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Abstract

The VDS tow cable has had a history of problems with the elastomer link that ties the fairing components together. Several changes have been made to the cable system and link to compensate but problems still exist. In this study, the results of the chemical, dynamic mechanical and thermal characterization of five polyurethane thermoplastic elastomers are reported. These were proposed as candidate materials to replace the poly(ether)urethane elastomer in use. The results are discussed in terms of the composition, percentage hard and soft segments, degree of phase mixing, and effect of hard segment length on the properties of the five poly(ether)urethane elastomers.

Résumé

Le lien en élastomère qui maintient ensemble les éléments carénés du câble servant au remorquage du sonar à profondeur variable a été l'objet de nombreux problèmes. Plusieurs modifications ont été apportées au système de câble et au lien, mais le problème persiste toujours. Dans cette étude, on fait état des résultats de la caractérisation chimique, dynamique-mécanique et thermique de cinq élastomères thermoplastiques de polyuréthane. On a proposé ces élastomères comme matériaux de remplacement possible de l'élastomère de poly(éther)uréthane actuellement utilisé. Les résultats sont examinés en termes de la composition, de la proportion de segments durs et de segments tendres, du degré de mélange des phases et de l'effet de la longueur des segments durs sur les propriétés des cinq élastomères de poly(éther)uréthane.

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CHARACTERIZATION OF POLY(ETHER)URETHANE THERMOPLASTIC ELASTOMERS

John A. Hiltz

EXECUTIVE SUMMARY

Introduction

The fairings on the VDS tow cable are tied together with elastomeric links. When these links fail, adjacent fairings can rotate relative to each other. This results in damage of the fairings during retrieval of the tow cable. In the late eighties, a decision was made to replace the nylon reinforced neoprene links with a thermoplastic elastomer (TPE) that was less prone to failure due to limited elasticity.

A thermoplastic elastomer (Texin 591-A) was selected to replace the neoprene link. However, the Texin 591-A link lacked rotational stiffness and failed in service. Another TPE, Estane 58300, was trialled but failed in-service in 1995.

In 1996, the LCMM (DMSS 7) requested that DREA/DL(A) aid in the failure investigation. Testing showed that Estane 58300 suffered plastic deformation at very low loads. This allowed greater movement of the links with respect to the fairing and led to fairing damage when the tow cable was retrieved.

DREA was also asked to suggest alternative TPEs for use as fairing links. Five poly(ether)urethane elastomers were selected for evaluation; Texin 990A, Texin 950D, Texin 970D, Elastollan 1195A, and Elastollan 1164D. A preliminary study indicated that Texin 950D and Elastollan 1195A should be further evaluated (A. Boehk, J. Hiltz and J.R. Matthews, "Investigation of VDS Tow Cable Link Materials", DREA RN/DL/96/5, October 1996).

To fully understand the properties of the poly(ether)urethanes requires a knowledge of the chemical make-up and phase structure of these compounds. In this paper the chemical, dynamic mechanical and thermal characterization of these materials are reported. These results are used to discuss the relationship between chemical composition, phase structure and properties of these materials.

Principal Results

Pyrolysis gas chromatography/mass spectrometry and Fourier Transform infrared spectroscopy can be used to identify TPEs and give some insight into the composition of TPEs. For instance, both techniques can be used to determine the relative proportions of hard and soft segments in the polymers that are related to hardness and modulus. Dynamic mechanical analysis gives glass transition temperature and information on the amount of phase mixing in the elastomers. Differential scanning calorimetry is sensitive to phase mixing and finer structural detail, such as the average length of the hard segments in the polymers.

Significance of the Results

Chemical, dynamic mechanical and thermal characterization techniques allow investigation of the structure of these polymers and therefore give insight into their properties and performance.

Future Plans

Thermoplastic elastomers are being considered for a number of defence applications including sound and vibration damping. Chemical, dynamic mechanical, and thermal characterization of these materials will be an important part of research aimed at their introduction into service.

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Introduction

In the late 1980s, the life cycle manager initiated a program to design a new fairing link for the AN/SQS-505 tow cable. It was reported[1] that the old fairing link, which was die cut from a nylon fibre reinforced neoprene rubber sheet, failed as the result of severely limited elasticity. That is, when the link was loaded it quickly reached its elongation to break and failed. This allowed adjacent fairings to rotate relative to each other. During retrieval rotation of adjacent fairings in excess of 20^{o} led to damage to the fairings. Damaged fairings resulted in system downtime and increased maintenance costs.

Based on these findings, a study was undertaken to find a material with high tensile strength and large elongation at break than the nylon reinforced neoprene. It was suggested that an injection moldable thermoplastic would be ideal since injection molding provided the most economical method of mass producing this part. Evaluation of several candidate materials resulted in the selection of a polyurethane-based thermoplastic elastomer, Texin 591-A. This thermoplastic elastomer was reported to have a tensile strength of 6000 psi and an elongation at break of 540%. Compared to the nylon fibre reinforced neoprene rubber links, this represented a 74% increase in tensile strength and a 420% increase in elongation at break.

In addition to the link material change, the link design was also altered. The Texin 591-A link was made thinner (0.200 inch versus 0.245) and the attachment holes were elongated. The increased tensile strength of the polyurethane elastomer was the rationale for the decrease in thickness, while it was thought that elongation of the slots would eliminate tensile loads on the links introduced when the tow cable was retrieved. However, the thinner Texin 591-A link showed a lack of rotational stiffness during tow trials and the elongated holes allowed the fairings to contact each other and this made pull out of the thinner link from an adjacent fairing easier[2,3].

To address these operational problems, further development work was undertaken. Round holes were reinstituted and the thickness of the links was increased from 0.200 inches to 0.250 inches. Several thermoplastic elastomers were tested to determine the effect of elastomer properties on rotational stiffness and cracking of the ABS fairing material. Rotational stiffness, tensile, and fatigue life tests were completed and it was recommended that a polyether-based polyurethane, Estane 58300 be trialled[4].

In 1995, a towed array with the Estane 58300 links failed in service. Links were reported to have broken during deployment of the VDS and when the cable was retrieved the fairings did not line up and were destroyed on the winch drum. DREA DL(A) was requested by DMSS 7 to aid in the failure investigation. Testing indicated that the failed link was the specified material (Estane 58300), had the specified thickness (0.25 inches), and placement and shape of holes. Mechanical testing, however, indicated that this material suffered plastic deformation at very low loads[5]. This would be critical in the area of the holes in the links as it would allow greater movement of the links with respect to the fairing.

This suggested that Estane 58300 might not have the flexibility and mechanical stiffness in tension required for the fairing link. A study of alternative poly(ether)urethane based thermoplastic elastomers was undertaken. Five poly(ether)urethane elastomers, Texin 990A, Texin 950D, Texin 970D, Elastollan 1195A and Elastollan 1164D were selected for further analysis. The load displacement behavior of these elastomers was investigated[5], and on the basis of this two of the thermoplastic elastomers chosen for further testing at Spectrum Engineering, Peterborough, Ontario.

To get a better understanding of the relationship between the structure and properties of poly(ether)urethanes, the composition and structure of Estane 58300, Texin 990A, Texin 950D, Texin 970D, Elastollan 1195A, and Elastollan 1164D have been investigated using pyrolysis gas chromatography/mass spectrometry, infrared spectrometry, dynamic mechanical analysis, and differential scanning calorimetry. The results are reported in this paper.

Experimental

Materials

Texin 990A, Texin 950D, and Texin 970D, were supplied by Bayer Polymers, Etobicoke, Ontario, Elastollan 1195A and Elastollan 1164D were supplied by BASF Corporation-Polymers, Wyandotte, Michigan, and Estane 58300 was supplied by B. F. Goodrich, Cleveland, Ohio. The Shore Type A or Shore Type D Durometer hardness of the six thermoplastic elastomers is shown in Table 1.

Table 1 - Manufacturer, trade name, and Shore Durometer hardness of the thermoplastic poly(ether)urethane elastomers.

Manufacturer	Trade Name	Shore Hardness
Bayer Polymers	Texin 990A	90A
Bayer Polymers	Texin 950D	50D
Bayer Polymers	Texin 970D	70D
BASF Plastics	Elastollan 1195A	95A
BASF Plastics	Elastollan 1164D	64D
B. F. Goodrich	Estane 58300	80A

Instrumentation

Pyrolysis gas chromatography/mass spectrometry (py-GC/MS) analysis of the elastomers was done using a Chemical Data Systems Model 122 pyroprobe coupled to a Fisons Platform II quadrupole GC/MS with a Fisons Model 8000 GC. Approximately 150 μg of each elastomer was heated at 20^{o}C/msec to 700^{o}C (20 second dwell time) in a 25 mm quartz tube.

The pyrolysis products were separated on a 30m long X 0.25 mm inside diameter ARX-5 capillary column with a 0.25μm thick stationary phase (5% phenyl-95%dimethylpolysiloxane). The GC was operated in the pressure control mode using Helium (linear flow rate 0.3m/sec at 40°C) as the carrier gas. To reduce deadspace between the pyroprobe and the head of the GC column, the column was threaded up through the pyroprobe interface and positioned adjacent to the end of the pyrolysis tube. The GC oven was programmed to hold at 40°C for 5 minutes, then ramped at a rate of 10°C/minute to 300°C, and finally held at 300°C for 9 minutes. Total run time was 40 minutes.

The quadrupole MS detector was operated in the full scan mode (25 atomic mass units (amu) to 500 amu).

Infrared spectra were acquired on a Nicolet Model 510P Fourier Transform infrared spectrometer in the transmittance mode. Thin films of the polymers were laid down on the NaCl plate from tetrahydrofuran or dimethylacetamide solutions.

Dynamic mechanical analysis (DMA) was carried out on a DuPont Instruments Model 983 Dynamic Mechanical Analyzer. The analyses were done in the fixed frequency mode and the storage modulus (E'), loss modulus (E") and tan δ were monitored as the temperature was ramped from -80.0°C to 60°C at a rate of 10°C/min. The glass transition temperature was taken as the maximum in the plot of E" versus temperature. Test coupons were approximately 42 mm long X 12.5 mm wide X 6.5 mm thick.

Differential scanning calorimetry was carried out on a DuPont Model 2910 Differential Scanning Calorimeter. Samples (~10mg) were heated at a rate of 10°C/min from 40°C to 250°C and then cooled to 40°C at a rate of 10°C/min.

Results and Discussion

Poly(ether)urethane Thermoplastic Elastomers

Thermoplastic polyurethanes elastomers are composed of hard and soft segments. The hard segments of polyether-based polyurethanes are composed of a diisocyanate and a diol (chain extender), while the soft segments are composed of polyethers (macroglycols) and diisocyanates. A typical diisocyanate, diol, and macroglycol are shown in Figure 1. Poly(ether)urethanes consist of alternating urethane rich, high glass transition temperature (T_g) hard segments and urethane sparce, low T_g soft segments that are connected by urethane linkages[5]. The alternating hard (A) and soft (B) segments result in a polymer with the structure $(AB)_n$. Unlike conventional elastomers that must be cross-linked to obtain their properties, thermoplastic elastomers do not contain cross-links and are therefore melt and solution processible above their melting points.

The elastomeric properties of thermoplastic polyurethanes arise from interactions between the polymer chains. The hard segments of the linear molecules contain functional groups that are capable of hydrogen bonding and these interactions lead to the aggregation of the urethane rich segments of the polymer. The urethane rich areas are connected by urethane poor polyether segments. The interactions of the urethane rich segments of the polymeric molecules result in what has been termed 'virtual cross-links'[6]. This interaction is shown in Figure 2. By varying the relative amounts of the hard and soft segments in the polymer, the physical properties of the polymer, such as hardness and modulus, can be altered substantially.

Chemical Characterization

Pyrolysis GC/MS

Texin Thermoplastic Elastomers

Pyrograms of Texin 990A, Texin 950D, and Texin 970D samples are shown in Figures 3a through 3c respectively. Analysis of the degradation products of these thermoplastic elastomers (TPEs) indicates they are diphenylmethanediisocyanate (MDI)-based Poly(ether)urethanes with 1,4-butanediol chain extender and poly(oxytetramethylene) soft segments. For instance, diphenylmethanediisocyanate, characteristic of the degradation of MDI-based polyurethanes, is found in each of the pyrograms; at 25.24 minutes in Figure 3a, at 25.23 minutes in Figure 3b and at 25.31 minutes in Figure 3c. Tetrahydrofuran (1.84 minutes in Figure 3a), butoxybutene (6.98 minutes in Figure 3a), and dibutylether (7.20 minutes in Figure 3a) are found in the degradation products of each of the Texin TPEs and are characteristic of the degradation of the poly(oxytetramethylene) portion of the polymer. Expansions of the pyrograms of Texin 990A, Texin 950D, and Texin 970D between 11.00 and 23.00 are shown in Figures 3d though 3f respectively. The similarity of the pyrolysis products of these three elastomers is evident from the pyrograms. Mass spectral analysis indicates that the compounds giving rise to these peaks result predominately from the degradation of the poly(oxytetramethylene) portion (soft segments) of the elastomers.

Mass spectral analysis indicated that the compound giving rise to the broad peak between 10.00 and 11.00 minutes was 1,4-butanediol. Diols, such as 1,4-butanediol, are used as chain extenders in polyurethane thermoplastic elastomers and are part of the urethane rich hard segments of these elastomers.

Because butanediol arises from the hard segment of the elastomer, it might reflect the relative proportions of hard and soft segments in the three Texin elastomers. That is, the amount of butanediol released should increase with the percent hard segment (and hardness) of the elastomers. The areas under the 1,4-butanediol peak and the peak at 11.60 minutes, which is released by the degradation of the soft segment of the polymer, were determined for the three Texin samples. The ratio of the areas (1,4-butanediol to 11.60 minute peaks) increased in going from the Texin 990A sample to the Texin 950D sample to the Texin 970D sample. The increase in ratio and therefore the amount of hard segment correlates with the increase in hardness of these elastomers.

Elastollan and EstaneThermoplastic Elastomers

Pyrograms of Estane 58300, Elastollan 1195A and Elastollan 1164D are shown in Figures 4a through 4c respectively. The pyrolytic degradation products of these thermoplastic elastomers are similar to those for the three Texin samples. Diphenylmethanediisocyanate is found in the degradation products of Elastollan 1195A (25.34 minutes) and Elastollan 1164D (25.38 minutes). It was not released following pyrolytic degradation of Estane 58300. However, a degradation product resulting from the degradation of a diphenylmethanediisocyanate-butanediol or a diphenylmethanediisocyanate-poly(oxytetramethylene) portion of the polymer chain was found at 32.23 minutes. The compound is shown in Figure 4d. The elastomers release a number of degradation products that are characteristic of the breakdown of the poly(oxytetramethylene) portion of the poly(ether)urethane, including tetrahydrofuran, butoxybutene, and dibutylether.

The pyrograms of Estane 58300, Elastollan 1195A and Elastollan 1164D between 11.00 and 23.00 minutes are shown in Figures 4e through 4g respectively. As was observed for the Texin thermoplastic elastomers, the pyrolytic degradation products for these elastomers are similar in this part of the chromatogram. Mass spectral analysis indicates that the compounds arise from the degradation of the soft segment (poly(oxytetramethylene)) portion of the elastomers.

1,4-butanediol was also released following pyrolysis of the Estane and Elastollan TPEs. As was noted for the Texin samples, 1,4-butanediol is a chain extender and arises from the degradation of the urethane rich hard segments of the elastomer. The ratio of the areas of the 1,4-butanediol and the peak at 11.60 minutes increased as the hardness of the samples increased from Shore A 80 to Shore D 64.

Infrared Analysis

Texin Thermoplastic Elastomers

Infrared (IR) spectra of Texin 990A, Texin 950D, and Texin 950D thermoplastic elastomers are shown in Figures 5a through 5c. The wavelengths of the major peaks in the IR spectra of the Texin thermoplastic elastomers are listed in Table 2. The IR spectra are typical of poly(ether)urethanes. For instance, in Figure 5a, the bands at 1730 cm^{-1} and 1703 cm^{-1} and the band at 1534 cm^{-1} are the amide I bands (C=O stretch) and amide II band (N-H deformation) respectively. These bands arise from the urethane functionality[7]. The band at 1223 cm^{-1} also arises from the urethane functionality (C-O stretch) while the band at 1076 cm^{-1} is attributed to the C-O stretch for first oxytetramethylene carbon contiguous with the urethane functional group. The bands at 1111 cm^{-1} and 772 cm^{-1} arise from the C-O stretch and the C-H out of plane vibration of the poly(oxytetramethylene) portion of the elastomer respectively.

Table 2

Absorption maxima (cm^{-1}) of the major functional groups of Texin 990A, Texin 950D, and Texin 970D thermoplastic Poly(ether)urethanes.

Absorption maximum (cm^{-1})

Vibration Mode	Texin 990A	Texin 950D	Texin 970D
N-H and O-H	3322	3326	3330
C-H stretch	2942	2942	2942
C-H stretch	2859	2859	2859
C=O stretch (amide I band)	1730	1730	1730
C=O stretch (amide I band)	1703	1703	1703
C=C in plane aromatic ring	1599	1597	1597
N-H (amide II band)	1534	1534	1530
C-O stretch (urethane)	1223	1225	1227
C-O stretch (polyether)	1111	1109	1109
C-O stretch (urethane)	1076	1080	1080
C-H out of plane aromatic ring	818	818	816
CH2 rocking (polyether)	772	772	772

Seymour *et. al.*[9] have used the ratio of the intensities of the two amide 1 bands to determine the level of hydrogen bonding in a series of poly(ether)urethanes. The two amide one bands at 1703 cm^{-1} and 1730 cm^{-1} are attributed to hydrogen bonded and non hydrogen bonded amide groups. As the relative concentration of urethane rich hard segments increases, the amount of hydrogen bonding in the polymer and therefore the ratio of the intensity of 1703 cm^{-1} to the 1730 cm^{-1} bands increases. The absorbance of these bands and their ratio for Texin 990A, Texin 950D, and Texin 970D samples are shown in Table 3. The ratios indicate that hydrogen bonding, and therefore the relative concentration of urethane rich hard segments, increases in going from Texin 990A to Texin 950D to Texin 970D.

The ratio of the intensities of the bands at 1111 cm^{-1} and 1076 cm^{-1}, which are due to C-O stretches in the polyether rich (soft) and urethane rich (hard) portions of the elastomers respectively, decrease in going from Texin 990A to Texin 950D to Texin 970D. The observed decrease is consistent with an increase in the relative proportion of hard segments in the elastomers. Further, the change correlates with the change in the hardness of the elastomers.

Table 3

The absorbance and ratio of absorbances for the hydrogen bonded and non-hydrogen bonded carbonyl peaks at 1703 cm^{-1} and 1730 cm^{-1} for the six Poly(ether)urethane thermoplastic elastomers.

Polymer	Texin 990A	Texin 950D	Texin 970D	Elastollan 1195A	Elastollan 1164D	Estane 58300
Absorption						
1703cm^{-1} (a)	0.27	0.19	0.22	0.45	0.31	0.17
1730cm^{-1} (b)	0.24	0.12	0.12	0.32	0.18	0.24
Ratio (a/b)	1.13	1.58	1.83	1.49	1.72	0.71

Estane and Elastollan Thermoplastic Elastomers

Infrared (IR) spectra of Estane 58300, Elastollan 1195A and Elastollan 1164D thermoplastic elastomers are shown in Figures 6a through 6c. The wavelengths of the major bands in the IR spectra of the Elastollan and Estane samples are listed in Table 4.

Table 4

Absorption maxima (cm^{-1}) of the major functional groups of Estane 58300, Elastollan 1195A and Elastollan 1164D thermoplastic Poly(ether)urethanes.

Absorption maximum (cm-1)

Vibration Mode	Estane 58300	Elastollan 1195A	Elastollan 1164D
N-H and O-H	3301	3330	3328
C-H stretch	2942	2942	2944
C-H stretch	2857	2859	2861
C=O stretch (amide I band)	1732	1730	1732
C=O stretch (amide I band)	1705	1701	1701
C=C in plane aromatic ring	1599	1597	1597
N-H (amide II band)	1536	1530	1532
C-O stretch (urethane)	1223	1225	1227
C-O stretch (polyether)	1111	1109	1109
C-O stretch (urethane)	1071	1080	1080
C-H out of plane aromatic ring	818	818	818
CH2 rocking (polyether)	772	772	772

The infrared spectra of the Estane 58300 and Elastollan samples were similar to the Texin samples. The ratios of the absorbance of the bands at 1703 cm^{-1} and 1730 cm^{-1} increase in going from Estane 58300 to Elastollan 1164A to Elastollan 1164D indicating that the amount of hydrogen bonding and therefore the relative concentrations of urethane rich segments is increasing.

The ratio of the intensities of the bands at 1109 cm^{-1} and 1080 cm^{-1} decrease in going from Estane 58300 to Elastollan 1164A to Elastollan 1164D. This is consistent with a decrease in the relative proportion of soft to hard segments in going from Estane 58300 to

Elastollan 1195A to Elastollan 1164D and the decrease correlates with the increase in hardness of the elastomers shown in Table 1.

Dynamic Mechanical Analysis (DMA)

Changes in the dynamic response of a material are related to a number of parameters including the structure of the polymer, the degree of cross-linking, crystallinity, and the presence of additives such as plasticizers and fillers. For instance, changes in the relative amounts of the two components in an $(AB)_n$ block copolymer, such as a poly(ether)urethane, result in changes in the amount of phase mixing of the hard and soft segments of the polymer. The amount of phase mixing in turn affects the dynamic response of the polymer. For instance, the temperature of the maximum in the plots of loss modulus (E") and tan δ, the ratio of loss and storage moduli (E'), against temperature and the width and intensity of the E" and tan δ peaks are all affected by the amount of phase mixing in these polymers.

Texin Thermoplastic Elastomers

Plots of E" versus T for samples of Texin 990A, Texin 950D, and Texin 970D are shown in Figure 7. Table 5 lists the T_g for the soft segment (poly(oxytetramethylene)) portion of the Texin samples. Both the temperature of the maximum in the plot of E" versus T, which is defined as the T_g, and the width of the peak in the plot of E" versus T increase in going from Texin 990A to Texin 950D to Texin 970D.

Estane and Elastollan Thermoplastic Elastomers

Plots of E" versus T for Estane 58300, Elastollan 1195A and Elastollan 1164D are shown in Figure 8 and the T_g of the samples are listed in Table 5. As was observed for the Texin samples, the T_g of the soft segments increased and E" versus T peak width increased in going from Estane 58300 to Elastollan 1195A to Elastollan 1164D.

The increase in T_g is consistent with increased phase mixing in the elastomers. That is, as the proportion of the hard segments increases so does the amount of phase mixing of the hard and soft segments. Phase mixing has been observed to increase the glass transition temperature of poly(ether)urethanes[10]. The broadening of the peak in the E" versus T plot is indicative of an increase in the heterogeneity[11], including hard segment length distributions, of the urethanes in going from Texin 990A to Texin 950D to Texin 970D or from Estane 58300 to Elastollan 1195A to Elastollan 1164D.

Table 5

Glass transition temperature (T_g) of the Texin, Elastollan and Estane thermoplastic polyurethane elastomers. T_g was taken as the maximum in the DMA plot of E" versus T in the fixed frequency mode at 1 Hz and a temperature ramp of 10^oC/min.

Material	T_g (^oC)
Texin 990A	-25.2
Texin 950D	-7.5
Texin 970D	34.8
Elastollan 1195A	-24.2
Elastollan 1164D	-18.6
Estane 58300	-29.7

Although T_g increases with increasing hardness for both the Texin and Elastollan TPEs, the relationship between T_g and hardness is not the same for the Texin and Elastollan TPEs. The T_g of the Texin samples increased from -25.2C to -7.5C to 34.8C as the hardness increased from Shore A90 to Shore D50 to Shore D70. In contrast to this, the T_g of the Elastollan samples increased from -24.2C to -18.6C as the hardness increased from Shore 95A to Shore 64D. This is indicative of more phase mixing in the Texin samples. There are several possible reasons for this. These include soft segment length and synthesis method[10,12]. This will be discussed in the section on differential scanning calorimetry.

Differential Scanning Calorimetry

The MDI/poly(oxytetramethylene)/1,4-butanedol based TPEs have multiphase structures as a result of the incompatibility of the hard and soft segments of the polymer[13]. The phase structure of TPEs depends on a number of factors including the hard segment content, soft segment length, hard segment length, thermal history, and synthesis method[10,12]. Seymour and Cooper[14] observed three endothermic peaks in the DSC traces of MDI/1,4-butanedol based TPEs. They concluded that the three peaks, at approximately 70°C (region I), 160°C (region II), and 180°C (region III), were morphological in origin[15]. The region I endotherm is time dependent and depends on thermal history (annealing temperature). It is attributed to poorly ordered hard segments. The region II endotherm is attributed to more ordered hard segments resulting from microphase separation of the hard and soft segments, and the region III is attributed to the melting of microcrystalline hard segments. Annealing led to changes in the position of the endotherms in regions I and II, that is, the peaks merged to form a single peak on the high temperature side of the peak in region III. Annealing at temperatures above 200°C, led to phase separation of the hard and soft segments and a DSC trace with one endothermic peak. TPEs with low hard segment content do not have an endothermic peak in region III. This may be due to the short hard segment length of the low MDI polymers which affects their ability to crystallize[16].

The DSC traces for the Texin 990A, Texin 950D, and Texin 970D samples between 40°C and 250°C are shown in Figure 9. The Texin 990A DSC trace had endotherms with minimums at approximately 70°C and 160°C, the latter peak indicating microphase separation of the hard and soft segments of this elastomer. The Texin 950 DSC trace had endotherms with minimums at approximately 70°C, 177°C, and at 200°C. The major endotherm was at 177°C, which is in region III, and indicates the presence of microcrystalline hard segments. The endotherm at 200°C is due the melting of crystalline hard segments resulting from increased phase separation in the elastomer and more long range order in the hard segments. This is consistent with the higher hard segment content of Texin 950D relative to Texin 990A. The DSC trace for Texin 970D has three endotherms at approximately 80°C, 186°C, and 200°C. The major endotherm for Texin 970D is at a higher temperature suggesting more long range order in the microcrystalline hard segments than was observed for Texin 950D.

The DSC traces for the Estane 58300, Elastollan 1195A and Elastollan 1164D samples between 40°C and 250°C are shown in Figure 10. The Estane 58300 DSC trace has three endotherms with minimum at 70°C, 100°C, and 145°C. The lack of an endothermic peak in Region III indicates the lack of microcrystalline hard segments and reflects the small percentage of hard segment in this elastomer. The Elastollan 1195A DSC trace has three endothermic peaks at 70°C, 176°C, and 187°C. The peaks at 70°C and 176°C are similar to those found for Texin 950D. However, the peak at 187°C (shoulder on the larger peak) was not observed for Texin 950D. This arises from domains in the hard phase of Elastollan 1195A with more long range order. The Elastollan 1164D trace has 5 endothermic peaks at 145°C, 176°C, 187°C, 203°C and 220°C. The peaks at 203°C and 220°C may result from domains in the hard phase with more order than is found in the other elastomers.

The differences in the DSC and DMA results for the Elastollan 1164D and Texin 970D TPEs suggest there may be a difference in the hard segment length distributions in the two polymers[12]. This could be due to the way in which the two elastomers were synthesized. Miller et. al. investigated the effect of single and multistep synthesis methods on the properties of MDI/butanediol/poly(oxytetramethylene) thermoplastic elastomers. They concluded, on the basis of IR, DSC and DMA results, that a multistep synthesis resulted in polymers with a higher percentage of hard segments containing a single MDI unit. Because short hard segments are more soluble than long hard segments in the soft phase, the multistep polymers exhibited a higher degree of phase mixing. Conversely, polymers made using a single step synthesis had a lower percentage of hard segments containing a single MDI unit and were therefore less soluble in the soft phase. This resulted in less phase mixing and greater percentage hard domain crystallinity.

The crystallization temperature (T_c) and heat of crystallization (H_c) for the six TPEs are shown in Table 6. The T_c for the three Texin elastomers decreases with monotonically with hardness, as does T_c for the Elastollan elastomers. However, the Elastollan samples recrystallize at a higher temperature than the Texin samples of comparable hardness, for instance, Elastollan 1164D recrystallized at 164.5°C while Texin 970D crystallized at 111°C. This is consistent with differences in the hard segment lengths of these elastomers and therefore the nature of their crystalline domains.

With the exception of the Texin 970D sample, the heat of crystallization (H_c) of the elastomers increased with hardness. The increase in H_c results from the greater percentage of hard segment in the Texin 950D and Elastollan 1164D samples relative to Texin 990A, Estane 58300 and Elastollan 1195A sample. The lower H_c for the Texin 970D sample may result from increased phase mixing in this elastomer.

Table 6

The crystallization temperature and heat of crystallization of the six poly(ether)urethanes.

Polymer	T_c (C)	H_c (J/g)
Texin 990A	86.2	9.1
Texin 950D	105.8	14.3
Texin 970D	111.0	12.7
Elastollan 1195A	149.0	10.4
Elastollan 1164D	164.5	18.9
Estane 58300	90.6	6.0

Conclusions

Py-GC/MS and FTIR analyses indicate that the six elastomers are all MDI/1,4-butanediol/poly(oxytetramethylene) based poly(ether)urethanes. The proportion of hard segments in a series of these polymers can be approximated from the amount of 1,4-butanediol released following pyrolysis. The ratio of the IR absorbance of hydrogen bonded and non-hydrogen bonded carbonyl peaks increases as the percentage hard segments in the poly(ether)urethanes increases. The hard segment concentration of a series of these elastomers can also be approximated from the ratio of the absorbances of the C-O stretches at 1111 cm^{-1} and 1076 cm^{-1} respectively. The ratio decreases as the proportion of hard segments in the polymer increases.

The increase in temperature of the maximum in the DMA plot of E" versus temperature was greater for the Texin elastomers than for the Elastollan elastomers as hard segment concentration increased. This indicated more phase mixing in the Texin samples than for the Elastollan samples.

DSC results confirmed increased phase mixing in the Texin samples. The higher melting point of crytalline domains in the Elastollan samples is consistent with increased long range order in these elastomers resulting from better phase separation. The Elastollan elastomers also have higher crystallization temperatures than the Texin elastomers. These data are consistent with the Texin samples containing shorter hard segment lengths than the Elastollan samples. This would result in more phase mixing in the Texin samples and a greater percentage hard domain crystallinity in the Elastollan samples.

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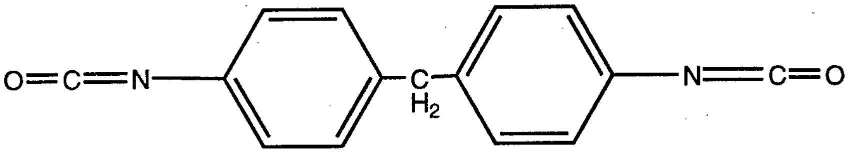

4,4'-methylene di(phenyl isocyanate) MDI

$HO—CH_2—CH_2—CH_2—CH_2—OH$

1,4-butanediol

$$\left(O—CH_2—CH_2—CH_2—CH_2 \right)_n$$

poly(oxytetramethylene)

Figure 1 - Chemical structures of a typical diisocyanate (4,4'-methylene di(phenyl isocyanate), diol (butanediol) and macroglycol (poly(oxytetramethylene)) used to prepare thermoplastic poly(ether)urethanes.

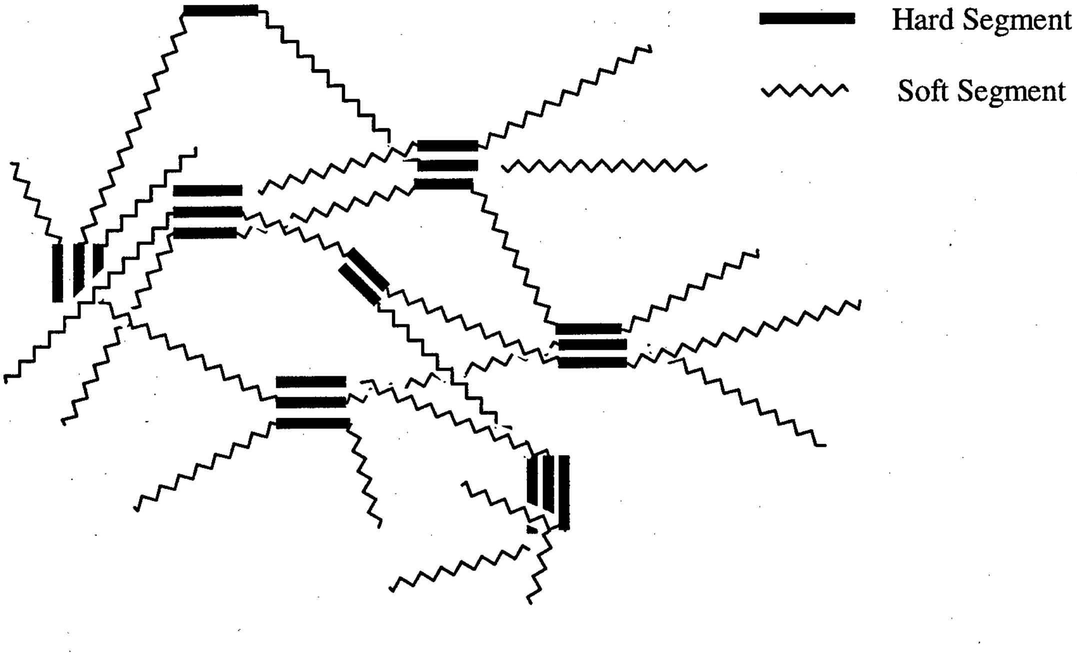

Figure 2 - Schematic representation of a virtually cross-linked thermoplastic poly(ether)urethane elastomer. The hard segments consist of the diisocyanate extended with the diol while the soft segments consist of the macroglycol coupled with the diisocyanate.

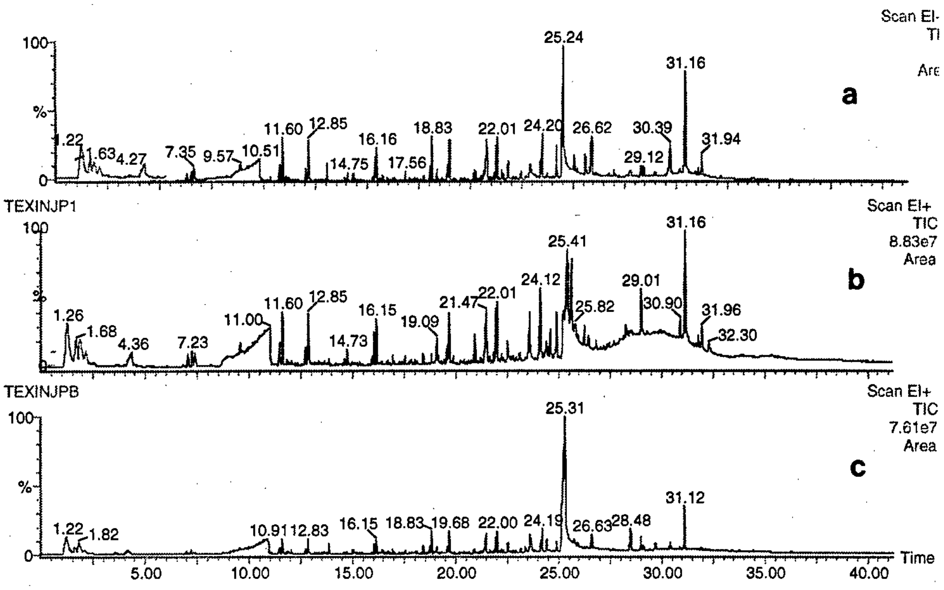

Figure 3 - Chromatograms of the pyrolytic degradation products of a) Texin 990A, b) Texin 950D, and c) Texin 970D following pyrolysis at 700°C.

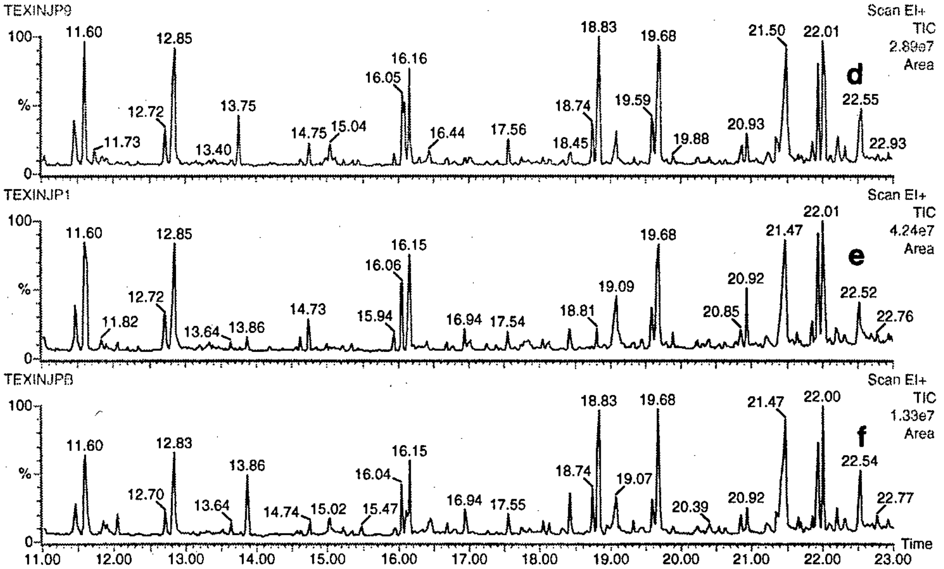

Figure 3 - Expansion of the chromatograms of the pyrolytic degradation products of d) Texin 990A, e) Texin 950D and f) Texin 970D between 11.00 and 23.00 minutes.

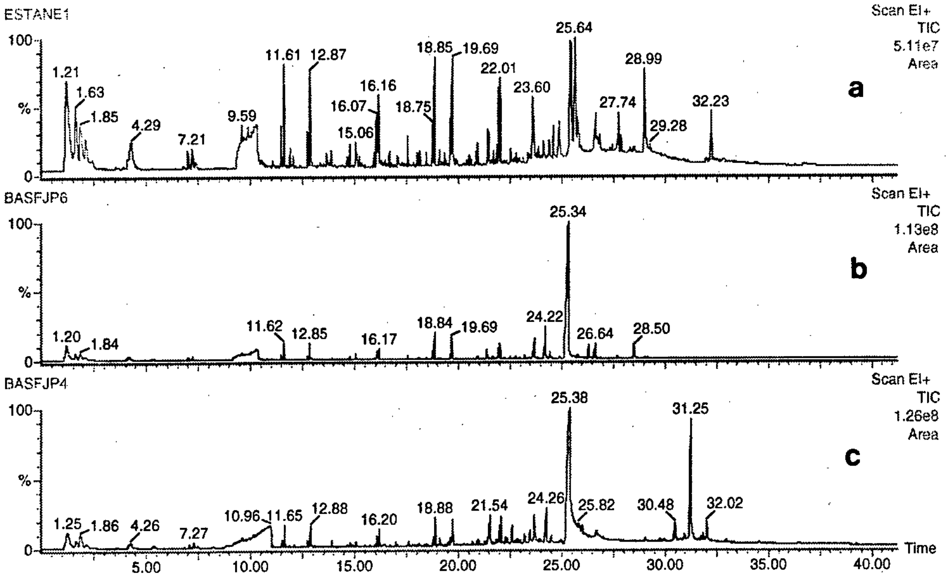

Figure 4 - Chromatograms of the pyrolytic degradation products of a) Estane 58300, b) Elastollan 1195A and c) Elastollan 1164D following pyrolysis at 700°C.

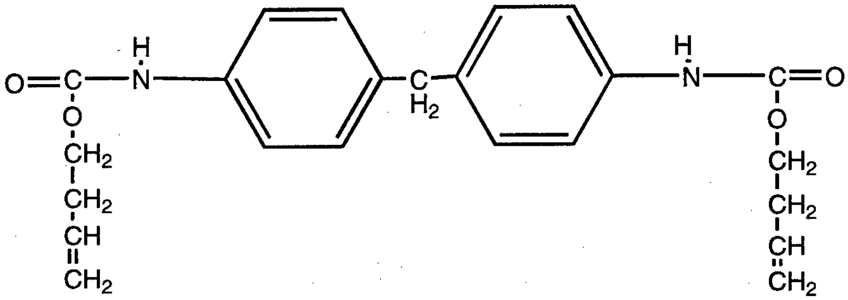

Figure 4d - Degradation product of Estane 58300 poly(ether)urethane (32.23 minutes) containing the diphenylmethanediisocyanate/butanediol - based fragment.

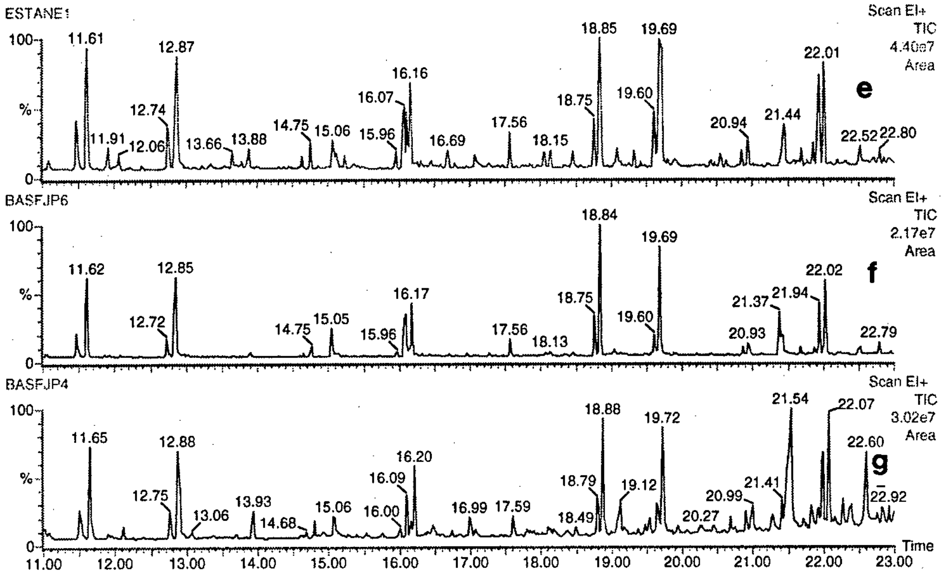

Figure 4 - Expansion of the chromatograms of the pyrolytic degradation products of e) Estane 58300, f) Elastollan 1195D and g) Elastollan 1164D between 11.00 and 23.00 minutes.

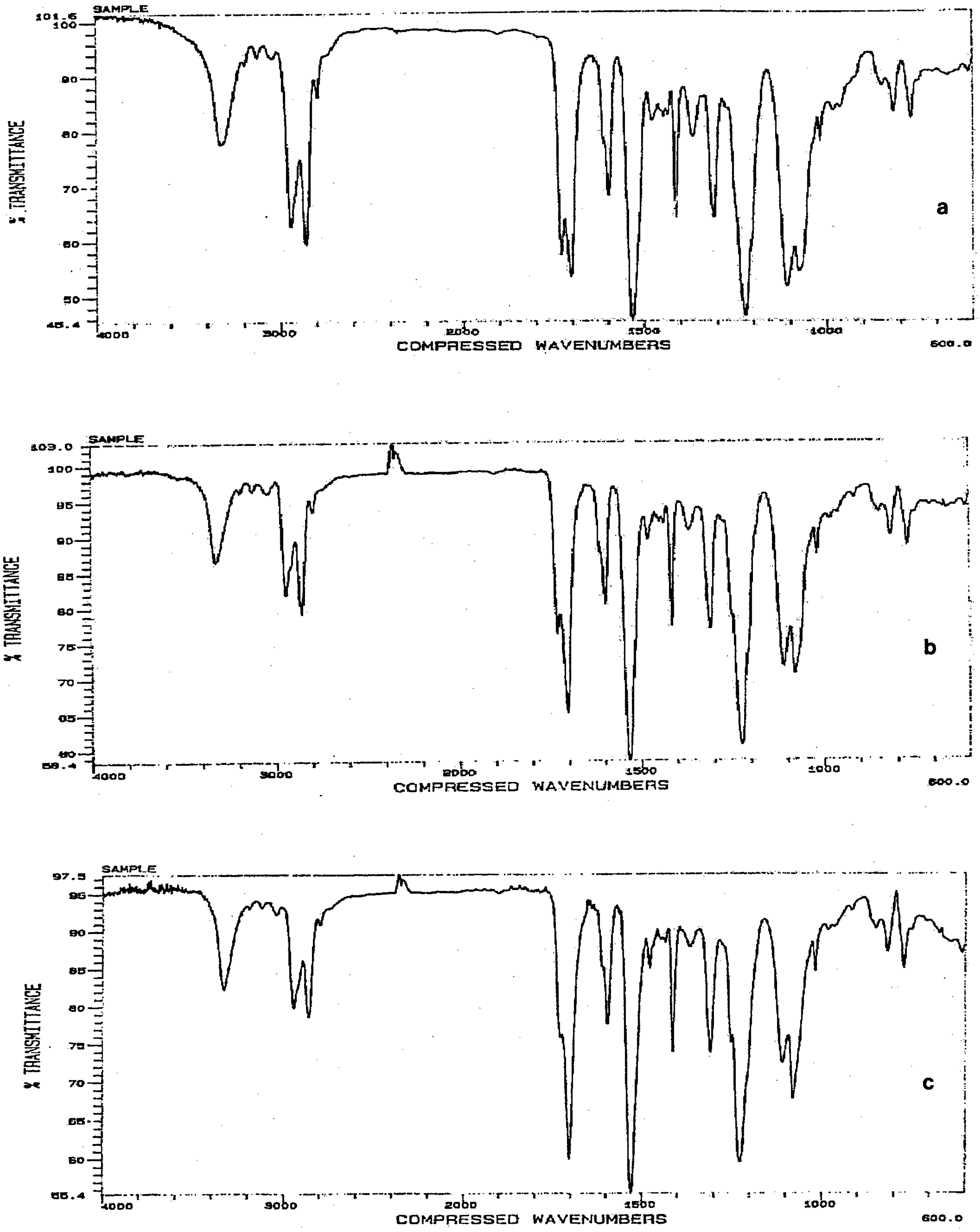

Figure 5 – Infrared spectra of a)Texin 990A, b)Texin 950D, and c) Texin 970D. The infrared were run in the transmission mode as films from tetrahydrofuran.

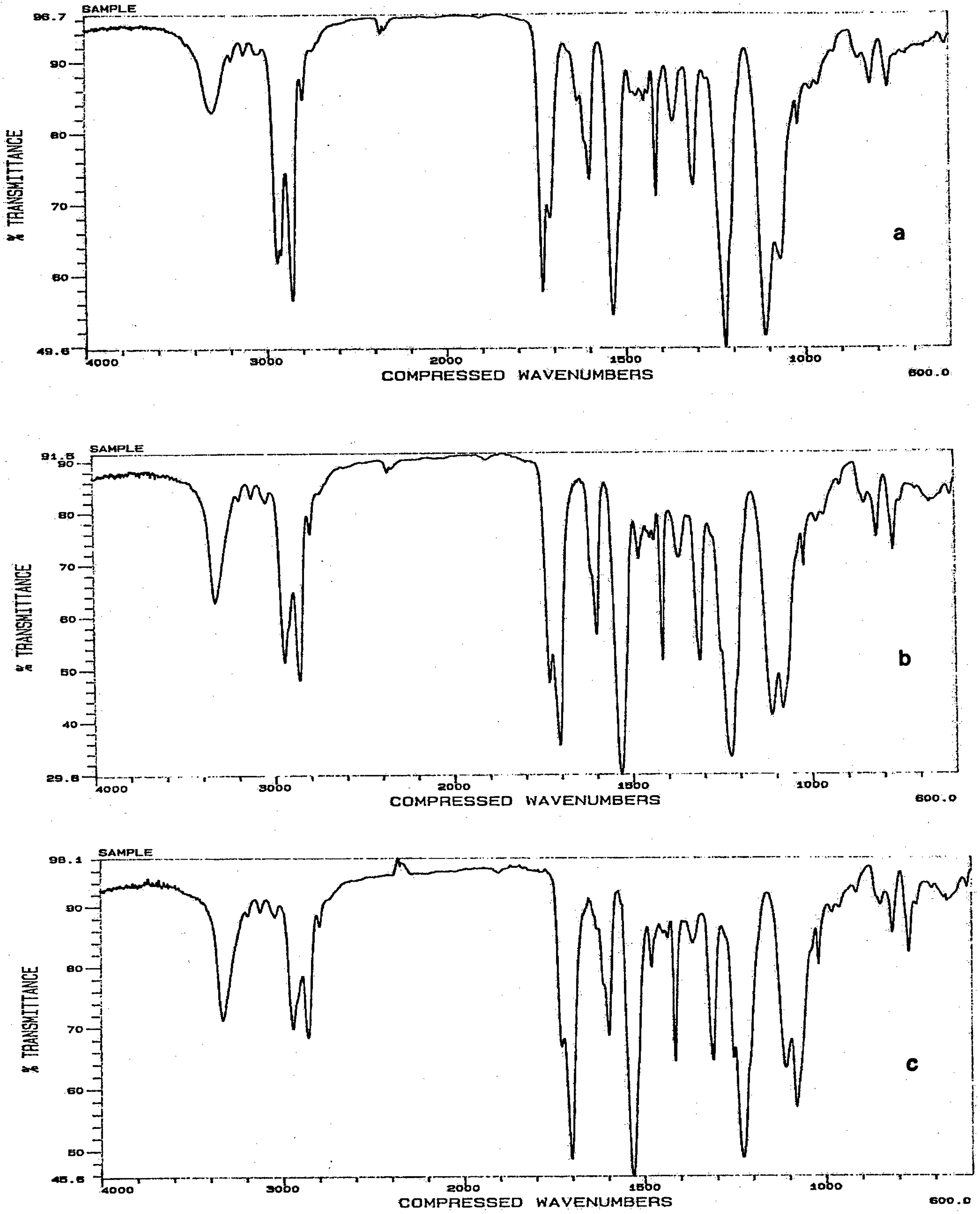

Figure 6 - Infrared spectra of a)Estane 58300, b)Elastollan 1195A, and c)Elastollan 1164D. The infrared were run in the transmission mode as films from tetrahydrofuran.

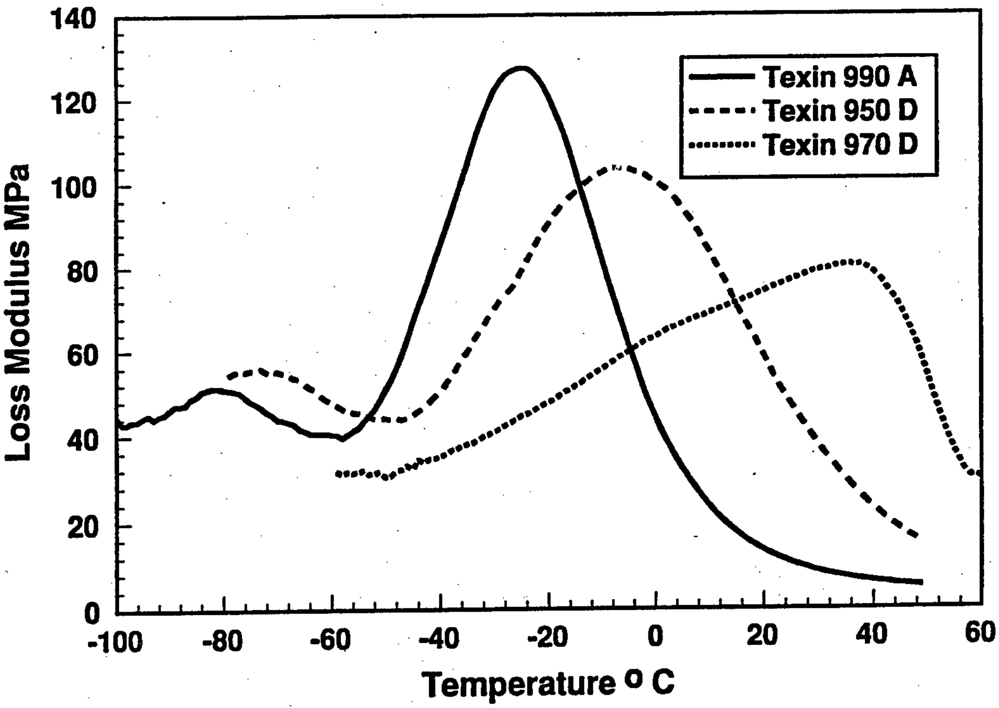

Figure 7 – Plots of loss modulus (E") versus temperature for Texin 990A, Texin 950D, and Texin 970D.

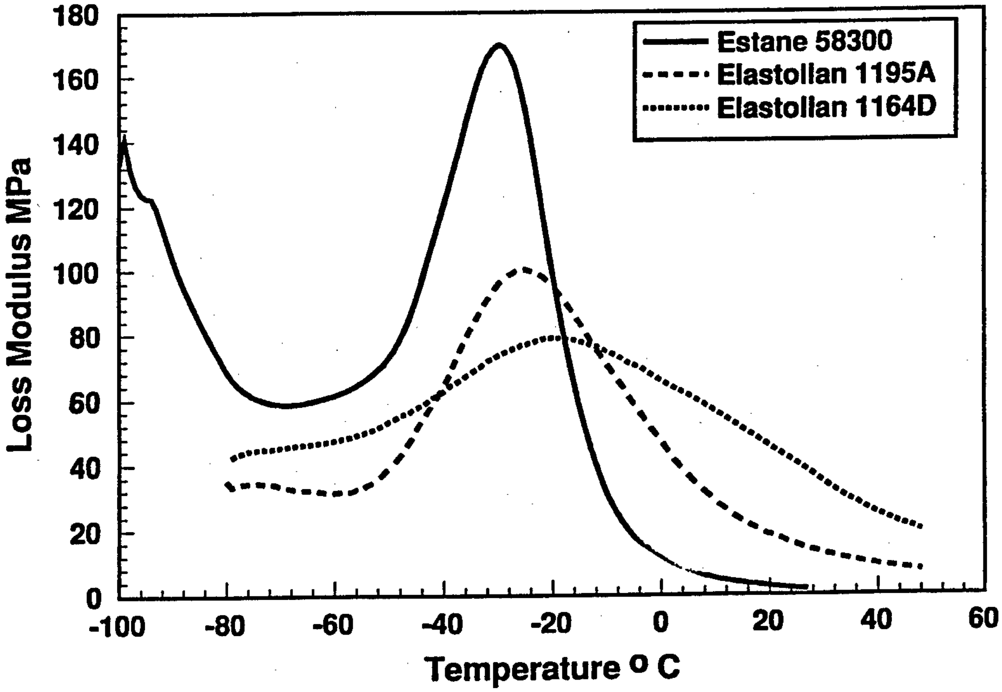

Figure 8 – Plots of loss modulus (E") versus temperature for Estane 58300, Elastollan 1195A, and Elastollan 1164D.

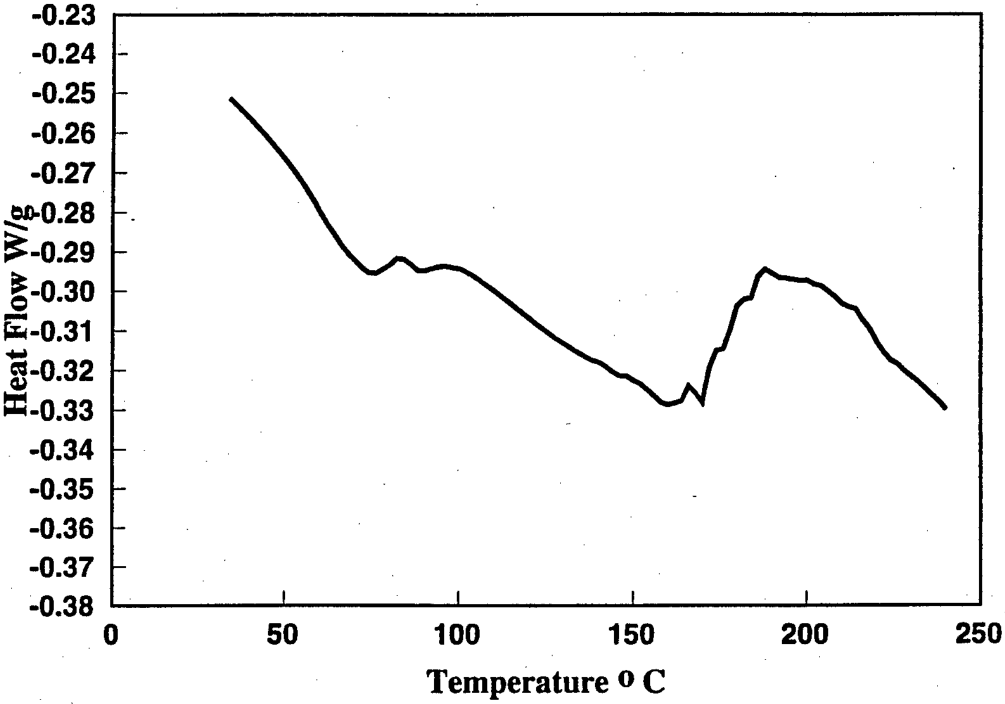

Figure 9a – Differential scanning calorimetry thermogram for Texin 990A.

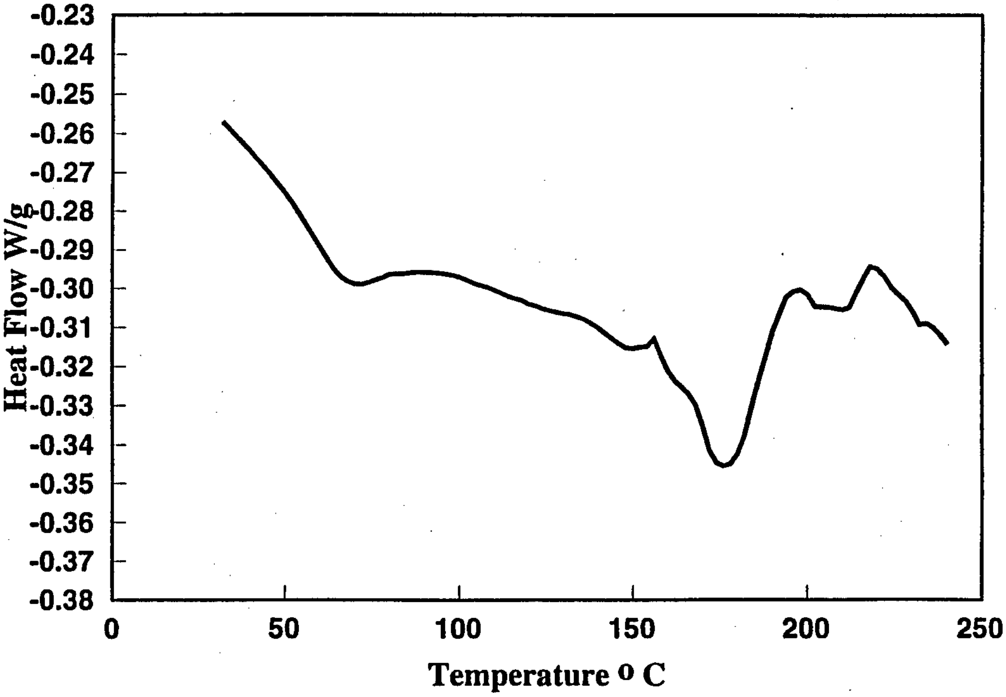

Figure 9b – Differential scanning calorimetry thermogram for Texin 950D.

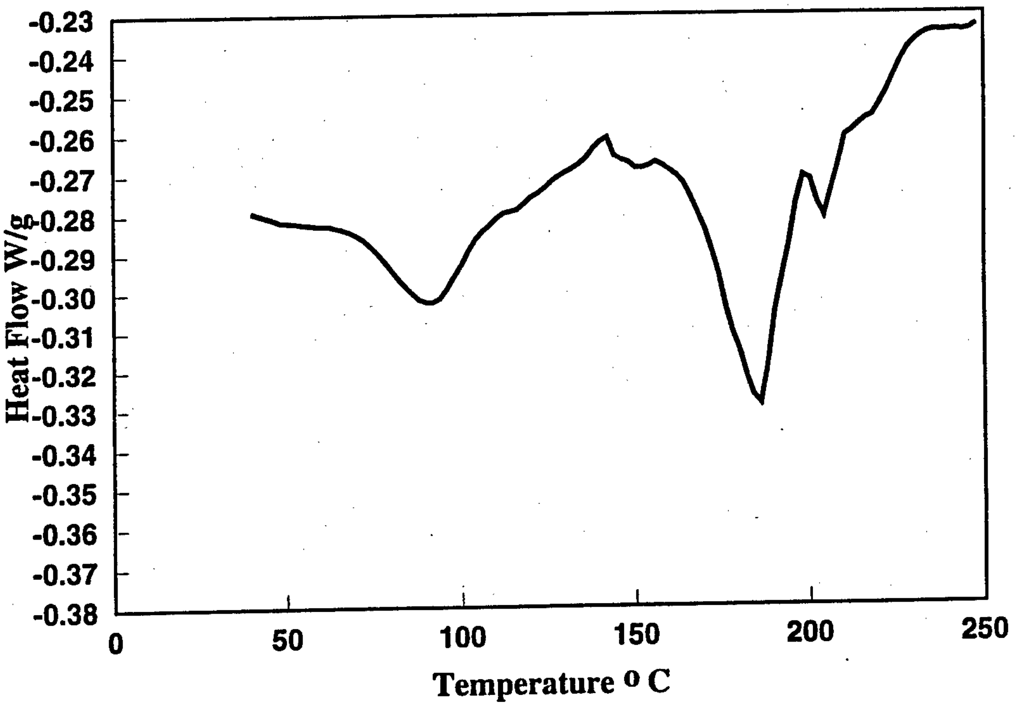

Figure 9c – Differential scanning calorimetry thermogram for Texin 970D.

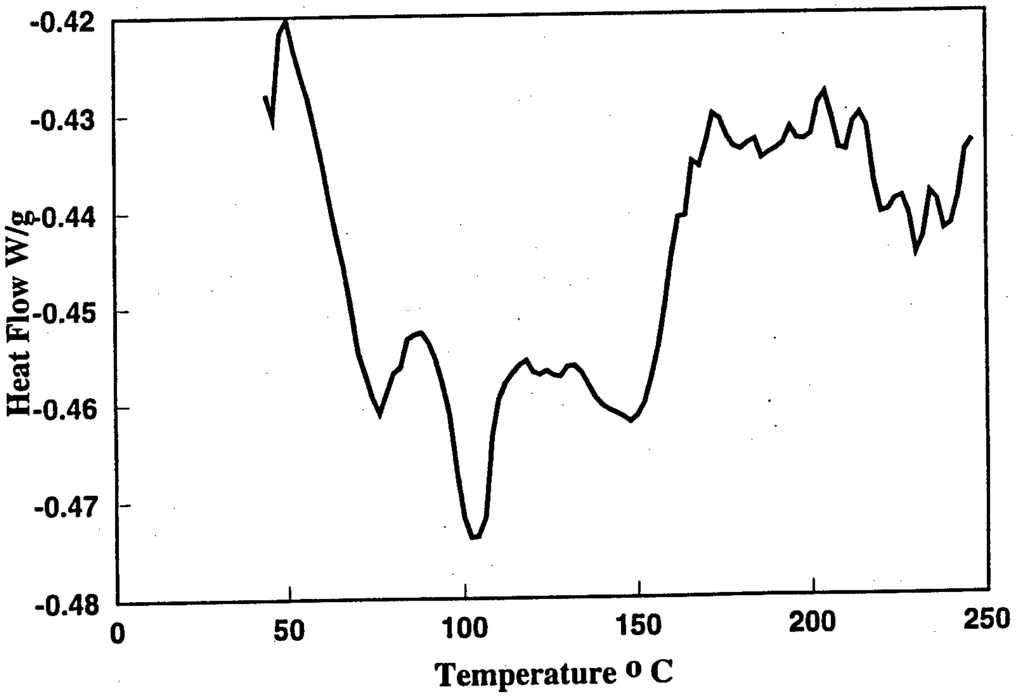

Figure 10a – Differential scanning calorimetry thermogram for Estane 58300.

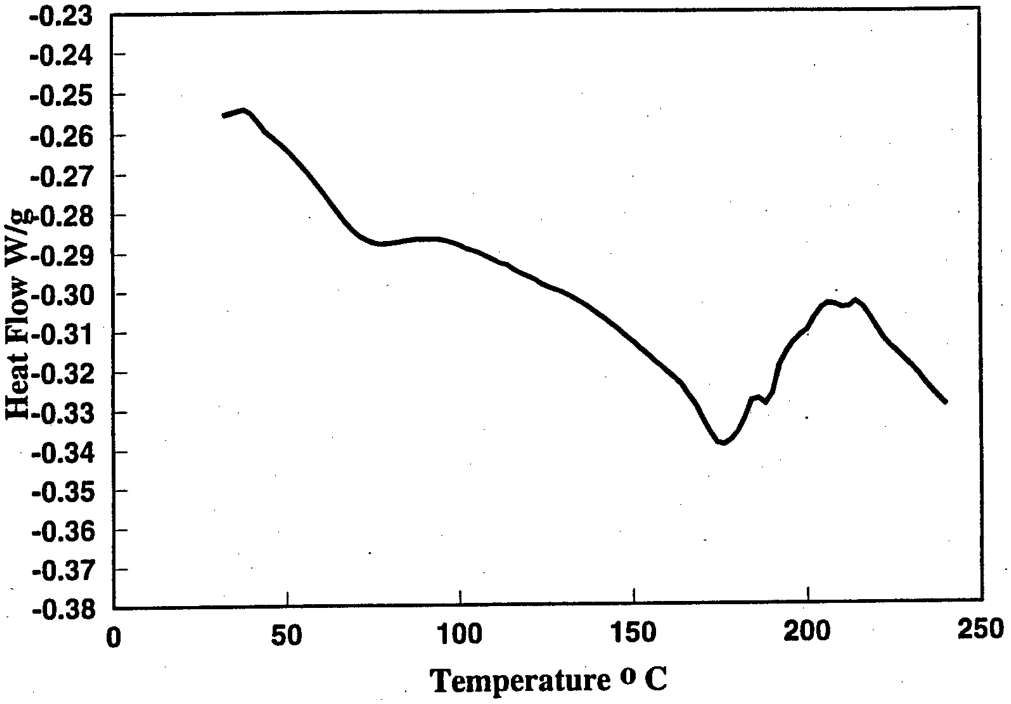

Figure 10b – Differential scanning calorimetry thermogram for Elastollan 1195A.

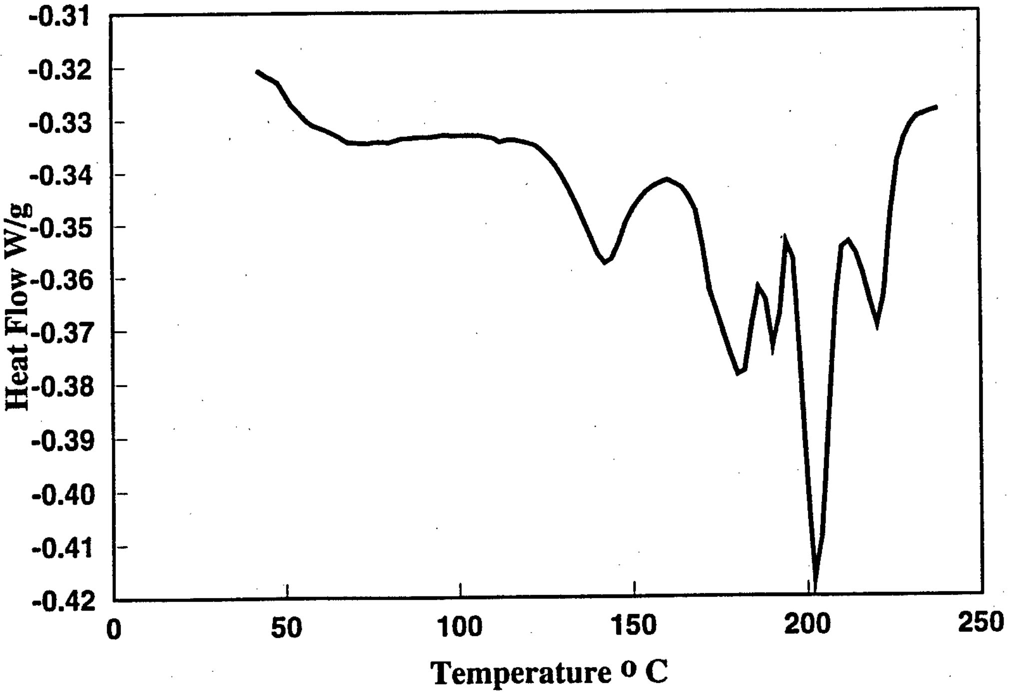

Figure 10c – Differential scanning calorimetry thermogram for Elastollan 1164D.

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The VDS tow cable has had a history of problems with the elastomer link that ties the fairing components together. Several changes have been made to the cable system and link to compensate but problems still exist. In this study, the results of the chemical, dynamic mechanical and thermal characterization of five polyurethane thermoplastic elastomers are reported. These were proposed as candidate materials to replace the poly(ether)urethane elastomer in use. The results are discussed in terms of the composition, percentage hard and soft segments, degree of phase mixing, and effect of hard segment length on the properties of the five poly(ether)urethane elastomers.

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poly(oxytetrameylene)
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Pyrolysis Gas Chromatography/Mass Spectrometry