

**JEFFAMINE™-EPOXY TOUGHENED UNSATURATED  
POLYESTER, INTERPENETRATING  
POLYMER NETWORK (IPN)**

Presented to the Graduate Council of Southwest Texas State University

in partial fulfillment of the requirements for the degree of

Master of Science

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## DEDICATION

*To My Mother (Zeina Mustafa Agha) and Father (Ghazi Shaker el-Jishi). Whom without, this would have not been possible.*

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## ABSTRACT

A series (15:85%) translucent intact IPNs made of a reactive rubber (Jeffamine™), a commercially available epoxy and unsaturated polyester were prepared. All IPNs showed increased toughness with incorporation of the Jeffoxy rubber. DMTA data showed a single T<sub>g</sub> phenomena and narrow peak widths with a shift in T<sub>g</sub> for all rubber containing IPNs. Jeffoxy DMTA data showed high molecular weight tri-amine T-5000 with highest tan  $\delta$  value (2xT-403). DSC calculations showed complete extent of cure at 90°C for an 8h cure time. A 45% increase in Izod impact strength (toughness) with least standard deviation recorded for T-509 containing IPN. T-509 strength was comparable to that of the pure PE. Stiffness and strength values documented for all IPNs using a three-point, bend flexural test. Material with the highest flexural modulus was that of linear di-amine D-2000. Highest strength recorded for T-403 and D-2000 IPNs. SEM images showed T-509 with no scattered particles (1-20 $\mu$ m) suggesting good distribution of rubber particles in polyester. TGA values compared well with that of the neat polyester the exception was that of T-403 which exhibited a 20°C decrease.

# **Jeffamine™-Epoxy Toughened Unsaturated Polyester InterPenetrating Network (IPN)**

## **1. BACKGROUND**

### **1.1 Interpenetrating Polymer Networks (IPNs)**

The first interpenetrating network was discovered by Aylsworth in 1914 and can be defined as a combination of two or more network polymers “synthesized in juxtaposition” (1). A better definition is offered by Kim (2): “An Interpenetrating Polymer Network (IPN) is a mixture of two or more cross-linked polymers with a physically interlocked network structure between the component polymers” ( Figure1).

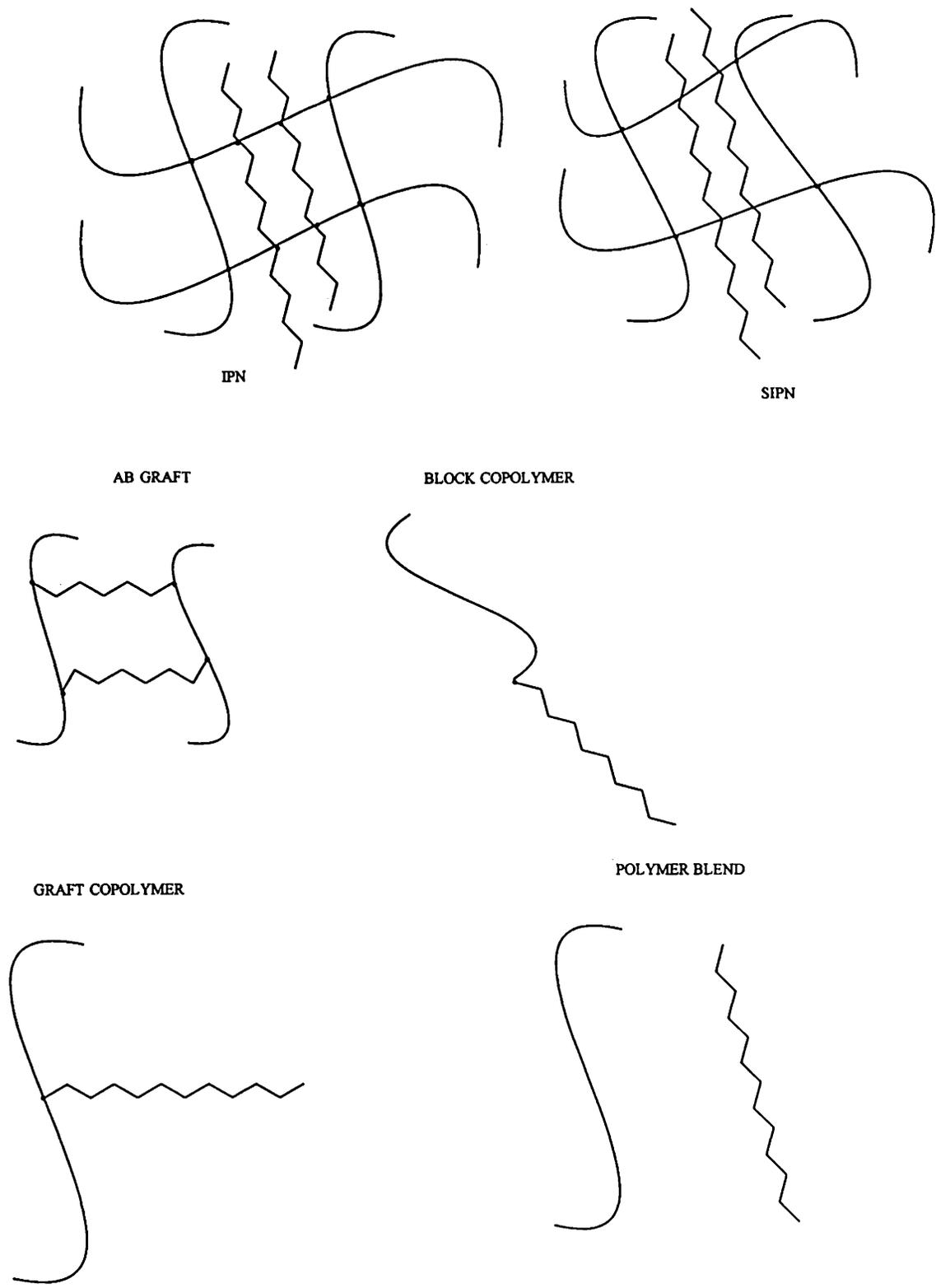


Figure 1: IPN, Semi -IPN vs. Other Polymers

IPNs form an extensive interlocked highly cross-linked structure, they differ from graft copolymers, polymer blends, and block copolymers in that they are thermosets whereas the former are thermoplastics. IPNs possess thermoset characteristics such as thermal and chemical resistance.

## 1.2 History and Development of Brittle Polymers

Use of brittle polymers, such as PVC and PS, was limited prior to the development of rubber-toughened polymers in the late 1930's and 1940's. Improvements in the low temperature resistance of these materials, was accomplished through graft or block co-polymerization. Toughness may be defined as resistance to impact with low-impact polymers having Izod impact strengths of greater than 105 J/M (3).

## 1.3 Polyesters

Polyesters have been used in engineering plastics since the early 1970's due to their physical integrity and mechanical properties. Two kinds of polyesters used are polyethylene terephthalate (PET or PETE) and polybutylene terephthalate (PBT) both semi-crystalline, they have found wide use in industry as pure thermoplastics or as toughened thermoplastic blends. Having physico-chemical properties similar to polyamides they have competed for the same applications along with the relatively tough polycarbonates (4). The first all-synthetic fiber was a flexible aliphatic polyester produced by Carothers and Hill in 1932 (3). The first rubber-toughened PET (Rynite) was produced by Dreyrup of du Pont in 1978 (3). Today however, in a move to induce even

stronger and more highly cross-linked materials, unsaturated polyesters have become the material of choice.

Unsaturated polyesters are highly cross-linked, undergoing rapid addition polymerization with the appropriate initiator (e.g benzoyl peroxide) and cross-linker (e.g. styrene). These materials though mechanically strong and chemically resistant, suffer from the problem of being brittle, a characteristic of low impact resistance.

#### 1.4 Rubber-Toughened Polymers

Unsaturated polyesters (UPs) combined with glass fiber-reinforced plastics (GRP or FRP) have because of their strong mechanical properties been long used in boat materials, pipes, tanks, car components and building panels (5). Though mechanically strong, they suffer from being of poor toughness possessing a low resistance to impact. They are hard and brittle and applied as low cost glass fiber-reinforced plastics (6).

Similarly, epoxies are commercially relevant materials with a wide range of applications and are even a stronger material, but, like unsaturated polyesters, still lack good toughness. Attempts to toughen epoxies have included incorporation of a rubber liquid (7-9), although reduction of  $T_g$ , tensile strength, and modulus, were negative side effects (6).

Thermoplastic modification through blending or addition to another thermoset was another possibility for toughening the thermoplastic (10-13). With recent extensive research in the blending of two thermosets to form IPNs (13-18), IPNs have been shown to display an improvement in mechanical properties (19-20) and improvement in

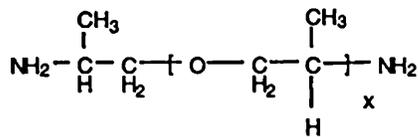
cracking energy-absorbing capability. Examples of this were improved crack resistance of an epoxy/acrylic IPN (20) and improved toughness for an epoxy/UP IPN (6).

Polyurethanes have long been used as a rubber component to toughen unsaturated polyesters (and vice versa). Kim (2) reported a four-fold improvement in impact strength for an 80/20 (w:w) UP/PU composition. Kim *et al.* (21) reported a two-fold increase in fracture toughness of a UPE system.

## 2. INTRODUCTION

Our approach is to improve the toughness (resistance to impact) of the UP by incorporating a new rubbery component. Our rubbery phase will be made of an epoxy modified by a Jeffamine™ reactive rubber. A desirable polyester system would have mechanical strength and chemical resistance while having a higher impact resistance. The incorporated rubbery phase is desired as a separate dispersed component in the polymer. This way, the toughness of the UP is improved without sacrificing significantly the overall mechanical property of the material, such as modulus or ultimate strength. An elastomer-modified, unsaturated polymer would therefore be comprised of an unsaturated polyester modified by a low molecular weight elastomer. Epoxy molecular weights are approx. 3500 g/mol our own reactive rubbers (Jeffamines™) range from 400-5000 g/mol in MW (see Figure 2).

Typical Chemical Structure of a Diamine. For D-2000 ( $x=33.1$ )



Typical Chemical Structure of a Tri-amine  
For T-403 ( $x+y+z = \sim 5.3$ )

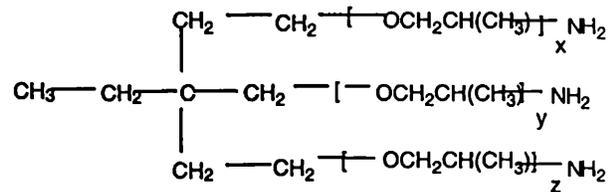
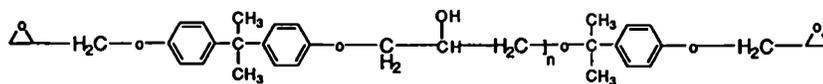


Figure 2: Typical Chemical Structures of Linear and Branched Jeffamines™

Idealized structure of unsaturated polyepoxide  
Avg. MW 350-3000



Idealized unsaturated polyester structure

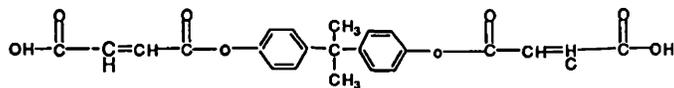


Figure 2a: Idealized Epoxy and Unsaturated Polyester

The low molecular weight mix ensures compatibility with the unsaturated polyester. Keeping the elastomer composition below 20% by weight of the whole polyester composition minimizes phase separation. Phase separation occurs during the polymerization step; but, due to the formation of the physical interlocking networks of the component polymers, phase separation is permanently stopped during polymerization when both component polymers reach their gel-point. The presence of the physical interlocking at the interface of the two component polymer domains enhances the adhesion between the matrix and dispersion which are one of the major factors in the performance of rubber-toughened plastics (2). The degree of toughening is strongly dependent on the phase-separated morphology; ideally a fine dispersion of the elastomer is desired in the UP matrix (particle size  $<1 \mu\text{m}$  by SEM ) (21,23).

McGarry has shown that initially the components are fully soluble and compatible, but as the reaction proceeds, the molecular weight of the products increases and phase separation results (23). Further, as the rubber component is kept under 9% (w:w) of the overall UPE, the continuous phase is the UPE; but above 9% a phase inversion takes place and the elastomer becomes the continuous phase as evidenced by SEM.

Another consideration for keeping the rubber incorporation to  $<20\%$  is that the addition of thermoplastic modifiers costs more than the thermoset resin itself. Therefore, it becomes necessary to develop thermosets with low thermoplastic concentrations in them (6).

Incorporation of high-performance thermoplastics into thermosets has recently been highlighted as a new approach to enhancing the toughness of thermosets without significantly lowering their thermal and mechanical properties (2,23-27).

In our study an unsaturated polyester resin containing a cross-linker (styrene) and an added initiator (benzoyl peroxide) was incorporated with a Jeffamine™-epoxy component (Jeffoxy) to form an IPN under heat. The epoxy resin is reacted with an amine-terminated flexible polymer before being mixed with the unsaturated polyester resin containing the curing reagent and cross-linker. The epoxy resin terminal groups on low molecular weight elastomers make the molecule sufficiently compatible with the polyester component that a homogeneous dispersion of elastomer particles can be achieved on cure.

McGarry (23) has shown through infrared spectroscopy experiments, that the Michael addition reactions of the amine-terminated elastomer occur less rapidly with the double bond of the UP when compared to the rapid attack that takes place between the carboxylic acid end groups of the UP and the epoxy. This leads to some grafting of the UP and some chain extension in addition to cross-linking (23).

Unsaturated polyesters that have increased fracture energy can be made from the reaction of an epoxy with an amine system in the presence of polyester resin with a vinyl cross-linking agent and initiator. McGarry (23) reports a ten-fold increase in toughness with a rubber content of 20%. Such primary di- or tri-amine-terminated elastomers (see Figure 2) are known as Jeffamines™ and are commercially available from Huntsman. The Jeffamine™ can be varied in MW or chemical structure/geometry ( di vs. tri) linear or branched (see Figure 2).

The amine-terminated flexible polymer segments are generally liquid polymers that enhance the toughness and pliability of polymers. The first letter preceding the Jeffmaine™ name indicates whether the Jeffamine is a di - or tri- amine. The number that follows is an indication of molecular weight. As an example Jeffamine™ D-2000 is a di-amine with a MW of 2000g/mol

The focus of this study is to investigate the incorporation of four different Jeffamines™(D-2000,T-403,T-509,T-5000) into an epoxy/UPE system with the desire of screening the best material that offers improvement in UPE toughness/resistance to impact. DMTA will be used to determine the degree of compatibility of the UPE/rubber through examination of Tg (tan  $\delta$  max.). Physical appearance, as well as tan  $\delta$  peak width will be measured to give an indication of IPN formation and compatibility (30). DSC will be used to examine extent of cure. Toughness measurements will be done by examining impact strength values of the various IPNs; using the Notched Izod Impact Test. Flexural Modulus and Strength at Break will be measured using a flexural three-point bend test. SEM photomicrographs will be obtained to determine the microstructure interactions of the IPNs and to get an indication of compatibility. TGA data will be documented to examine thermal decomposition properties of the IPNs by comparing them to the neat PE.

### 3. EXPERIMENTAL

The styrene-containing (40-65%) unsaturated polyester resin (Polylite) was obtained from Reichhold, Inc. Benzoyl peroxide was used as received from Aldrich. The epoxy resin used was Dow's D.E.R. Bisphenol A type liquid resin with EEW (Epoxy Equivalent Weights) of 182-193. Jeffamines™ were obtained from Huntsman Corp. and were used as received (D-2000, T-403, XTJ-509, and T-5000), MW range 400-5000 g/mol. All Jeffoxy (Jeffamine™+epoxy)/UP mixtures were 15:85 % (w:w) in composition. The mold release used was Ultra 2 Yellow Label Universal Mold release supplied by Price-Driscoll Corp.

Thermogravimetric analysis (TGA) data collected on a Rheometric Scientific TGA at test conditions of 20°C/min nitrogen and air 15-20mg. Differential Scanning Calorimetry (DSC) data were collected on a Rheometric Scientific DSC with a heating rate of 20°C/min (5mg weighed samples). Dynamic Mechanical Thermal Analysis (DMTA) data were collected with single cantilever bending mode for all IPNs over a temperature range of -150°C to 250°C, with applied force conditions of 0.01%, 1 Hz, 5°C/ min.

DMTA for Jeffoxy samples were done in compression mode at applied force conditions of 1 HZ, 0.05%, 5°C/ min. All Jeffoxy samples were prepared by curing in oven for 8h at 90°C and allowed to sit at room temperature for 3 days. Only T-403 was fully cured when removed from the oven all other samples cured following the 3 day period.

Flexural three-point bend samples were prepared according to ASTM D 790-97. Samples were 3 inches long, 0.5 inches wide, 1/8<sup>th</sup> inch thick with 2 inches support.

Toughness was measured using an Izod Notch TMI Monitor/Impact instrument. Samples of 2.5 inches long, 1/2 inch wide were prepared according to ASTM D 256-92. SEM pictures were taken by Dr. Helga Sittertz-Bhatkar, Electron Microscopy Center; Texas A&M University.

### 3.1 Preparation of Polyester

A 225g amount of Polyester was poured into a 600 mL beaker and 3.94g of benzoyl peroxide was added. Polyester was transferred to a 500 mL, round-bottom flask and mixed/de-gassed for 1 hour on a rotaryevaporator at 35-40°C.

### 3.2 Preparation of Jeffamine™-Epoxy Mixtures

A 33.12 g of Jeffamine™ D-2000 was poured into a 400 mL beaker. A quantity of 11.92 g of epoxy were added and mixed well until a homogenous mixture was obtained.

### 3.3 Preparation of Jeffoxy-UPE Mixture

A 37.5g of Jeffoxy 2000 (JO-2000) was poured into a 600 mL beaker containing 212.5 g of the polyester (1.75-2% BPO). The solution was mixed well and transferred to a 500 mL, round-bottom flask and degassed on a rotary-evaporator for 3-3.5 h at 35°C. The degassing was critical to avoid cracking as well as to avoid bubbles in the final cast.

### 3.4 Preparation of the Molds

Both sides of the mold were sprayed with mold release. The mold was set upright and the JO/UPE mixture was poured in it. The cast was placed in a preheated oven (90°C) and allowed to cure for 8 h. The cast was allowed to cool in the oven before it was disassembled.

## 4. RESULTS AND DISCUSSION

### 4.1 Background

#### 4.1.1 A Compatible Elastomer/UPE System

The enhanced mechanical property of a toughened unsaturated polyester depends greatly on the degree of compatibility between the toughening agent and the unsaturated polyester. This compatibility can be tailored into the elastomer components by adjusting chemical structure and molecular weight. In our case, the reactive rubber (Jeffamine) component of our elastomer was varied in both molecular weight (400 to 5000g/mol) and in chemical structure/geometry (linear vs. branched see Figure 2).

#### 4.1.2 Mechanism and Rubber Particle Size

McGarry *et al.* (23) have shown that a two phase structure ensues upon mixing the elastomer and unsaturated polyester; one phase has no rubber while the other contains domains in the order of a few hundred angstroms of rubber distributed uniformly throughout. Below 9% (by weight) elastomer concentration, the continuous phase is that of the unsaturated polyester containing no rubber, whereas above 9% (as in our case) a phase inversion occurs and the continuous phase is now that containing the rubber with

the discontinuous phase having none. Further, it was demonstrated that a certain amount of chain extension takes place owing to the chemical reaction of the epoxy groups in the elastomer and the carboxylic acid end groups of the polyester. This reaction (between epoxy and carboxylic acid) is more rapid than the Michael addition reaction that takes place between the amino groups of the reactive rubber and double bonds of the unsaturated polyester. The resulting network (IPN) is then made up of chain extensions, some grafting, and cross-linking via the styrene and the reactive rubber of the unsaturated polyester chains.

Crosbie *et al.* (28) suggested that in order to produce a successful toughening additive for a polyester it is necessary to use a rubber, which is compatible with the uncured resin. This is so that the rubber will dissolve readily into the liquid resin and remain homogenous until curing begins. At the curing stage, the rubber precipitates out as a fine dispersion of particles (for example, hydroxyl-terminated poly (ether epichlorohydrin) has been found to be compatible with polyester to above 10% composition).

Low molecular weight epoxies (3500-4000 g/mol) mixed with reactive rubber-terminated amine resins enhance compatibility with the unsaturated polyester resin (5). D.S Kim *et al.* (21) concurred that a fine dispersion of particles gave significant improvement in toughness values. Particle size, adhesion strength between rubber particle and matrix and chemical structure of rubber particles are determinant factors in effecting physical toughness and toughening mechanisms of the modified polyester. Crosbie (29) noted that ideal particle sizes should be about 1-10 microns, with smaller numbers being more favored for enhancement of toughness properties.

### 4.1.3 Percent Composition of the Rubber

Yu-Seung *et al.* (31) highlighted the advantages for a percent composition of below 20% rubber incorporation in modified polyester resins. These advantages were discussed in the context of how the degree of toughening of thermoplastic modified thermosets, are strongly dependent on the phase-separated morphology. Kim *et al.* (2) showed the process of this phase separation to occur during the polymerization step. Due to the formation of physically interlocked networks of the component polymers (Jeffoxy and UPE in our case) phase separation was permanently stopped when both component polymers reach their gel point during polymerization.

The presence of the physical interlocking at the interface of the two component domains enhances the adhesion between the matrix and dispersion. This is one of the dominant factors in rubber-toughened plastics.

### 4.2 Dynamic Mechanical Thermal Analysis (DMTA)

Compatibility and Tg values of rubber and polyester IPNs can be determined by dynamic mechanical thermal analysis (DMTA) (30).

Tan  $\delta$  values can be compared for a mixture of discrete samples (polymer blends) or samples containing another component (IPN) to determine the loss modulus E' and storage modulus E'' of the material.

$$\text{Tan } \delta = E'' / E' \dots\dots\dots \text{(Equation 1)}$$

In DMTA a sample is subjected to an oscillating (dynamic) force while its thermal and mechanical behavior is recorded. E'' is a measure of the material's ability to dissipate or transform the energy of impact it encounters to heat or other. This loss modulus (E'')

value is directly related to the toughness physical property of our material.  $E'$ , on the other hand, describes the material's ability to store energy. A toughened material will exhibit an increase in its  $E''$  (ability to dissipate energy and therefore will possess a higher  $\tan \delta$  value (see equation 1).

The Flory-Fox equation can predict what the value of an IPN should be if complete miscibility of the two components is achieved leading to a single-phase homogeneous solid state (30). For phase-separated materials with some degree of miscibility (as in our case) an intermediate situation occurs. A shift will occur in the  $T_g$  of the first component if another component is present.

$$T_{\max, \text{blend}} = V_1 T_{\max,1} + V_{11} T_{\max,11} \dots \dots \dots \text{(Equation 2)}$$

Where  $V_1$  and  $V_{11}$  are the volume fractions of the two components and  $T_{\max,1}$ ,  $T_{\max,11}$  are the  $\tan \delta$  loss peak maxima for the two components.

In our case the obtained  $T_{\max}$  of the different IPNs did conform to the values predicted by the Flory-Fox equation as in the case of T-509, and D-2000 but did not conform as in the case of T-5000 and T-403 (see Table 1). This indicated full IPN formation probably taking place in T-509 and D-2000 while less miscibility takes place in T-403 and T-5000.

That separation indicated that we enjoyed an intermediate situation, where along with phase separation, some miscibility had taken place in some of the IPN mixtures.

The presence of small shoulders in our DMTA graphs, in some of our IPNs confirms this and that some degree of phase separation does indeed take place.

Table 1: Flory-Fox Tg vs. IPN Obtained Tg

| <i>IPN</i> | <i>Flory-Fox<br/>Tg(C)</i> | <i>PE (197 C)<br/>IPN Obtained<br/>Tg(C)</i> | <i>Jeffoxy (C)<br/>Tg(C)</i> |
|------------|----------------------------|--|------------------------------|
| JO-5000    | 165                        | 181  | -20                          |
| JO-509     | 167                        | 165  | -5                           |
| JO-2000    | 167                        | 168  | -6                           |
| JO-403     | 188                        | 83   | 104                          |

#### 4.2.1 IPN DMTA Results

A downward shift in Tg value was noted for the pure polyester resin in all IPNs examined when the elastomer was incorporated. Ideally, if an IPN is formed the material would have exhibited a single Tg phenomena and would have behaved as if it were one material. Further, it would have produced a relatively narrow peak width comparable to that of the pure component (for example the neat polyester). In addition, little or no shoulder would be present in the DMTA curves and one Tg at the  $\tan \delta$  maximum would be observed.

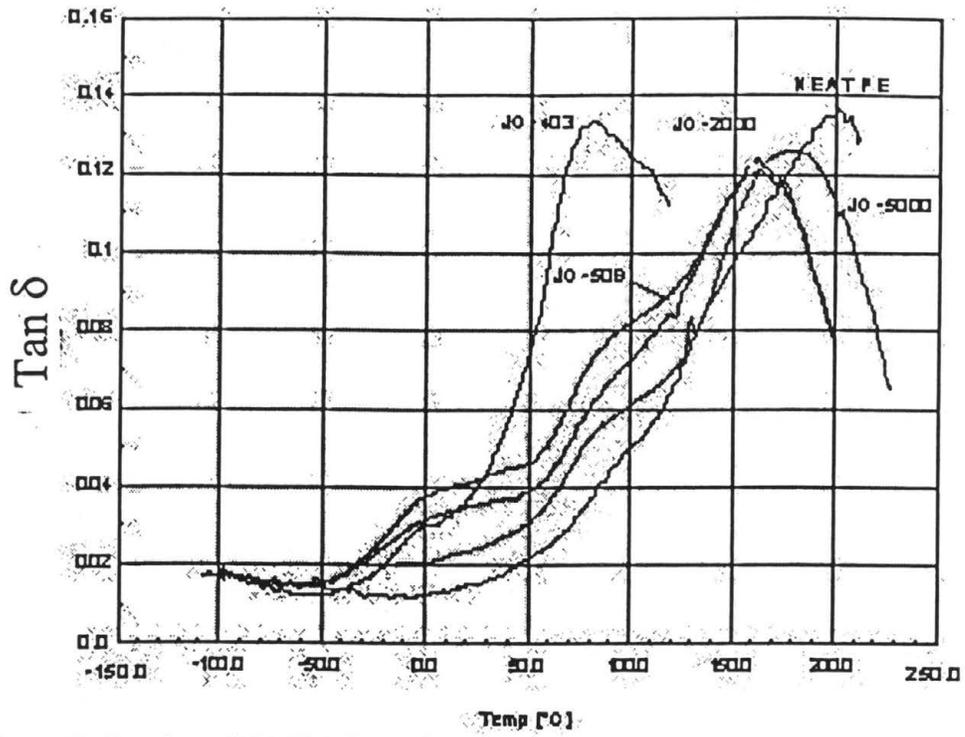


Figure 3: Overlay of DMTA Data for All IPNs and Pure PE

All our IPNs (D-2000, T-5000, T-509, T-403) exhibited a single Tg phenomenon (Figure 4) with little or no shoulder detected. Peak width at half-maximum was comparable to that of the neat polyester resin. Tg values were decreased upon incorporation of elastomer.

The most significant Tg shift occurred in the T-403 IPN. Approximately a 100°C decrease. The Tg indicated a more rubbery material formed.

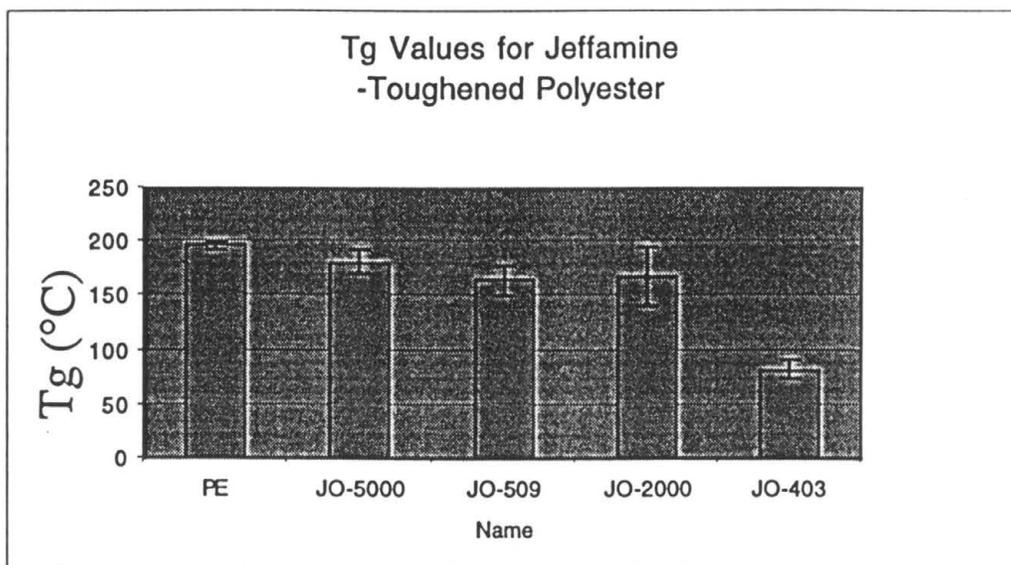


Figure 4: Tg Values of IPNs and Neat PE

We did not detect any differences in  $\tan \delta$  values in our IPNs (Figure 5), probably because the effects produced by the relatively low concentrations of elastomer (15% by weight) was below the sensitivity of the instrument.

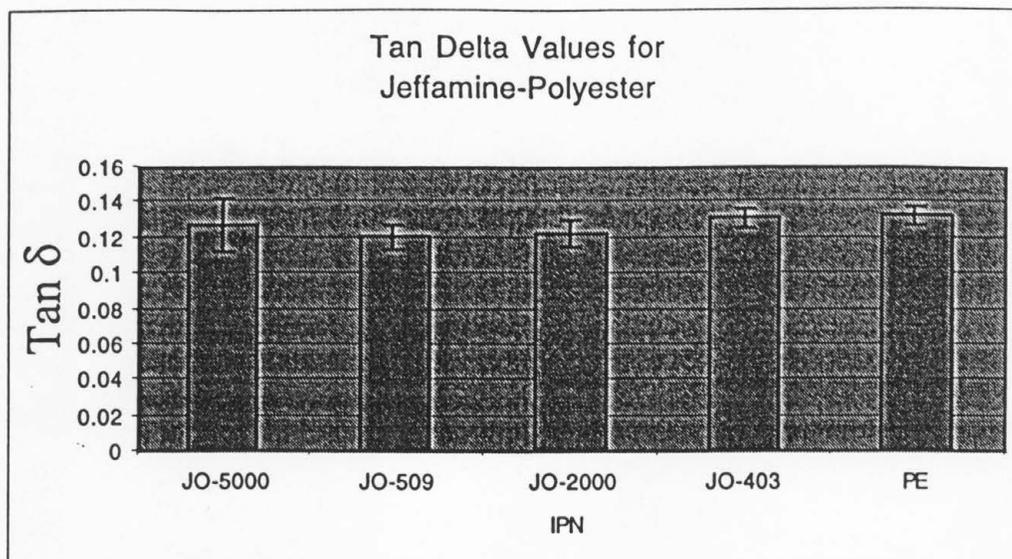


Figure 5: DMTA Tan  $\delta$  Values for IPNs and PE

DMTA data showed good reproducibility with tan  $\delta$  and Tg values agreeable to 2-4% error based on 3 sigma standard deviation calculations (see Figure 6).

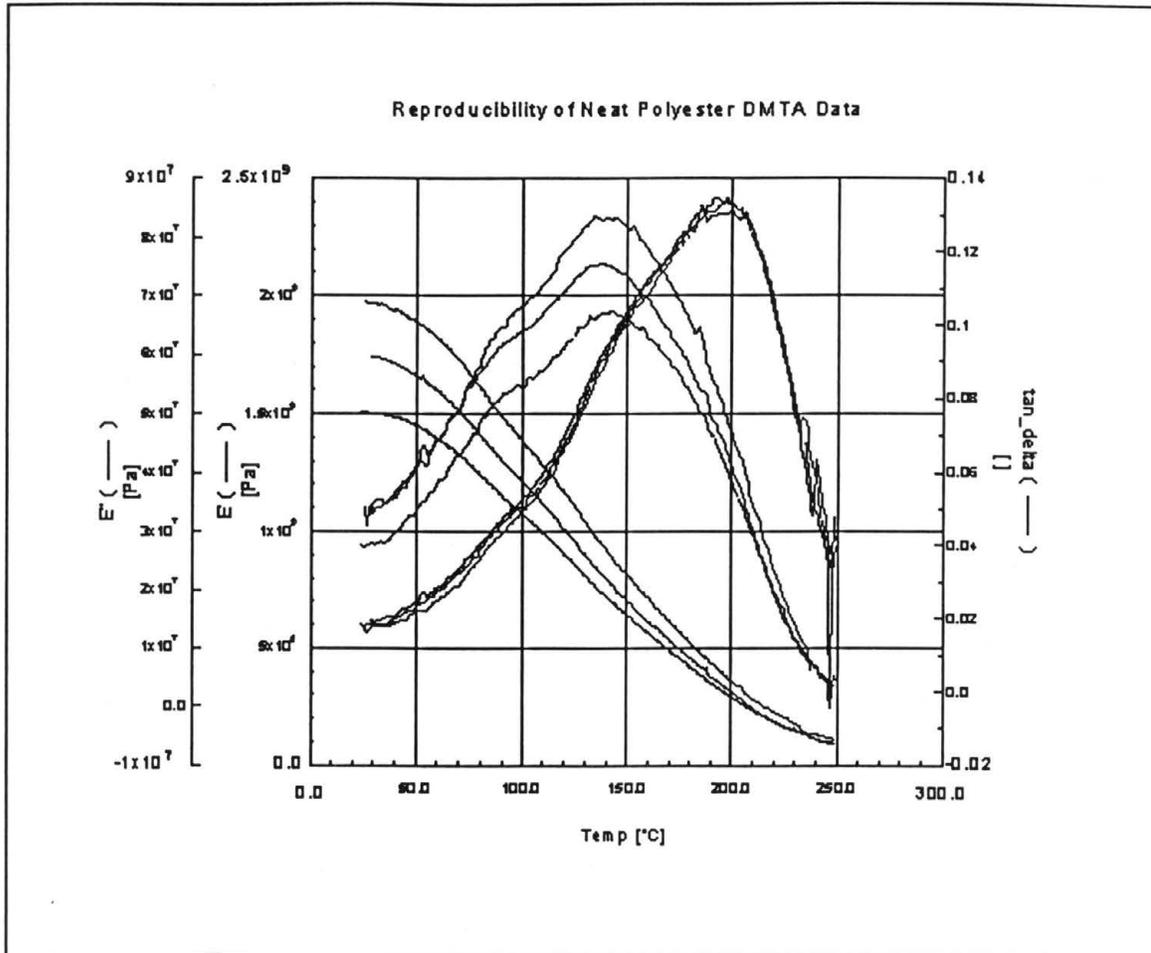


Figure 6: Reproducibility and Peak Width of Pure Polyester DMTA Data

#### 4.2.2 Jeffoxy DMTA Results

Jeffoxy weight composition is determined using the following equation:

$$(AHEW)=1000/2*\text{primary amine content (meq/g)}\dots\dots\dots(\text{Equation 3})$$

The primary amine content value is provided by the manufacturer and is substituted into the equation to give the amine hydrogen equivalent weight (AHEW). Once the AHEW value has been determined for the Jeffamine™, the Epoxy equivalent gram amount is calculated from the following equation:

$$AHEW/\text{Epoxy EW}= Xg \text{ Amine}/Xg \text{ Epoxy}\dots\dots\dots(\text{Equation 4})$$

Examining the DMTA data of pure Jeffoxies showed Jeffoxy T-5000 (our highest molecular weight tri-amine Jeffoxy) produced the toughest reactive rubber material with epoxy giving the highest post cure  $\tan \delta$  value of approximately 2. This was approximately 20 times larger than neat PE and was twice as large as T-403 (our lowest molecular weight Jeffamine).  $\tan \delta$  values of all Jeffoxies show a narrow peak width which indicated good compatibility of Jeffamine and epoxy (see Figure 7).

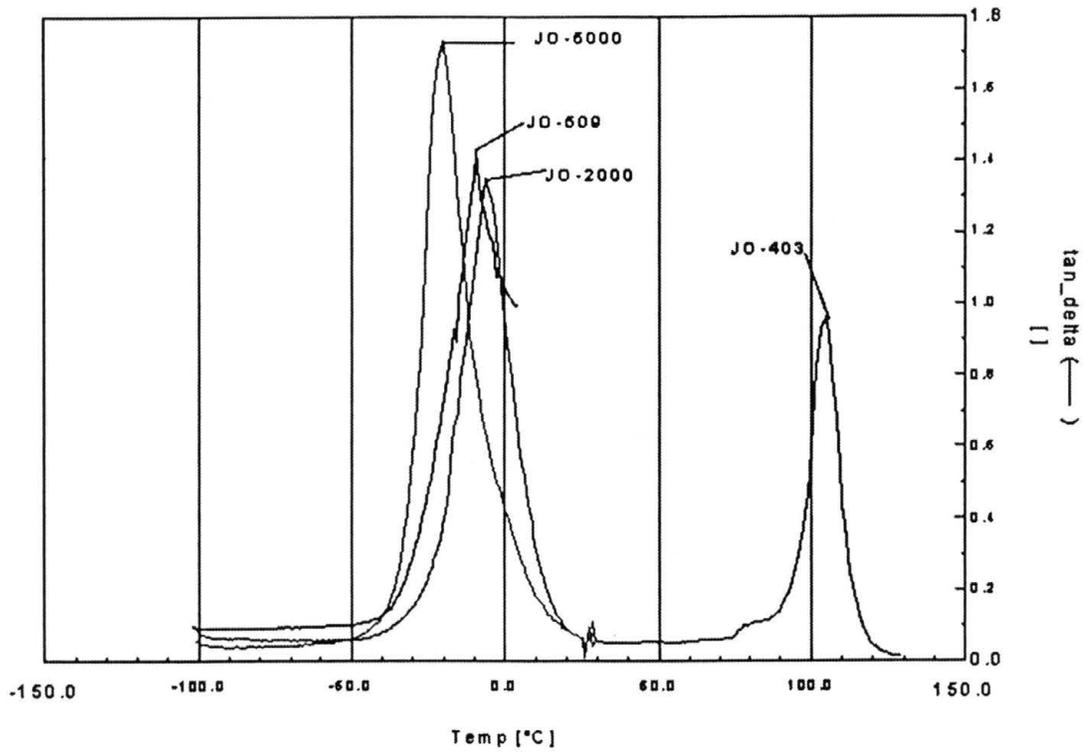


Figure 7: DMTA Overlay Data for Pure Jeffoxies Tg

### 4.3 Izod Notch Toughness Results

All IPNs showed an increase in toughness when compared to neat PE (Figure 8).

The best toughness increase with lowest standard deviation was for that of the tri-branched 3000 g/ mol MW T-509. This increased impact strength value correlated to an improvement in toughness of 27 J/M (a 45% increase in value) when compared to the 18 J/M for pure polyester.

The lowest standard deviation in the Notched Izod tests of T-509 was perhaps indicative of better distribution of T-509 rubber particles within the polyester resin than any of the other Jeffoxy/PE IPN samples.

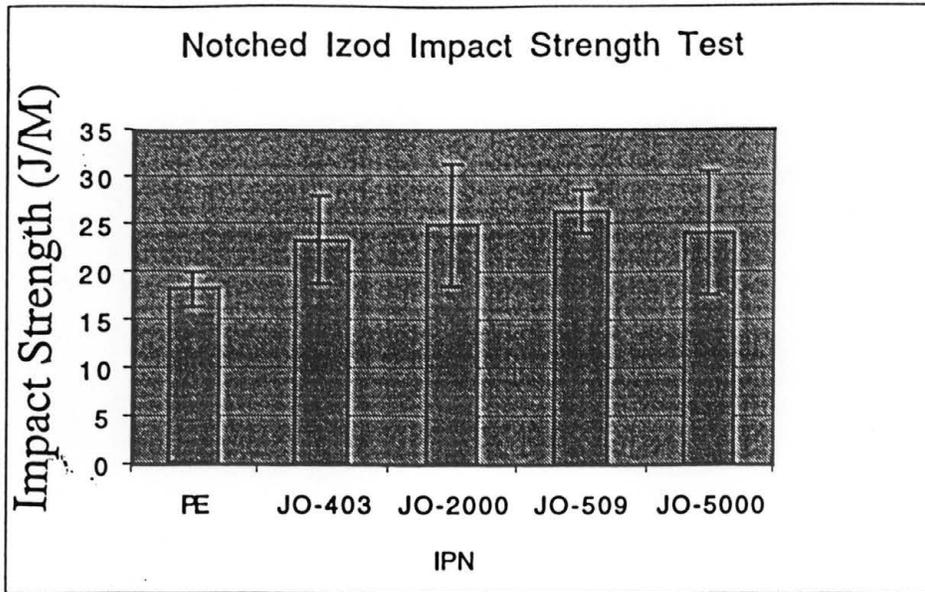
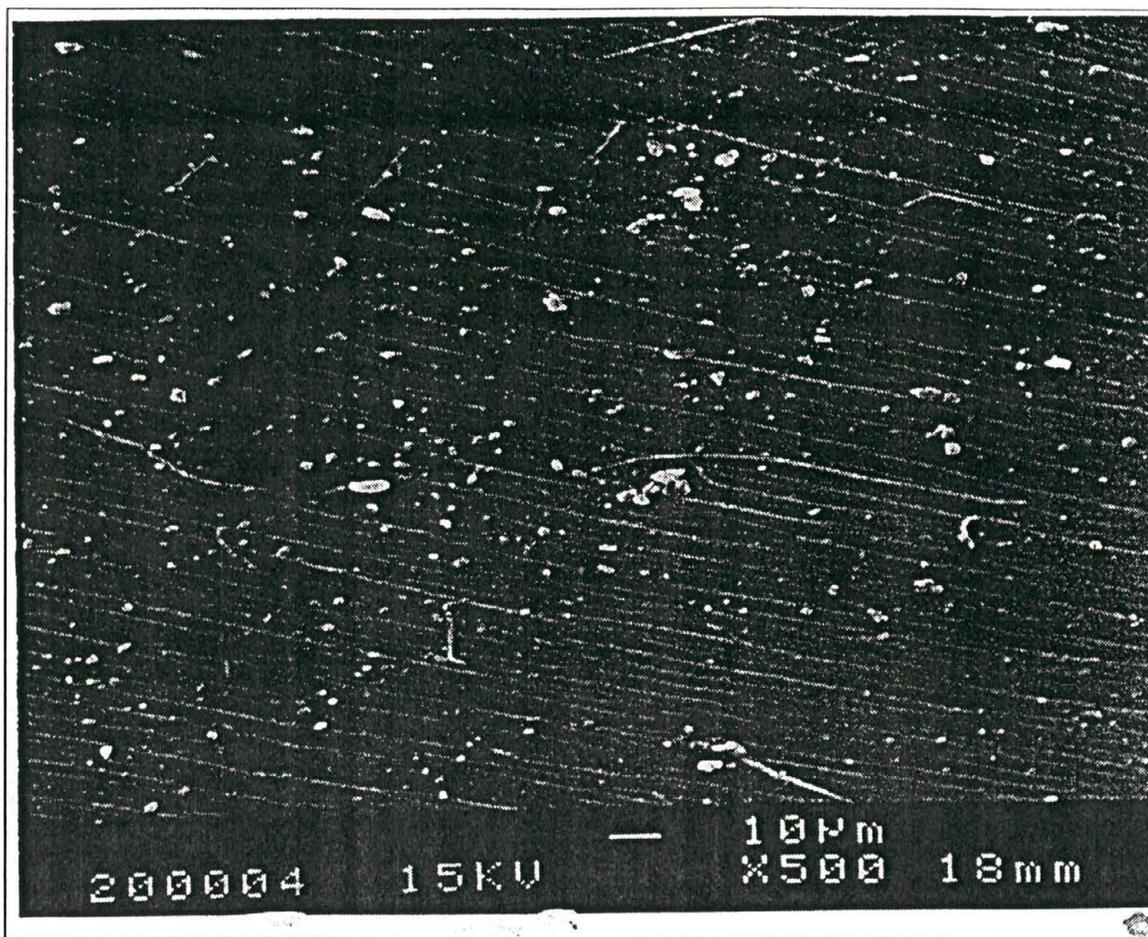


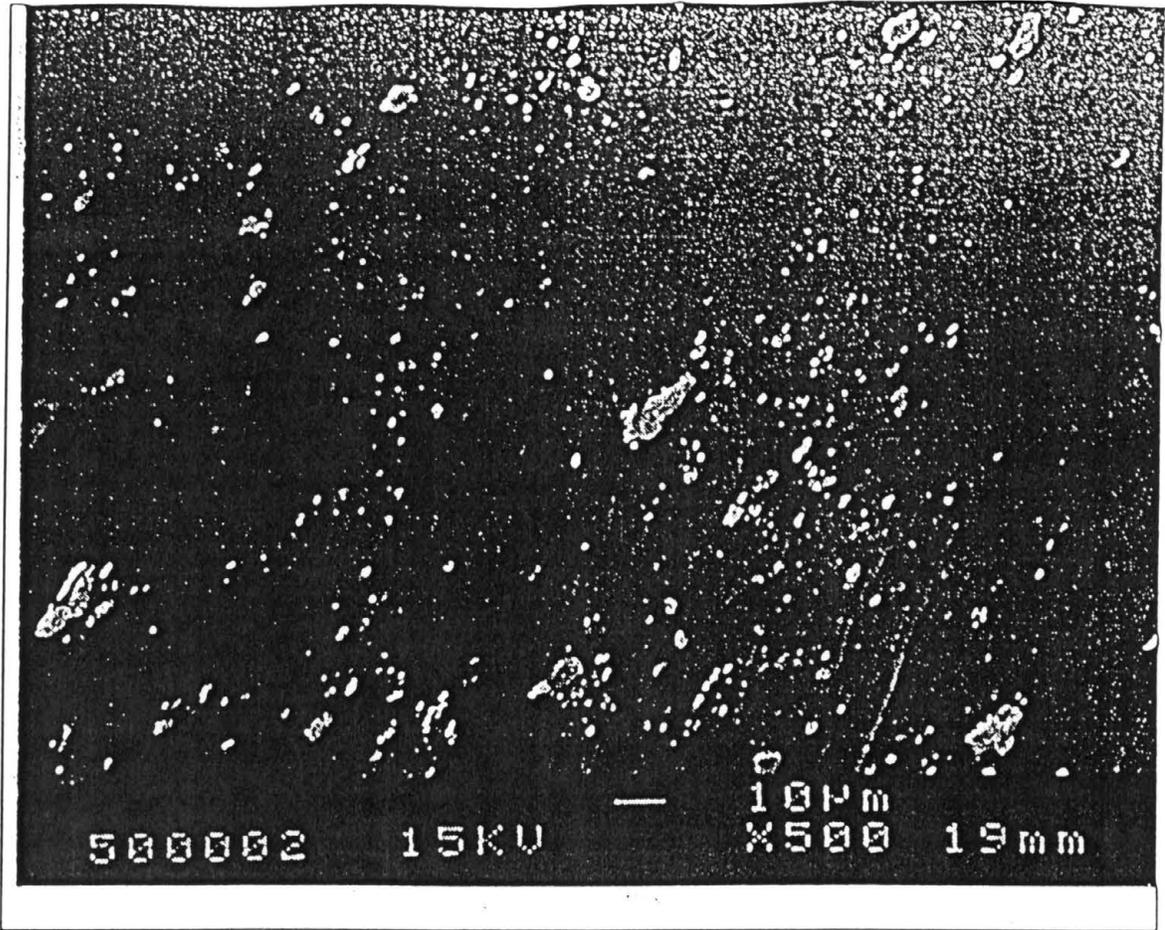
Figure 8: Notched Izod Impact Values with Standard Deviation for Various IPNs

#### 4.4 SEM Photo Micro-Graphs

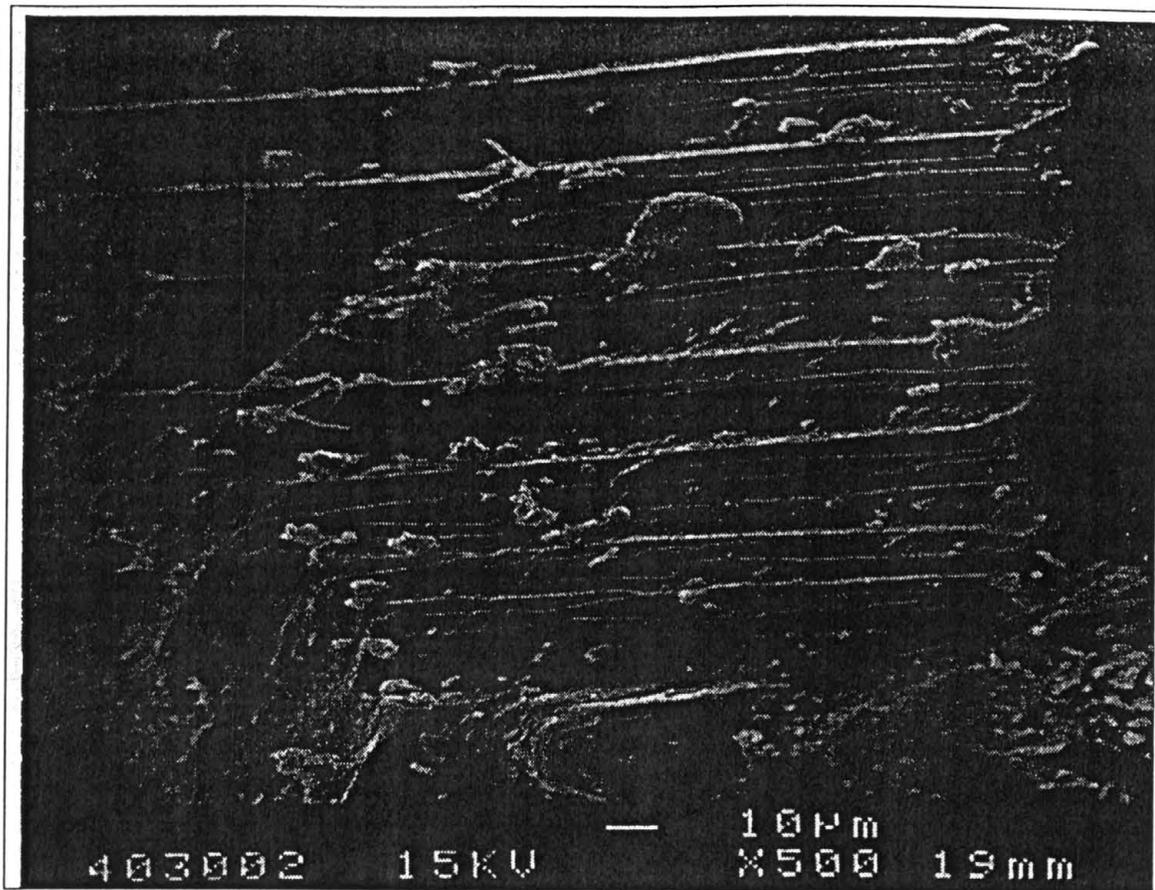
The above results are further confirmed by SEM images of T-509 that show the absence of discrete particles which were present in T-403, D-2000, and T-5000.



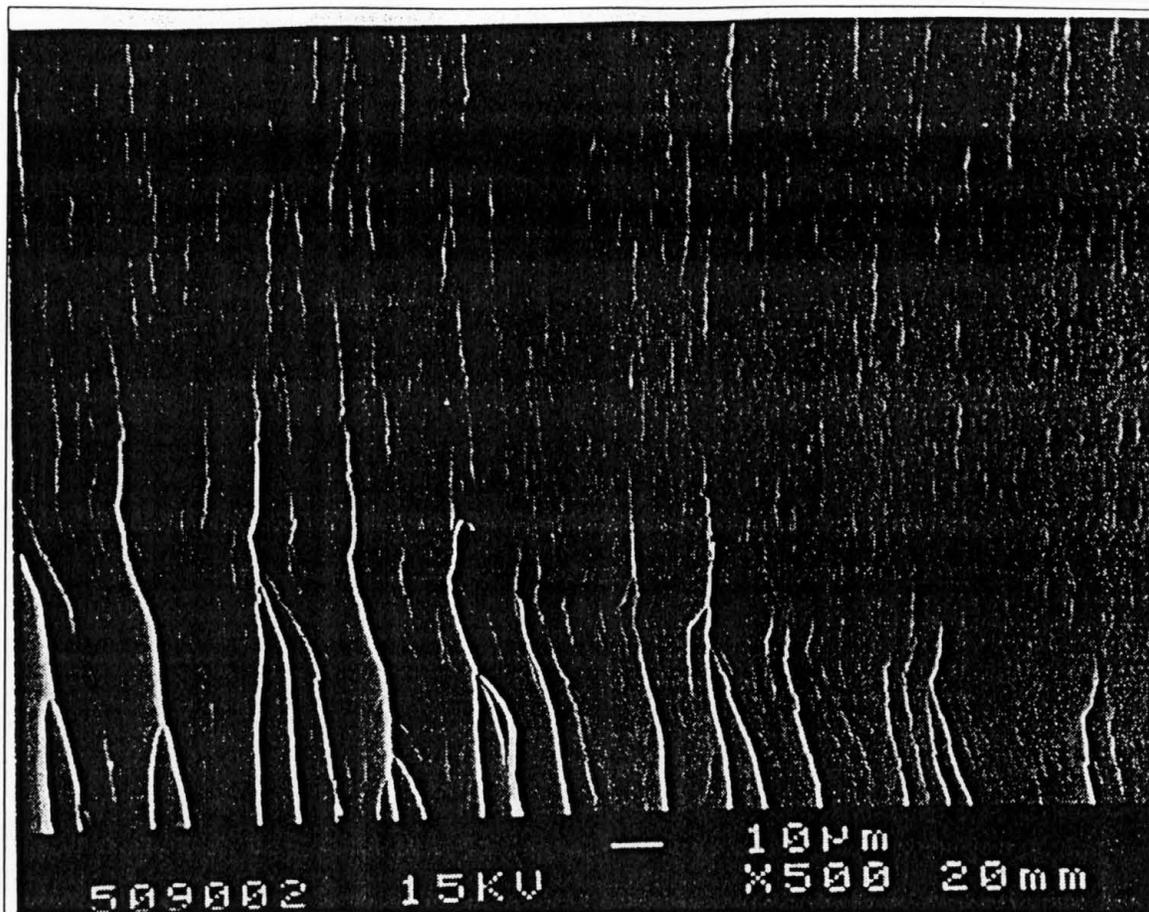
a) SEM Micrograph of D-2000 IPN



b) SEM Micrograph of T-5000 IPN



C) SEM Micrograph of T-403 IPN



d) SEM Micrograph of T-509 IPN

Figure 9: SEM Images of IPNs; T-509 (d) is clear of dispersed particles found in D-2000 (a), T-5000 (b), and T-403 (c).

#### 4.5 Three-point Bend Strength and Stiffness

Three-point bend tests show strength at break (Figure 10) and stiffness (Figure 11) for all IPNs and neat PE.

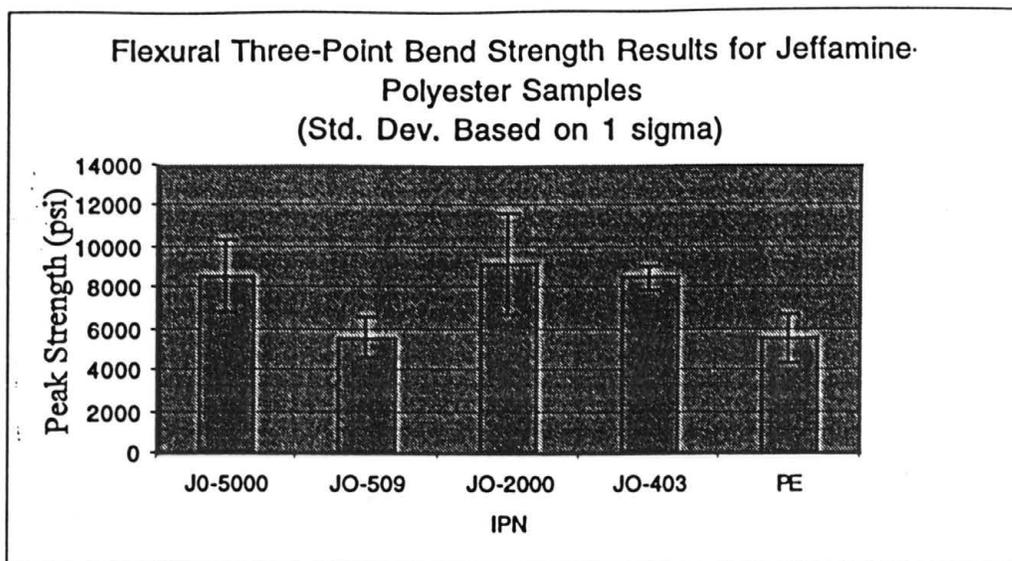


Figure 10: Strength Values for Various IPNs and PE Neat

Although percentage error can be as high as 27% , T-509 compared favorably with PE neat having a similar strength at break value of 6000 psi (20% error). The low molecular weight, tri-branched amine T-403 IPN, was the strongest material with a strength at break value of 8500 psi (42% increase) and error variation of 7%. Stiffness results for the various IPNs are shown below.

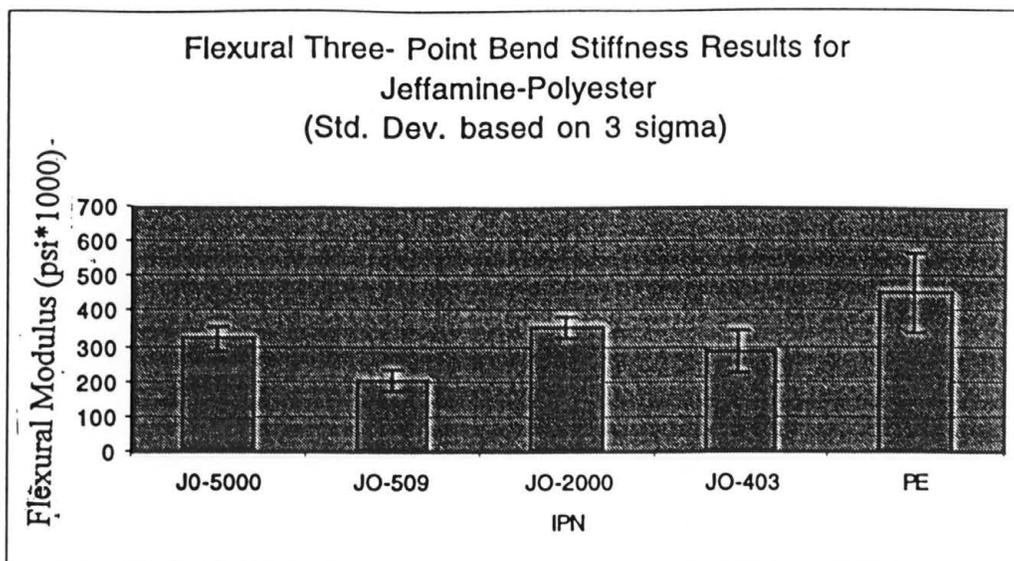


Figure 11: Flexural Modulus Results for Various IPNs and PE Neat.

Error for stiffness calculations (4-8%) was low indicating the instrument much more capable of reporting stiffness values than strength. T-509 showed the least stiffness of all samples a value of approximately 200 kpsi compared to a value of approximately 450Kpsi of the pure PE resin (a decrease in stiffness of 55%). The stiffest material was the IPN containing the linear di-amine D-2000 which showed a decrease of stiffness of only 22% upon addition of rubber component.

#### 4.6 Extent of Cure Results by DSC

DSC calculations through subtraction of heat of reaction values at different time intervals (pre-cure, partial-cure, and post cure) showed the cure behavior of our polyester resin (Figures 12-14). After 4h of cure time, pure PE resin had a 93% extent of cure. Curing was complete after 8h as no more heat of reaction was detected by DSC.

#### 4.7 TGA Data

TGA results showed the Jeffoxy IPNs have similar thermal decomposition properties to that of pure polyester, with the exception of T-403 (Tables 5-7). A decomposition temperature in nitrogen within 10°C (393-402°C) for all IPNs (4% char yield) was measured with the exception of T-403 which had a TGA of 382 °C a 20 °C depression (see Figures 12,13).

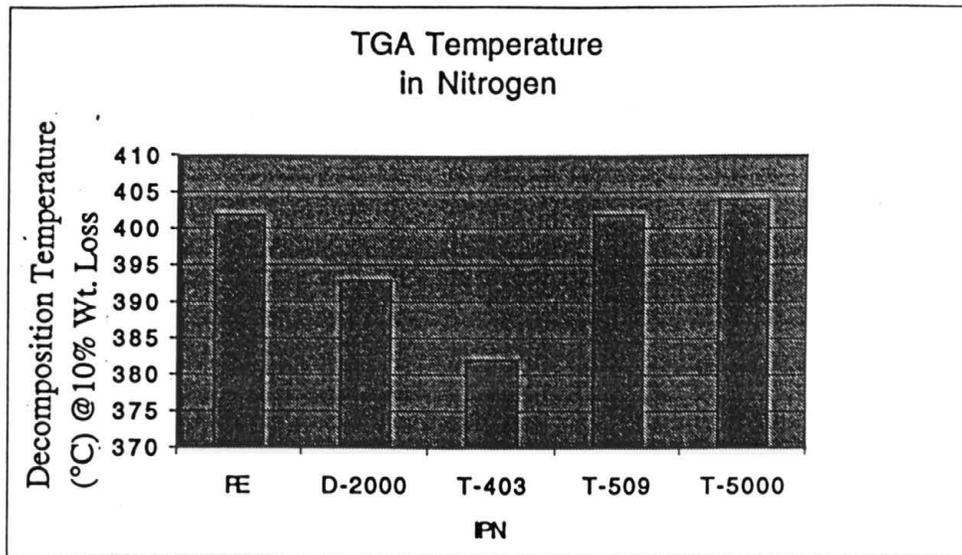


Figure 12: TGA Data for IPNs and PE in Nitrogen

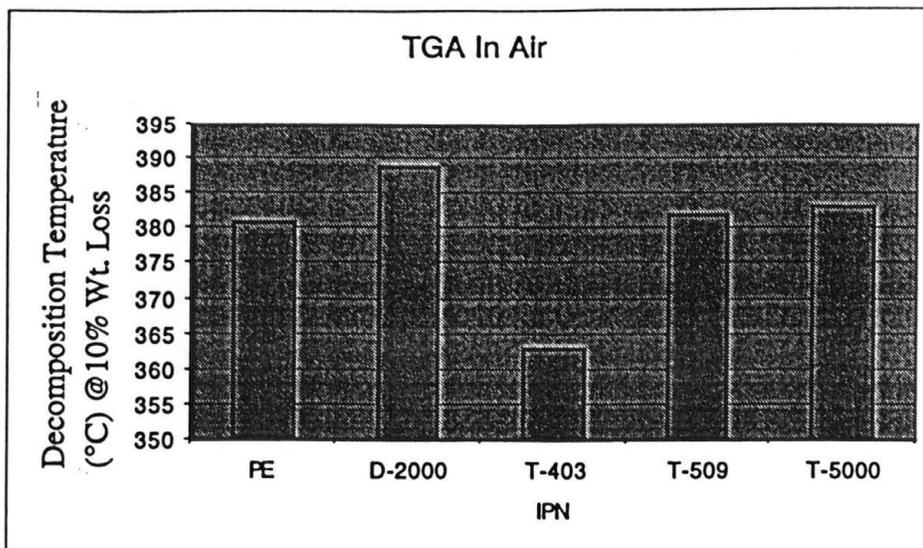


Figure 13: TGA Data for IPNs and PE in Air

## 5. CONCLUSIONS

1-A series of translucent, intact, and compatible molds using Jeffamine™ reactive rubbers were prepared.

2- Notched Izod impact strengths for all IPNs increased upon incorporation of rubber showing PE to be toughened.

3-The best toughness value with least standard deviation was that of tri-branched (3000 g/mol) T-509 IPN. This corresponded to a 45% increase in toughness with least standard deviation comparable to that of the neat PE.

4- DMTA data for all IPNs showed a decrease in T<sub>g</sub> upon incorporation of the rubber as was expected.

5- The largest T<sub>g</sub> decrease was that of low molecular weight branched T-403.

6- DMTA curve widths for all IPNs were comparable to that of the neat PE showing good compatibility of Jeffoxy and PE. Little or no shoulders were present in DMTA curves indicating for the most part IPN formation.

7- Flory-Fox calculations showed IPN formation likely in T-509 and D-2000 whereas a less compatible (some miscibility) intermediary IPN system likely to be present in T-403 and T-5000.

8- Jeffoxy DMTA data showed high molecular weight, branched, T-5000 to be the toughest material with  $\tan\delta$  values twice that of low molecular weight, branched, T-403.

9- Flexural three-point bend results showed linear D-2000 with highest flexural modulus value, which corresponded to a 22% decrease in flexural modulus upon incorporation of rubber. T-509 decreased to 55% of its flexural modulus value upon incorporation of the rubber.

10- Three-point bend strength at break results showed T-403 and D-2000 to have the highest values upon incorporation of the rubber. T-509 retained the strength at break value of the PE upon incorporation of the rubber.

11- DSC results showed complete extent of cure for all IPNs as evident by the disappearance of the heat of reaction peak upon curing.

12- TGA data showed the thermal stability of IPNs to compare well with that of the pure polyester. An exception was that of T-403 which had a 20°C decrease in TGA value.

13- Photomicrographs of T-509 showed the absence of discrete white particles (1-20 $\mu\text{m}$ ) present in D-2000, T-403, and T-5000 IPNs. This corresponded well with the

lowest standard deviation values obtained for T-509 by the Notched Izod Impact test. This suggested perhaps a more compatible system is to be found in the T-509 IPN.

## 6. SUGGESTIONS FOR FUTURE RESEARCH

Structural modifications of more Jeffamines™ can be undertaken as part of product development efforts. As an example, a linear di-amine more than 2000 in molecular weight can be investigated for different physical properties. Similarly variations in molecular weight for tri-branched Jeffamines™ can be further investigated. Copolymers of different Jeffamine™ structures can be screened for best toughness/compatibility IPN systems (di + tri, low molecular weight tri + high molecular tri, etc.). More SEM work can be done to decipher the nature of the white particles present in the IPNs. Varying the composition of the elastomer to greater or lower than 15% by weight in the IPN elastomer composition may show changes in morphology by SEM and/or changes in toughness, and/or changes in other mechanical properties as well as Tg values.

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## APPENDIX I:

### Tables

This appendix provides the raw data presented in the thesis. Tables 2 and 3 present the DMTA  $\tan\delta$  and  $T_g$  data for a comparison of all IPNs and neat PE. Table 3 provides Notched Izod impact strength results for all IPNs and the neat PE. Tables 5 and 6 present flexural three-point bend tests for IPN and PE flexural modulus and strength at break mechanical properties. Tables 7 and 8 present TGA data for all IPNs and PE in nitrogen (% char yield) and air.

Table 2: DMTA Tg values

| Sample Name | #1    | #2    | #3    | Mean    | Std. Dev | 3sigma  | %error based on 3sigma |
|-------------|-------|-------|-------|---------|----------|---------|------------------------|
| PE          | 197.8 | 195.3 | 197.7 | 196.933 | 1.41539  | 4.24617 | 2.15614                |
| JO-5000     | 179.1 | 185.7 | 178.9 | 181.233 | 3.86953  | 11.6086 | 6.40534                |
| JO-509      | 168.8 | 164.9 | 160.2 | 164.633 | 4.30619  | 12.9185 | 7.84688                |
| JO-2000     | 178.5 | 163.8 | 163   | 168.433 | 8.72716  | 26.1814 | 15.5441                |
| JO-403      | 85.1  | 79.1  | 83.7  | 82.6333 | 3.13900  | 9.41700 | 11.3961                |



Table 4: Notched Izod Impact Strength Results

|         | Impact Strength<br>(J/M) |       |       |       | Mean  | Std Dev. | 3sigma          |
|---------|--------------------------|-------|-------|-------|-------|----------|-----------------|
|         |                          |       |       |       |       |          |                 |
| FE      | 19.44                    | 19.44 | 15.52 | 19.44 | 17.48 | 18.264   | 1.75307 5.25923 |
| JO-403  | 21.4                     | 27.28 | 29.24 | 19.44 | 19.44 | 23.36    | 4.59660 13.7898 |
| JO-2000 | 21.4                     | 19.44 | 27.28 | 35.12 | 21.4  | 24.928   | 6.41132 19.2339 |
| JO-509  | 27.28                    | 29.2  | 27.28 | 25.32 | 23.36 | 26.488   | 2.22250 6.66750 |
| JO-5000 | 19.44                    | 19.44 | 31.2  | 31.2  | 19.44 | 24.144   | 6.44121 19.3236 |

Table 5: Three-Point Bend Strength Results

| Name    | Mean Avg. for 5 samples | Std. Dev. | %Error based on 1sigma |
|---------|-------------------------|-----------|------------------------|
| JO-5000 | 8588                    | 1719      | 20.01830182            |
| JO-509  | 5622                    | 1018      | 18.10743508            |
| JO-2000 | 9190                    | 2504      | 27.24700762            |
| JO-403  | 8507                    | 596       | 7.005895083            |
| FE      | 5589                    | 1175      | 21.09894056            |

Table 6: Three-Point Bend Flexural Modulus Results

| Stiffness(Modulus)(psi*1000) |                         |  |           |        |                        |
|------------------------------|-------------------------|--|-----------|--------|------------------------|
| Name                         | Mean Avg. for 5 samples |  | Std. Dev. | 3sigma | %error based on 3sigma |
| JO-5000                      | 324                     |  | 12        | 36     | 11.11111111            |
| JO-509                       | 208                     |  | 10        | 30     | 14.5631068             |
| JO-2000                      | 360                     |  | 10        | 30     | 8.33333333             |
| JO-403                       | 289                     |  | 20        | 60     | 20.76124567            |
| FE                           | 458                     |  | 38        | 114    | 24.89082969            |

Table 7: TGA in Nitrogen and %Char Yield

| Name   | Temp.<br>(10%Wt.Loss) | % Char<br>Yield |
|--------|-----------------------|-----------------|
| PE     | 402                   | 4               |
| D-2000 | 393                   | 3               |
| T-403  | 382                   | 7               |
| T-509  | 402                   | 4               |
| T-5000 | 404                   | 4               |

Table 8: TGA in Air

| Air    | Temp. (10% Wt. Loss) |
|--------|----------------------|
| FE     | 381                  |
| D-2000 | 389                  |
| T-403  | 363                  |
| T-509  | 382                  |
| T-5000 | 383                  |

## APPENDIX II:

### Figures

This appendix provides all graphs from which results were presented in this thesis. Figures 14-16 present DSC heat of reaction calculations to determine extent of cure. Figure 17 is a bar graph depiction of TGA char yield results for all IPNs and neat PE. Figures 18-22 depict all DMTA graphs for neat polyester and IPNs examined. Figures 23-27 show TGA results for all IPNs and neat PE in nitrogen. Figures 28-32 show TGA results for all IPNs and neat PE in air. Figures 33-37 show flexural three-point bend tests for all IPNs and neat PE.

Figure 14: DSC for Neat Polyester

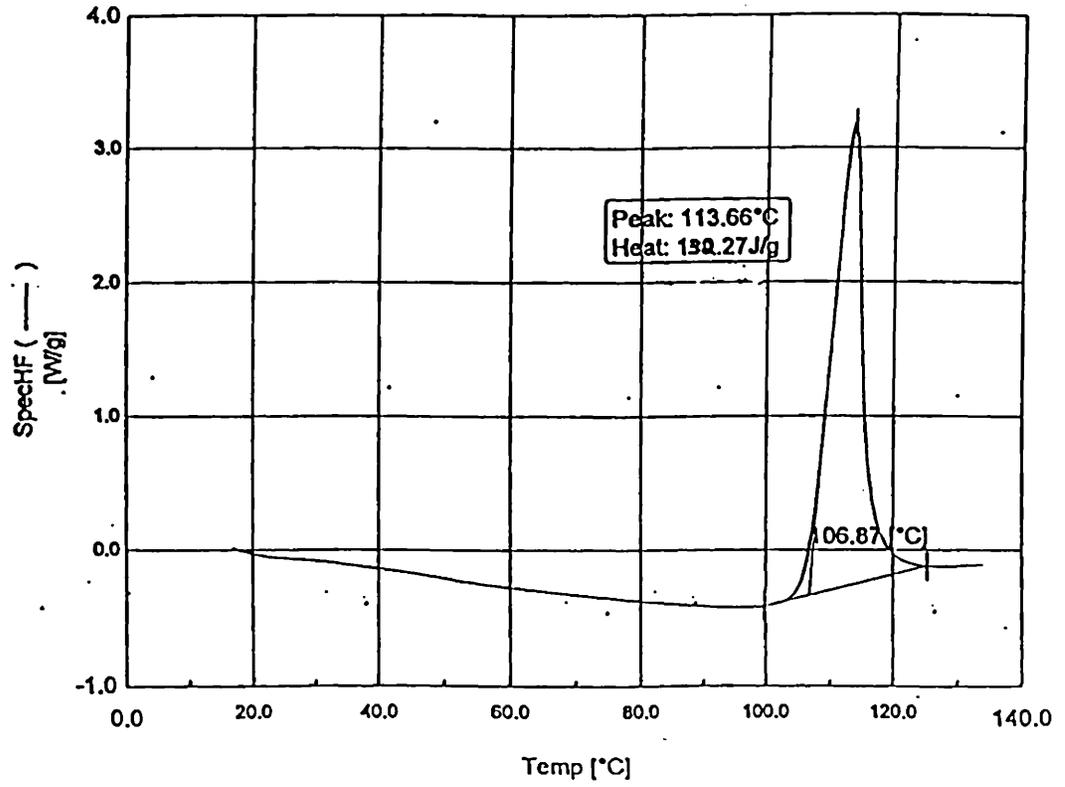


Figure 15: DSC for Neat Polyester Cured for 4h. at 90°C

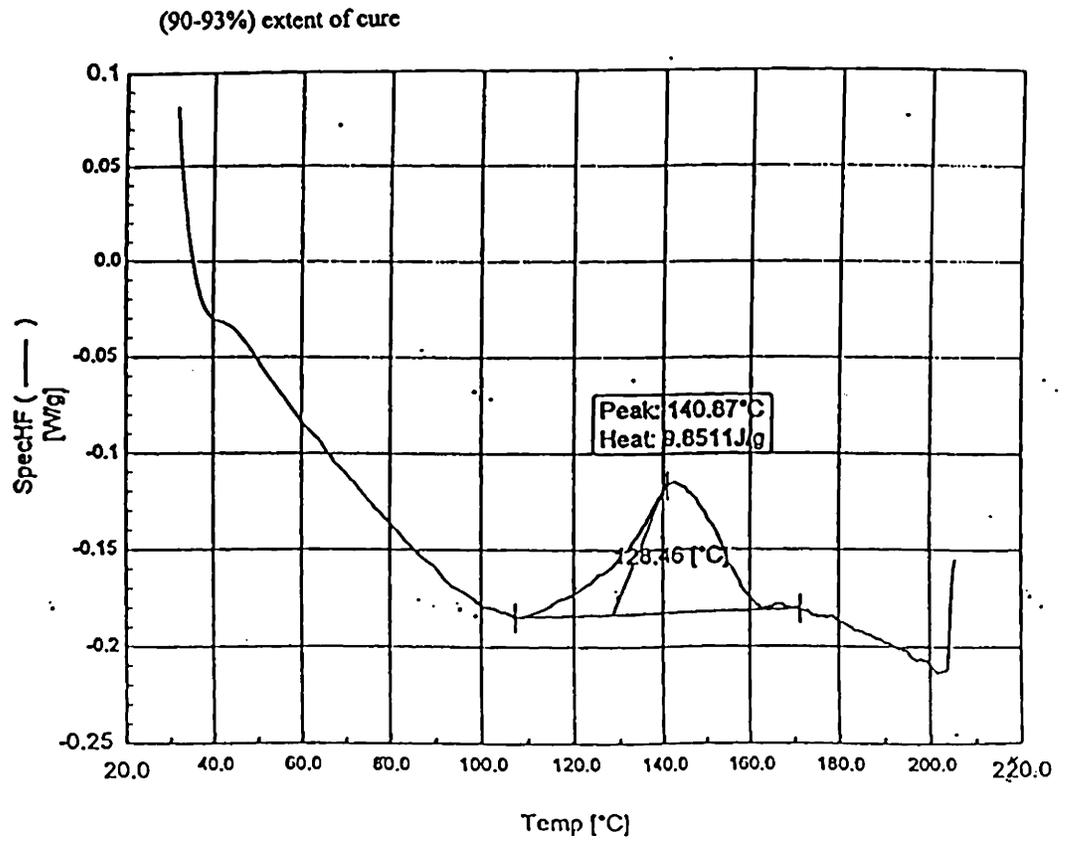


Figure 16: DSC for Neat Polyester Completely Cured @8h. 90°C

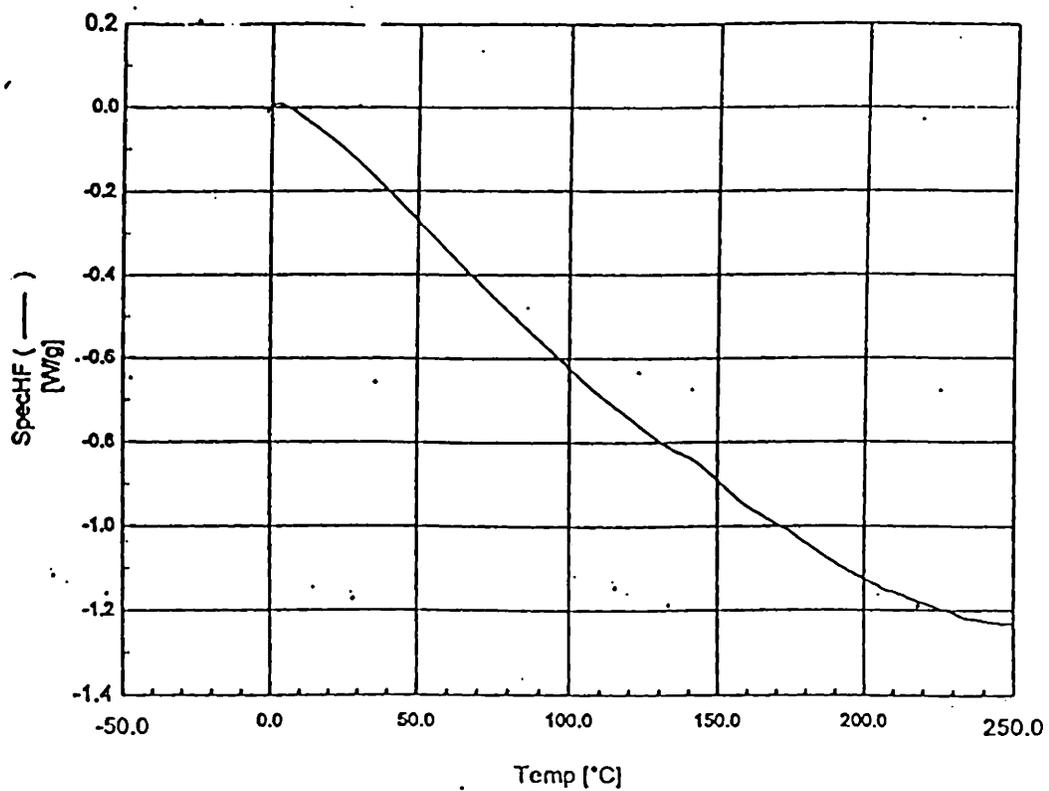


Figure 17: TGA % Char Yield

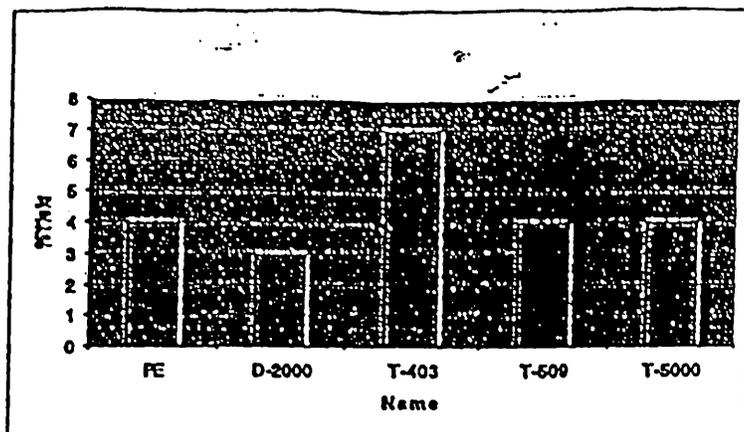


Figure 18: DMTA of Neat Polyester

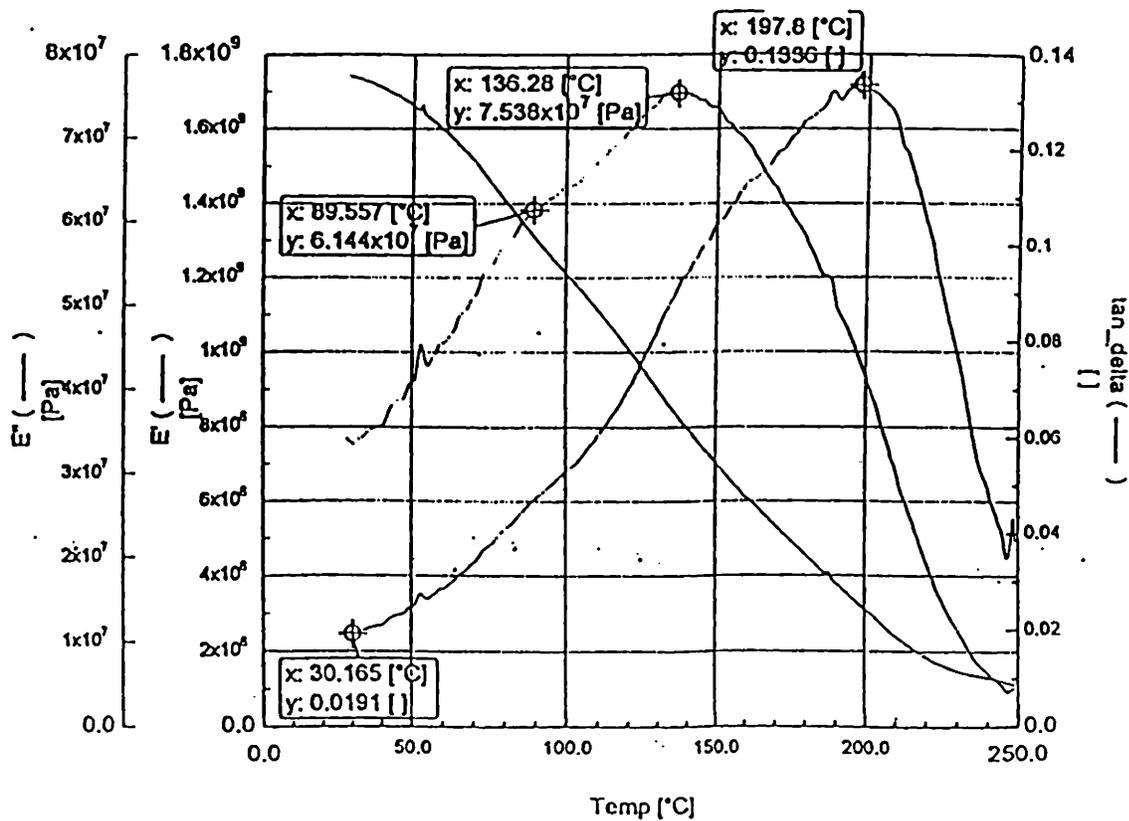


Figure 19: DMTA of JO-403

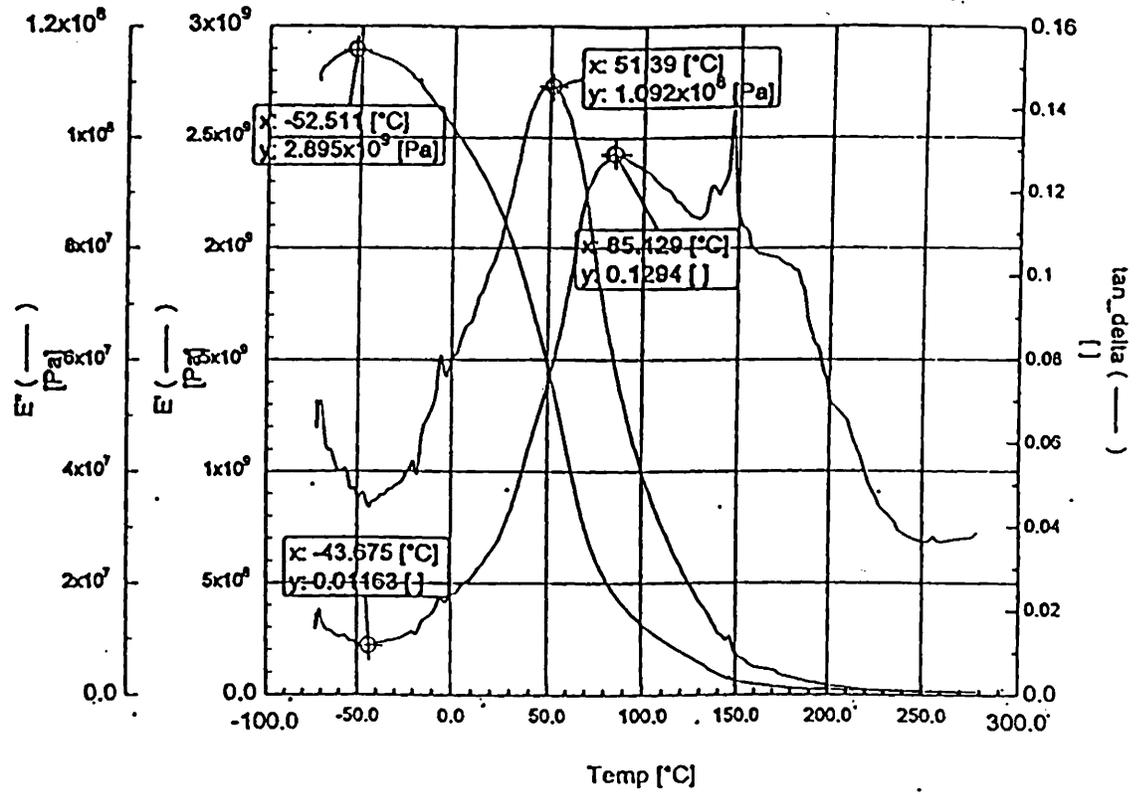


Figure 20: DMTA of JO-509

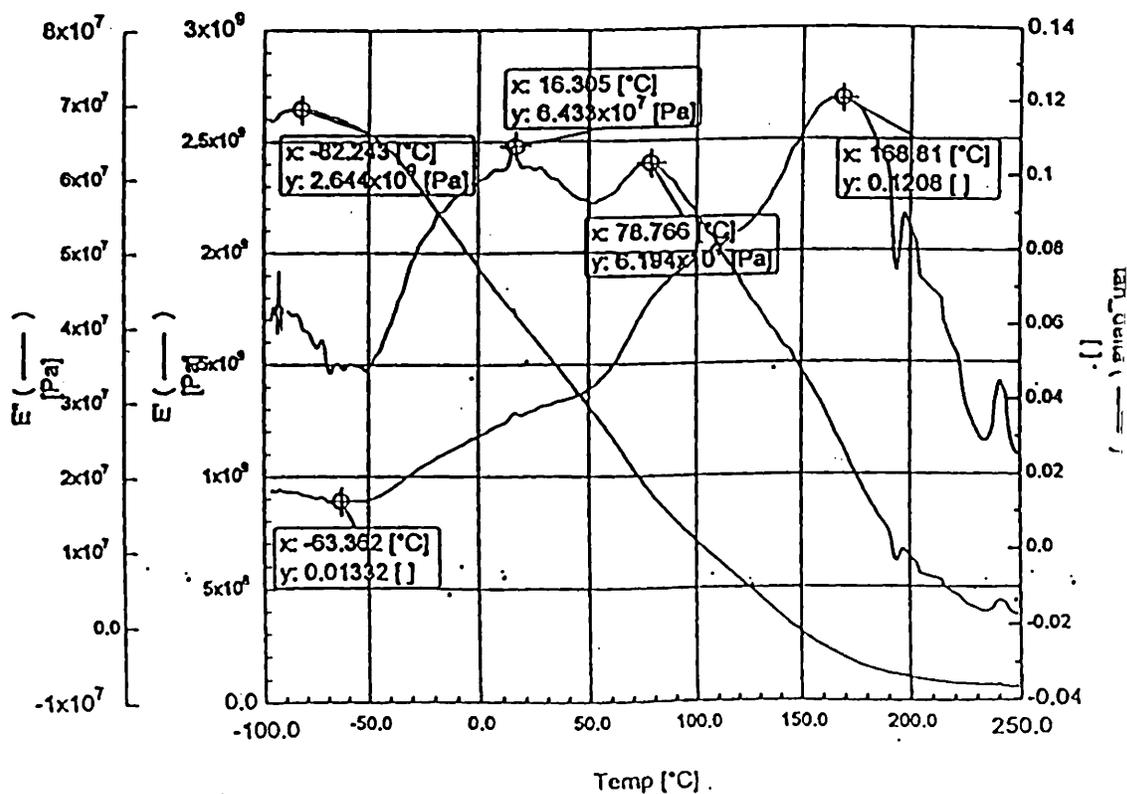


Figure 21: DMTA of JO-2000

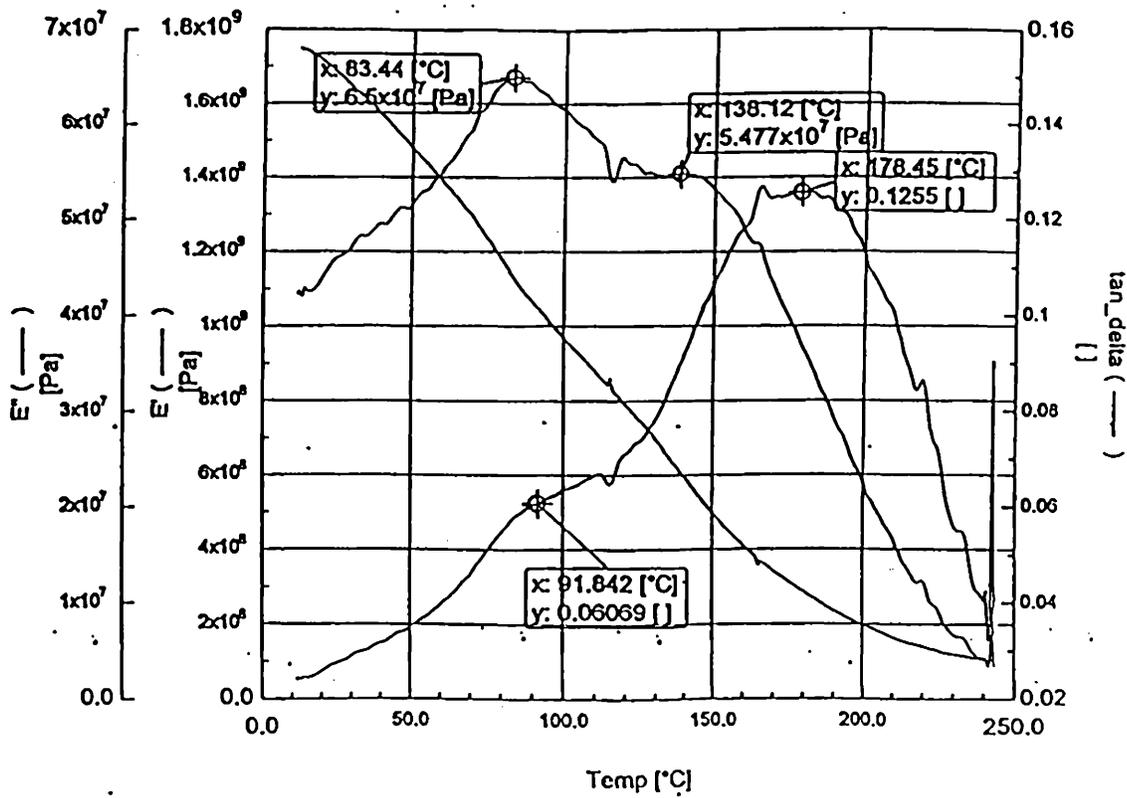


Figure 22: DMTA of JO-5000

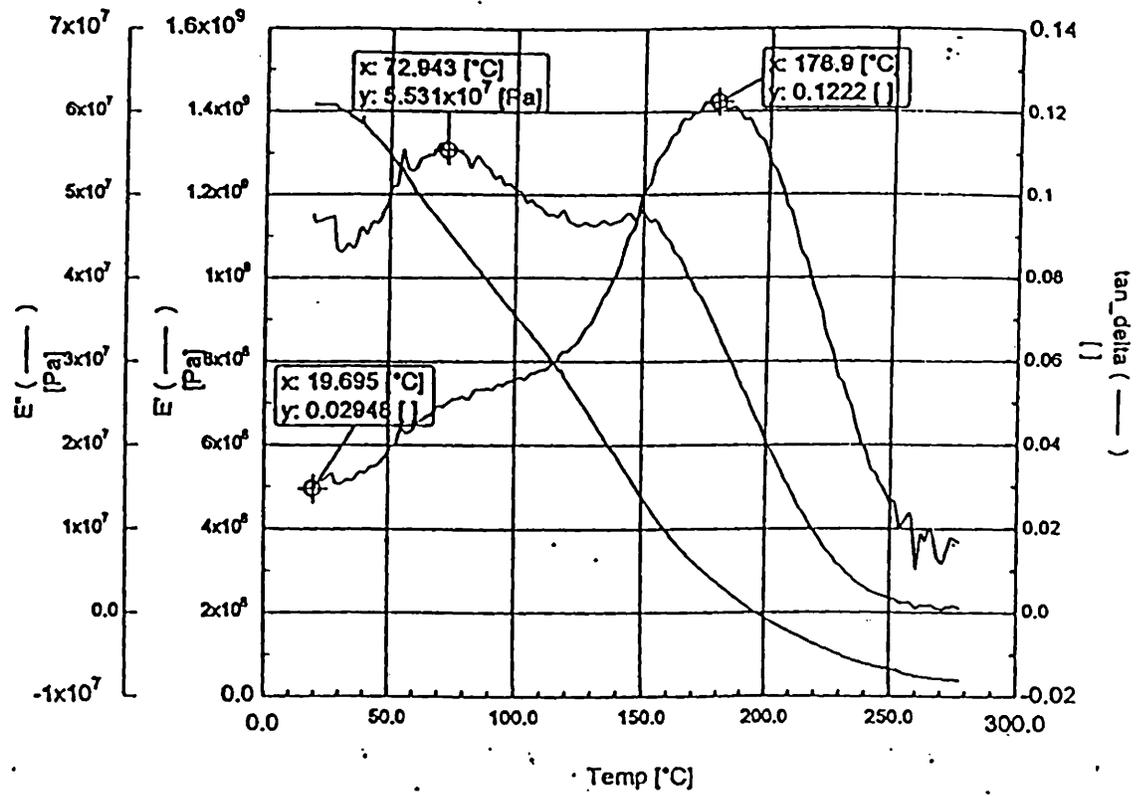


Figure 23: TGA of Neat Polyester in Nitrogen

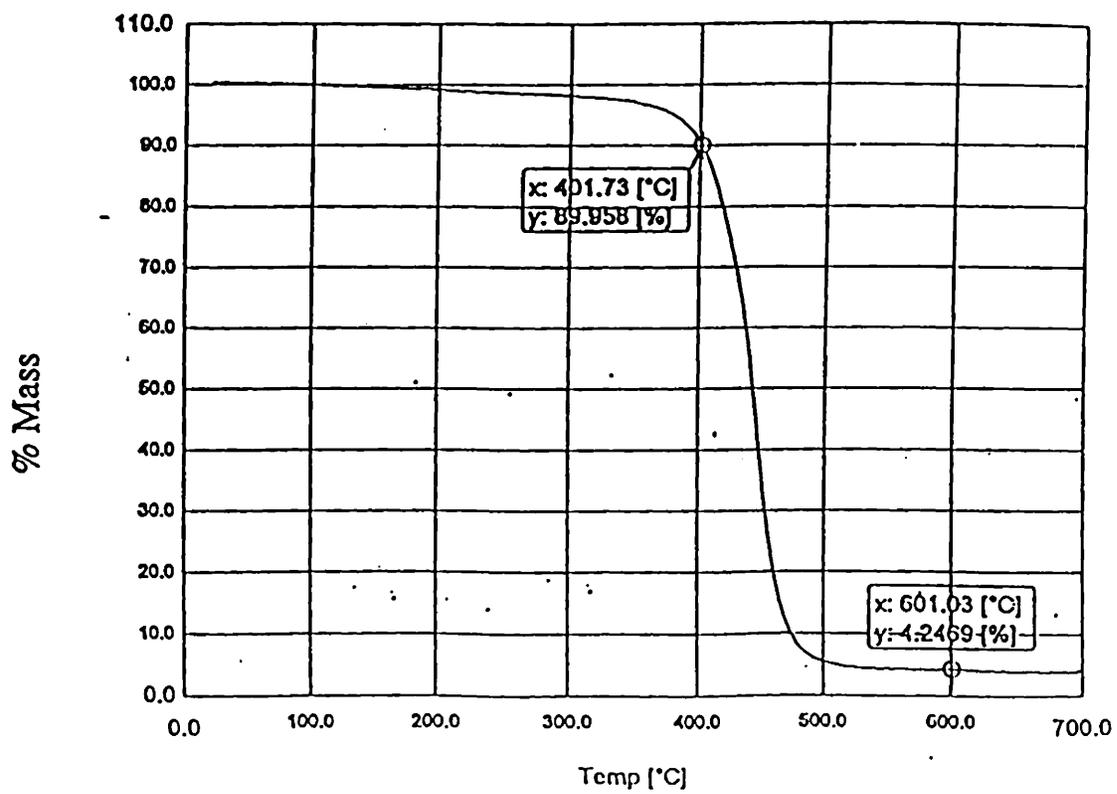


Figure 24: TGA of JO-403 in Nitrogen

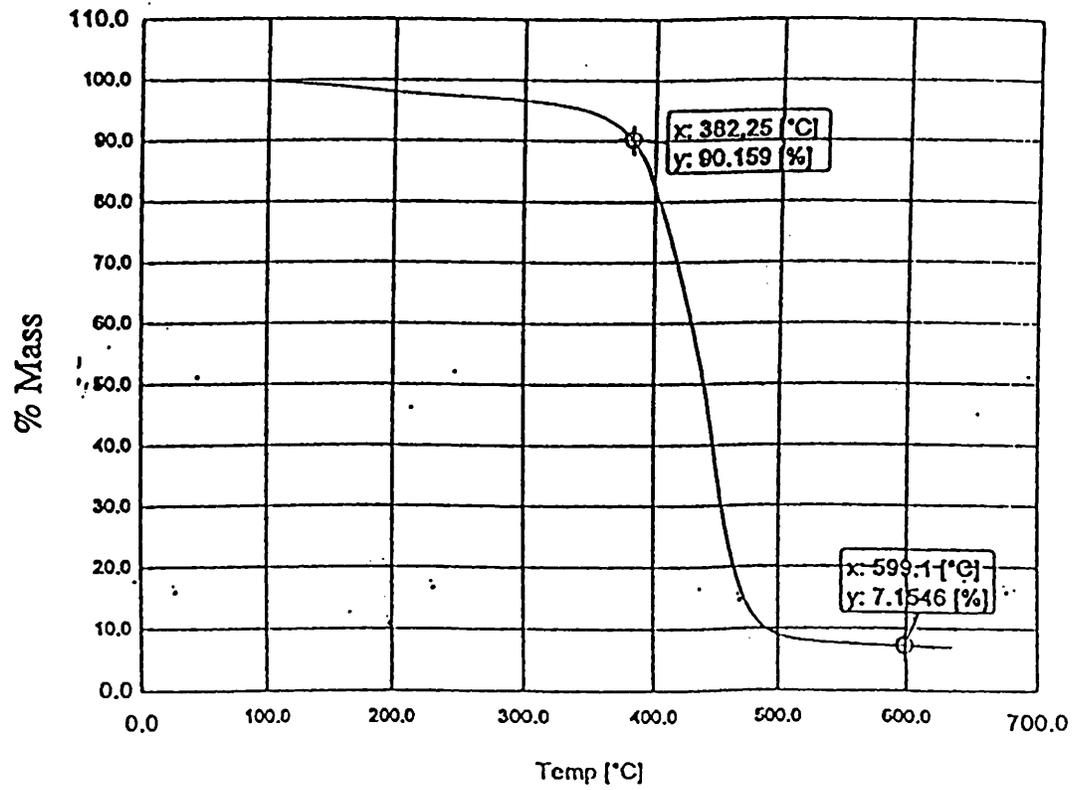


Figure 25: TGA of JO-509 in Nitrogen

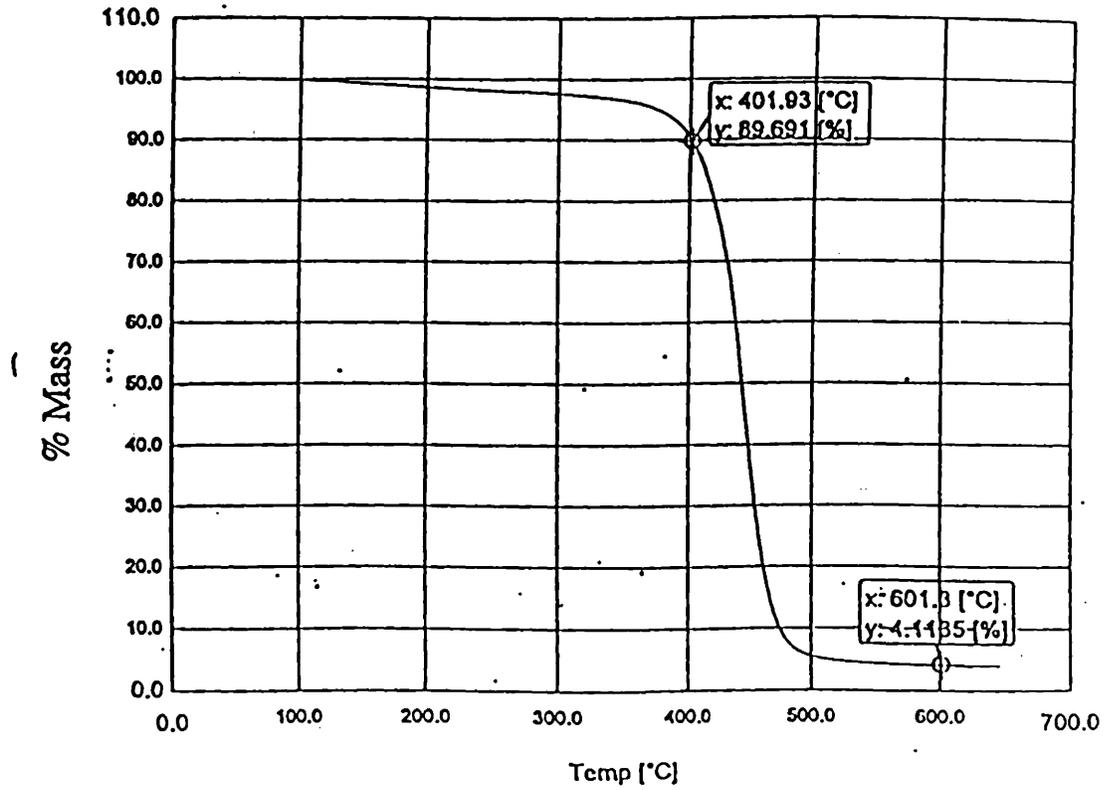


Figure 26: TGA of JO-2000 in Nitrogen

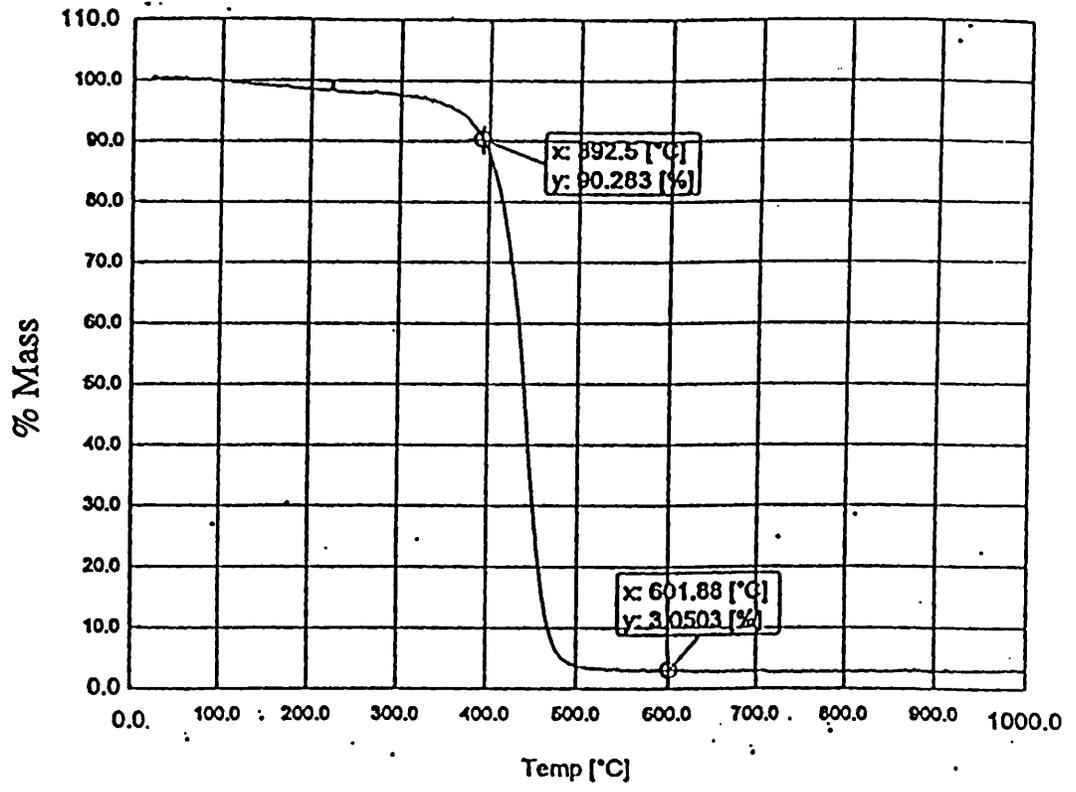


Figure 27: TGA of JO-5000 in Nitrogen

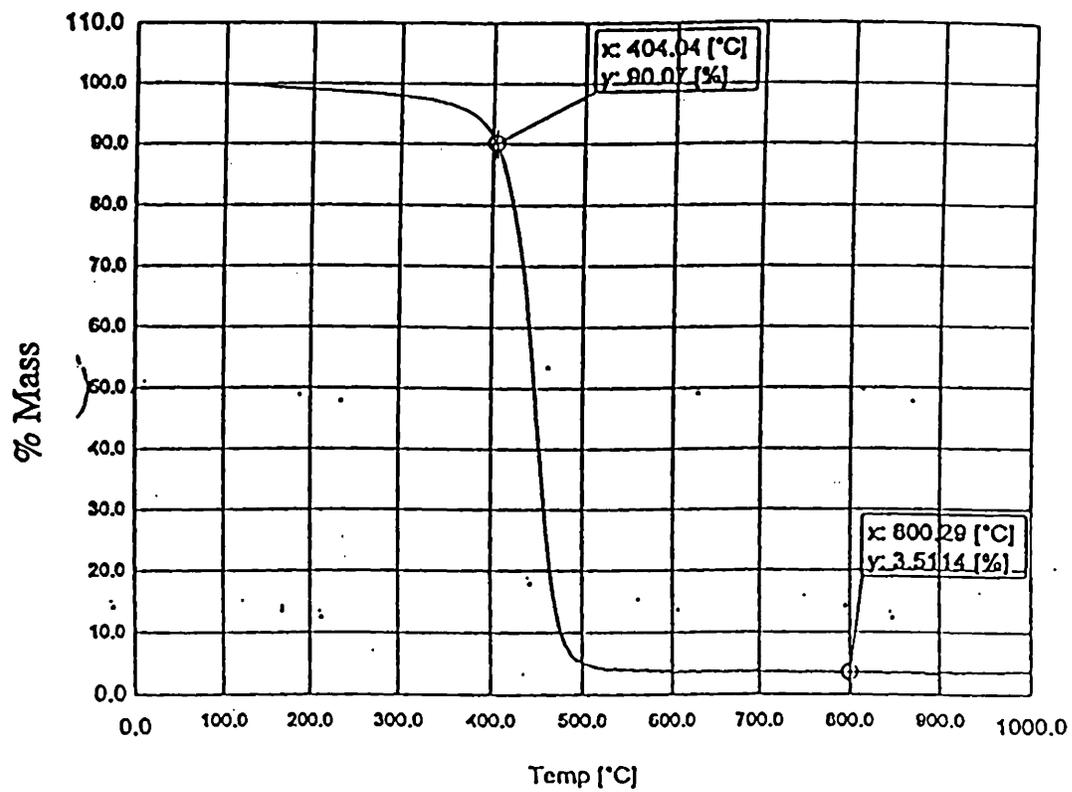


Figure 28: TGA of Neat polyester in Air

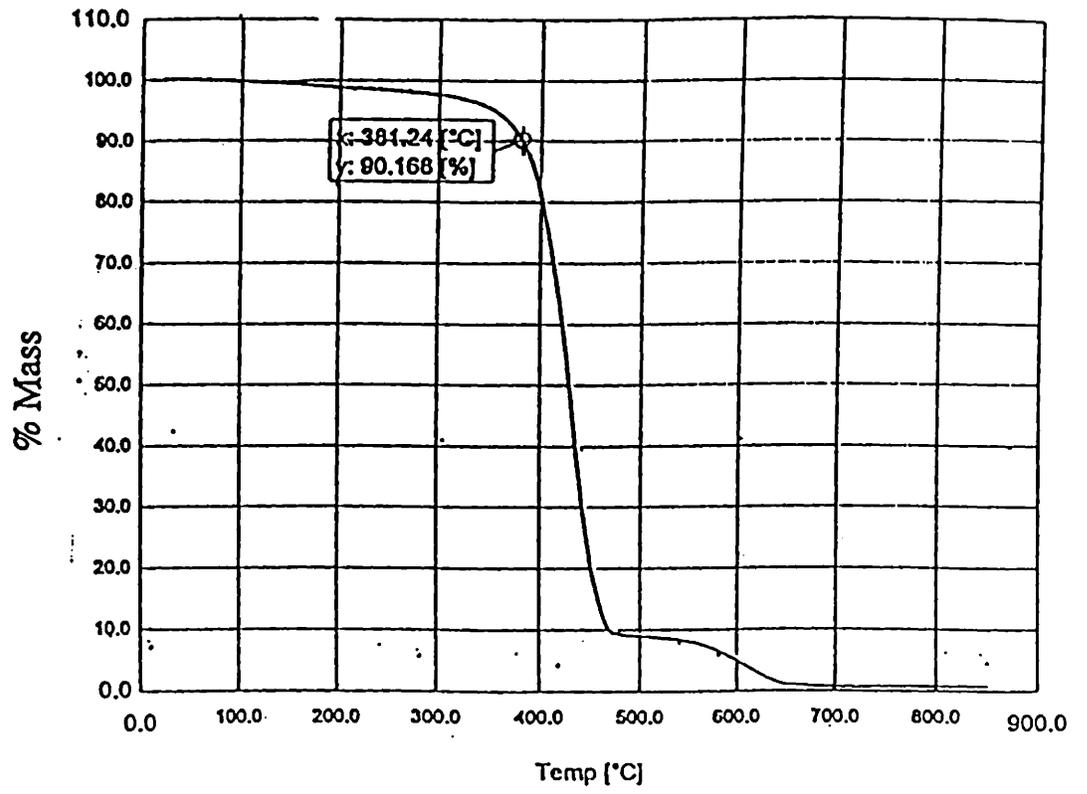


Figure 29: TGA of JO-403 in Air

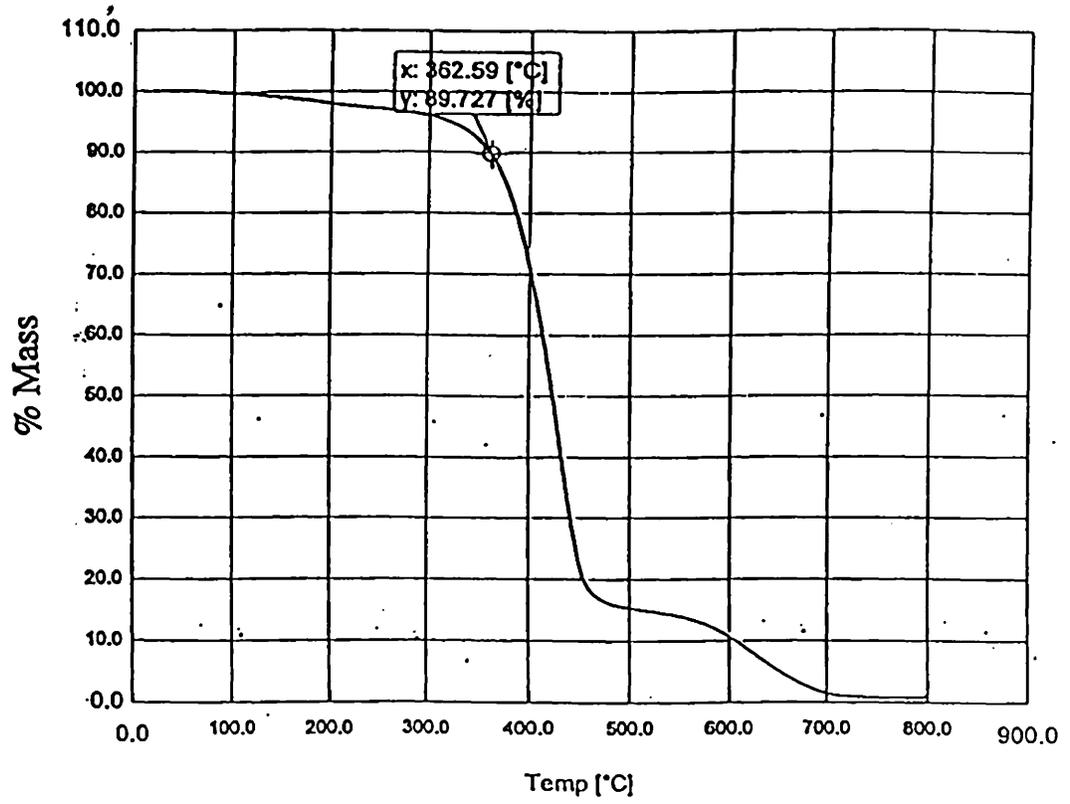


Figure 30: TGA of JO-509 in Air

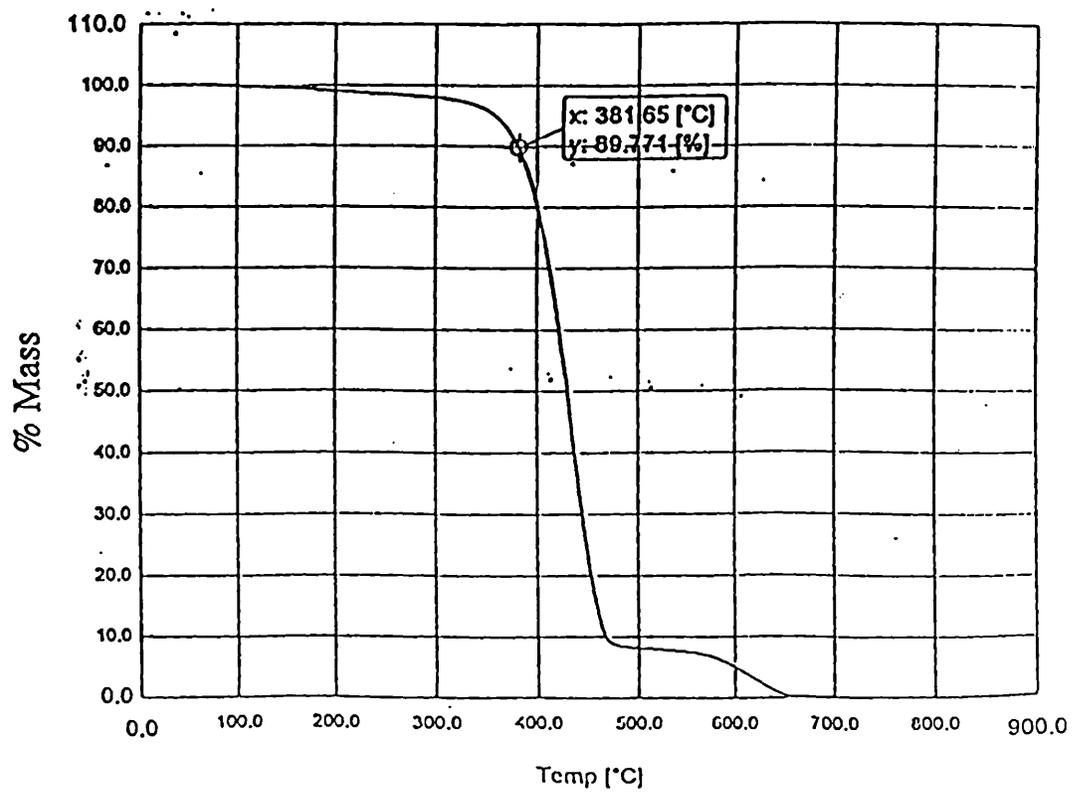


Figure 31: TGA of JO-2000 in Air

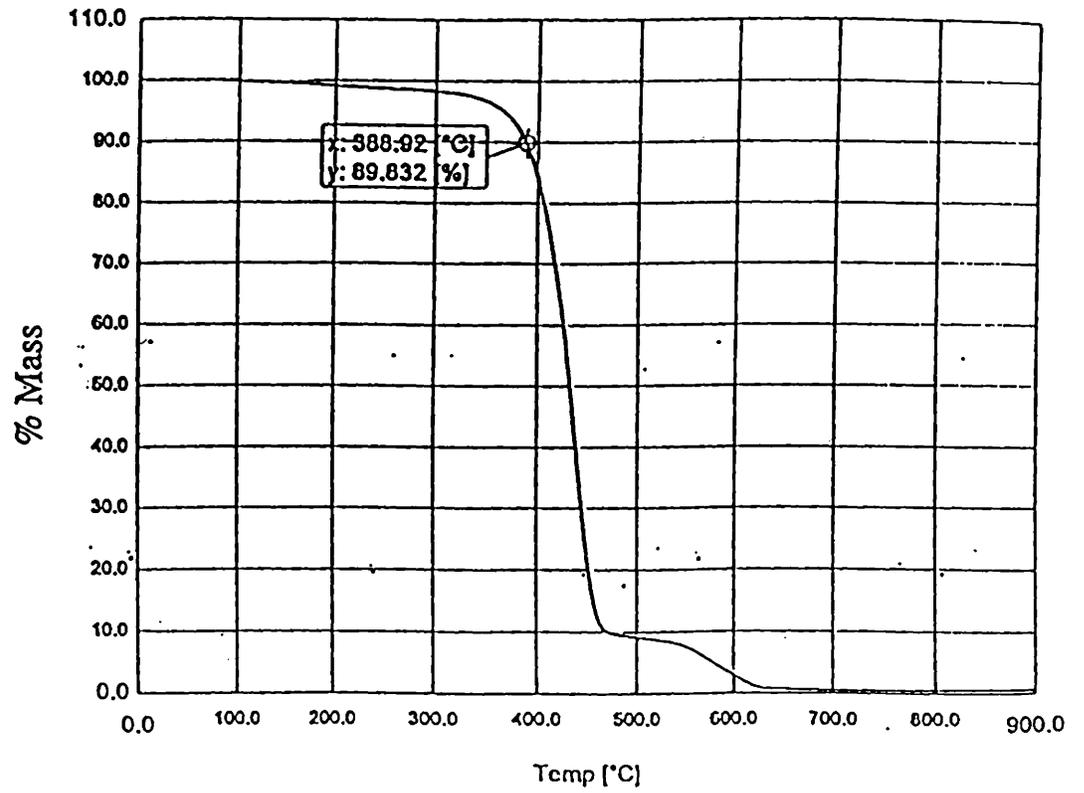


Figure 32: TGA of JO-5000 in Air

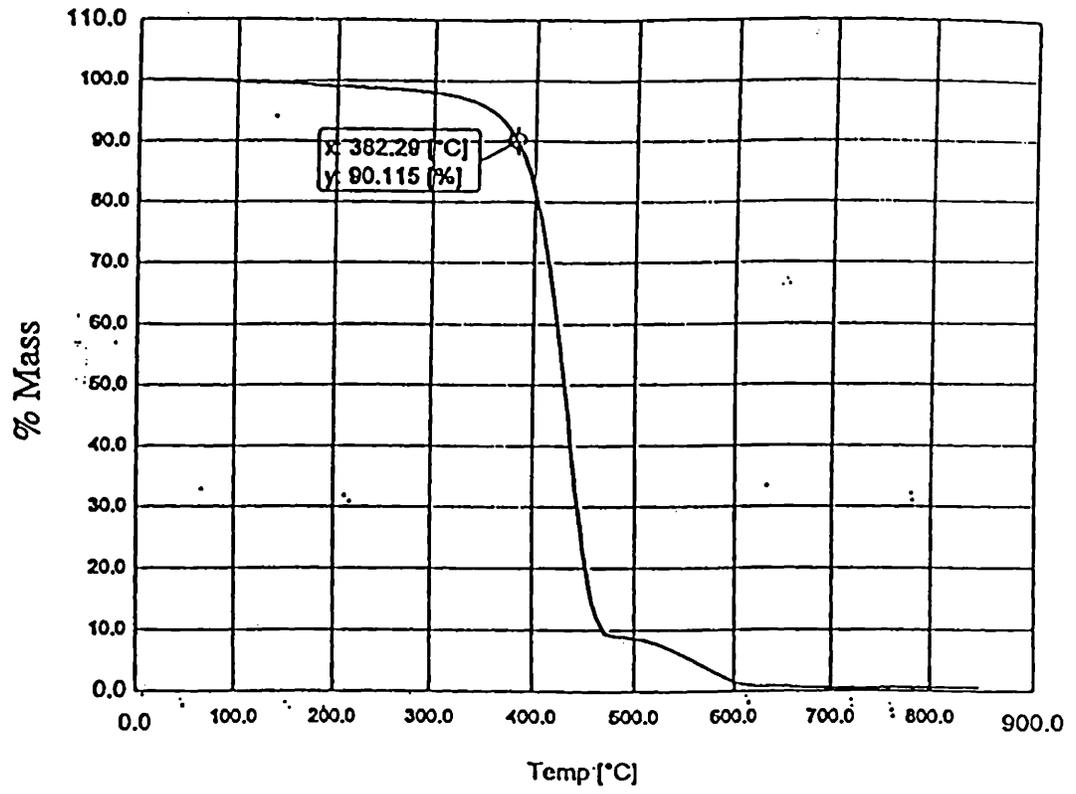


Figure 33: Three-Point Flexural Bend of Neat Polyester

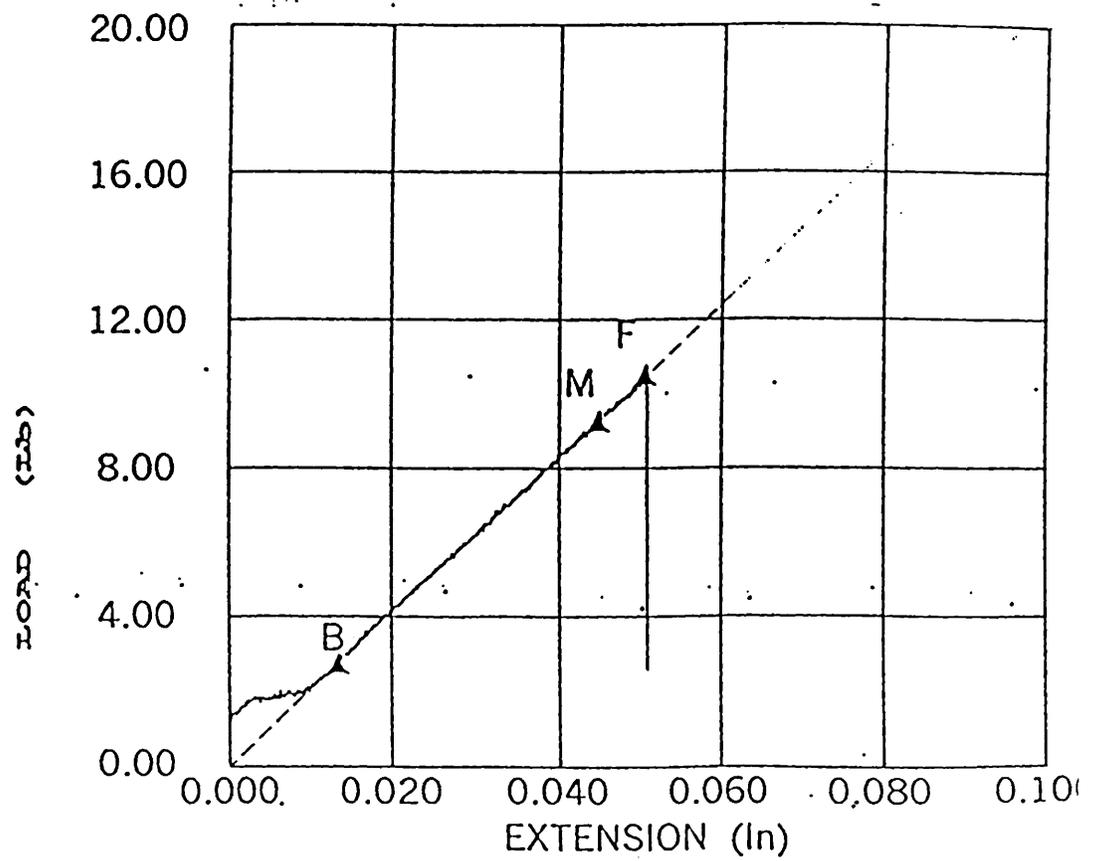


Figure 34: Three-Point Flexural Bend of JO-403

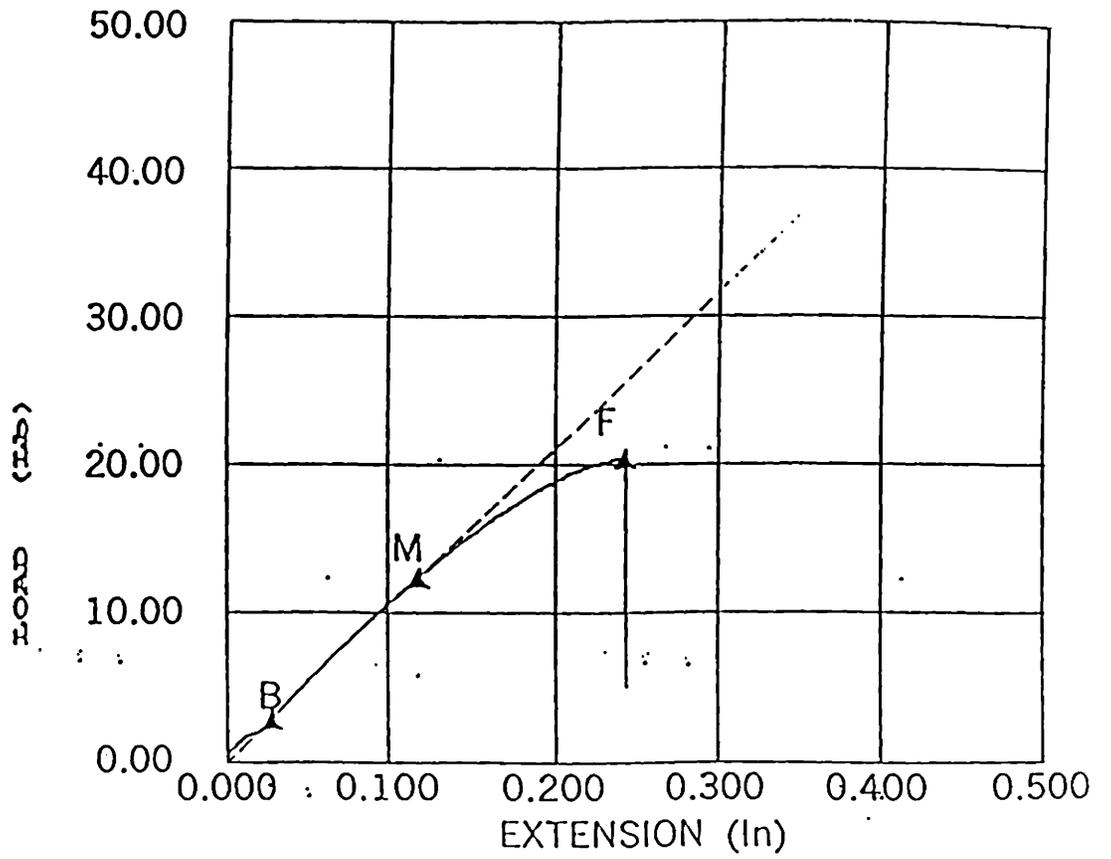


Figure 35: Three-Point Flexural Bend of JO-509

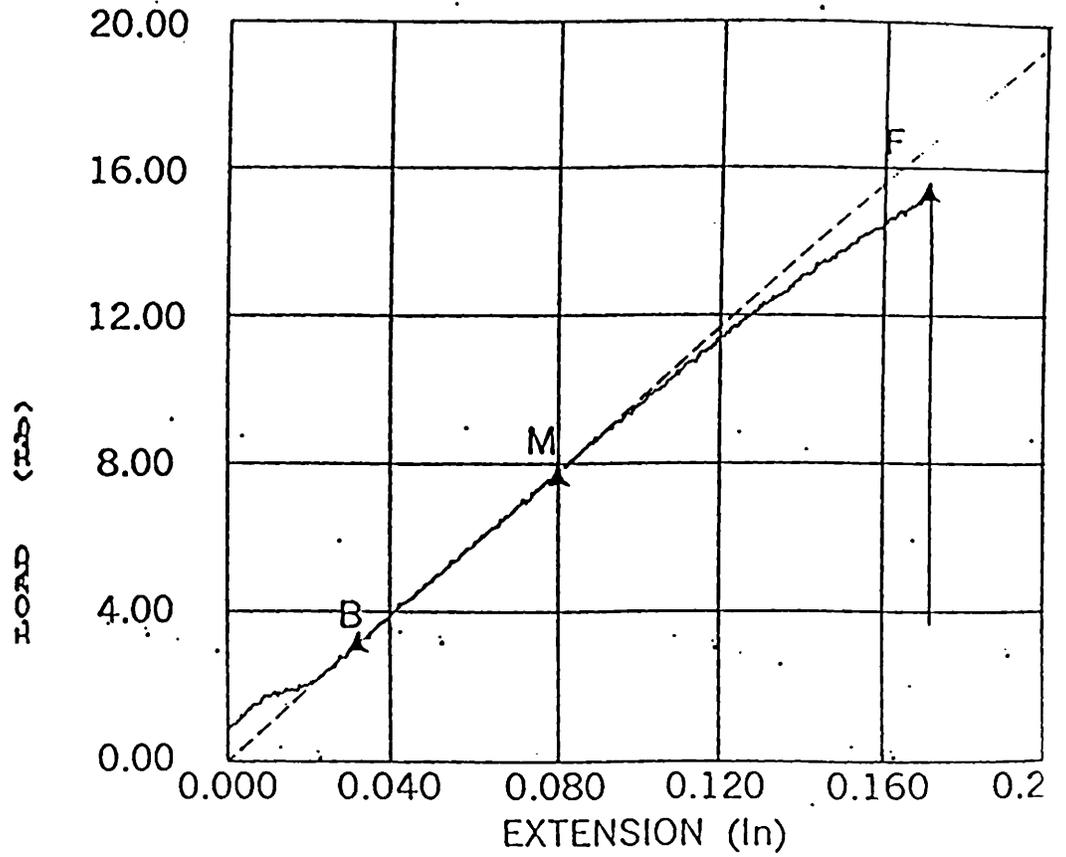


Figure 36: Three-Point Flexural Bend of JO-2000

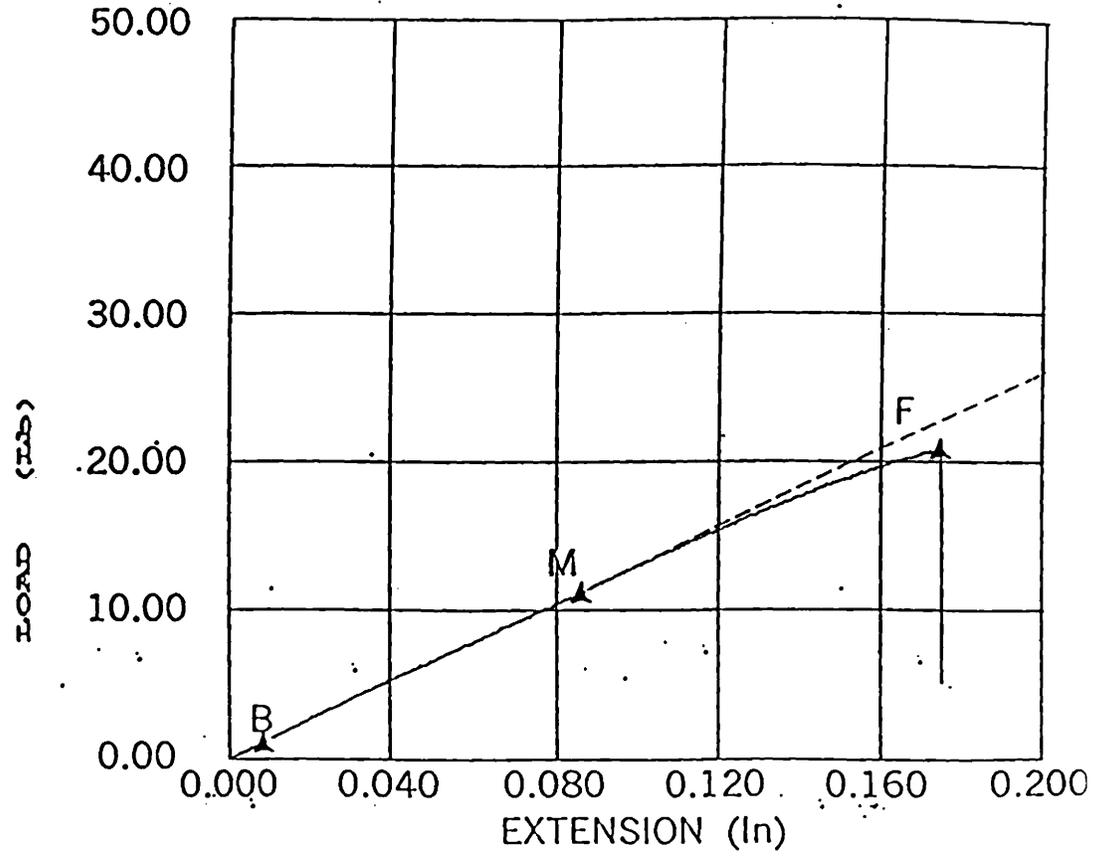


Figure 37: Three-Point Flexural Bend of JO-5000

