Celsius. The samples were then increased to 285 degrees Celsius at a rate of 10 degrees Celsius per minute. The samples were then cooled to zero degrees at the same rate. For each sample this test was repeated with no time elapsed in between tests such that each sample was held isothermally at zero degrees twice and held at 285 degrees twice. After the second isothermal hold at 285, the samples were cooled back down to zero degrees. At each high and low endpoint the sample was held isothermally for five minutes.

4.3 TGA

Some of the samples exhibited a yellow tint after melt processing. Thermal Gravimetric Analysis (TGA) was performed to determine if this yellowing occurred

because of degradation of the sample when melt processed at 285 degrees Celsius. TGA determines the amount of weight lost as a sample is heated. Thermal energy can break covalent bonds, especially in the presence of oxygen. TGA was conducted in air to examine any thermal degradation that may have occurred. The powders of original Iupilon™, FX™ Control and the FX™ Triptycene as well as the FX™ Control blend and FX™ Triptycene blend were tested. A sample of each powder and blend was subjected to an increase in temperature of 10 degrees Celsius per minute up to 285 degrees Celsius where it was maintained isothermally for 40 minutes.

A sample of each powder and blend was also subjected to an increase in temperature up to 400 degrees Celsius at five degrees Celsius per minute. This test was performed to determine how much the samples would degrade at a temperature much higher than the melting temperatures.

5 Results

5.1 Compression

The results that were gathered under the compression test were in terms of force applied by the Zwick/Roell and the distance traveled from the point of initial contatct. To analyze this data correctly these values were converted into true stress and true strain. Equation 1 illustrates how using the force applied with the cross-sectional area of the sample gives rise to the engineering stress, where F is the force applied and d is the diameter of the sample. Engineering strain can be found by dividing the sample Area A_0, by the distance traveled ΔA, as shown by Equation 2. Engineering stress is converted to true stress using engineering stress and engineering strain as exhibited by Equation 3. True strain is a function of only engineering strain illustrated in Equation 4. The results obtained have negative true strain because the system underwent compression. The opposite of the true strain was used in the various figures for easy viewing.

$$\sigma_E = F \cdot \frac{1}{\pi \left(\dfrac{d_0}{2}\right)^2} \qquad\qquad \textbf{Equation 1}$$

$$\varepsilon_E = \frac{\Delta A}{A_0} \qquad\qquad \textbf{Equation 2}$$

$$\sigma_T = \sigma_E \cdot \left(1 + \varepsilon_E\right) \qquad\qquad \textbf{Equation 3}$$

$$\varepsilon_T = \ell n \cdot \left(1 + \varepsilon_E\right) \qquad\qquad \textbf{Equation 4}$$

The true stress vs. true strain results were consistent for all three strain rates. the same. Figure 8] [Figure 9] [Figure 10] The compressive yield stress of the FX™ Triptycene blend was higher across all three strain rates than almost all of the FX™ Control blend samples. There was one value for compressive yield stress of FX™ Control at 0.1 strain % per second that was higher than the FX™ Triptycene blends. All other values for FX™ Control at all strain rates were below FX™ Triptycene values. It is also interesting to note that the FX™ Control blend had a greater compressive yield stress than pure Iupilon™. For all strain rate tests at a true strain above 0.6, the stress values of the three blends were amount of stress exerted on each of the three blends was the same.

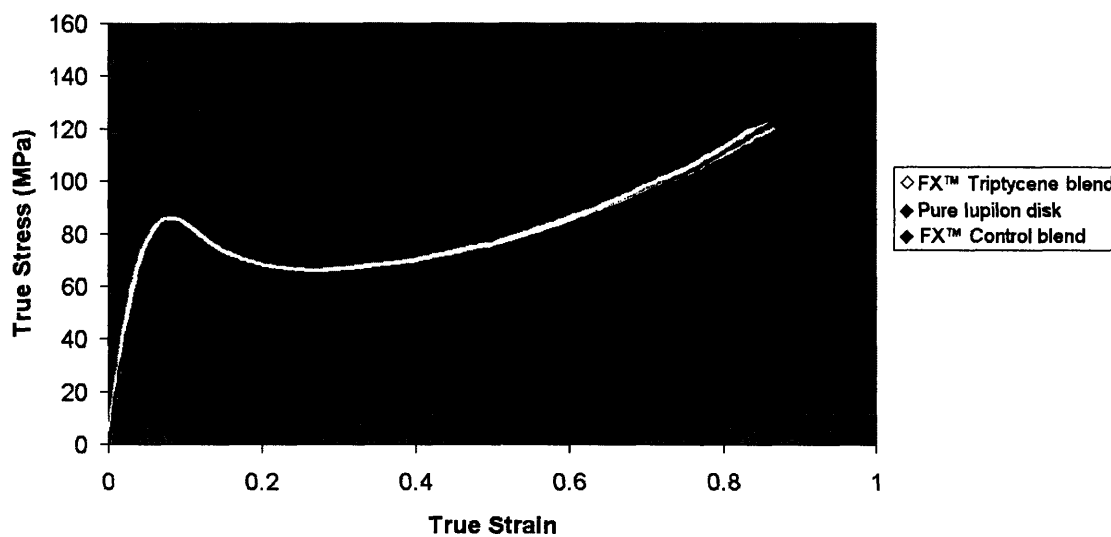**Figure 8**: True Stress vs. True Strain. 0.1 % per second strain rate

Figure 9: True Stress vs. True Strain. 0.01% per second strain rate
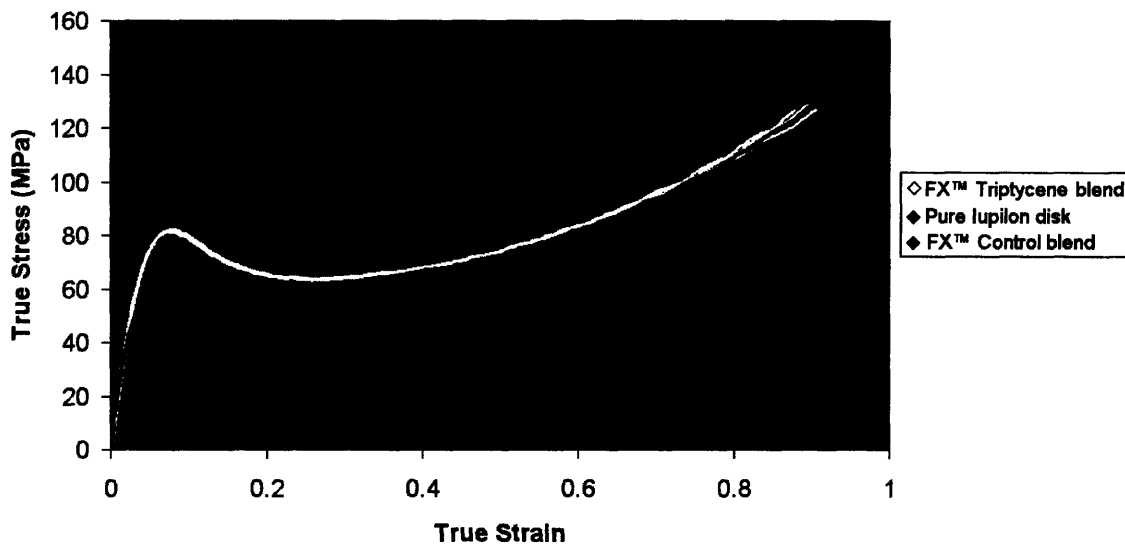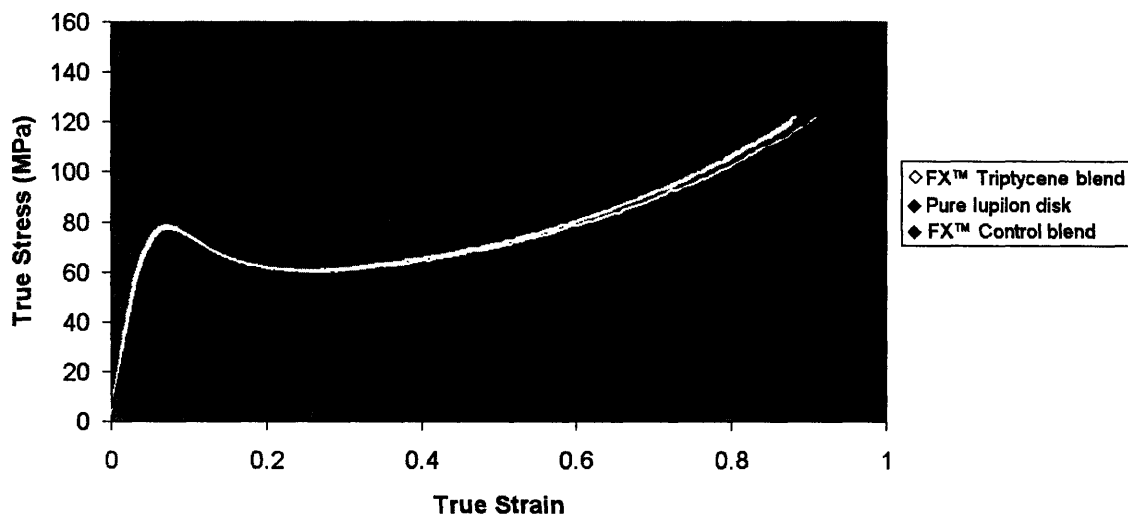

Figure 10: True Stress vs. True Strain. 0.001 % per second strain rate

5.2 DSC

Differential Scanning Calorimetry was conducted by thermally scanning the sample with temperature ranging from zero degrees Celsius to 285 degrees Celsius. However, the results are from different cycles of scanning. The results used for the

powder samples are from the second cycle of the increasing temperature scan. This was done so that the data used in analysis was of material that already had a compact solid form when it was heated. The first cycle of the increasing temperature scan was used for the already solid blended materials. It should also be noted that the data from the decreasing temperature scans was not used, and that only the increasing temperature scans from zero to 285 degrees were used in analysis. The values of Heat Inflow in Figure 11 and Figure 12 are not absolute values, but relative values for a given curve. Constants were added to the values of heat inflow to spread out the curves vertically for easy analysis and viewing. The amount of heat inflow is not relevant to the analysis of the DSC because it depends upon sample size. However, a change in the curve is of high interest.
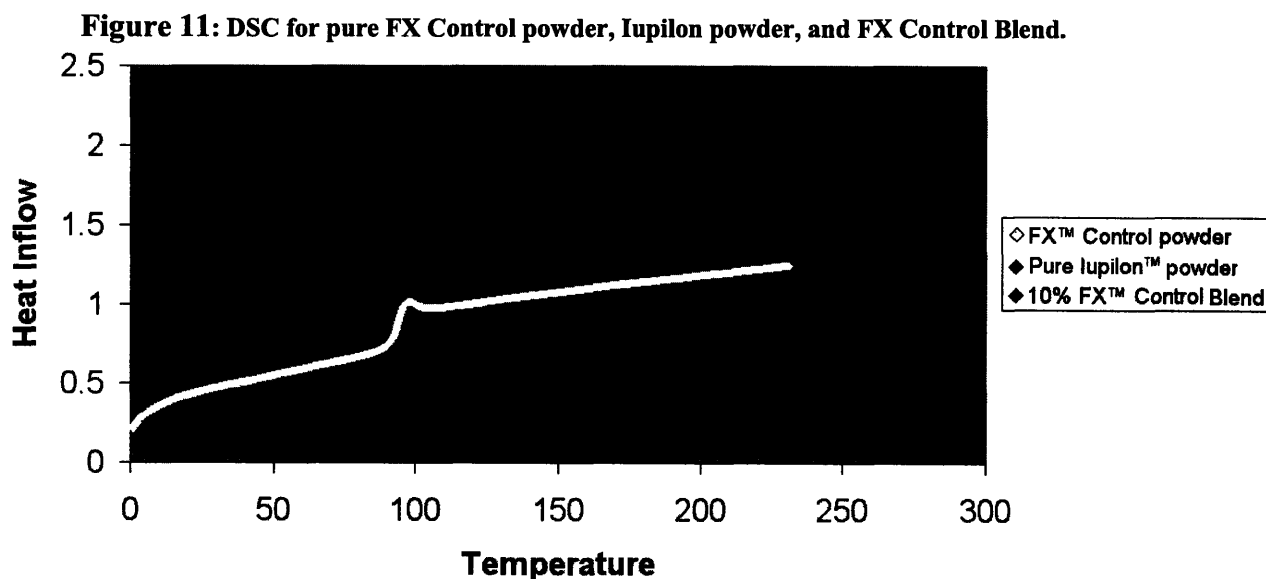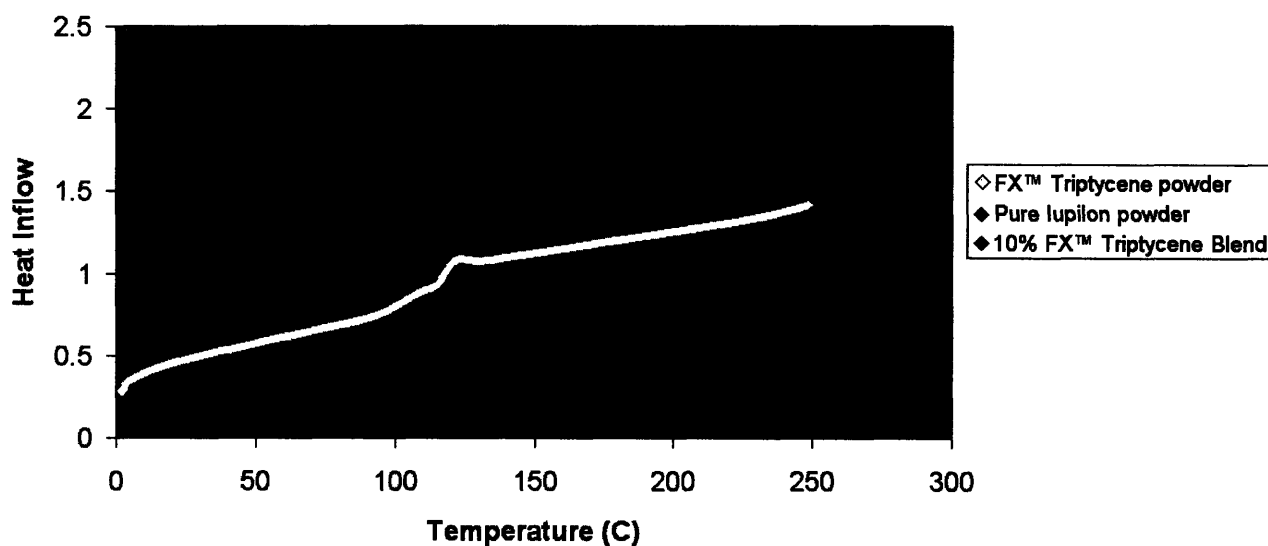
Figure 11: DSC for pure FX Control powder, Iupilon powder, and FX Control Blend.

Figure 12: DSC for pure FX Triptycene powder, Iupilon powder, and FX Triptycene blend.


In Figure 11 the glass transition temperatures of both powders, as well as the blend, are visible as areas of temporarily increased slope in the heating curve. Iupilon™ powder is shown to have a glass transition temperature (Tg) of 152 degrees Celsius. The FX™ Control powder is shown to have a Tg of 93 degrees Celsius. The blend of the Iupilon™ and FX™ Control powders does not deviate from the smooth curve at either 93 or 152 degrees Celsius. The Tg of the FX™ Control blend is 139 degrees. If the two powders had phase separated in the blend there would be a change in slope in the Heat Inflow at the glass transition temperatures of both powders. Instead we see that the glass transition temperature of the blend falls in between the Tg values for the two powders. It is also much closer to the Tg of Iupilon™. This is to be expected due to Iupilon™'s overwhelming 90% weight presence in the blend.

The same results are seen in Figure 12. The Tg of Iupilon™ is again 152 degrees Celsius and the powder of FX™ Triptycene has a Tg of 117 degrees Celsius. The blend exhibits a Tg of 145 degrees Celsius, and does not have any changes in slope in Heat Inflow at either of the Tgs of the powders. The blend does not exhibit any signs of phase separation.

5.3 TGA

During the preparation of the samples it was noted that the FX™ Control samples as well as the FX™ Triptycene samples were yellowish in color. Triptycene as an additive typically causes a material to yellow, but the FX™ Control was not expected to yellow. TGA was performed to determine if this yellowing of the samples was due to thermal degradation. The results from the TGA (Thermo Gravimetric Analysis) tests show very little degradation in the Iupilon™ powder. For the test that increased temperature by 10 degrees Celsius per minute and held the samples at 285 degrees Celsius, the lower molecular weight FX™ Control and FX™ Triptycene samples both degraded. This test was an attempt to mimic the conditions of the melt processing that the sample underwent in preparation. Both the FX™ Control and FX™ Triptycene samples degraded four weight percent as shown in [Figure 13].

Figure 13: TGA for 10 degree ramp and held at 285 degrees Celsius for 40 minutes
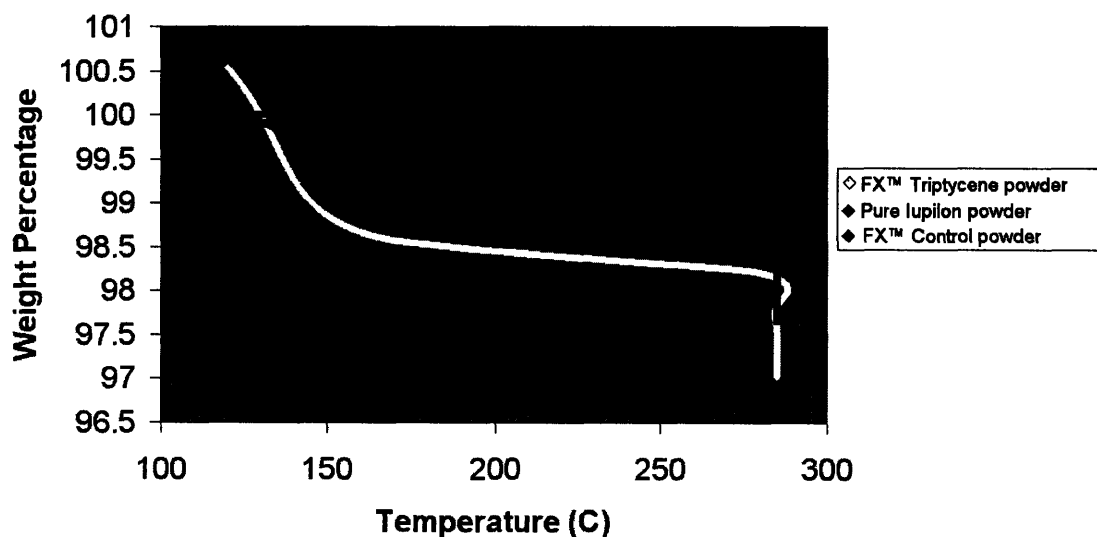
The second TGA test increased temperature by 5 degrees per minute up to 400 degrees Celsius. Iupilon™ was stable for this test, but FX™ Control lost 6% of its mass. Data of FX™ Triptycene was not available for this test due to a malfunction in the Thermogravimetric Analyzer during the test of that sample. The machine was broken for the remainder of the testing period and unfortunately no data could be collected on FX™ Triptycene. [Figure 14]

Figure 14: TGA for 5 degree ramp up to 400 degrees Celsius
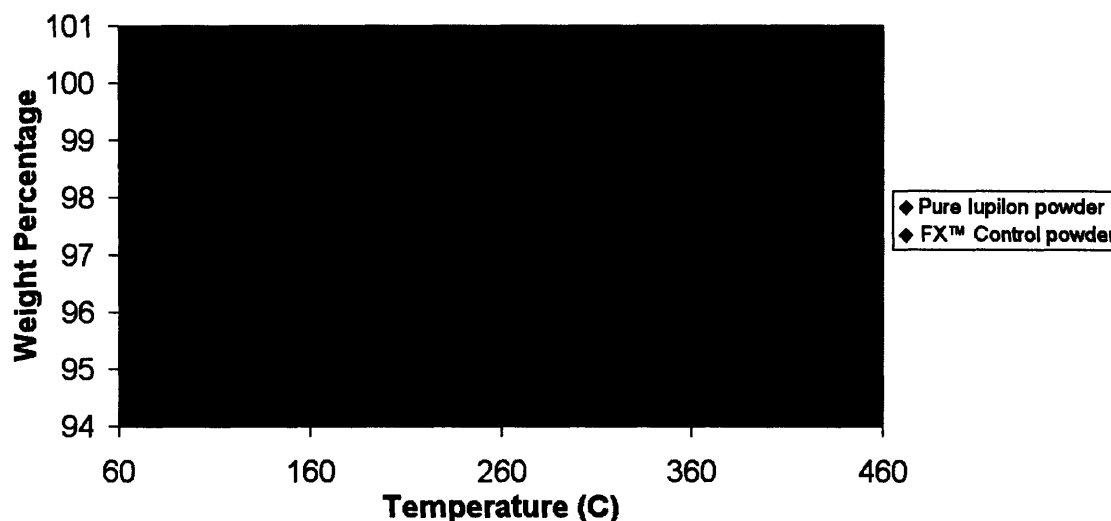
6 Discussion

6.1 Compression

The compression test results show that the FX™ Triptycene blend had a larger compressive yield stress under all static strain rates than the FX™ Control blend. [Figure 15] This can be attributed to changes in behavior induced by the presence of triptycene units. One possibility is that during the outward radial flow of material the polymer chains flowed past one another and the triptycene units may have threaded as described earlier in tension. This would have increased the modulus and the yield stress of the samples because threading holds chains together in a network. Another means that triptycene could have caused an increase in the yield stress of the samples could be due to steric hindrance of the triptycene side units. Triptycene is a large side unit on the polymer chain, and this bulkiness could have increased the amount of stress required to compress the sample and cause the sample to flow radially.

Figure 15: Compressive Yield Strengths
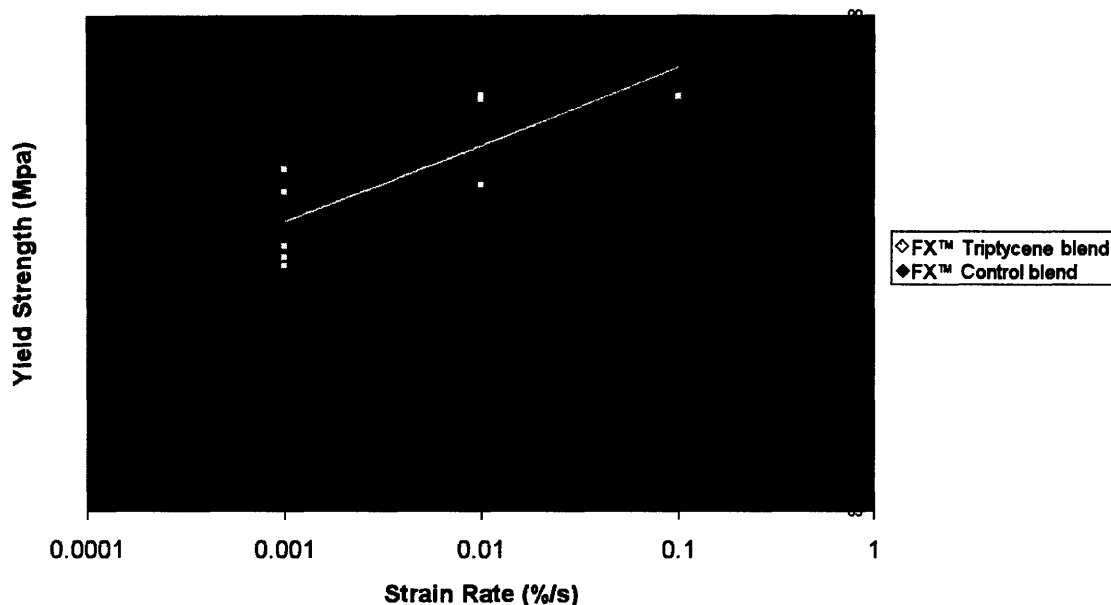
The blend of FX™ Control powder and Iupilon™ had a larger compressive yield stress under all static strain rates than pure Iupilon™ . This is surprising since it was assumed that FX™ Control powder was similar to commercial-grade polycarbonate. This could be due to the presence of the substituted phosphorus group for the carbonate group. It could also be due branching that may have occurred during the manufacturing of the powder by Triton Systems Inc. The low molecular weight of both the FX™ Control and FX™ Triptycene powders changes the characteristics of material. For a polymer to exhibit the same properties due to entanglement there needs to be a sufficient molecular weight to cause this entanglement. The critical entanglement molecular weight of polycarbonate is 1500, which is quite close to the molecular weight values of the FX™ powders.[8] Also the Polydispersity Index (PDI) is very high for both of the FX™ powders. This means that the distribution curve of the molecular weight value is very large. There are individual polymer chains that will be much lower molecular weights than the values given as well as some higher.

Triton Systems may have created FX™ Control powder under different conditions than polycarbonates are usually created. This would cause the pure Iupilon™ baseline to be less valuable. Additionally, if Triton created FX™ Control powder and FX™ Triptycene powder using very different processes, the results obtained could be due to these processing differences and not the triptycene unit.

6.2 DSC

The results from the DSC graphs show that both the FX™ Control blends and the FX™ Triptycene blends were not phase separated. The glass transition temperatures of the blends fell between the composition powders. This is exactly what we expect from a homogeneous blend. If the blends were phase separated, we would expect multiple glass transitions and lower physical properties such as compressive yield stress.

6.3 TGA

The TGA tests were originally performed to determine if there was significant degradation of the samples when they were melt processed into blended disks. The tests were performed in oxygen and did show some signs of degradation in the test where the samples were held isothermally for 40 minutes at 285 degrees Celsius. This was cause for concern, especially because the samples turned a yellow-brownish color. The samples remained transparent, but a dark yellow tint was clearly visible. It is also clear from the TGA tests that Iupilon™ is a far superior product that is very stable even at high temperatures. It appears that FX™ Control and FX™ Triptycene are not as stable at higher temperatures in the presence of oxygen. This is surprising considering that the phosphorus group substituted in FX™ Control was created to make the polymer more resistant to flame. It is difficult to be resistant to flame if the polymer degrades by as much as five or six percent as seen in the TGA experiment. This further proves the low quality of the Triton Systems Inc. FX™ samples. If the samples did not degrade, it is likely that the physical properties such as compressive yield stress may have shown an increase even greater than that seen.

7 Suggested Further Work

The research conducted in this thesis could be further enhanced through two main avenues. A recurring theme in the discussion of the results was the extremely low sample powder quality. To further this research it would be wise to work with more reliable, higher molecular weight, and more stable starting materials. Iupilon™ was an excellent selection, but the sample powders of FX™ Control and FX™ Triptycene were very poor. It would also be wise to do more research with tension tests to further study the effects of triptycene interlocking, as well as the role of the beta transition.

More testing should be done with the current blends. Dynamic Mechanical Analysis would hopefully show a thermal transition associated with the triptycene side units. [Figure 16] Also, testing at much higher rates $(10^{-4}\,\mathrm{s}^{-1})$ using a Split Hopkinson bar would help further prove the application of polycarbonates with triptycene side units as ballistic impact resistant materials. Triptycene units have the potential to increase physical characteristics of many polymers with little cost and effort.

Figure 16: Expected polycarbonate molecular motion transitions. Expect a gamma transition to occur due to triptycene unit effect
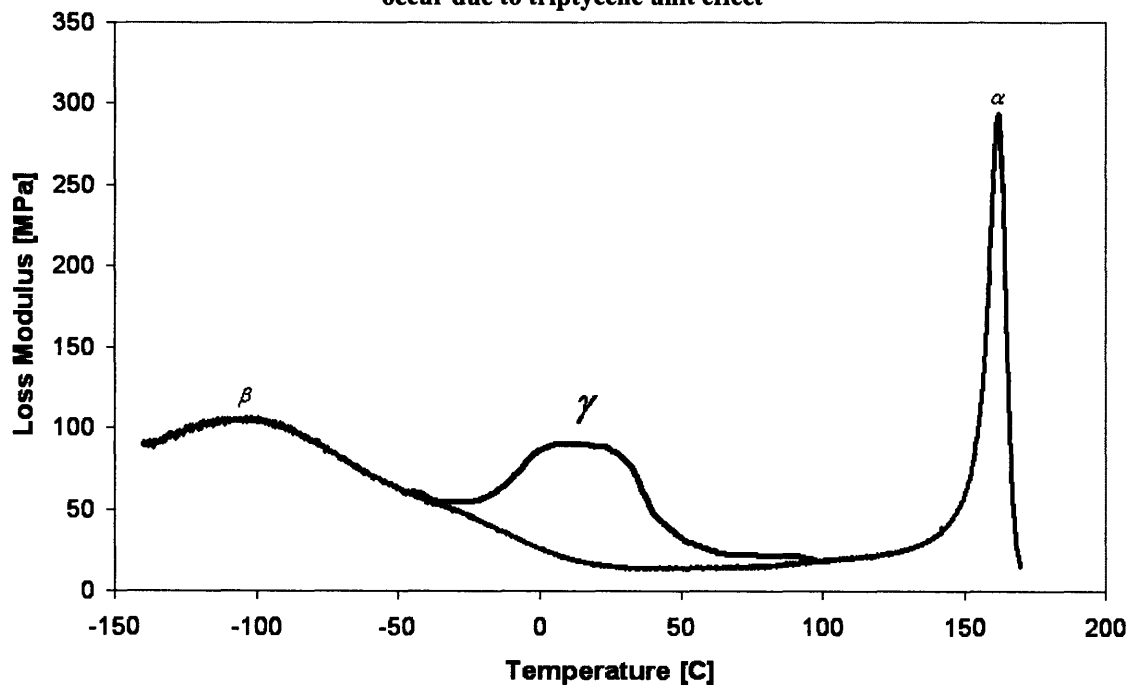
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