Report No. NAWCADWAR--96-31-TR

ANALYSIS OF PLYOPHEN ADHESIVES USED IN SELF-LUBRICATING BEARINGS

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8 April 1996

INTERIM REPORT

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Prepared for
NAVAL AIR SYSTEMS COMMAND (AIR- 435)
Washington, DC 20361-6000

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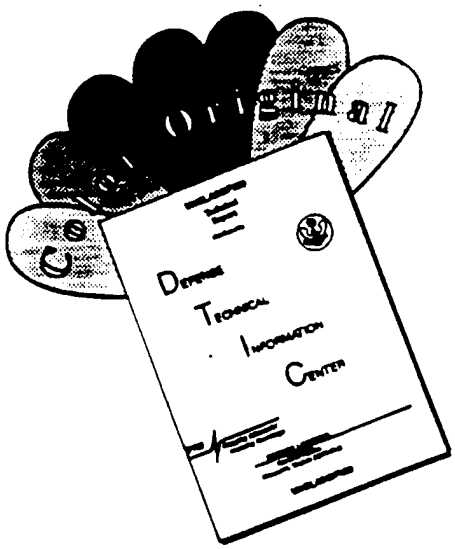

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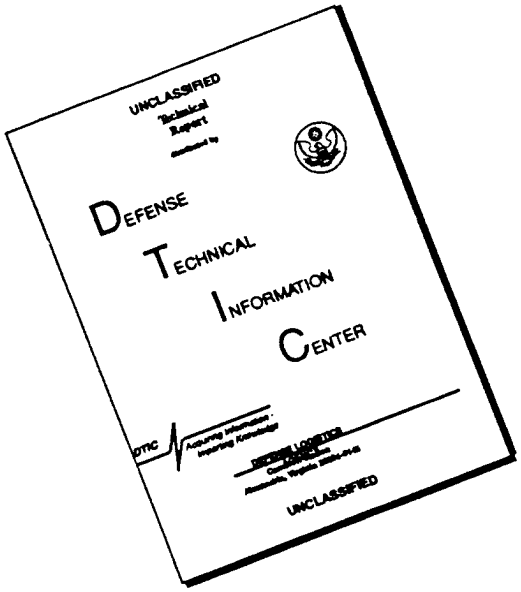

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	8 APRIL 1996	Interim Report

4. TITLE AND SUBTITLE

Analysis of Plyophen Adhesives Used in Self-Lubricating Bearings

5. FUNDING NUMBERS

6. AUTHOR(S)

B. Lam Ta

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

NAWCADWAR
Air Vehicle Engineering Department (Code 4352)
P.O. Box 5152
Warminster, PA 18974-0591

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AIR- 435
Naval Air Systems Command
Arlington, VA 22243-5120

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

NAWCADWAR--96-31-TR

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Authorized for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Plyophen 23-900 and 23-057, two phenolic adhesives widely used in self-lubricating bearing applications, are being replaced with Plyophen 23-900X and 23-057X. The proposed alternatives are supposedly no different from the original adhesives since the change was made in the choice of catalyst used and then later removed during processing. A program was developed in which the basic material characteristics such as the chemical, mechanical, physical and thermal properties of the original adhesives are evaluated and compared with those of the proposed alternatives. The study includes floating roller peel test, Fourier transform infrared analysis, single lap shear test, thermomechanical analysis and viscosity measurements. Although this is an interim report, results so far indicate that there are definite differences between the original adhesives and the proposed alternatives.

14. SUBJECT TERMS

Adhesives, Bearings, Catalyst, Occidental Chemical, Phenolic, Plyophen, Self-Lubricating Bearings

15. NUMBER OF PAGES

55

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

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SUMMARY

Occidental Chemical, the manufacturer of Plyophen 23-900 and 23-057, two phenolic adhesives being widely used in self-lubricating bearing applications, has decided to replace them with alternative adhesives, 23-900X and 23-057X. The manufacturer claimed that the proposed alternatives are no different from the original adhesives since it was just a change in the catalyst, which is removed during processing, and not in the final product.

To verify that the proposed alternatives are the same as the original adhesives, a test plan was developed to evaluate and compare the basic material characteristics of both the original adhesives and the proposed alternatives. Testing of the chemical, mechanical, physical and thermal properties of the four adhesives include floating roller peel tests, Fourier transform infrared spectroscopies, single lap shear tests, thermomechanical analyses and viscosity measurements.

Even though this is an interim report and not all the tests have been completed, results indicate that the proposed alternatives are not the same as the original adhesives. Not only are they different in critical properties, the handling of these adhesives are also different from each other as indicated in the viscosity measurement results and in the specimen preparations for thermomechanical analyses. To determine how different the original adhesives are from the proposed alternatives, a batch to batch variation analysis should be included in the next round of testing.

1.0 OBJECTIVE

The purpose of this study is to fully evaluate the properties and characteristics of two phenolic adhesives, Plyophen 23-900 and 23-057, which are widely used in the manufacture of self-lubricating airframe bearings, and compare the results with those of the two proposed alternative adhesives, Plyophen 23-900X and 23-057X.

2.0 BACKGROUND

Occidental Chemical Corporation produces two phenolic adhesives, Plyophen 23-900 and 23-057, which are widely used in the manufacture of bearings. Specifically, these adhesives are used to bond self-lubricating liners in airframe bearings and also as raw material in the manufacture of self-lubricating liner materials. These bearings are used extensively in both military and commercial aircraft and helicopters.

In the manufacture of the 23-900 and 23-057 adhesives, a toxic catalyst (barium) is used which is later removed during processing, thus becoming a hazardous waste. Waste disposal cost for the barium catalyst is high; therefore, Occidental Chemical plans to terminate the production of the 23-900 and 23-057 resins. Occidental Chemical has developed two other adhesives which use an amine based catalyst and is now offering them as alternatives to the 23-900 and 23-057. The manufacturer claims that these two alternative adhesives, 23-900X and 23-057X, are identical to 23-900 and 23-057. Since it is only a change in the catalyst, the difference supposedly lies only in the processing of the adhesive and not in the final product.

Currently, Occidental Chemical still produces 23-900 and 23-057. However, it is urgent that we find suitable alternative adhesives. Hopefully, both the 23-900X and 23-057X adhesives will provide the characteristics required for their use in the manufacture of self-lubricating bearings.

3.0 TEST PROGRAM

Thermal analysis as well as physical, chemical and mechanical tests were performed to fully establish the material properties of the adhesives under investigation. A test program was developed to evaluate the baseline characteristics of the two original adhesives, 23-900 and 23-057, and compare the results with those obtained from the two proposed alternatives, 23-900X and 23-057X. The entire test program is depicted in Table 1. The shaded areas indicate testing that has been completed to date and will be discussed in this report.

Table 1. Test Matrix of Phenolic Adhesives Analysis

TESTS		ADHESIVES			
Methods	**Conditions**	**23-900**	**23-900X**	**23-057**	**23-057X**
FLOATING ROLLER PEEL	cured	*	*	*	*
	cured & exposed for 1 week @ 77°C and 95-100% RH	*	*	*	*
INFRARED SPECTROSCOPY	uncured				
	cured				
SINGLE LAP SHEAR	cured and test @ 25°C	*	*	*	*
	cured and test @ 163°C	*	*	*	*
	cured and test @ -55°C	*	*	*	*
THERMAL MECHANICAL ANALYSIS	cured				
	cured and exposed for 24 hr. @ 163°C				
	cured & exposed for 1 week @ 77°C and 95-100% RH				
	cured & immersed in MIL-H-83282 hydraulic fluid @ 82°C for 24 hr.				
VISCOSITY	uncured and test @ 25°C				

* Tests performed at Picatinny Arsenal as reported in Reference (1)

Floating roller peel and single lap shear tests are included for mechanical properties analyses; infrared spectroscopy is a form of chemical analysis. Both the thermal mechanical analysis and the viscosity measurement are methods used for evaluating thermal and physical properties, respectively. The usefulness of these tests are described in the following paragraphs.

3.1 Floating Roller Peel Test

A major problem always encountered in using a structural adhesive is how to determine the strength of its bonded joint. The most severe test ever performed on an adhesive is the peel test because it constitutes a test of the adhesive in its weakest stress mode. When the adhesive in a bonded joint tears from the edges inward, this phenomenon is called

peeling. The peel strength of an adhesive is then defined as the resistance of an adhesive bond to further failure. Peel strength is a critical property because peeling can be caused by a relatively small normal load as compared to the high shear stress that most adhesives can withstand. However, this will result in a disaster if the unbonded area is subjected to a sufficiently high static or cyclic loads. The unbonded area will propagate a crack through the bond, causing total failure.

In bearing applications the bearing is a small structure, therefore, the same principle applies to the adhesives used. In this case, we are using an adhesive to bond the liner to the metallic substrate of a bearing. It is critical that we determine how well the liner adheres to the bearing substrate because this affects how the self-lubricating bearing wears. The self-lubricating liner material relies on the structural integrity of the adhesive for its performance. When both adhesive and cohesive bonds are intact, the liner material is properly supported and is able to fulfill its role of providing a low-friction and low-wear sliding surface within the bearing. If the liner starts to peel, the liner will wear unevenly which will adversely affect its performance.

3.1.1 Test Method

The peel resistance of the adhesives were determined according to ASTM Test Method D3167-76, Floating Roller Peel Resistance of Adhesives.

3.1.2 Specimen Preparation

Surface Preparation. Two flexible member 2024-T3 bare aluminum adherends, one panel 0.025 inch thick and the other 0.064 inch thick, were cleaned by wiping the surface with methyl ethyl ketone (MEK) until no visible residue remained. The panels were then immersed for 5 minutes in a solution of hexavalent chromium and fluoride (4 wt%) and deionized water (96 wt%), rinsed with deionized water, then phosphoric acid anodized according to ASTM Test Method D3933. The panels were then rinsed with deionized water and dried for 30 minutes at 75°C.

Bonding Procedure. The panels were coated with the appropriate adhesive and then bonded together with a random mat polyester scrim cloth in between the panels. The entire assembly was then placed in an autoclave of a laboratory platen press and cured at 350°F for 1 hour under 80 psi of nitrogen.

Test Specimen Configuration. Test specimens were obtained by cutting the bonded panels into 1 inch width specimens. The specimen configuration for a floating roller peel test is shown in Figure 1.

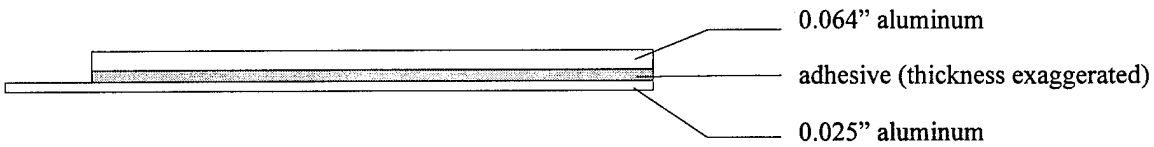


Figure 1. Cross Section of a Floating Roller Peel Test Specimen

3.2 Fourier Transform Infrared (FTIR) Spectroscopy

When determining the chemical components of a material, the preferred method is FTIR analysis if it is available. This method is less tedious and is extremely clean as compared to the conventional chemical analysis. An FTIR is used to identify all the chemical functional groups existing in a particular adhesive and requires only a very small sample for the test.

In this method, a small sample of the adhesive is exposed to an infrared light. The chemical functional group within each molecule will absorb the energy at a certain discrete wavelength. The spectrometer then detects the wavelengths at which the energy is being absorbed and outputs the chemical analysis in a form of a graph. The curve on this graph contains numerous peaks; each peak represents a vibration of the chemical bond within a functional group found in the adhesive. These peaks are then compared against a standard which identifies exactly the chemicals they represent. When used in comparing the uncured vs. the cured adhesive, one can immediately see which chemicals are consumed during the curing process. An FTIR is like the fingerprint of a material and is an extremely valuable method used in differentiating various adhesives. As a quality control tool, an FTIR assures the user that the adhesive has the same chemical properties as that used in the past.

3.2.1 Test Method

Chemical analysis of the adhesives were done utilizing the Perkin-Elmer 1800 Fourier Transform Infrared Spectrometer.

3.2.2 Specimen Preparation

FTIRs for all 4 adhesives were performed in the as received liquid condition as well as in the post cured condition. Analysis for the as received adhesives required only a few drops of the liquid per sample to be placed into the machine. Analysis for the post cured

adhesives required cured scrapings from the floating roller peel or single lap shear bonded panel overflow. The scrapings were then crushed into powder and placed into the infrared spectrometer.

3.3 Single Lap Shear Test

A bonded structure is considered to be in shear when it is subjected to a load acting in the plane of the adhesive. Shear stresses are produced when the adhesive layer resists the movement of the adherends in the opposite directions. The most common test performed in the analysis of adhesives is the single lap shear strength test. It is popular because the specimens are easy to fabricate, the test is economical to conduct, and many designs used in industry rely on this overlap geometry as their foundation. However, its greatest appeal and usefulness lies in its realistic simulation of the types of stresses and loads that are normally experienced by most structural metal adhesives.

The single lap shear test provides the bearing manufacturer with a quantitative value of an adhesive's strength. This test is used both to characterize the adhesive's performance (strength) and also as a quality control indicator during production.

3.3.1 Test Method

The lap-shear strengths of the adhesives were determined according to ASTM D1002-72, Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal).

3.3.2 Specimen Preparation

Surface Preparation. 2024-T3 bare finger aluminum panels were cleaned by wiping the surface with MEK until no visible residue remained. The panels were then immersed for 5 minutes in a solution of hexavalent chromium and fluoride (4 wt%) and deionized water (96 wt%), rinsed with deionized water, then phosphoric acid anodized according to ASTM Test Method D3933. The panels were then rinsed with deionized water and dried for 30 minutes at 75°C.

Bonding Procedure. Two 0.063 inch thick aluminum panels were bonded with the adhesives in between the 0.500 inch overlapping area. The panels were first coated with the appropriate adhesive and then bonded together with a random mat polyester scrim cloth in between the panels. The entire assembly was then placed in an autoclave of a laboratory platen press and cured at 350°F for 1 hour under 80 psi of nitrogen.

Test Specimen Configuration. Test specimens were obtained by cutting the bonded panels into 1 inch width specimens. The specimen configuration for a single lap shear test is shown in the figure below.

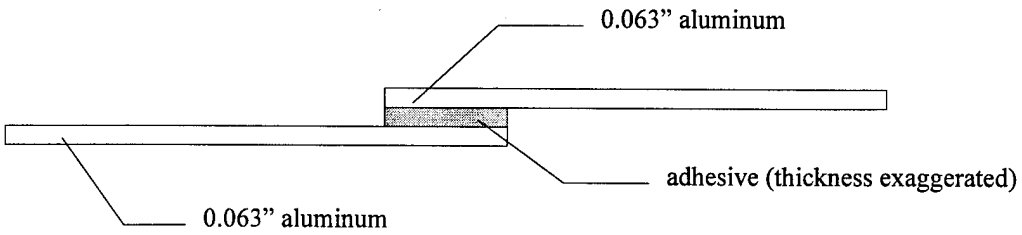


Figure 2. Cross Section of a Single Lap Shear Test Specimen

3.4 Thermomechanical Analysis (TMA)

TMA is a method of thermal analysis that can be used to measure the glass transition temperature (Tg) of an adhesive. The glass transition temperature is a basic characteristic of amorphous materials. Below this temperature the adhesive exhibits a glass-like behavior -- hard, stiff and brittle. This behavior is due to the restriction of its molecular motion. Above the Tg the adhesive is typically limp and flexible and may even exhibit a viscoelastic behavior. Viscoelasticity is a term used to describe the properties of a material that falls between those of a solid (elastic) and those of a liquid (viscous). At the Tg all properties of an amorphous material which are dependent on molecular motion will show a marked change. For most polymers, the Tg is not at one specific point, rather it typically is a range of temperature within which the material will exhibit a gradual change in its glass-like behavior. The Tg is a useful tool to determine the operating temperature range of an adhesive as well as identify and differentiate between various adhesives.

For bearing applications, the high end of the operating temperature range of a bearing is limited by its Tg. Checking the Tg of an adhesive is a quick and useful quality control tool for ensuring that the performance of the bearing remains consistent. The Tg is also an important factor in the selection of an adhesive to be used in a self-lubricating bearing system. If an alternative adhesive is to be used, the ideal choice would be one which has the Tg closest to the replaced adhesive.

The Tg of a material can be obtained through various types of thermal analyses. These

include differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) as well as thermomechanical analysis (TMA). In this study, both the DSC and the DMA were performed on the 23-900, 23-900X, 23-057 and 23-057X. However, it was an extremely frustrating process. The Tg obtained from DSCs were extremely inconsistent since the liquid resin is actually monitored by the DSC during the curing process. In addition to the chemical reactions occurring while curing, these adhesives also contained so much solvents which were trying to escape that it was difficult to pinpoint the Tg of any of these adhesives. The DSC was then abandoned for the DMA technique instead. However, good results were difficult to obtain. These adhesives were so brittle that they were not able to withstand the flexural bending deformation mode of strain produced by the DMA. Many specimens cracked in the fixture before the test was completed. As a last resort, the TMA was chosen to replace the DMA and good consistent results were finally obtained.

3.4.1 Test Method

The glass transition temperature (Tg) of each adhesive was measured using the Perkin-Elmer 7 Series Thermal Analysis System.

3.4.2 Specimen Preparation

To obtain a valid Tg from the TMA, the cured adhesive sample must be absolutely void free and totally flat with parallel surfaces. Since these four adhesives are not "pourable" in the raw state, the manufacturer supplies them to the user in solutions of solvents which must be removed prior to curing. The solvents are driven off either by room or elevated temperature vacuuming of the adhesive in a large beaker. Then the adhesive is subjected to higher temperature to drive off additional solvents. During this process the resin must be stirred to break the skin that normally forms over the surface of the adhesive, enabling the solvents to escape. Once the solvents have been driven off, the adhesive is then poured into a mold and cured at 350°F for one hour. Figures 3 to 7 depict the difficulty in obtaining solvent-free, void-free, flat and parallel surfaced TMA specimens. As demonstrated in these figures, the procedure for preparing TMA specimens is complex and unique to each adhesive and can be found in Appendix A.

Once the adhesive samples have been cured, they must be cut into approximately 0.250 inch square by 0.125 inch thick specimens. Each specimen must be polished with sand paper to eliminate surface ripples and/or bubbles formed on the surface while curing. The specimen may then be placed into the TMA and heated up to 350°C. The TMA result of each adhesive was recorded and displayed as a curve on a graph from which the Tg was derived. See Appendix B.

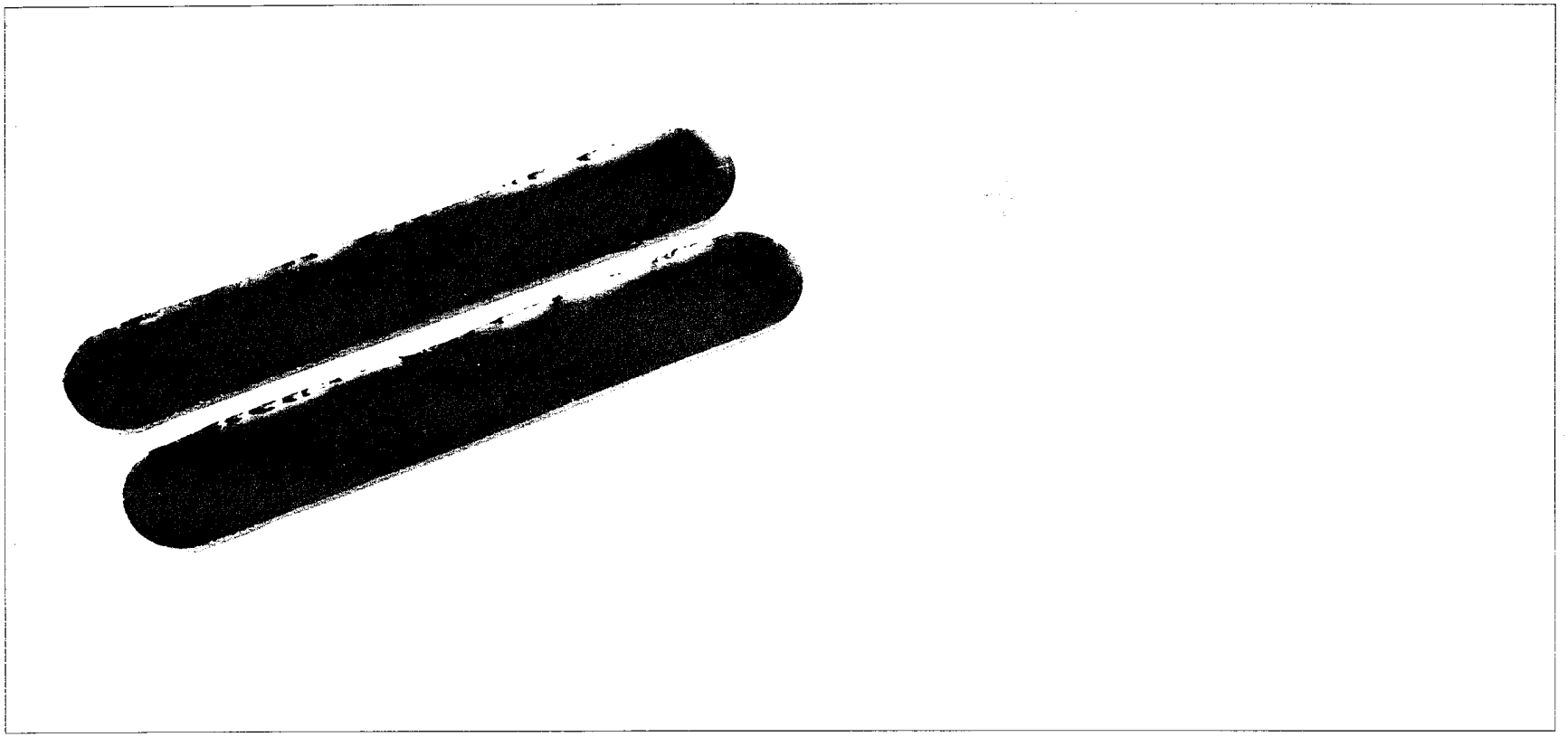


Figure 3. Cured and Uncured 23-900 TMA Specimens

The two cured 23-900 TMA specimens are on the left and the two uncured 23-900 TMA specimens are on the right. This figure depicts a good example of the typical difference between an uncured sample and a good cured sample of the plyophen adhesives. The uncured samples are lighter in color and full of solvents as indicated by the formation of numerous bubbles when heated. The cured samples are darker in color and if prepared properly, as shown here, should have very few bubbles within as well as on the surface of the specimens. The uncured samples were scrapped because the solvents were not completely driven off before the adhesive was poured into the mold.

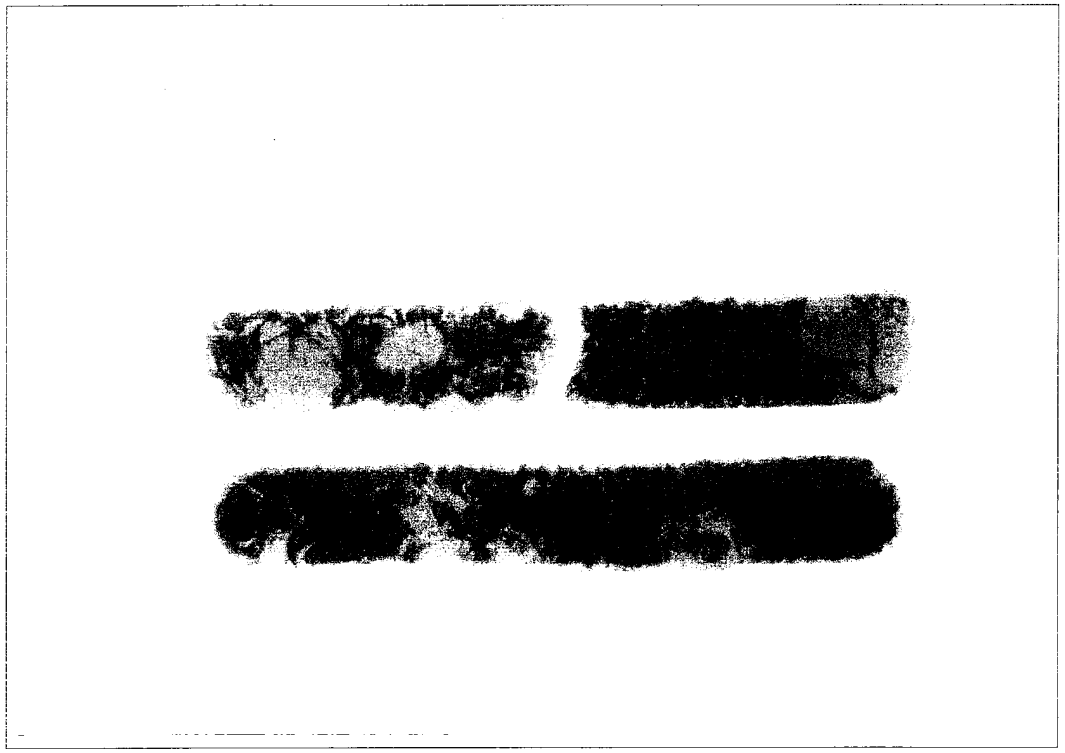


Figure 4. Cured 23-900X TMA Specimens

These two cured 23-900X TMA specimens were not usable. This particular adhesive had been subjected to the process used for driving off the solvents in the 23-900 adhesive. The 23-900X had reached the uncured state in which it seemed to be solvent-free; however, numerous bubbles were found trapped within the specimens after curing.

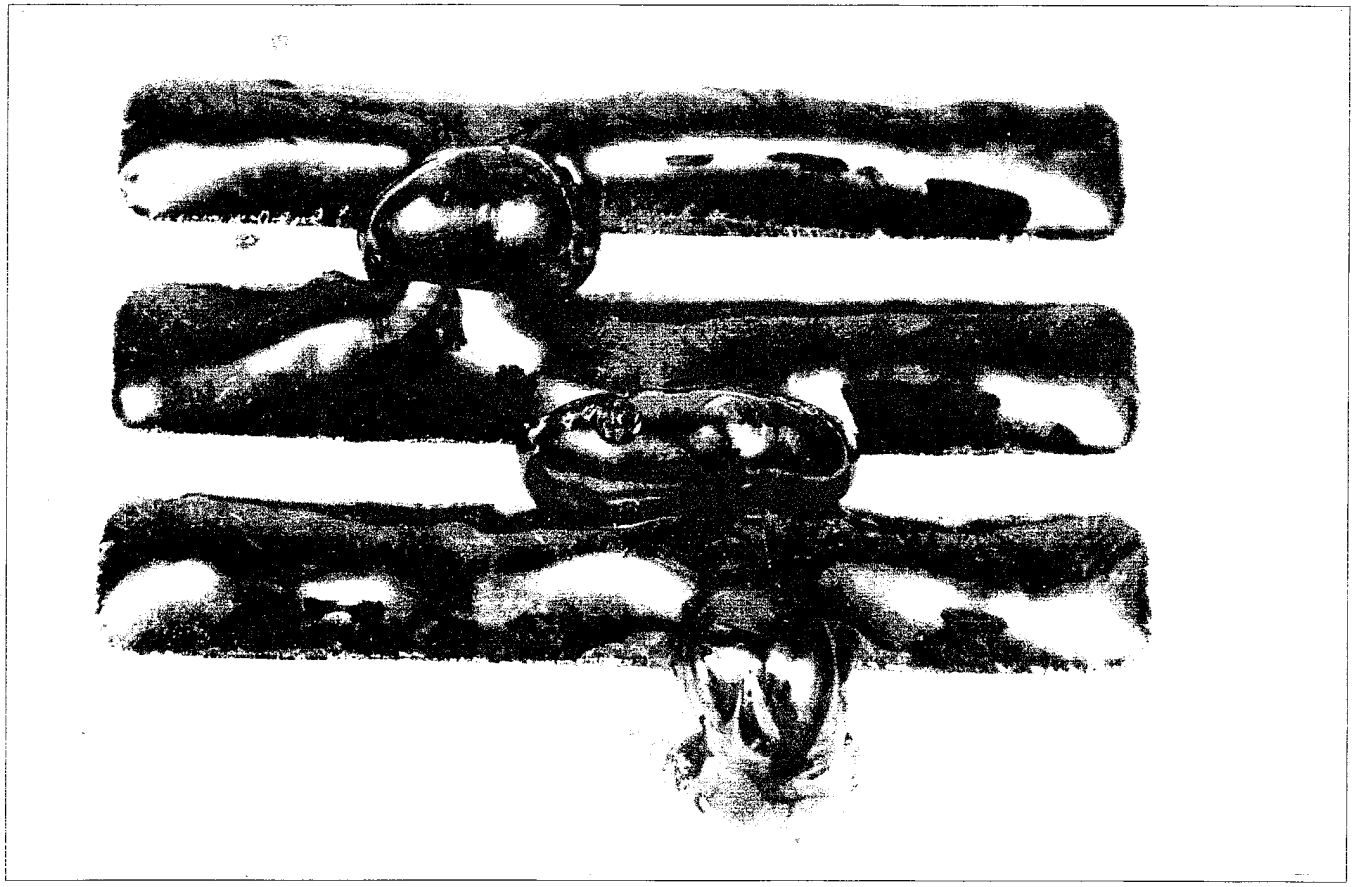


Figure 5. Cured 23-057 TMA Specimens

These cured 23-057 TMA specimens were also discarded. As with the specimens shown in Figure 4, there were so much solvents left within the adhesive that, it in this case, it actually oozed while curing.

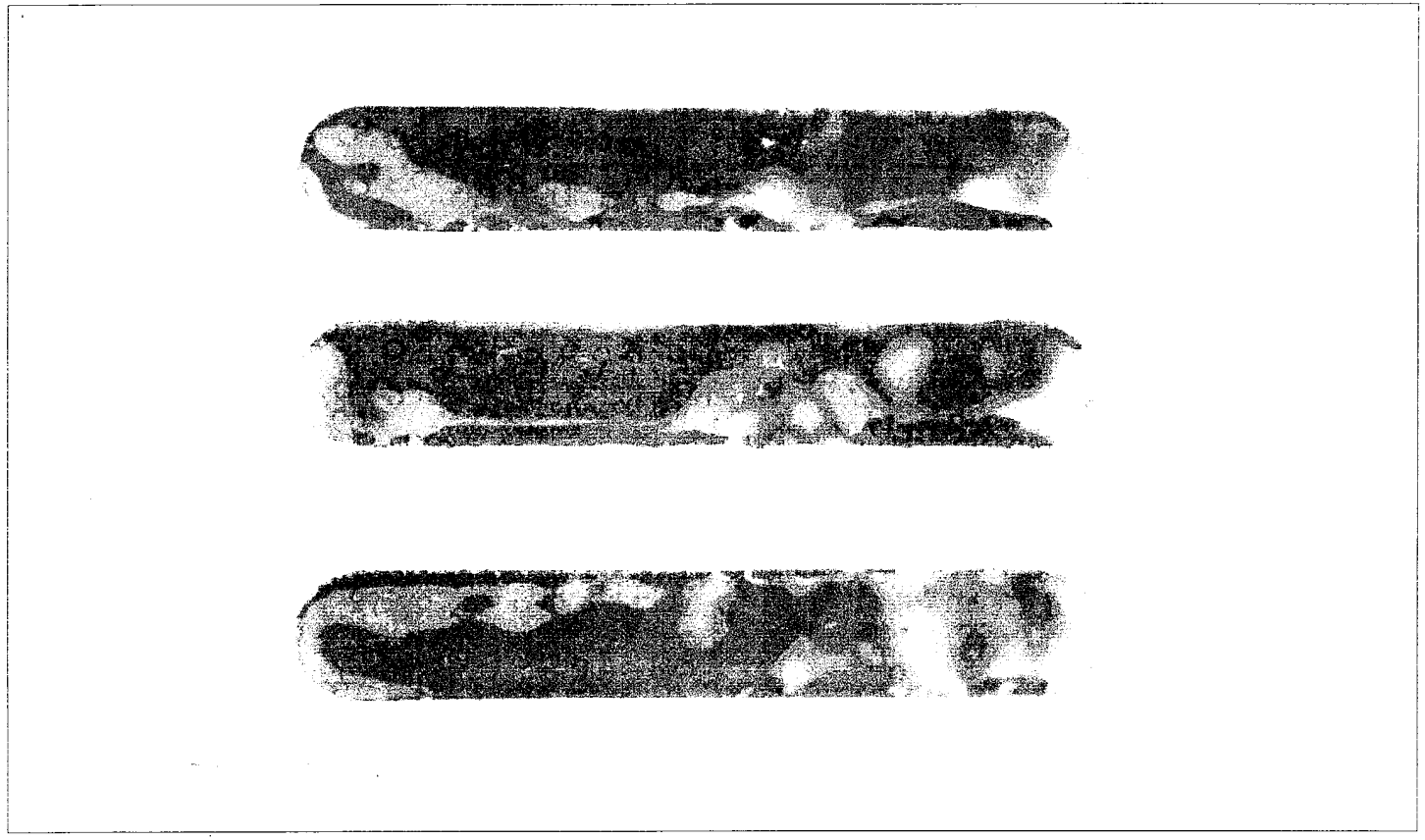


Figure 6. Cured 23-057 TMA Specimens

These cured 23-057 TMA samples are almost perfect. They were the best specimens obtained in terms of the amount of solvents left within the adhesive. Notice, however, that there are a few bubbles near the bottom surface and that the top surface is rippled. Both surfaces must be sanded to remove the bubbles and to achieve parallel planes.

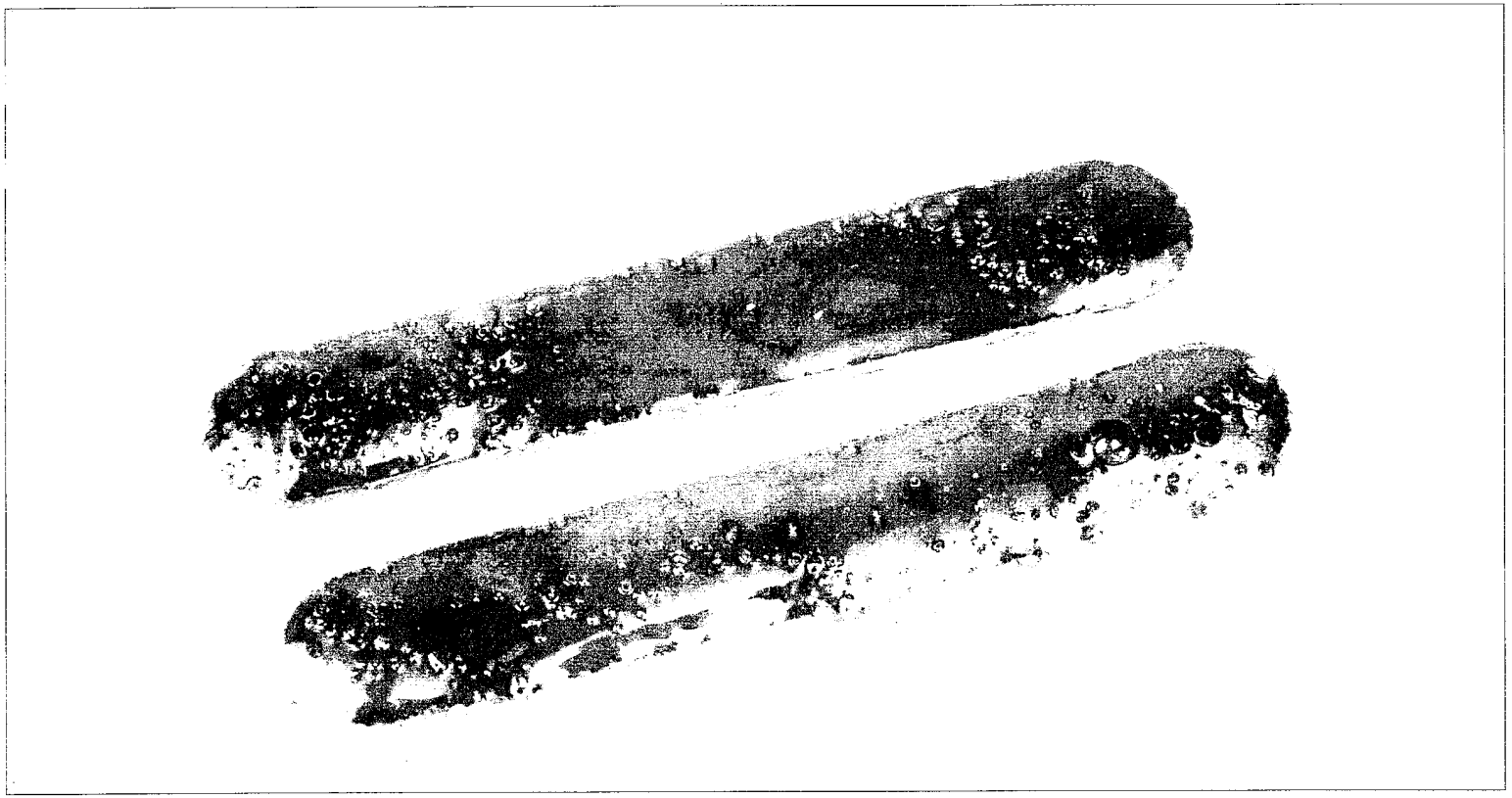


Figure 7. Cured 23-057X TMA Specimens

It may not seem so at first glance but this figure shows a usable sample of cured 23-057X TMA specimens. Even though there are many bubbles on the surface of the specimens, they can be sanded away. It is more important not to have these bubbles or voids within the specimens for TMA testing.

3.5 Viscosity

The viscosity of a liquid is its resistance to flow, caused by the internal friction of its molecular components. Viscosity is a basic property of an uncured adhesive and is a useful tool in understanding its molecular size. It is usually measured by determining how much an adhesive flows under a given load at a specific temperature. Viscosity measurement is also used to determine whether the chemical reactions during the manufacture of the adhesive are complete. For bearing application purposes, the viscosity reveals the ease at which the adhesive can be applied.

3.5.1 Test Method

The viscosities of the adhesives were measured with a Cannon Fenske Kinematic Viscometer according to ASTM D445-88, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity).

3.5.2 Specimen Preparation

Approximately 15 ml of the adhesive were poured into a capillary inside a #500 size tube. The resin was then allowed to flow under gravity and at room temperature through two marks on the tube. Measurement of time was initiated when the meniscus of the adhesive flowed through the first mark. Time was recorded when the meniscus passed through the second mark. The viscosity measurement was then calculated and includes a factor for the size of the tube used.

4.0 RESULTS

4.1 Floating Roller Peel Test

The peel strength results of all four adhesives are listed in Tables 2 and 3, including the means (μ) and the standard deviations (σ) calculated. A replicate of five specimens per each adhesive were tested.

Table 2. Floating Roller Peel Strength - Cured and Test @ 25°C

Adhesive	Results (piw)					μ	σ
23-900	1.60	1.60	1.60	1.60	1.80	1.64	0.09
23-900X	1.20	1.20	1.20	1.20	1.20	1.20	0.00
23-057	1.60	1.60	1.60	1.80	1.80	1.68	0.11
23-057X	1.80	1.60	1.40	1.80	1.80	1.68	0.18

Table 3. Floating Roller Peel Strength Tested @ 25°C
Cured, Exposed for 1 Week @ 77°C and 95-100% RH

Adhesive	Results (piw)					μ	σ
23-900	1.00	1.80	2.00	2.20	1.40	1.68	0.48
23-900X	1.60	1.60	1.20	1.40	1.60	1.48	0.18
23-057	2.00	1.60	2.00	1.40	1.60	1.72	0.27
23-057X	1.40	2.00	1.80	1.80	2.00	1.80	0.24

Even though these specimens had 100% cohesive type failures, the average peel strengths for all 4 adhesives were less than 2 lb/inch width (piw). These results are considered invalid according to ASTM D3187; they should be between 15-85% of the load cell full scale range. The full scale load used was 20 lb. which means that the results should fall between 3-17 lb. These low values indicated that the adhesive is extremely brittle and that there is a significant difference between the flexural stiffness of the 2024-T3 aluminum adherend used and the low peel resistance of the adhesives tested. If a thinner gauge aluminum adherend was used, higher values might have been observed. No statistical analysis was done on the peel strength results because they were considered invalid. However, even with the low values the results were generally consistent. The standard deviation (σ) calculated for each set of tests were all less than 1, which is extremely good. Note that the mean values (μ) of the 23-900 and the 23-900X were not as close to each other as were those of the 23-057 and the 23-057X. Since the results were so low, this test will be repeated utilizing a 0.007 inch thick flexible aluminum adherend rather than the 0.025 inch previously used.

4.2 Fourier Transform Infrared (FTIR) Spectroscopy

Figures 8 through 12 show the FTIR (chemical analysis) results of the uncured and cured adhesives we have completed so far. In the uncured state, the FTIRs of the original adhesives and their proposed alternatives are similar (Figures 8 and 9). Figure 8 displays practically identical analyses for the uncured 23-900 and 23-900X, and Figure 9 displays

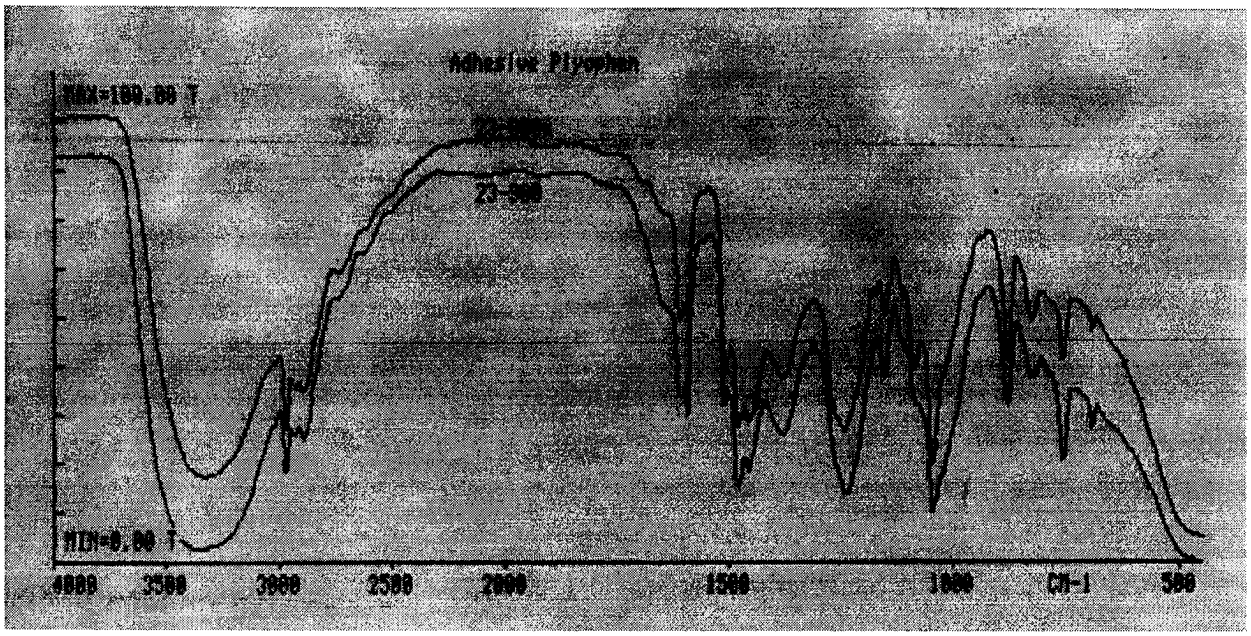


Figure 8. FTIR Analyses of Uncured 23-900 and 23-900X

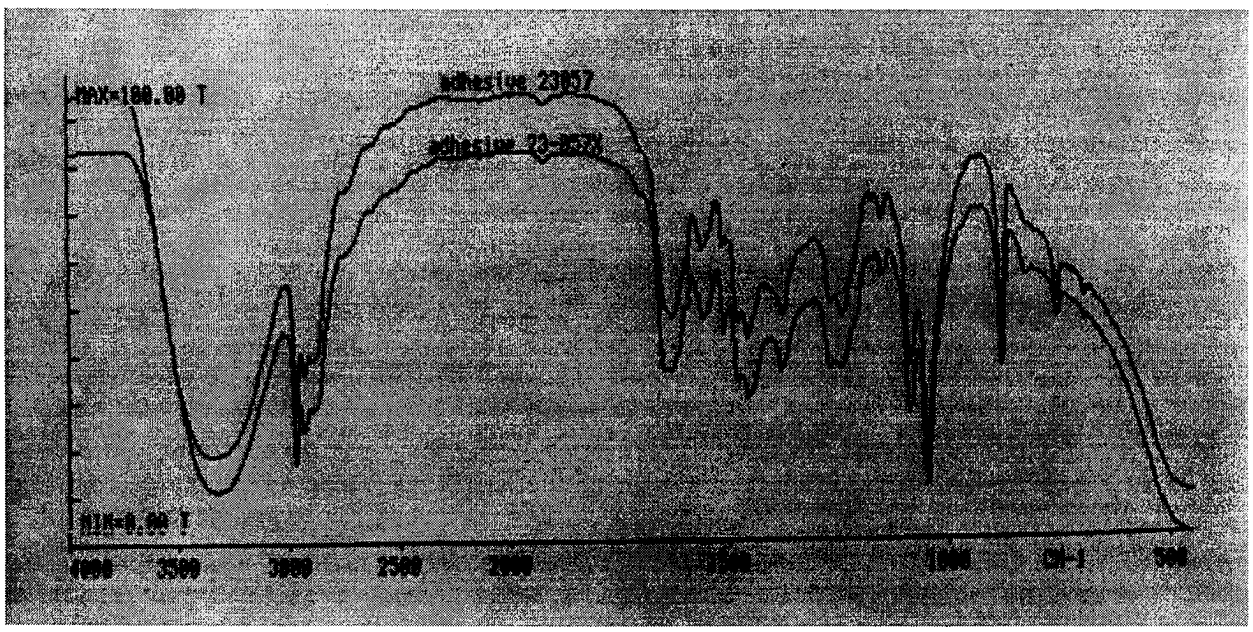


Figure 9. FTIR Analyses of Uncured 23-057 and 23-057X

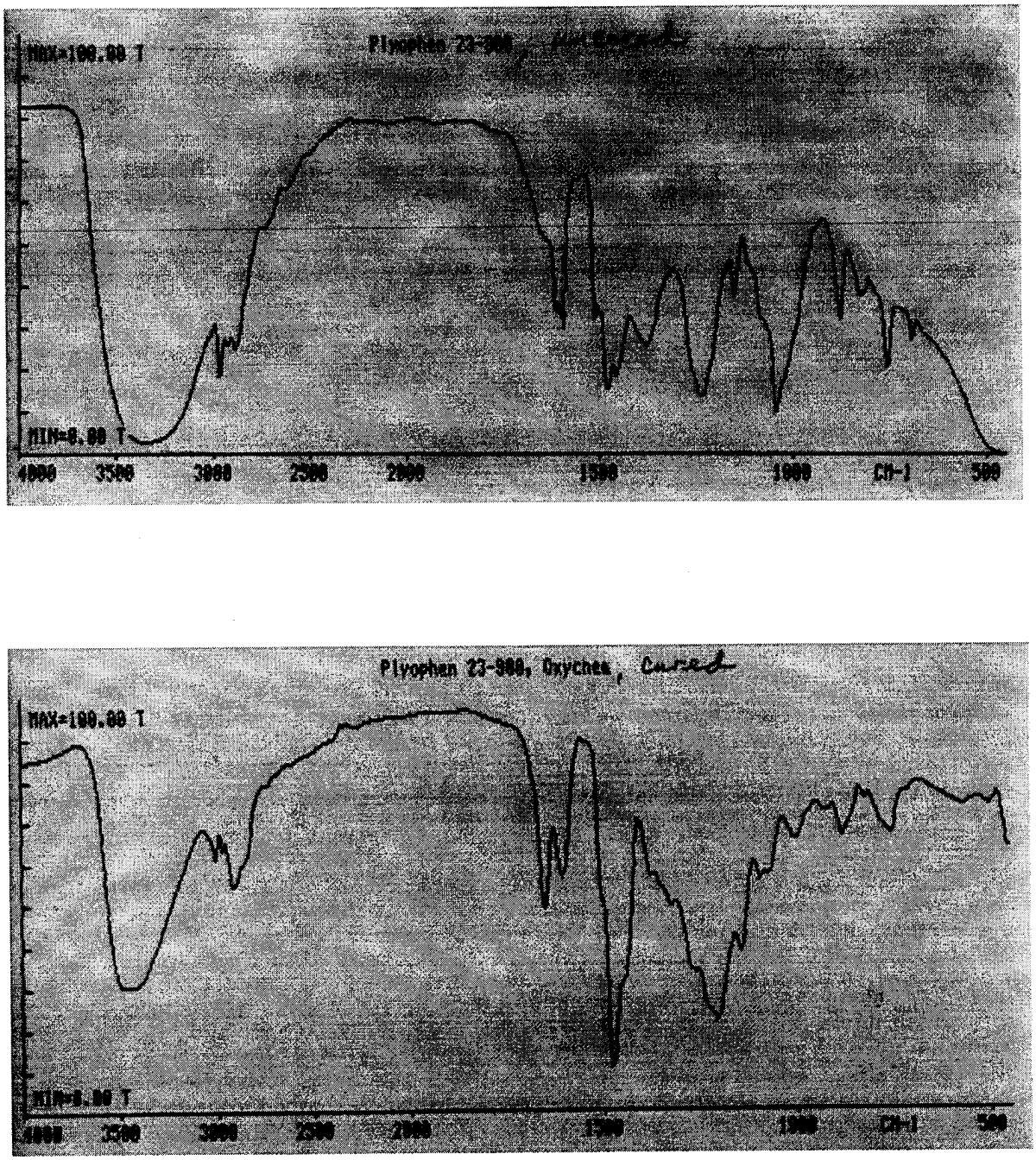
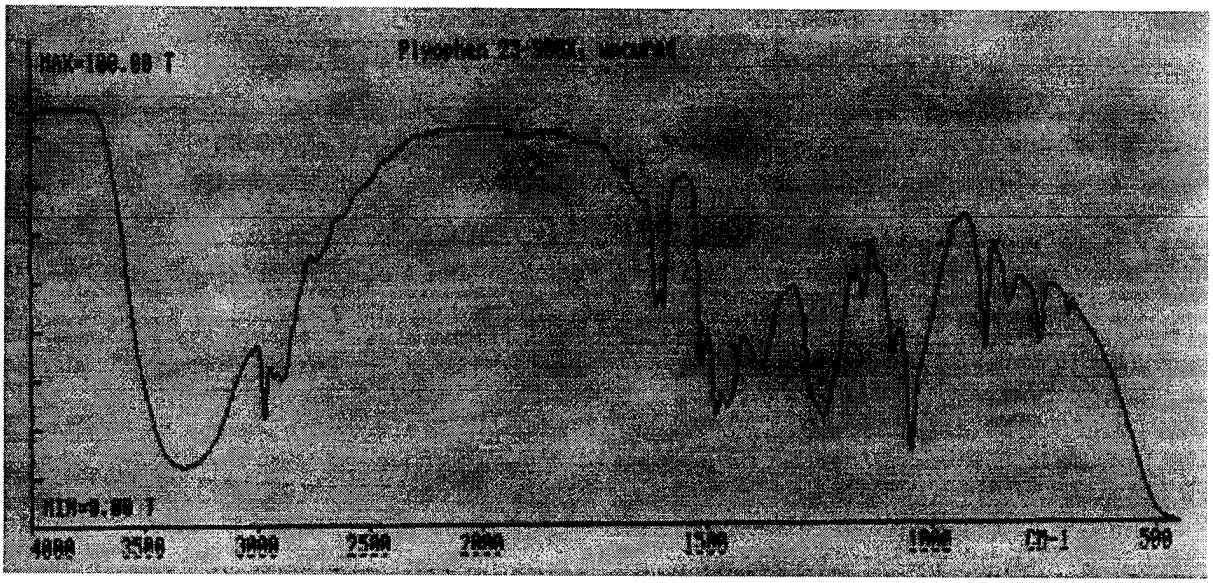


Figure 10. FTIR Analyses of Uncured and Cured 23-900



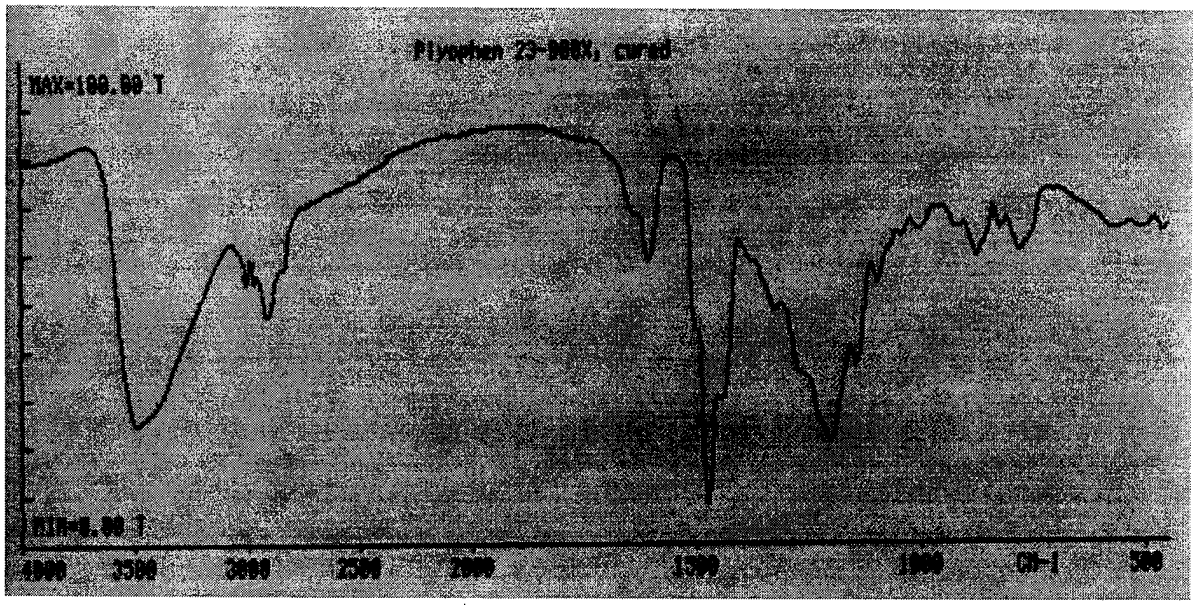


Figure 11. FTIR Analyses of Uncured and Cured 23-900X

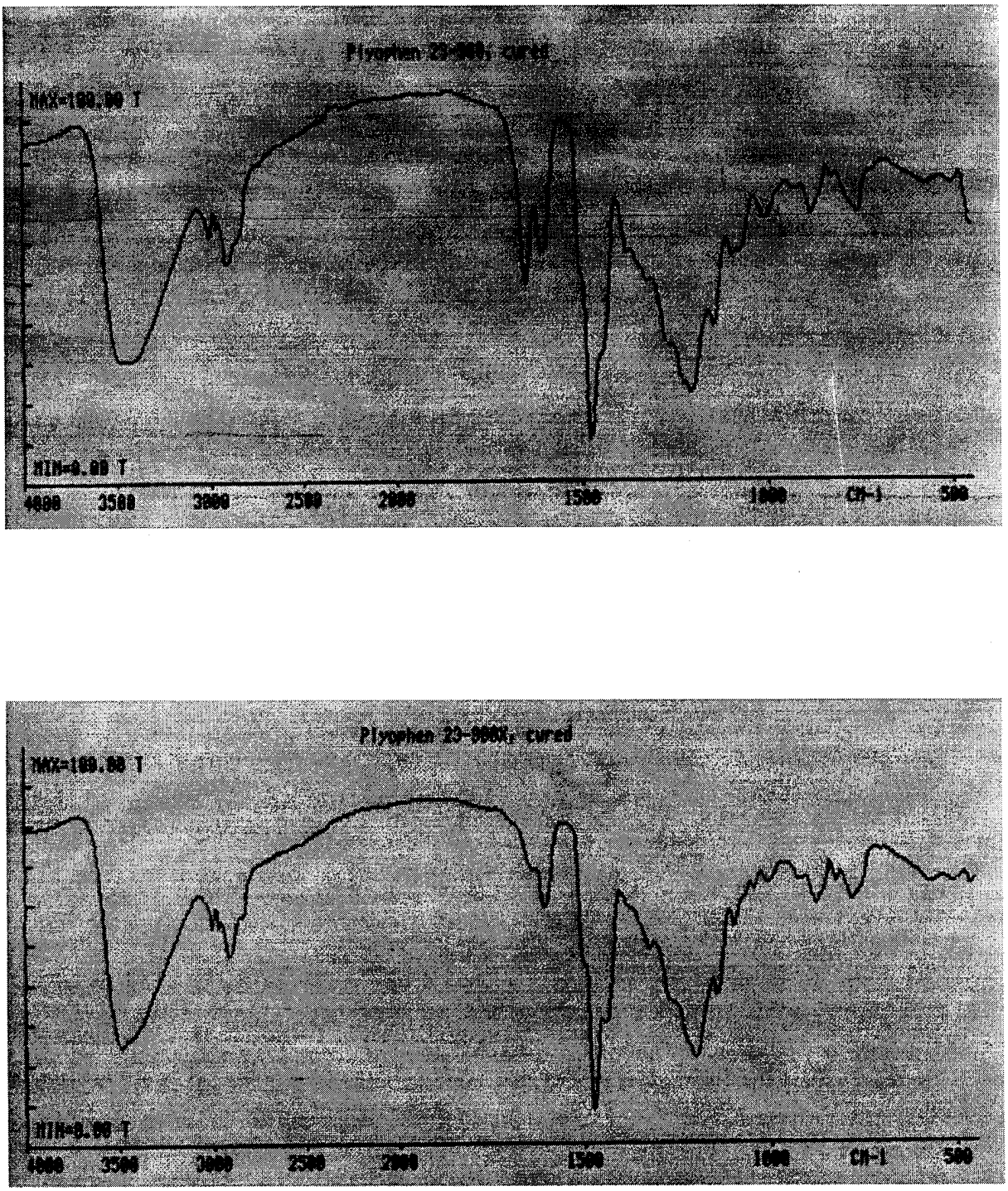


Figure 12. FTIR Analyses of Cured 23-900 and Cured 23-900X

practically identical analyses for the uncured 23-057 and 23-057X. Figures 10 and 11 depict the chemical difference between uncured and cured adhesives (23-900 and 23-900X), and one can immediately see which chemical components have been consumed during the curing process. When comparing the FTIR of cured 23-900 with cured 23-900X (see Figure 12), a significant difference is seen in the peaks at approximately 1600 cm^{-1}. Although we did not observe this difference in the FTIRs of the uncured 23-900 and 23-900X, it is seen in the cured materials. There is no explanation for this difference; however, it does raise concern as to whether the 23-900X is truly the same as the 23-900 which it is intended to replace. Even though the FTIRs for the cured 23-057 and 23-057X have not been completed, there probably will also be a difference between these adhesives in the cured state.

4.3 Single Lap Shear Test

Single lap shear test results of 23-900, 23-900X, 23-057 and 23-057X are listed in Tables 4 through 7 and the statistical analyses of these data are shown in Tables 8 through 11. The purpose of the statistical analyses was to determine if the shear strengths of the 23-900 and 23-057 adhesives are significantly different than those of the proposed alternatives, 23-900X and 23-057X. In addition, as part of the statistical analyses, outlier tests were also performed on the lap shear strength data for each adhesive. Outliers are data points which should be rejected because they were too extreme and did not fit within the normal range of all the data received for a particular adhesive tested at a specific condition.

Table 4. Single Lap Shear Strength of 23-900

Conditions	Results (psi)					μ	σ
Cured and test @ 25°C	1260	1180	1260	1120	1260	1216	64
Cured and test @ 163°C	*1220	1040	1060	980	1020	1064	92
Cured and test @ -55°C	1280	1240	1320	1320	1300	1292	33

* Suspected outlier

Table 5. Single Lap Shear Strength of 23-900X

Conditions	Results (psi)					μ	σ
Cured and test @ 25°C	900	940	900	880	980	920	40
Cured and test @ 163°C	920	900	820	920	860	884	43
Cured and test @ -55°C	860	960	980	920	960	936	48

Table 6. Single Lap Shear Strength of 23-057

Conditions	Results (psi)					μ	σ
Cured and test @ 25°C	1620	1480	1560	1420	1420	1500	88
Cured and test @ 163°C	1340	1360	1340	1340	*1000	1276	155
Cured and test @ -55°C	1560	1680	1440	1400	1520	1520	110

* Suspected outlier

Table 7. Single Lap Shear Strength of 23-057X

Conditions	Results (psi)					μ	σ
Cured and test @ 25°C	1700	1660	1760	1720	1840	1736	68
Cured and test @ 163°C	1320	1540	1520	1260	1360	1400	124
Cured and test @ -55°C	1480	1640	1720	1780	1580	1640	117

4.3.1 Statistical Analyses

Several statistical analyses were performed. The first analysis was performed at the 95% confidence level and included all the data. The second analysis also included all the data but was performed at the 90% confidence level. The third and fourth analyses were performed both at the 95% and the 90% confidence levels, respectively, but rejected the outliers.

In this study, the statistical technique used to determine whether the two adhesives being compared are significantly different from each other is the "t-Test". For each analysis, there is a range of "non-critical t" values which is used to compare with a "calculated t" value. If the "calculated t" value is beyond the range of the "non-critical t" values, then the difference between the two samples is considered significant. The range of "non-critical t" values is obtained from a "t-Distribution Table". However, the sample sizes (n_1 and n_2), the degrees of freedom (ν) and the confidence level must be determined prior to using this table. Sample sizes are the number of data points in each sample and depend on whether there are outliers and if the outliers are included or excluded in the analysis. Sample sizes are important because they are used to determine the degrees of freedom as defined in the equation below.

$$\nu = (n_1 - 1) + (n_2 - 1)$$

The sample means (μ) and standard deviations (σ) obtained from the lap shear strength data of both adhesives are used to calculate the "t" value. The standard deviations of both samples (σ_1 and σ_2) as well as the sample sizes (n_1 and n_2) are used first to calculate the "pooled variance" which is defined as follows:

$$(\sigma_p)^2 = \frac{(n_1 - 1)\cdot(\sigma_1)^2 + (n_2 - 1)\cdot(\sigma_2)^2}{n_1 + n_2 - 2}$$

The pooled variance and the means (μ_1 and μ_2) are then used to calculate the "t" value in the following equation:

$$t = \frac{\mu_1 - \mu_2}{\sqrt{(\sigma_p)^2 \cdot \left(\frac{1}{n_1} + \frac{1}{n_2}\right)}}$$

4.3.1.1 Example of Statistical Analysis

An example of determining whether results of the 23-900 single lap shear specimens tested at 163°C is significantly different than those of the 23-900X is demonstrated below.

Adhesive 23-900 is sample 1; adhesive 23-900X is sample 2. Each has a sample size of 5; therefore, $n_1 = 5$ and $n_2 = 5$. Both n_1 and n_2 are used to determine the degrees of freedom in the following equation:

$$\nu = (n_1 - 1) + (n_2 - 1) = (5 - 1) + (5 - 1) = 8$$

In the t-Distribution Table (see Appendix C), the range of the "non-critical t" value for 8 degrees of freedom and 90% confidence level is $-2.306 < t < 2.306$. At the 95% confidence level, the range of the "non-critical t" value is $-1.860 < t < 1.860$. The next step is to calculate the "t" value and determine whether it is within the non-critical ranges of the 90% and 95% confidence levels.

The pooled variance is calculated first.

$$(\sigma_p)^2 = \frac{(n_1 - 1)\cdot(\sigma_1)^2 + (n_2 - 1)\cdot(\sigma_2)^2}{n_1 + n_2 - 2} = \frac{(5 - 1)\cdot(92)^2 + (5 - 1)\cdot(43)^2}{5 + 5 - 2} = 5156.50$$

The pooled variance is then used to calculate the "t" value in the equation below.

$$t = \frac{\mu_1 - \mu_2}{\sqrt{(\sigma_p)^2\cdot\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}} = \frac{1064 - 884}{\sqrt{5165.50\left(\frac{1}{5} + \frac{1}{5}\right)}} = 3.954$$

When the "calculated t" value of 3.954 is compared with the ranges of "non-critical t" values obtained for both 90% and 95% confidence levels, it is obviously outside both ranges. This means that results of the 23-900 and the 23-900X single lap shear specimens tested at 163°C are significantly different from each other, hence the "yes" in Table 8.

4.3.1.2 Example of Statistical Analysis Excluding Outliers

The same technique applies when outliers are excluded. Table 4 lists the 23-900 results of specimens tested at 163°C. The 1220 psi is a suspect outlier and if it is rejected in this analysis, the mean (μ_1) now changes from 1064 psi to 1025 psi, and the standard deviation (σ_1) changes to 34 instead of 92. Furthermore, the degrees of freedom would now be 7 rather than 8 as demonstrated below.

$$\nu = (n_1 - 1) + (n_2 - 1) = (4 - 1) + (5 - 1) = 7$$

In the t-Distribution Table (Appendix C), the range of "non-critical t" values for 7 degrees of freedom at 95% confidence level is $-2.365 < t < 2.365$ and at 90% confidence level is $-1.895 < t < 1.895$.

Excluding the outlier (1220 psi) also changes the calculation of the pooled variance as follows:

$$(\sigma_p)^2 = \frac{(n_1 - 1)\cdot(\sigma_1)^2 + (n_2 - 1)\cdot(\sigma_2)^2}{n_1 + n_2 - 2} = \frac{(4 - 1)\cdot(34)^2 + (5 - 1)\cdot(43)^2}{4 + 5 - 2} = 1552.00$$

This new pooled variance is now used to calculate the "t" value.

$$t = \frac{\mu_1 - \mu_2}{\sqrt{(\sigma_p)^2\cdot\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}} = \frac{1025 - 884}{\sqrt{1552\left(\frac{1}{4} + \frac{1}{5}\right)}} = 5.298$$

When the "calculated t" value of 5.298 is compared with the range of "non-critical t" values for both the 90% and 95%, it is still outside of both ranges. This means that the results of both adhesives are significantly different from each other when tested at 163°C whether the outlier, 1220 psi, is included or excluded in the analyses.

4.3.1.3 Summary of Statistical Analyses

Based on these factors, the "yes" in Tables 8 through 11 means that the adhesives are

significantly different at that confidence level and the "no" means that the difference is not significant. If an outlier is rejected, one of the "factors" has changed, which in turn affects the range of the "non-critical t" values as well as the "calculated t" value (see Tables 9 and 11).

Table 8. Shear Strength t-Test Results for 23-900 and 23-900X: Including Outliers

	23-900	23-900X	t	90%	95%
μ @ 25°C	1216	920	8.782	yes	yes
μ @ 163°C	1064	884	3.954	yes	yes
μ @ -55°C	1292	936	13.652	yes	yes

At 90% confidence level, the non-critical range for t: $-2.306 < t < 2.306$
At 95% confidence level, the non-critical range for t: $-1.860 < t < 1.860$

Table 9. Shear Strength t-Test Results for 23-900 and 23-900X: Excluding Outliers

	23-900	23-900X	t	90%	95%
μ @ 25°C	1216	920	8.782	yes	yes
μ @ 163°C	1025	884	5.298	*yes	*yes
μ @ -55°C	1292	936	13.652	yes	yes

At 90% confidence level, the non-critical range for t: $-2.306 < t < 2.306$
At 95% confidence level, the non-critical range for t: $-1.860 < t < 1.860$

*Outliers were rejected - At 90% confidence level, the non-critical range for t: $-2.365 < t < 2.365$
*Outliers were rejected - At 95% confidence level, the non-critical range for t: $-1.895 < t < 1.895$

Table 10. Shear Strength t-Test Results for 23-057 and 23-057X: Including Outliers

	23-057	23-057X	t	90%	95%
μ @ 25°C	1500	1736	-4.724	yes	yes
μ @ 163°C	1276	1400	-1.399	no	no
μ @ -55°C	1520	1640	-1.671	no	no

At 90% confidence level, the non-critical range for t: $-2.306 < t < 2.306$
At 95% confidence level, the non-critical range for t: $-1.860 < t < 1.860$

Table 11. Shear Strength t-Test Results for 23-057 and 23-057X: Excluding Outliers

	23-057	23-057X	t	90%	95%
μ @ 25°C	1500	1736	-4.724	yes	yes
μ @ 163°C	1345	1400	-0.987	*no	*no
μ @ -55°C	1520	1640	-1.671	no	no

At 90% confidence level, the non-critical range for t: $-2.306 < t < 2.306$
At 95% confidence level, the non-critical range for t: $-1.860 < t < 1.860$

*Outliers were rejected - At 90% confidence level, the non-critical range for t: $-2.365 < t < 2.365$
*Outliers were rejected - At 95% confidence level, the non-critical range for t: $-1.895 < t < 1.895$

In all four analyses the results were consistent, including and excluding outliers. The statistical analyses indicated that there is a significant difference between the 23-900 and 23-900X adhesives for all test conditions. As for 23-057 and 23-057X adhesives, the only significant difference detected was with specimens tested at room temperature.

4.4 Thermomechanical Analysis

TMA results of the four adhesives are listed in Table 12. The actual graph output from the TMAs are shown in Appendices F through R. Due to the difficulty in producing void-free samples and because it was essential to have flat parallel surfaces to obtain consistent results, 5 TMAs on the 23-900X adhesives had to be done before reproducible results were obtained. The shaded areas in Table 12 showed the two Tg's that are closest within normal fluctuation range of that particular adhesive. Note that it was more difficult to exactly pinpoint the Tg's of the proposed alternative adhesives, 23-900X and 23-057X.

Table 12. TMA Results - Tg in °C

23-900	23-900X	23-057	23-057X
178	200	167	209
179	214	153	204
179	220	153	
	229		
	233		

4.5 Viscosity

Table 13 shows the viscosity measurements in centipoise (cps) for all four adhesives. These results were measured at room temperature. Note that the original adhesives were a lot less viscous than the proposed alternatives which means that they definitely are not the same and that the proposed alternatives may be more difficult to handle in subsequent processing. This accounted for the numerous problems encountered in trying to prepare specimens for thermal analyses (TMA & DMA). The resins do not flow easily when most of the solvents are gone so it was not easy to pour them into the mold. They must be constantly heated to keep them flowing. Furthermore, when the resins are exposed to air, a skin is formed on the surface which traps the solvents from escaping. The resins must be constantly stirred while they are being heated for thermal analysis specimen preparation.

Table 13. Room Temperature Viscosity Measurements - cps

23-900	23-900X	23-057	23-057X
231.6	860.0	1470.7	2447.0

5.0 CONCLUSIONS

5.1 Plyophen 23-900 and 23-900X

Results indicate that there is a definite difference between the 23-900 and the 23-900X adhesives. We can see it clearly in the following test results:

In the **FTIRs**, which are chemical analyses of the cured samples (Figure 12), at approximately 1600 cm^{-1} along the horizontal axis, there is a peak in the curve of the 23-900 that is not in the 23-900X. Other results also supported this difference. These include a drastic difference between the **viscosity** of the 23-900 and the viscosity of the 23-900X, which was four times greater. The **TMA** results also showed that Tg of the 23-900X was approximately 50°C higher than the Tg of the 23-900. Statistical analyses of **single lap shear** tests also concur that there is a significant difference between the 23-900 and the 23-900X for all test conditions. Overall raw data showed that the single lap shear strength of the 23-900 is higher than 23-900X. Even though **floating roller peel** test results were too low to be considered valid, the raw data were consistent enough that we can see that the peel strength of the 23-900X were lower than those of the 23-900. Whether this is considered a significant difference or not, we will not know until we repeat this test.

5.2 Plyophen 23-057 and 23-057X

Overall, results seem to indicate that there is a definite difference between the 23-057 and the 23-057X adhesives. The following discussions support this conclusion:

Again, results of the **TMA** show that there is approximately a 50°C difference between the Tg of the 23-057 and the Tg of the 23-057X. The alternative adhesive, 23-057X, has a higher Tg. Results of the **viscosity** measurements show that the viscosity of the 23-057X is approximately twice that of the 23-057. The statistical analyses of the room temperature **single lap shear** test results also show a significant difference between the two adhesives. Yet, the difference is not considered significant when tested at elevated and at low temperatures, 163°C and -55°C respectively. Overall raw data indicate that the **floating roller peel strength** of the 23-057X is higher than 23-057. Although the test will be repeated, raw data of the floating roller peel test also indicated that the 23-057X is slightly higher than the 23-057. The **FTIRs** for the cured adhesives have not been completed so we cannot conclude that they are chemically different at this point even though we suspect that they will be due to the differences found in the Tg's and in the viscosity measurements.

5.3 Determination of the Tg

Although the Tg can be obtained through various types of thermal analyses, the preferred method for the 23-900, 23-900X, 23-057 and 23-057X adhesives is the TMA. In the liquid form, these adhesives are full of solvent which resulted in inconsistent DSC measurements. In the cured state, the adhesives were too brittle to withstand the mechanical stress produced by the DMA.

5.4 Modified Floating Roller Peel Test Method

The peel resistance of the adhesives were determined according to ASTM Test Method D3167-76, Floating Roller Peel Resistance of Adhesives. The thickness of the thin gauge adherend used in this method is 0.025 inch which is too thick for testing a brittle adhesive. There is a significant difference between the flexural stiffness of the adherend and the adhesives which resulted in low values for peel strength. These values are considered invalid by ASTM Test Method D3167-76; the results should be between 15% to 85% of the load cell full scale range. The full scale load was 20 lb. which means that the results should fall between 3-17 lb. The results obtained were all $\leq$ 2.00 piw which means that we should be using a thinner gauge adherend in order to reduce the difference between the flexural stiffness of the adherend and the adhesives.

6.0 RECOMMENDATIONS

The test program implemented in this study is the first time that we have tried to evaluate the properties of the Plyophen 23-900, 23-900X, 23-057 and 23-057X. We had expected that there will be modifications to the methods we intended to use. Each material is different and test methods and sometimes even specimen preparations needed to be developed and or adapted for each specific test. We have discovered that there are changes and or modifications that should be made and suggest that the following procedures should be used:

6.1 Determining the Tg

- The preferred method for determining the Tg of these adhesives is the TMA.
- The specimen preparation procedures for the TMA of these adhesives should follow Appendix A.
- Prior to placing specimens into the test fixture of the TMA, the each specimen should be sanded to eliminate surface bubbles and ripples and to ensure totally flat parallel planes.

6.2 Floating Roller Peel Test

When utilizing ASTM Test Method D3167-76 for determining the peel strength of these adhesives, the thinner gauge aluminum adherend used should be 0.007 inch thick 2024-T3 aluminum rather than 0.025 inch.

6.3 Test Program

Now that the specifics for each test have been developed, the test program should be completed for the additional conditionings as outlined in the test matrix.

6.4 Batch Variations

With all the testing that has been done and the additional conditionings that still need to be evaluated, there has only been one batch per adhesive tested. Although results so far are rather conclusive that there is a difference between the original adhesives and the proposed alternatives, we would feel even more confident had we tested for batch variations. Since the specifics for each test have been developed, we recommend that the next step is to repeat the same test matrix but with different batches of adhesives. It would better define the difference between the original adhesives and the proposed alternatives. We may find that although there are differences, they may or may not be as significant as the results obtained in this study.

REFERENCES

1. DePiero, William S. and Brescia, Joseph A., "Evaluation of Adhesives for Use in Self-Lubricating Bearings," Technical Report ARAED-TR-95010, August 1995.

2. Hartshorn, S.R., Structural Adhesives-Chemistry and Technology, Plenum Press, 1986.

3. Cagle, Charles V., Handbook of Adhesive Bonding, McGraw-Hill, 1973.

4. Wendlandt, Wesley W., Thermal Methods of Analysis, John Wiley & Sons, Inc., 1974.

5. ASTM D1002-72, Standard Test Method for Strength Properties of Adhesives in Shear by Tension Loading (Metal-to-Metal).

6. ASTM D3167-76, Standard Test Method for Floating Roller Peel Resistance of Adhesives.

7. ASTM D445-88, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity).

8. Crow, Edwin L., Davis, Frances A., and Maxfield, Margaret W., Statistics Manual, Dover Publications, 1960.

9. Smith, G. Milton, A Simplified Guide to Statistics, Holt, Rinehart and Winston, Inc., 1970.

APPENDIX A

TMA TEST SPECIMEN PREPARATION PROCEDURES

TMA Test Specimen Preparation of Plyophen 23-900 Adhesive

1. Pour approximately 50 ml of the adhesive into a 600 ml plastic beaker.

2. Place the beaker into a vacuum oven with a Teflon sheet or any nonstick surface underneath the beaker in case the contents overflow.

3. The exhaust of the vacuum oven should be vented through a trap and the trap should be placed under a fume hood.

4. Pull a room temperature vacuum of 28-30 inches of Hg on the adhesive for 1 hr to remove the solvents.

5. Remove the beaker and place it in a circulating oven which was preheated at approximately 90°C.

6. Every 3-5 minutes, stir the adhesive to break the film on its surface enabling any solvents which did not escape during the room temperature vacuum to come to the surface and escape.

7. Remove the beaker from the oven when no more bubbles break to the surface after stirring.

8. Clean a release mold (usually made of Teflon) which contains recesses for samples approximately 3" long by 1/2" wide by 1/8" thick.

9. Slowly pour the adhesive into the mold so that no bubbles are formed.

10. After the mold has been filled, use a sharp metal point to break any bubbles formed either on the surface or within the adhesive.

11. Place the mold for a few minutes into the oven which was preheated at 90°C to make sure that the mold is completely filled.

12. Place the mold into the autoclave of a benchtop platen press and cure at 350°F, under 80-100 psi of nitrogen for 1 hour.

TMA Test Specimen Preparation of Plyophen 23-900X Adhesive

1. Pour approximately 50 ml of the adhesive into a 600 ml plastic beaker.
2. Place the beaker into a vacuum oven with a Teflon sheet or any nonstick surface underneath the beaker in case the contents overflow.
3. The exhaust of the vacuum oven should be vented through a trap and the trap should be placed under a fume hood.
4. Pull a room temperature vacuum of 28-30 inches of Hg on the adhesive until the adhesive has almost stopped bubbling from solvents "boil-off".
5. Remove the beaker from the vacuum oven; the adhesive is dry at this point.
6. Place a sheet of porous material over the beaker to keep dust out and leave standing at normal room temperature and humidity for 3 days.
7. Place the beaker in a circulating oven which was preheated at approximately 90°C.
8. After 1 minute, stir the adhesive to break the film on its surface enabling any solvents which did not escape during the room temperature vacuum to come to the surface and escape. Continue stirring the adhesive every 2-3 minutes.
9. Remove the beaker from the oven when no more bubbles break to the surface after stirring.
10. Clean a release mold (usually made of Teflon) which contains recesses for samples approximately 3" long by 1/2" wide by 1/8" thick.
11. Slowly pour the adhesive into the mold so that no bubbles are formed.
12. If the adhesive becomes hard to pour, place the beaker back into the oven to soften it. Repeat this step until the recesses are filled.
13. After the mold has been filled, use a sharp metal point to break any bubbles formed either on the surface or within the adhesive.
14. Place the mold for a few minutes into the oven which was preheated at 90°C to make sure that the mold is completely filled.
15. Place the mold into the autoclave of a benchtop platen press and cure at 350°F, under 80-100 psi of nitrogen for 1 hour.

TMA Test Specimen Preparation of Plyophen 23-057 Adhesive

1. Pour approximately 50 ml of the adhesive into a 600 ml plastic beaker.

2. Place the beaker into a vacuum oven with a Teflon sheet or any nonstick surface underneath the beaker in case the contents overflow.

3. The exhaust of the vacuum oven should be vented through a trap and the trap should be placed under a fume hood.

4. Pull a room temperature vacuum of 28-30 inches of Hg on the adhesive for 2-3 hr to remove the solvents.

5. Remove the beaker and place it in a circulating oven which was preheated at approximately 90°C.

6. Every 3-5 minutes, stir the adhesive to break the film on the surface of the adhesive enabling any solvents which did not escape during the room temperature vacuum to come to the surface and escape.

7. Remove the beaker from the oven when no more bubbles break to the surface after stirring.

8. Clean a release mold (usually made of Teflon) which contains recesses for samples approximately 3" long by 1/2" wide by 1/8" thick.

9. Slowly pour the adhesive into the mold so that no bubbles are formed.

10. After the mold has been filled, use a sharp metal point to break any bubbles formed either on the surface or within the adhesive.

11. Place the mold for a few minutes into the oven which was preheated at 90°C to make sure that the mold is completely filled.

12. Place the mold into the autoclave of a benchtop platen press and cure at 350°F, under 80-100 psi of nitrogen for 1 hour.

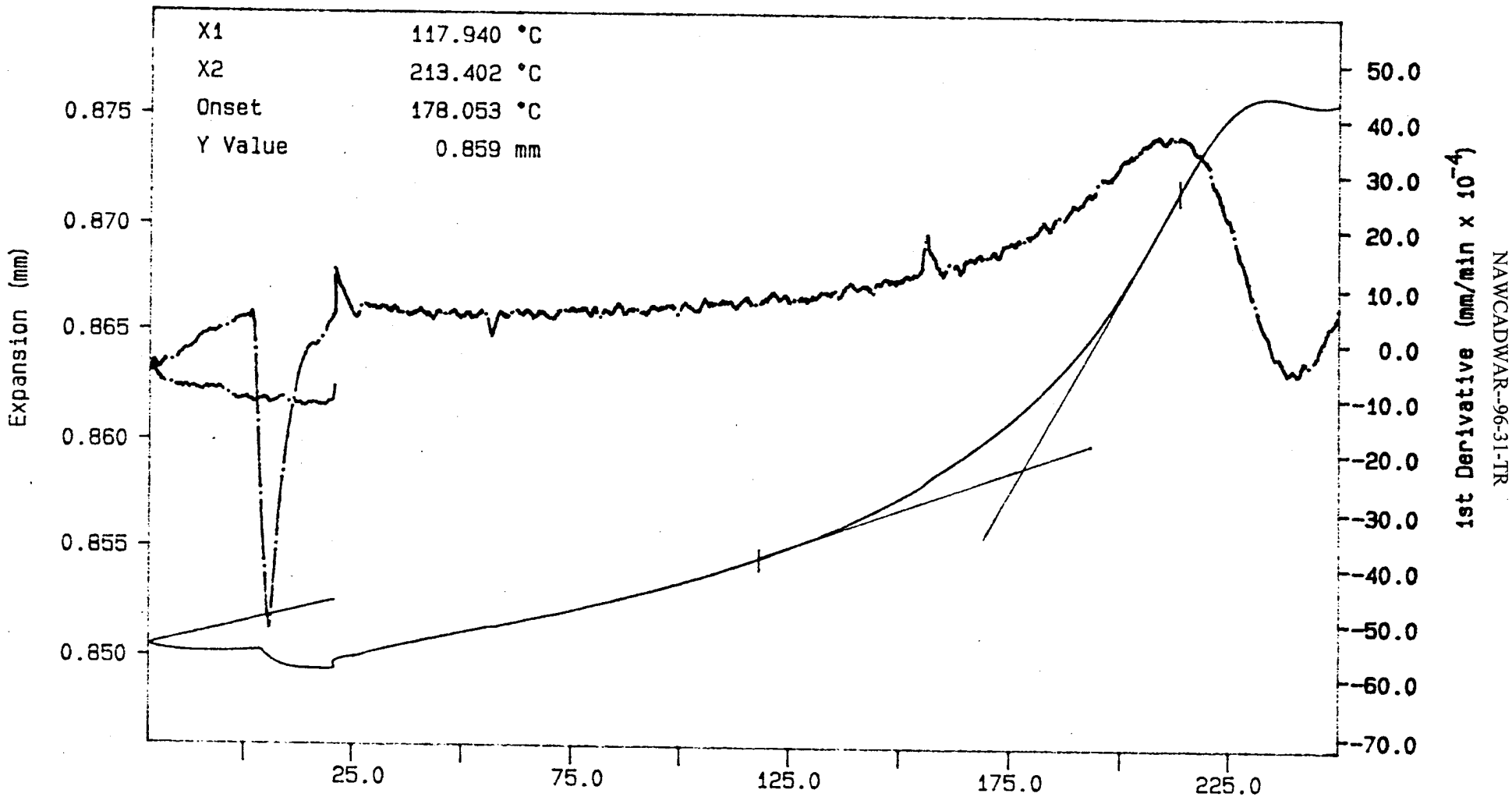
TMA Test Specimen Preparation of Plyophen 23-057X Adhesive

1. Pour approximately 50 ml of the adhesive into a 600 ml plastic beaker.
2. Place the beaker into a vacuum oven with a Teflon sheet or any nonstick surface underneath the beaker in case the contents overflow.
3. The exhaust of the vacuum oven should be vented through a trap and the trap should be placed under a fume hood.
4. Pull a vacuum of 28-30 inches of Hg at 80°C on the adhesive until the adhesive has stopped bubbling from solvents "boil-off".
5. Remove the beaker from the vacuum oven; the adhesive is very dry at this point.
6. Place a sheet of porous material over the beaker to keep dust out and leave standing at normal room temperature and humidity for 7 days.
7. Place the beaker in a circulating oven which was preheated at approximately 90°C.
8. After 1 minute, stir the adhesive to break the film on its surface enabling any solvents which did not escape during the room temperature vacuum to come to the surface and escape. Continue stirring the adhesive every 2-3 minutes.
9. Remove the beaker from the oven when no more bubbles break to the surface after stirring.
10. Clean a release mold (usually made of Teflon) which contains recesses for samples approximately 3" long by 1/2" wide by 1/8" thick.
11. Slowly pour the adhesive into the mold so that no bubbles are formed.
12. When the adhesive becomes hard to pour, place the beaker back into the oven to soften it. Repeat this step until the recesses are filled.
13. After the mold has been filled, use a sharp metal point to break any bubbles formed either on the surface or within the adhesive.
14. Place the mold for a few minutes into the oven which was preheated at 90°C to make sure that the mold is completely filled.
15. Place the mold into the autoclave of a benchtop platen press and cure at 350°F, under 80-100 psi of nitrogen for 1 hour.

APPENDIX B

TMA EXPANSION CURVES

Curve 1: TMA in Expansion
File info: PLY000 Tue May 2 14:58:35 1995
Sample Height: 0.844 mm
C23-900

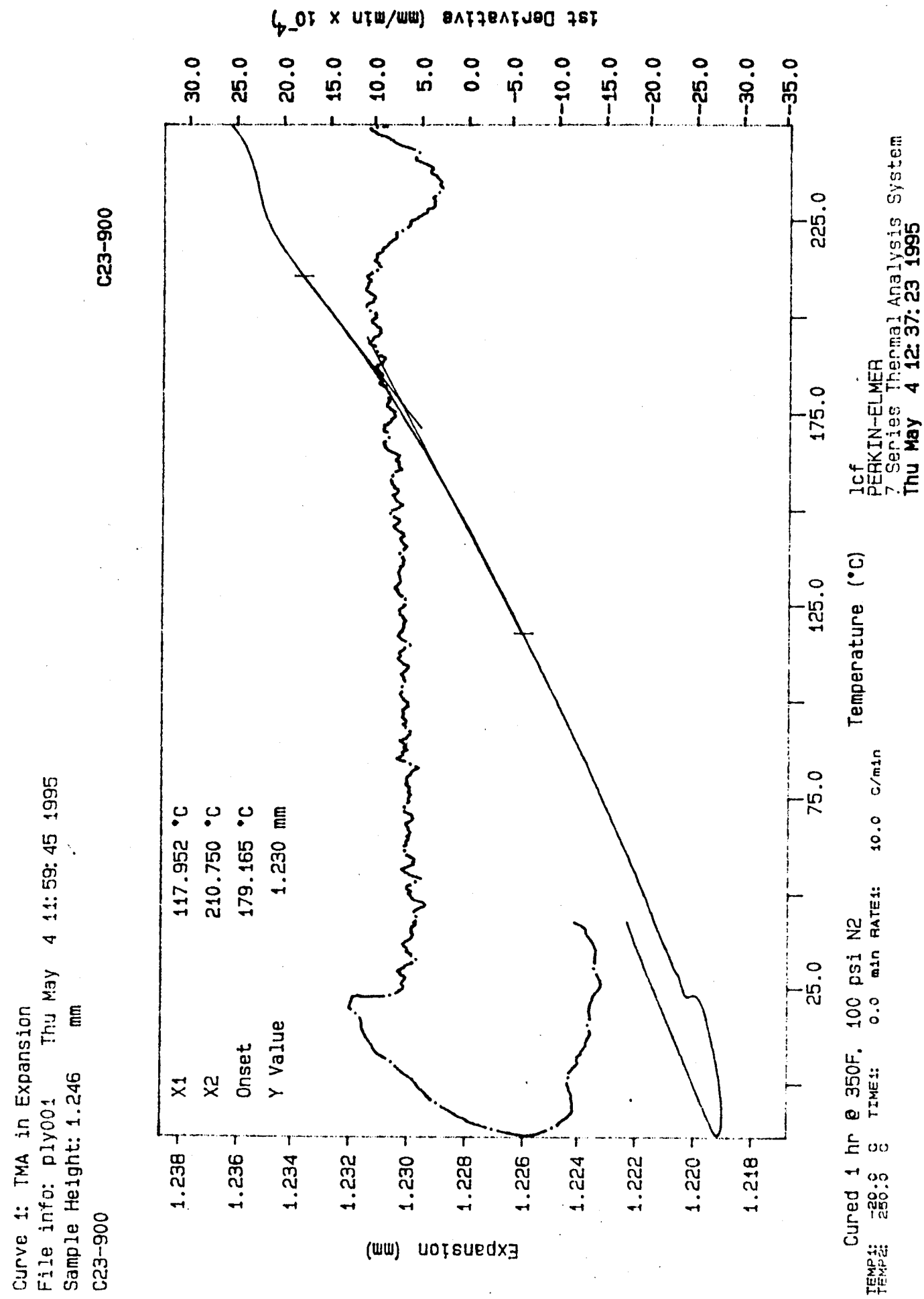


Cured 1 hr @ 350F, 100 psi N2
TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 250.0 C

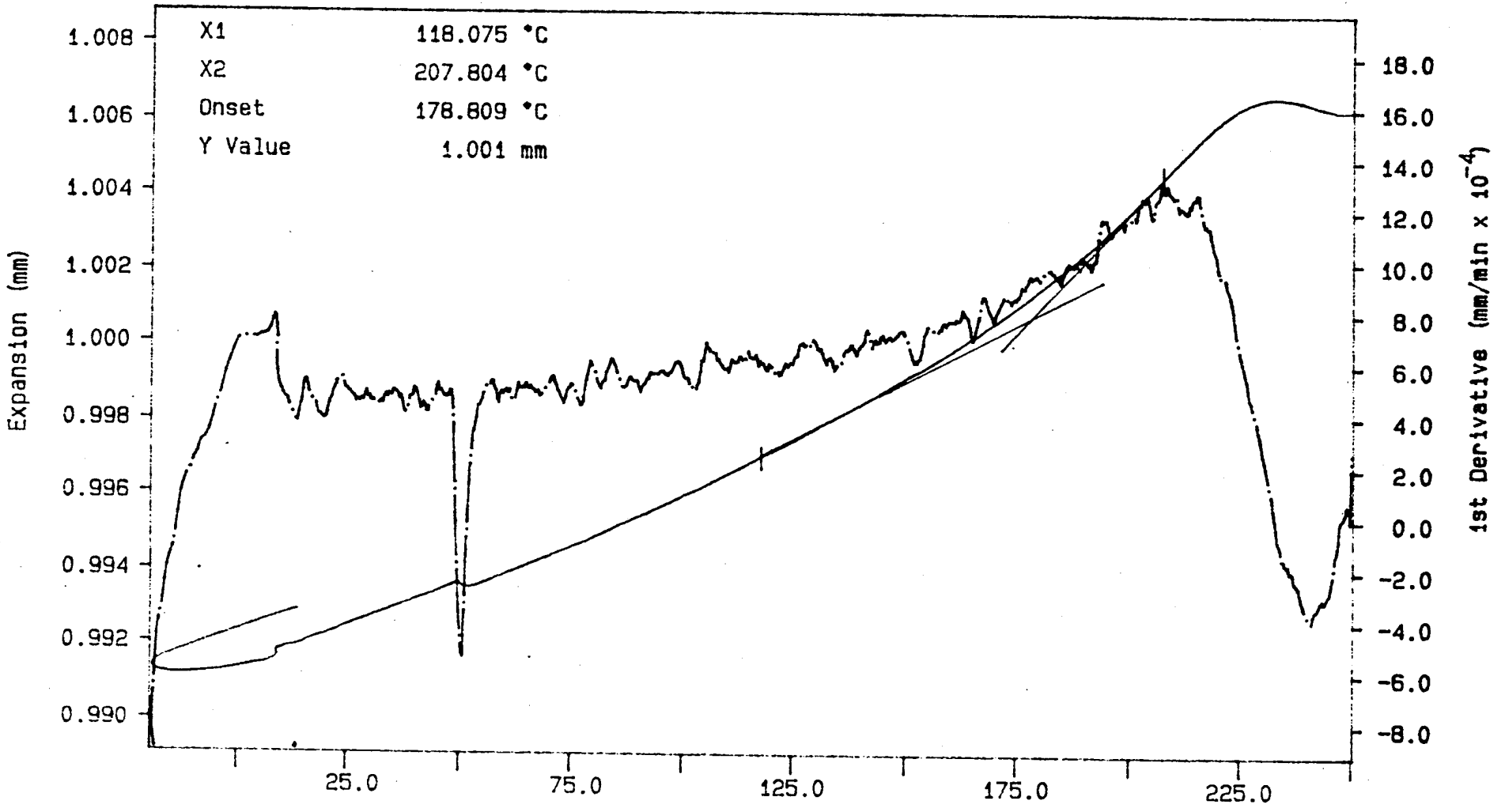
lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Thu May 4 10:41:58 1995

B2

NAWCADWAR--96-31-TR


Curve 1: TMA in Expansion
File info: ply001 Thu May 4 11:59:45 1995
Sample Height: 1.246 mm
C23-900
C23-900
1st Derivative (mm/min x 10^-4)
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
-10.0
-15.0
-20.0
-25.0
-30.0
-35.0
1.238
1.236
1.234
1.232
1.230
1.228
1.226
1.224
1.222
1.220
1.218
Expansion (mm)
X1 117.952 °C
X2 210.750 °C
Onset 179.165 °C
Y Value 1.230 mm
25.0
75.0
125.0
175.0
225.0
Temperature (°C)
Cured 1 hr @ 350F, 100 psi N2
TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 250.0 C
lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Thu May 4 12:37:23 1995

Curve 1: TMA in Expansion
File info: ply004a Fri May 5 14:05:40 1995
Sample Height: 0.993 mm
C23-900 (ply004 stopped - annealed)



Cured 1 hr @ 350F, 100 psi N2
TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 250.0 C

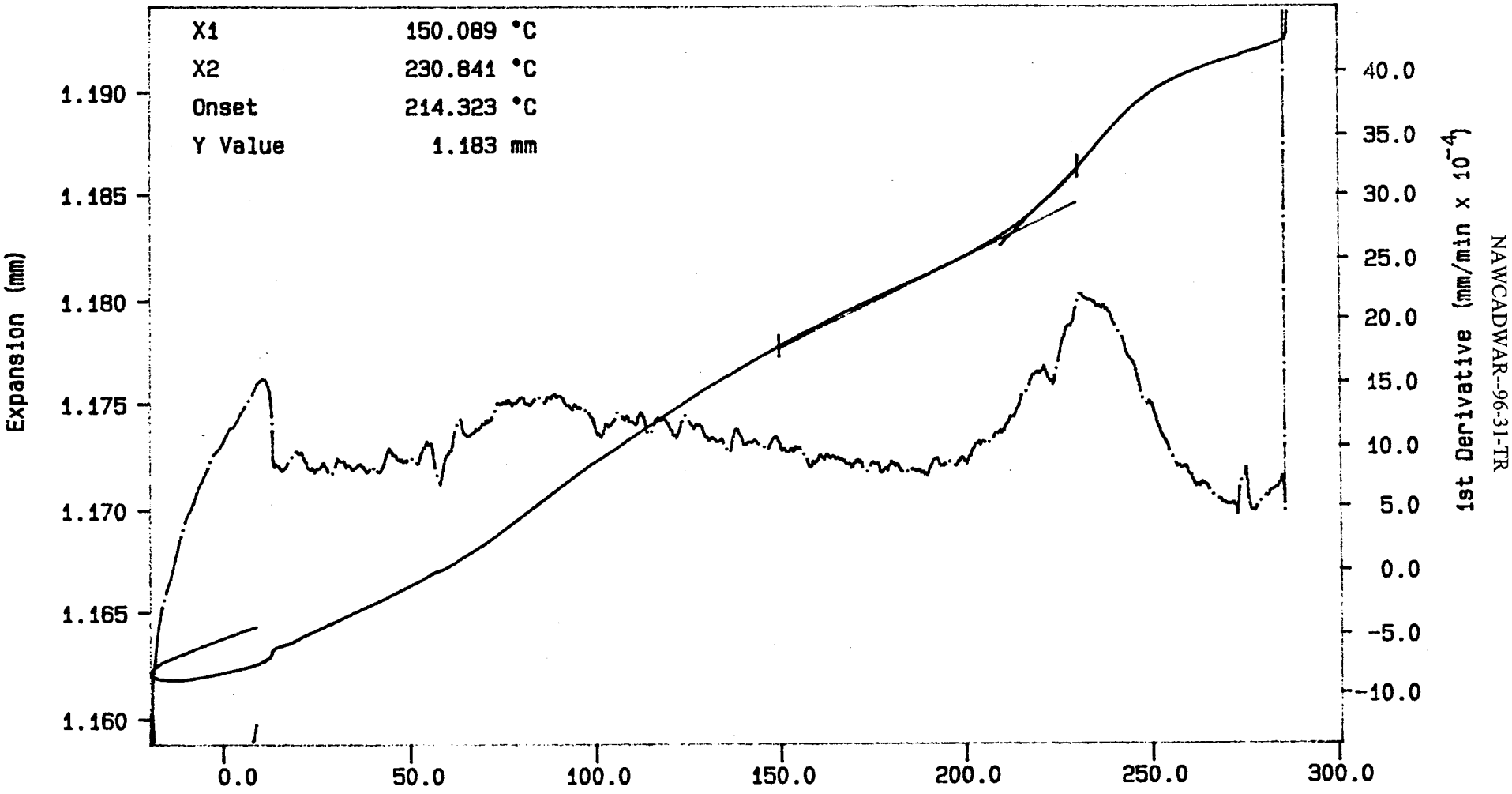
lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Fri May 5 14:17:23 1995

B4

NAWCADWAR-96-31-TR

Curve 1: TMA in Expansion
File info: c23900x006 Tue Aug 1 15:03:49 1995
Sample Height: 1.164 mm
C23-900X (Sample #4)

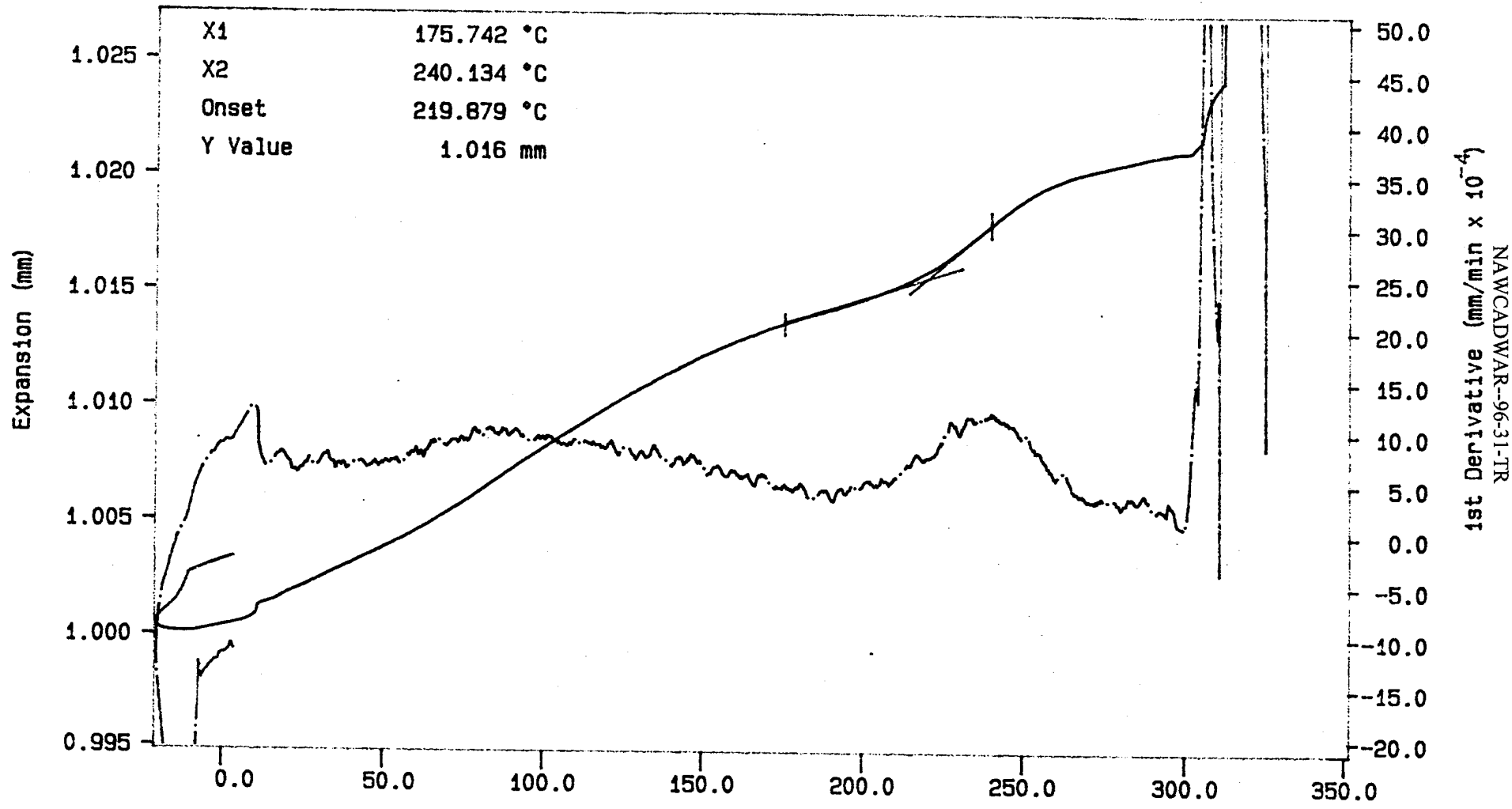
C23-900X (Sample #4)



Cured, no conditioning
TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 300.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Tue Aug 1 15:21:46 1995

Curve 1: TMA in Expansion
File info: c23900x007 Wed Aug 2 12:51:59 1995
Sample Height: 1.003 mm
C23-900X (Sample #5)

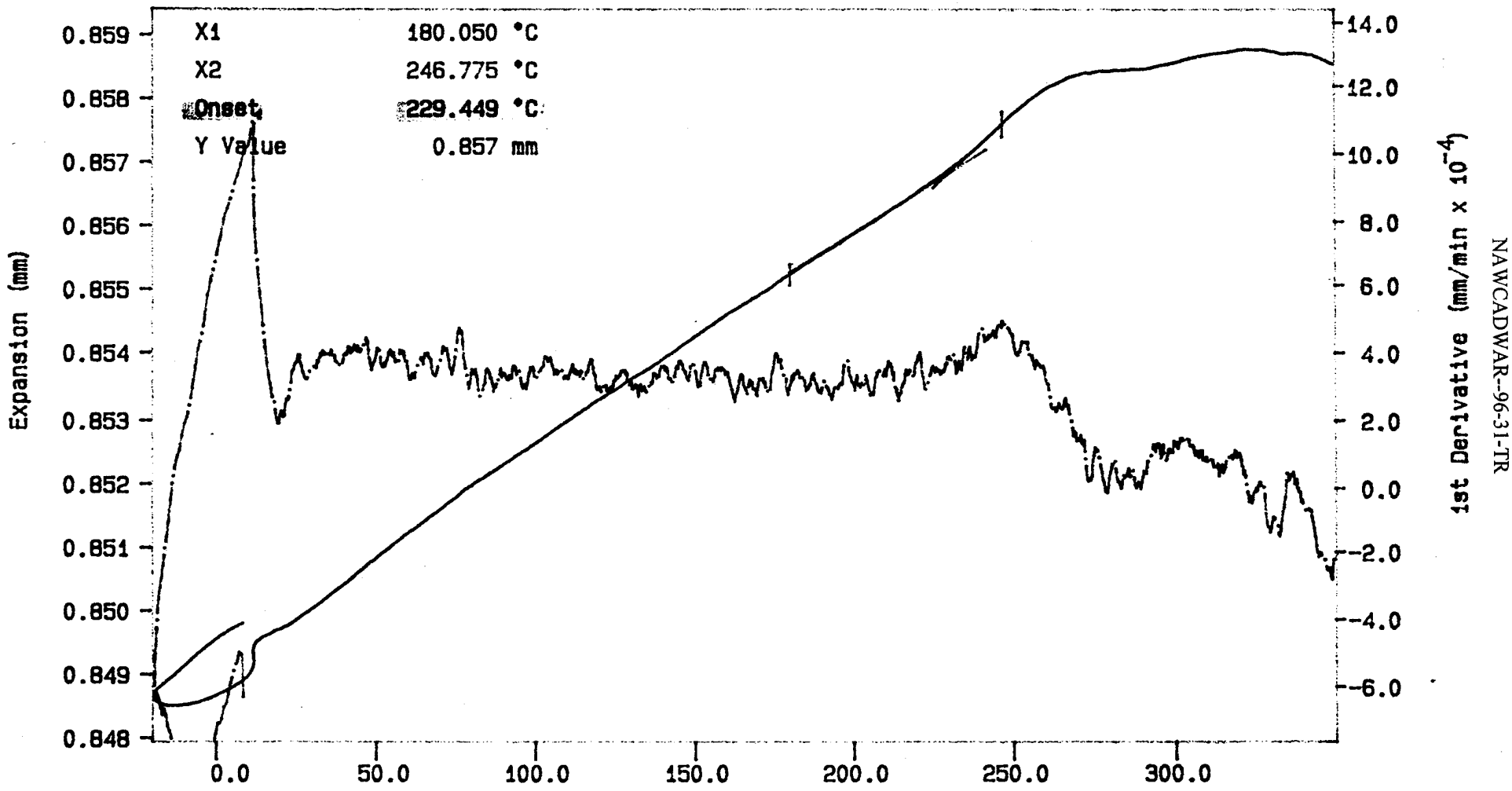


Cured, no conditioning
TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 350.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Wed Aug 2 14:02:27 1995

Curve 1: TMA in Expansion
File info: c23900o000 Tue Aug 8 11:25:49 1995
Sample Height: 0.850 mm
C23-900X (Old Sample) (Sample 1 - He)

C23-900X (Old Sample) (Sample 1 - He)

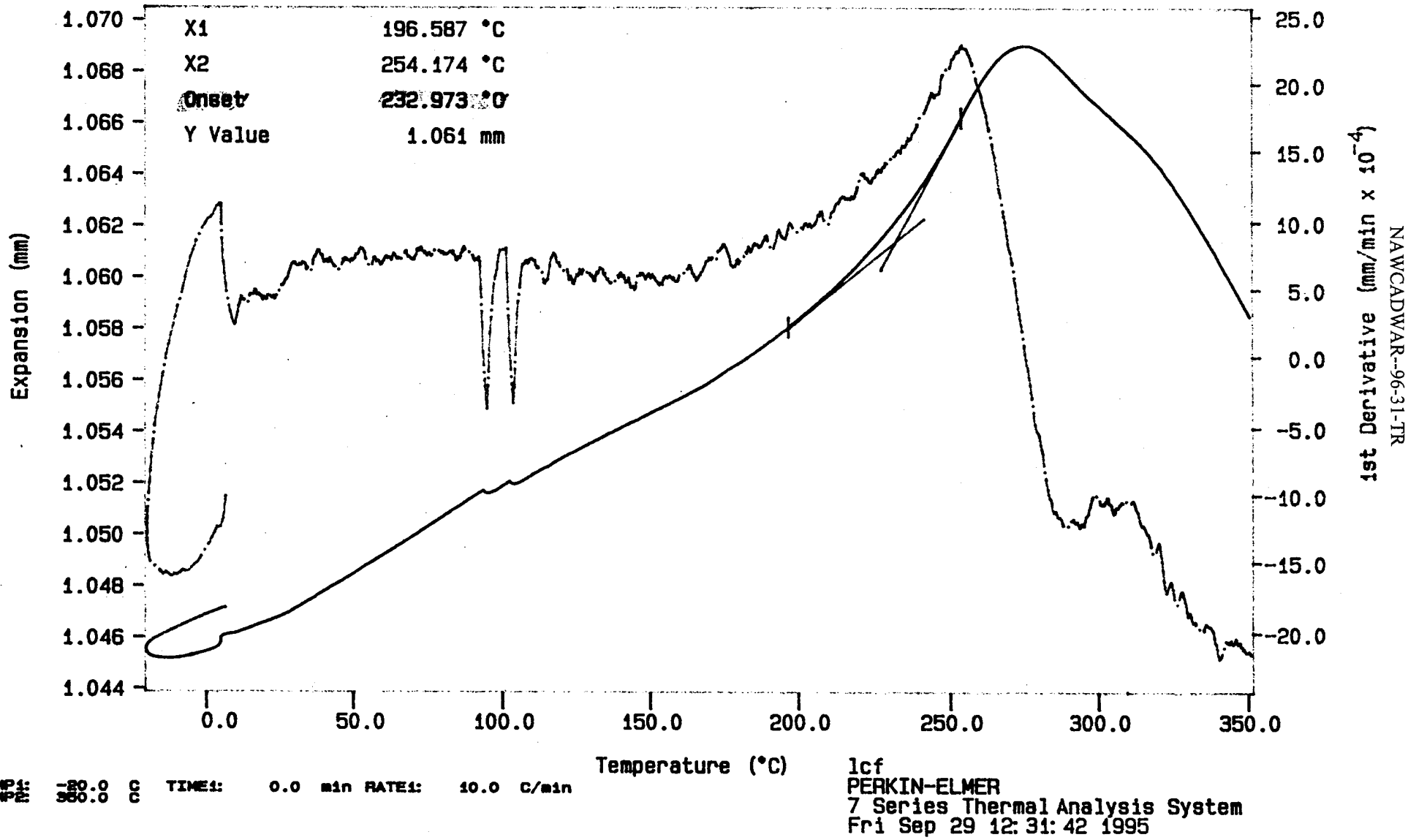


Cured 1 Hr @ 350F, 100 psi N2

TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 350.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Tue Aug 8 11:44:20 1995

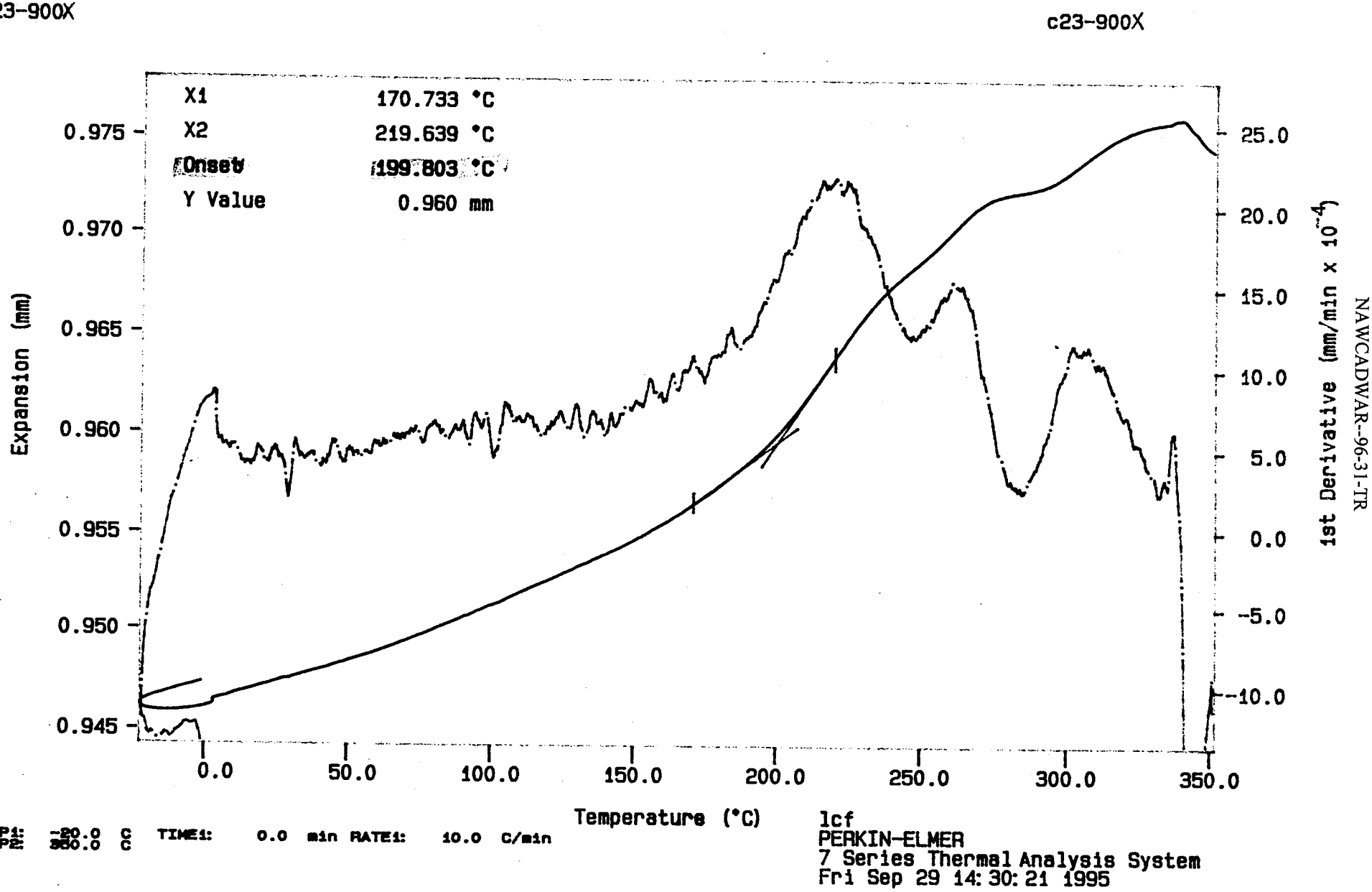
Curve 1: TMA in Expansion
File info: c23900001 Fri Sep 29 12:11:14 1995
Sample Height: 1.047 mm
c23-900X



TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 360.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Sep 29 12:31:42 1995

Curve 1: TMA in Expansion
File info: c23900002 Fri Sep 29 13:14:05 1995
Sample Height: 0.948 mm
c23-900X

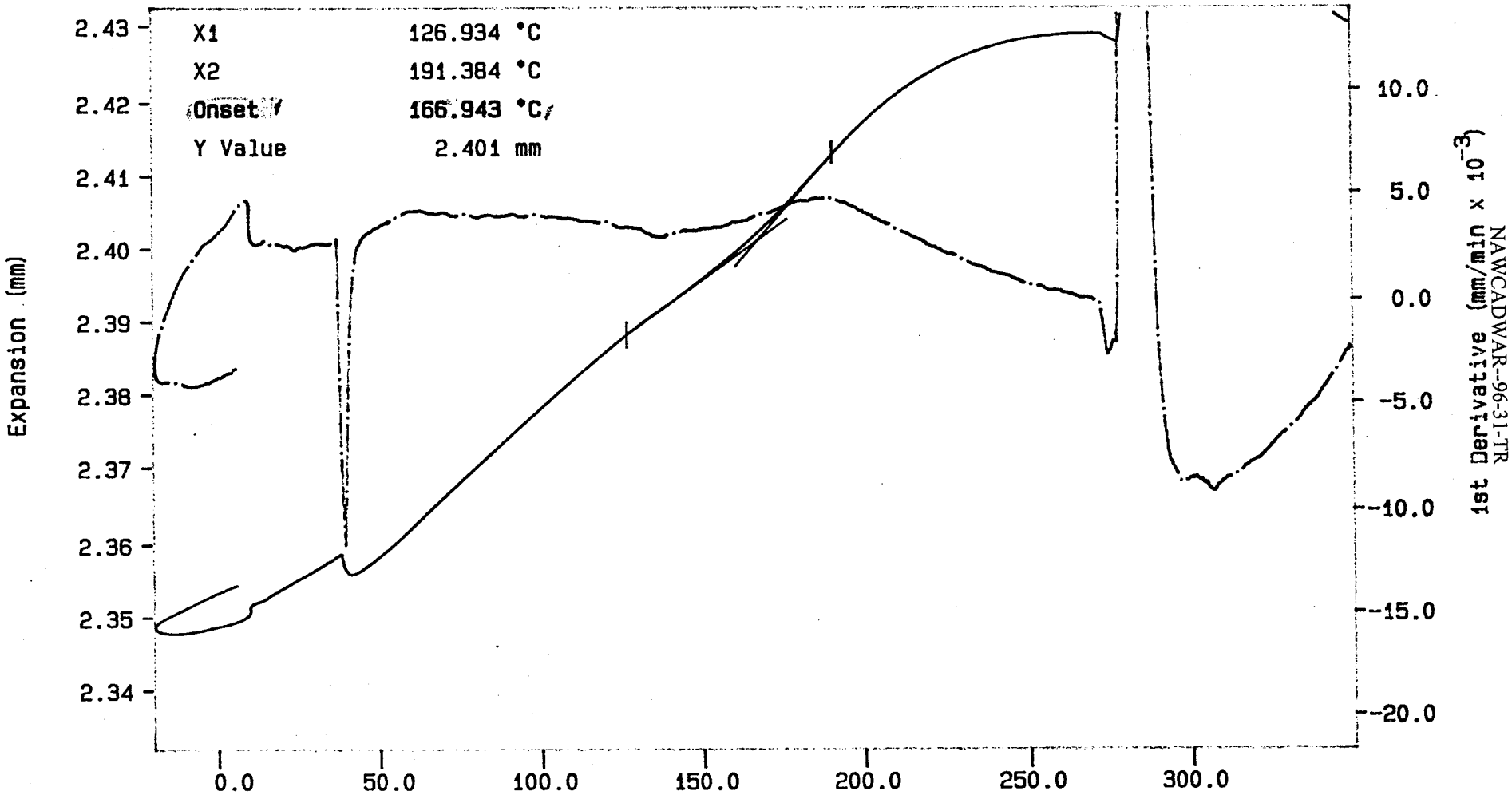


TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 350.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Sep 29 14:30:21 1995

Curve 1: TMA in Expansion
File info: c23057000 Thu Sep 28 16:42:06 1995
Sample Height: 2.355 mm
C23-057

C23-057



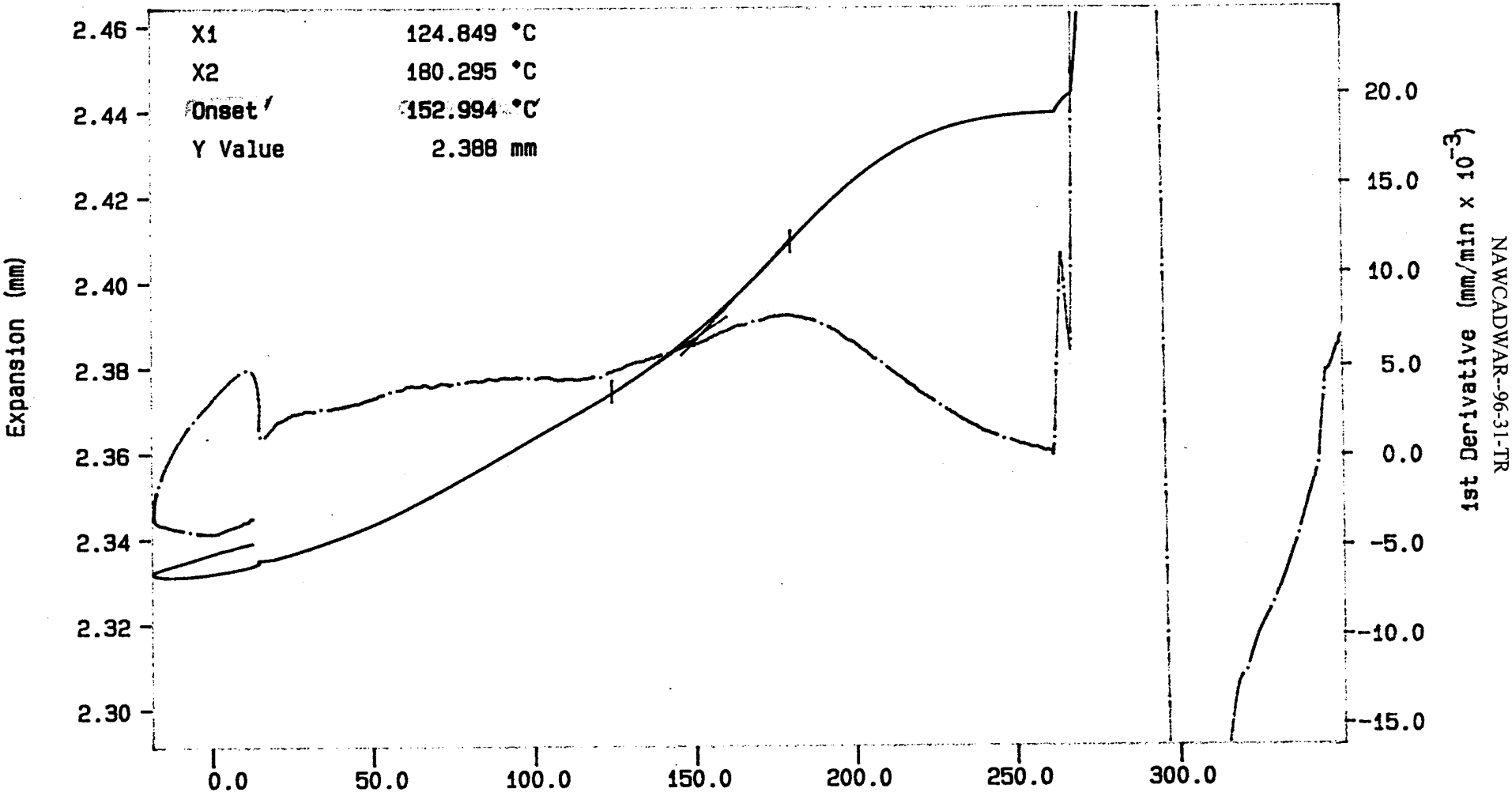
TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 350.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Thu Sep 28 16:54:07 1995

NAWCADWAR-96-31-TR

Curve 1: TMA in Expansion
File info: c23057001 Thu Sep 28 17:34:35 1995
Sample Height: 2.340 mm
C23-057

C23-057

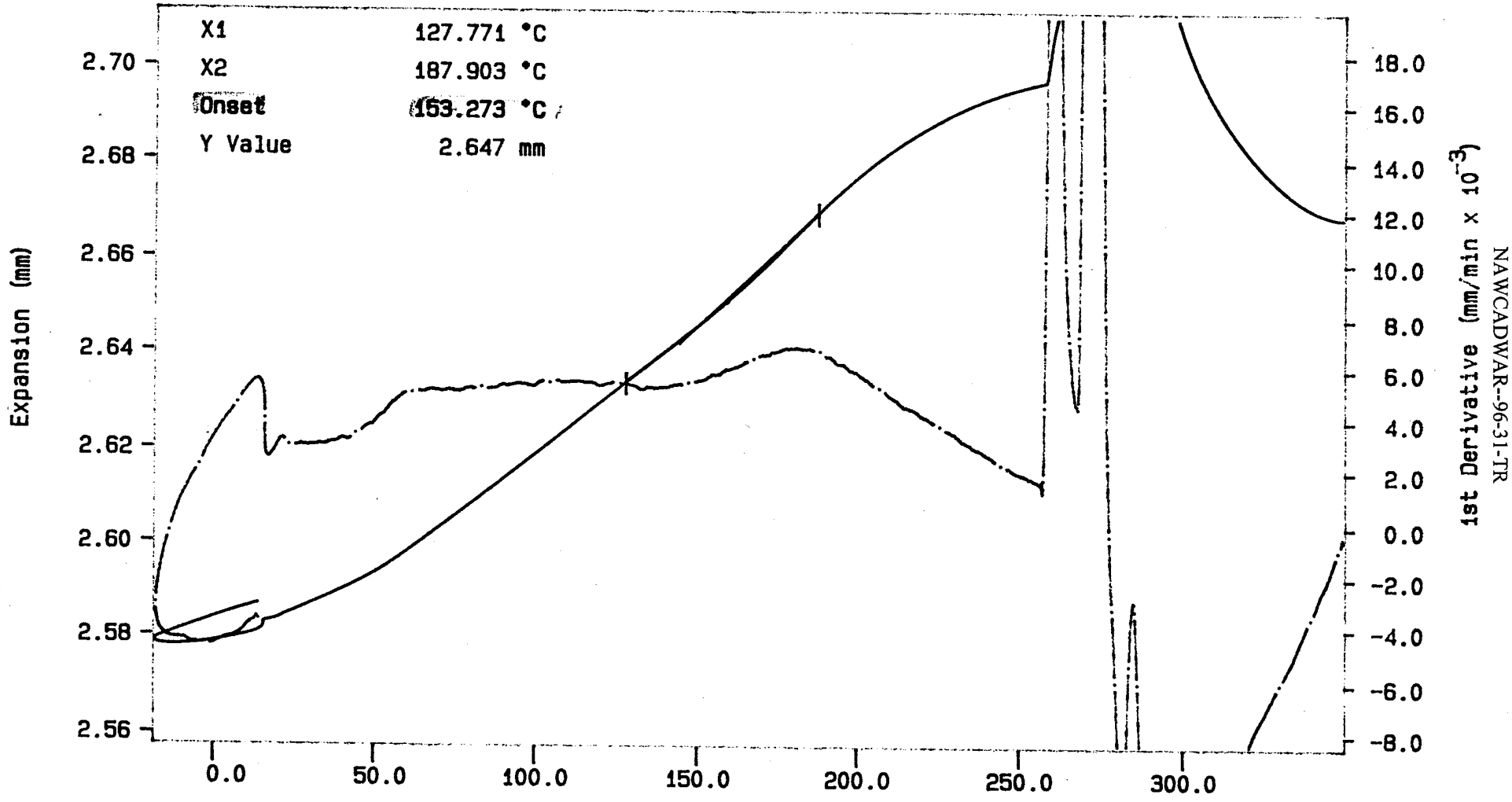


TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 350.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Sep 29 09:16:02 1995

NAWCADWAR-96-31-TR

Curve 1: TMA in Expansion
File info: c23057002 Thu Sep 28 18:31:49 1995
Sample Height: 2.587 mm
C23-057

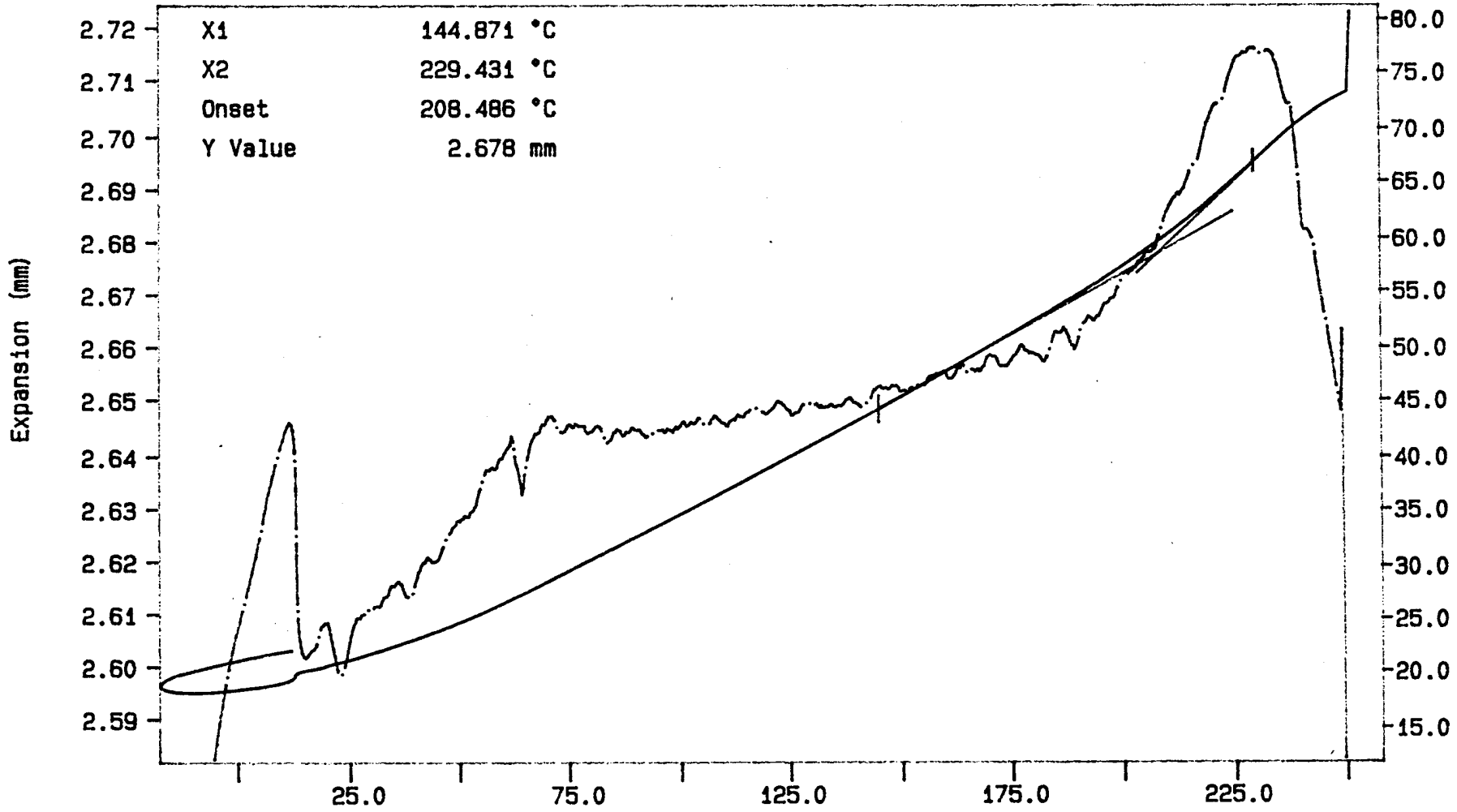


TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 350.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Thu Sep 28 18:49:13 1995

Curve 1: TMA in Expansion
File info: c23057x002 Mon Jul 31 13:50:08 1995
Sample Height: 2.603 mm
C23-057X (Sample #2)

C23-057X (Sample #2)

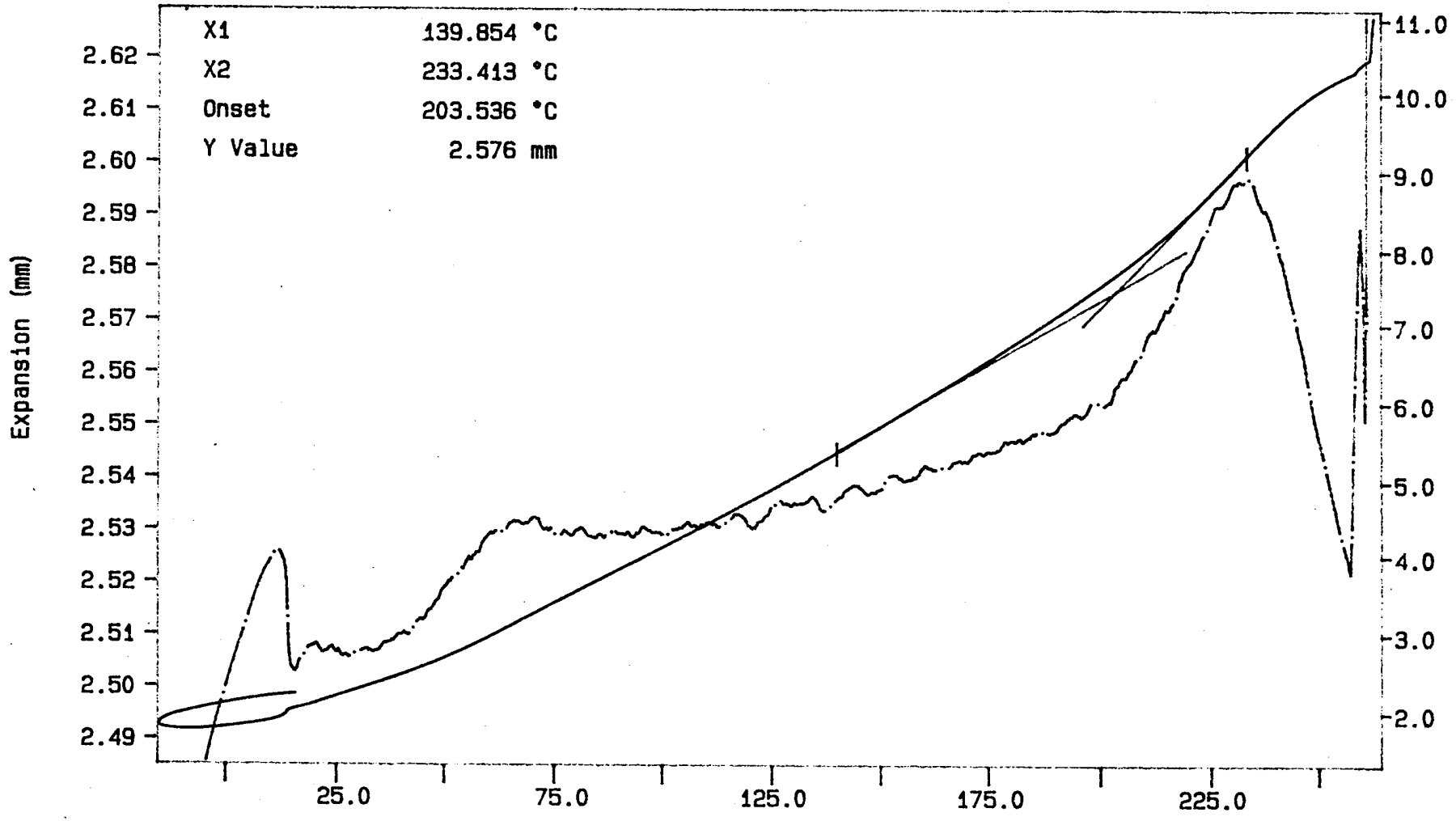


Cured, no conditioning
TEMP1: -80.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 300.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Wed Aug 2 14:55:14 1995

Curve 1: TMA in Expansion
File info: c23057x004 Mon Jul 31 15:15:33 1995
Sample Height: 2.502 mm
C23-057X (Sample #3)

C23-057X (Sample #3)



Cured, no conditioning
TEMP1: -20.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 300.0 C

lcf
PERKIN-ELMER
7 Series Thermal Analysis System
Mon Jul 31 15:35:10 1995

NAWCADWAR--96-31-TR

APPENDIX C

CRITICAL VALUES OF THE t-DISTRIBUTION

Critical Values of the t-Distribution

Degrees of Freedom	Confidence Level		
ν	99%	95%	90%
1	63.657	12.706	6.314
2	9.925	4.303	2.920
3	5.841	3.182	2.353
4	4.604	2.776	2.132
5	4.032	2.571	2.015
6	3.707	2.447	1.943
7	3.499	2.365	1.895
8	3.355	2.306	1.860
9	3.250	2.262	1.833
10	3.169	2.228	1.812
11	3.106	2.201	1.796
12	3.055	2.179	1.782
13	3.012	2.160	1.771
14	2.977	2.145	1.761
15	2.947	2.131	1.753
16	2.921	2.120	1.746
17	2.898	2.110	1.740
18	2.878	2.101	1.734
19	2.861	2.093	1.729
20	2.845	2.086	1.725
21	2.831	2.080	1.721
22	2.819	2.074	1.717
23	2.807	2.069	1.714
24	2.797	2.064	1.711
25	2.787	2.060	1.708
26	2.779	2.056	1.706
27	2.771	2.052	1.703
28	2.763	2.048	1.701
29	2.756	2.045	1.699
∞	2.576	1.960	1.645

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