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MATERIAL SELECTION AND EVALUATION OF NEW ENCAPSULATION COMPOUNDS FOR ELECTRIC CABLES FOR LAUNCH SUPPORT SYSTEM

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Finally, special thanks are due to Robert Frankfort for conducting the flammability test and coordinating the hypergolic compatibility test and to Steve Sojourner of Boeing Aerospace Operations for providing technical data and making the samples for the hydrolytic stability and flammability tests.

ABSTRACT

Eight urethane compounds were evaluated as possible replacement for the existing encapsulating compounds for electrical cables for the Launch Support System at Kennedy Space Center (KSC). The existing encapsulating compound, PR-1535, contains the curative MOCA 4-4'-Methylene-BIS (2-chloroaniline), which is a suspect carcinogen and hence may be the subject of further restrictions of its use by the Occupational Safety and Health Administration (OSHA). The samples made in the configuration of cable joints and in the form of disks were evaluated for flammability and hypergolic compatibility. These also underwent accelerated weatherability tests that measured the residual hardness of the exposed samples. Three candidates and the existing compound passed the hardness test. Of these, only one candidate and the existing compound passed the flammability test. The thermal and hydrolytic stability (weatherability) of these samples was studied using thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and differential scanning calorimetric (DSC) techniques. The TMA and DSC data correlated with the residual hardness data; whereas, the TGA data showed no correlation.

A hypergolic compatibility test will be conducted on the compound V-356-HE80, which passed both the flammability and accelerated weatherability tests.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

1.0 INTRODUCTION

1.1 Background Information

The connectors used in the Launch Support electrical cables are encapsulated with a polyurethane potting compound to ensure protection against tropical temperature and humidity. One component of the current encapsulation compound PR-1535, made by Product Research and Chemical, Inc., contains the curative MOCA [4-4'-Methylene-BIS (2-chloroaniline)], which is a suspect carcinogen and may be subject to OSHA restrictions of its use (1). A direct substitute of this material would be very desirable if not necessary.

1.2 Overall Scope of the Project [Boeing Aerospace Operations (BAO) and KSC]

The following procedures are used for Qualification Test Requirements for encapsulation compounds for electrical cables for Launch Support.

a. Boeing Aerospace Operations encapsulated electrical cable components using the appropriate molding process for each compound (seven candidates and the current material).

b. Boeing Aerospace Operations evaluated electrical properties and processibility (molding).

c. The Materials Science Laboratory (MSL) evaluated chemical and physical properties.

d. KSC will generate an Approved Product List (APL) for electrical cable insulating compounds and revise molding procedures due to change of potting materials.

1.3 Scope of This Project (Materials Science Laboratory)

The scope includes the evaluation of the thermal and hypergolic stability, weatherability, and flammability of the seven candidates and current electrical cable insulating compounds.

2.0 MATERIALS AND METHODS

2.1 Encapsulating Chemical Compounds

Eight chemical compounds were chosen from the Qualified Products List of products qualified under Military Specification QPL.24041-16 and the current encapsulating compound:

a. PR-1535: A polyether polyol polymer with totuene diisocyanate (TDI) with MOCA is used as a curing agent.

b. PR-1574: Same as PR-1535, except 2-hydroxypropyl aniline is used as a curing agent.

c. PR-1592: Same as PR-1535, except an aromatic diamine is used as a curing agent.

d. PR-1590: Same as PR-1535, with slight modification of the chemical composition of the curative.

e. PS-799: Same as PR-1535, except with polyamine used as a curing agent.

Note: All the above compounds are manufactured by Product Research and Chemical Corporation.

f. Conathan EN-9 (CONAP Inc.): Poly (oxy-1,4-butane diyl)-hydro-hydroxy trimethylol pentane with TDI and (methyl thio) toluene diamine used as a curing agent.

g. Conathan EN-1556 (CONAP Inc.): Ethohexadiol with TDI and 2-propanol-1, 1' phenyl aminobis diamine used as a curing agent.

h. V-356-HE80 (BP Chemicals): Polytetramethylene glycols with isophorone diisocyanate and a polyol curative (non-TDI, non-MOCA polyurethane) used as a curing agent.

The preparation of urethane polymers is a two-step reaction. The first step is the formation of prepolymer by the reaction of a diol and diisocyanate. The second step is the chain extension by reacting with a curing agent, which is typically an amine.

2.2 Encapsulation of Electrical Cable Joints (Boeing)

The electrical cable components were encapsulated in special molds by applying the potting polyurethane compounds using an air pressurized injection gun fitted with a cartridge and allowing the encapsulated parts to cure according to specifications provided by the manufacturers and procedures used by Boeing at KSC (MIL-M-24041, KSC-SPEC-E-0029, and KSC-STD-132).

These components yielded as-used configuration samples. Special samples in the form of disks were made using special molds that were used for the evaluation of accelerated weatherability.

2.3 Thermal and Hydrolytic Stability (Weatherability)

The high temperature-humidity conditioning was done inside a desiccator containing a saturated solution of potassium sulfate in a forced convection oven with the precision of ±0.5 degree Centigrade (°C). The conditioning of 28 days at 100 °C and 95 percent relative humidity (RH) is intended to simulate about ten years of service at 35 °C and 95 percent RH (2). This is a reasonable simulation used for many of the military applications.

The samples, in the form of disks (2.8 millimeters in diameter and 1 millimeter in thickness), were taken out of the desiccator/oven every seventh day, air cooled, cleaned with tap water and deionized water, and subjected to hardness measurements. The samples were cut, removed for thermal analyses, and then put back in the desiccator/oven.

2.4 Hardness Measurement

The hardnesses of the samples were measured using Shore Durometer (Type A). The data reported are averages of three samples, five measurements per sample.

2.5 Flammability Test

The flammability test was done using the Upward Flame Propagation Test (NASA Handbook 8060.1C, Test 1), which is a slight modification of ASTM D568 with the requirement that the specimen be "self-extinguishing." The samples in user-configuration form (cable joints) were held at 45 degrees to the flame and supported by a needle rather than a clamp to reduce heatsink size. In order to pass,

the sample had to survive a direct current (dc) of 55 amperes through 16 American wire gauge (AWG) (MIL-W-5086, polyvinyl chloride insulated) for a period of 30 seconds versus 2.5 minutes for ASTM D568, without ignition and charring.

2.6 Hypergolic Compatibility Test

The hypergolic compatibility tests on the samples were conducted by Wiltech Corporation (a KSC contractor) that followed the procedures described in KSC Report 91-5331. This test is conducted by placing 0.5 millimeter (ml) of the appropriate fluid [hydrazine (N_2H_4), monomethylhydrazine (MMH), and nitrogen tetroxide (N_2O_4)] on the top of the sample and monitoring the temperature for 10 minutes. A temperature increase of 2.8 °C constitutes failure.

2.7 Thermal Analysis

Dynamically programmed thermogravimetric analyses of the samples were carried out using a Dupont TGA 951 module, controller, and Dupont 2100 Thermal Analyst data analyzer in a nitrogen atmosphere. The Thermal Analyst 2100 controlled and tracked the progress of the experiment, collected data, and printed or plotted the results of the experiments.

A Dupont Thermomechanical Analyzer 943 was used to study the depth of penetration of a probe on the surface of the samples as a function of temperature. A weight of 10 grams (g) was used on the weighing pan attached to the end of the probe. TMA analyses were carried out using Dupont TMA module, controller, and Thermal Analyst 2100.

Differential Scanning Calorimetric analyses were carried out with a Dupont DSC 2910 module, controller, and Thermal Analyst 2100. A nitrogen purge flow rate of 50 milliliters per minute was used. Samples for the DSC runs were cooled to near 0 °C using a special cooling accessory with crushed ice as the coolant.

A heating rate of 10 °C per minute was used in all the TGA, TMA, and DSC runs.

3.0 RESULTS AND DISCUSSIONS

3.1 Hydrolytic and Flammability Studies

The results of the hydrolytic stability and flammability tests are summarized in table 1. Of the eight candidates and the existing encapsulation compounds, only the existing encapsulation compounds and one of the candidate compounds (V-356HE80) passed the flammability test.

Figure 1 represents the results of weatherability in the form of residual hardness versus time of exposure for the eight compounds. The compounds EN-9 and PR-1574 exhibited very little loss of hardness with exposure in 100 °C, 95 percent RH for a period of four weeks. The compound PR-1535 (current product) showed appreciable loss of hardness with exposure time and barely passed the minimum Shore A hardness of 40 requirement. The compounds PS-799 and EN-1556 exhibited a drastic decrease in hardness with values approaching zero after three weeks of exposure. The compound V-356-HE80 demonstrated good hydrolytic stability with little loss of hardness after the first week of exposure. This agrees with the vendor data (figure 2) which shows loss of hardness for the first week but very little loss of hardness at exposure time beyond that. The starting hardness of this compound could not be determined properly, probably because the curing process had not been completed at the time of hardness measurements. The hardness of ~50 is much lower than the hardness value of 80 specified by the vendor. Improper formulation and/or molding could be the cause of this low hardness. Previous hydrolytic stability tests conducted on this material started with the Shore A hardness of 82 and had final Shore A hardness of 64.

The sample PR-1590 did not survive one week of exposure as the hardness reduced to zero at that point.

3.2 Thermal Analysis

3.2.1 Thermogravimetric Analysis

Thermal and hydrolytic degradation (accelerated weatherability) of samples would be expected to lead to scission of the polymer chains, decreased crosslinked density, and molecular weight changes affecting mechanical and thermal

Table 1. Hydrolytic Stability and Flammability of Polyurethane Compounds

		Shore Durometer, Type A				
Sample	Flammability	Week 0 (Zero)	Week 1	Week 2	Week 3	Week 4
PR-1535	Passed	85	70	58	44	38
V-356-HE80	Passed	--	49	48	44	44
PR-1574	Failed	92	90	84	80	83
PR-1592	Failed	92	70	53	33	23
EN-9	Failed	93	89	83	82	82
PS-799	Failed	84	57	26	0	--
EN-1556	Failed	82	39	19	0	--
PR-1590	Failed	66	0	--	--	--

properties. TGA measures weight loss as a function of temperature.

Figures 3, 4, 5, and 6 show the TGA data of the current compound, PR-1535, and the candidate, V-356-HE80, the two compounds which successfully passed the flammability and the hydrolytic stability tests. The weight loss started about 300 °C for the zero, one, two, three, and four weeks of exposed samples of PR-1535 (figure 4). These temperatures did not correlate to the trend in the hardness versus exposed time data; that is, the incipient temperature of weight loss should decrease with a decrease in hardness due to polymer degradation. Since the TGA monitors only volatilization and weight loss, this does not exclude the possibility that other thermal degradation reactions not producing volatile products,are involved in the failure process.

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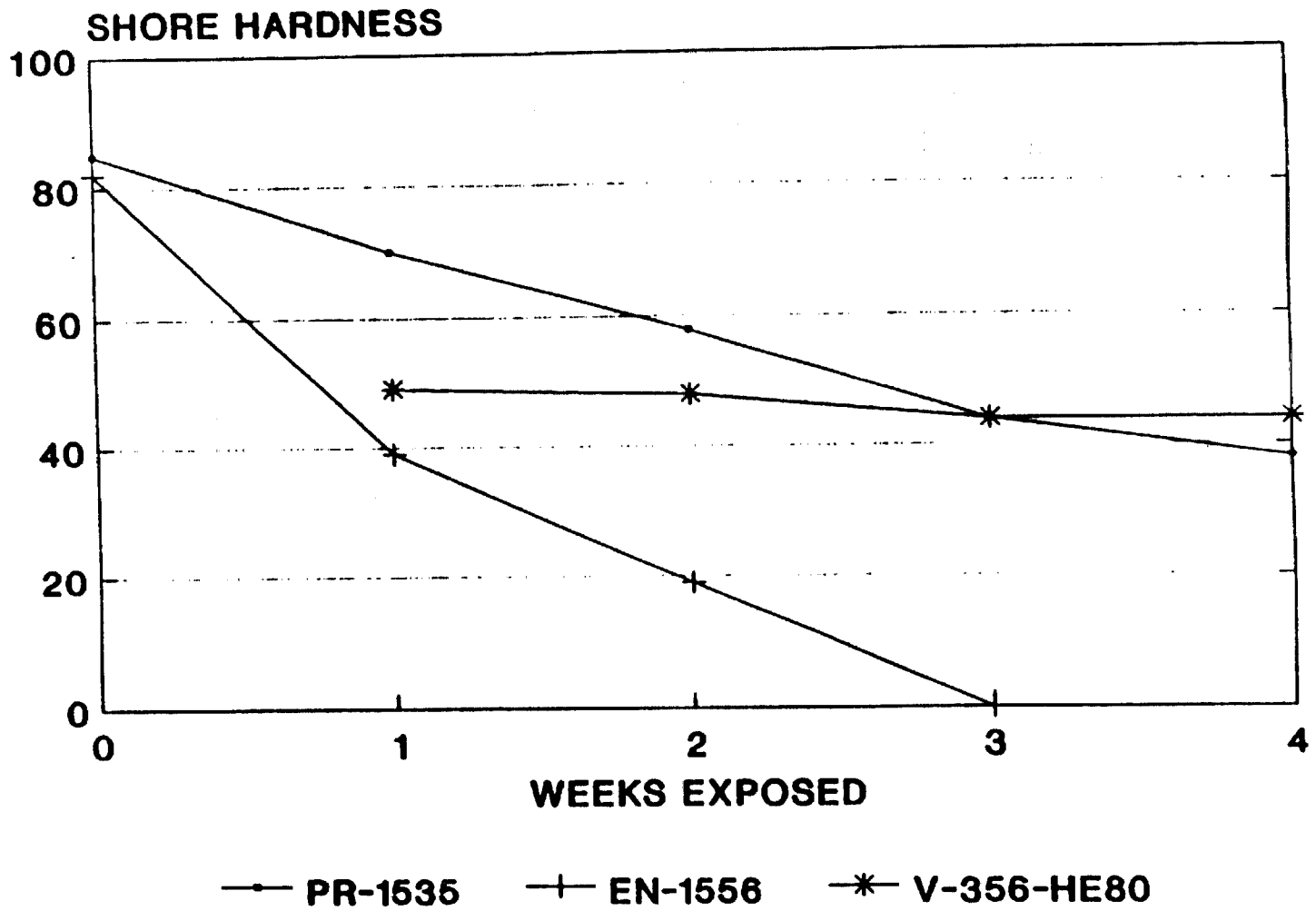

Figure 1. Residual Hardness of Polyurethane Samples (Sheet 1 of 2)

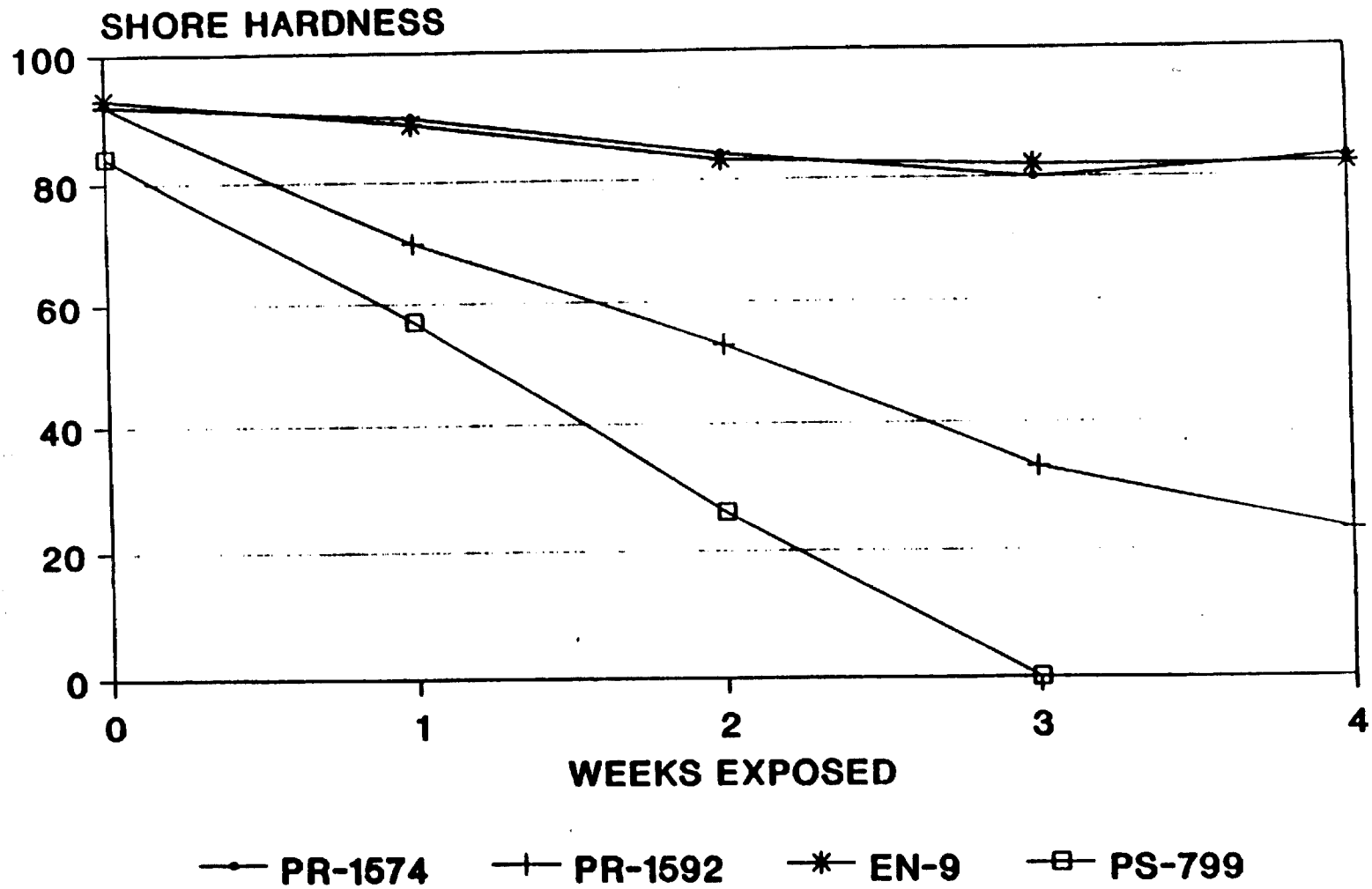

Figure 1. Residual Hardness of Polyurethane Samples (Sheet 2 of 2)

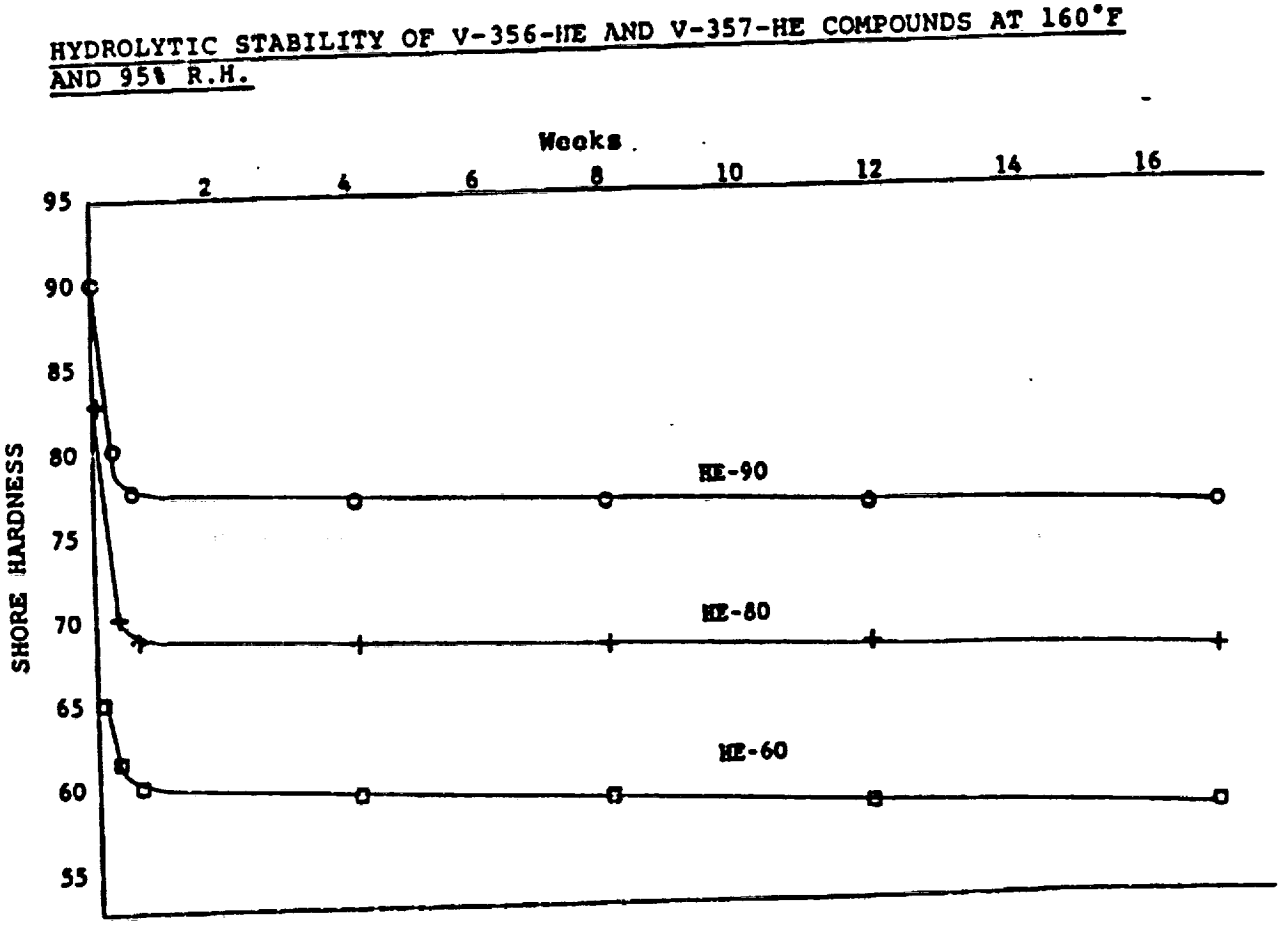

Figure 2. Residual Hardness of Polyurethane V-356-HE80 (Vendor Data)

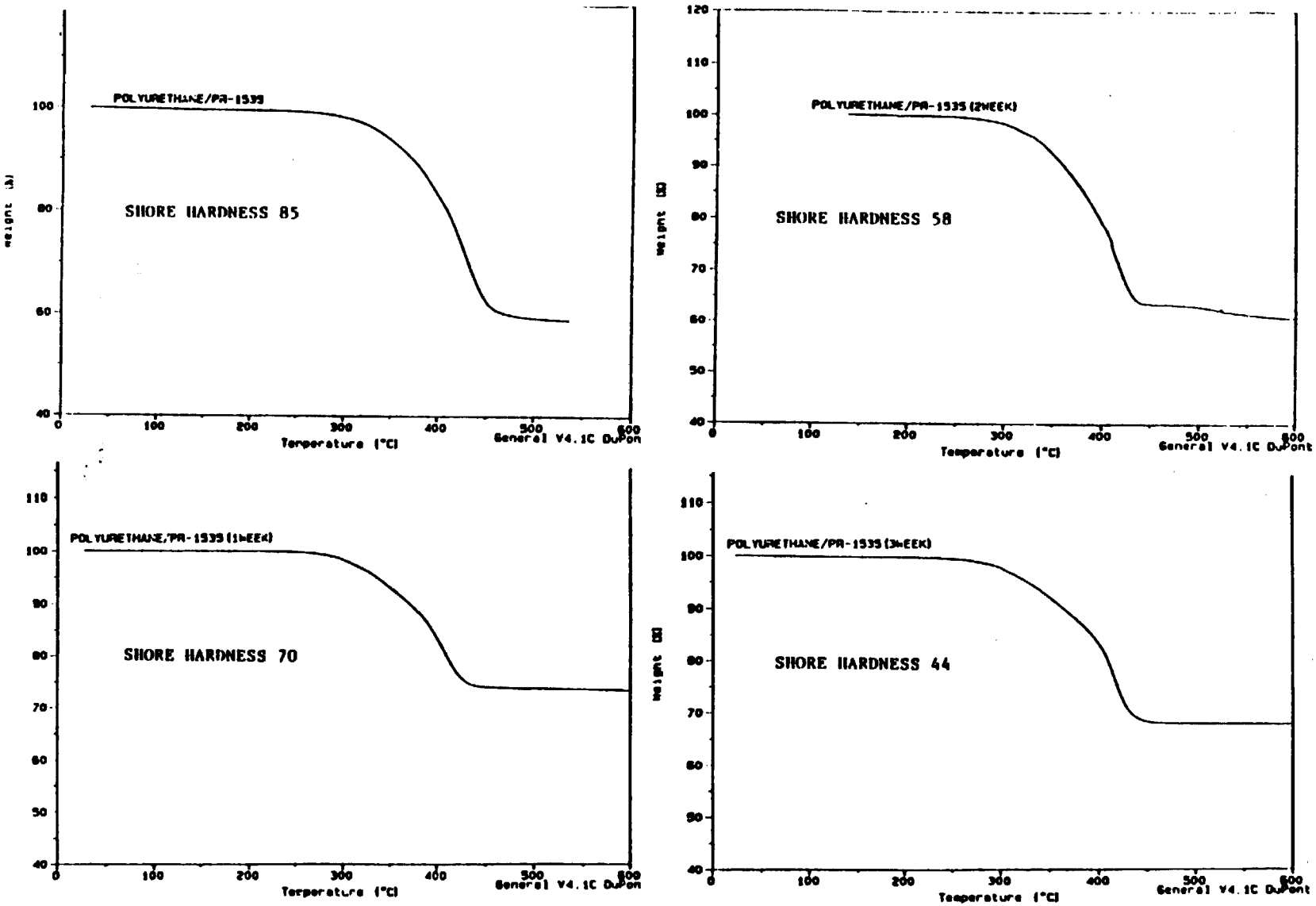

Figure 3. Thermogravimetric Curves of Polyurethane PR-1535

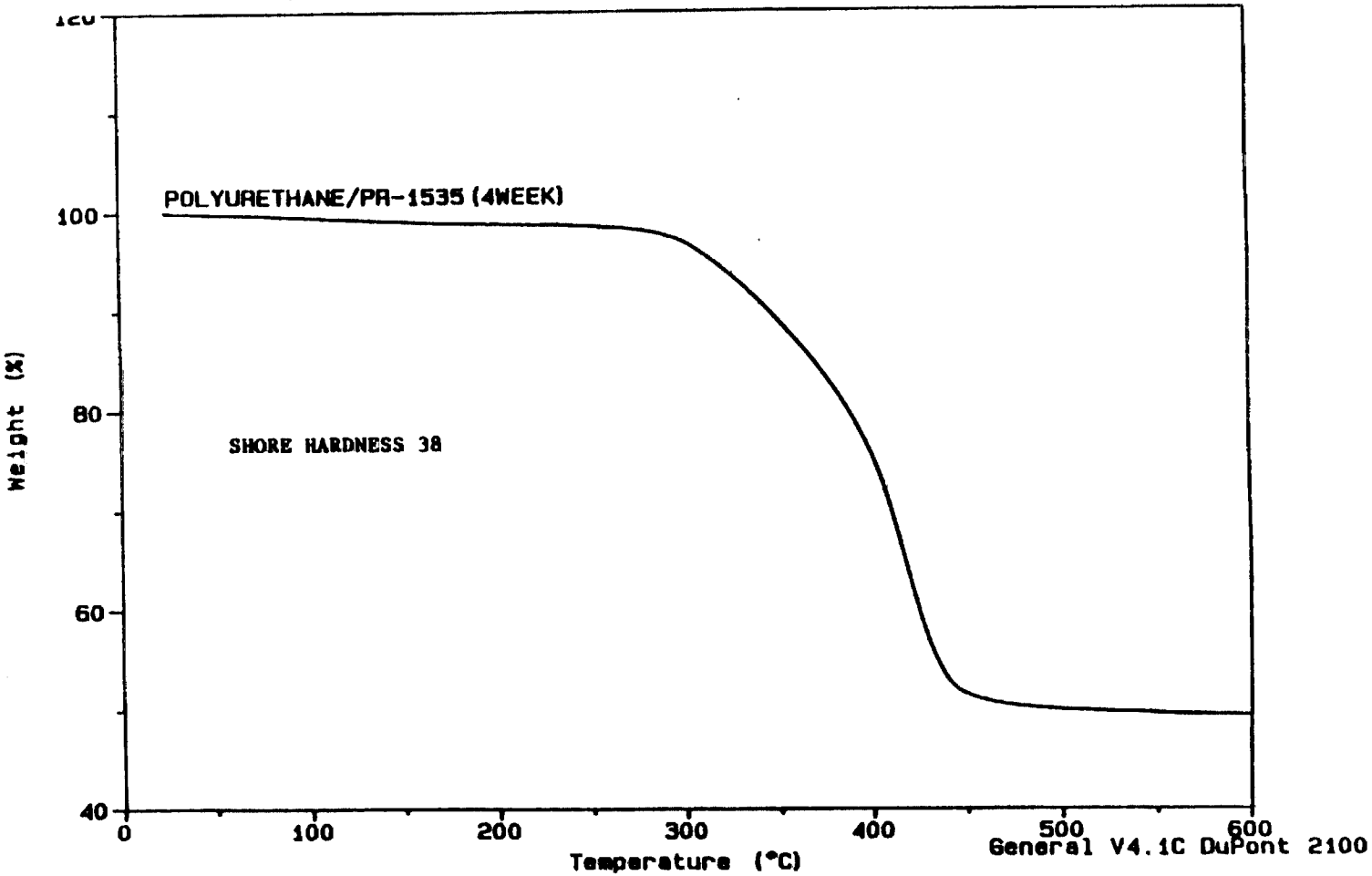

Figure 4. Thermogravimetric Curve For Polyurethane PR-1535 (Week 4)

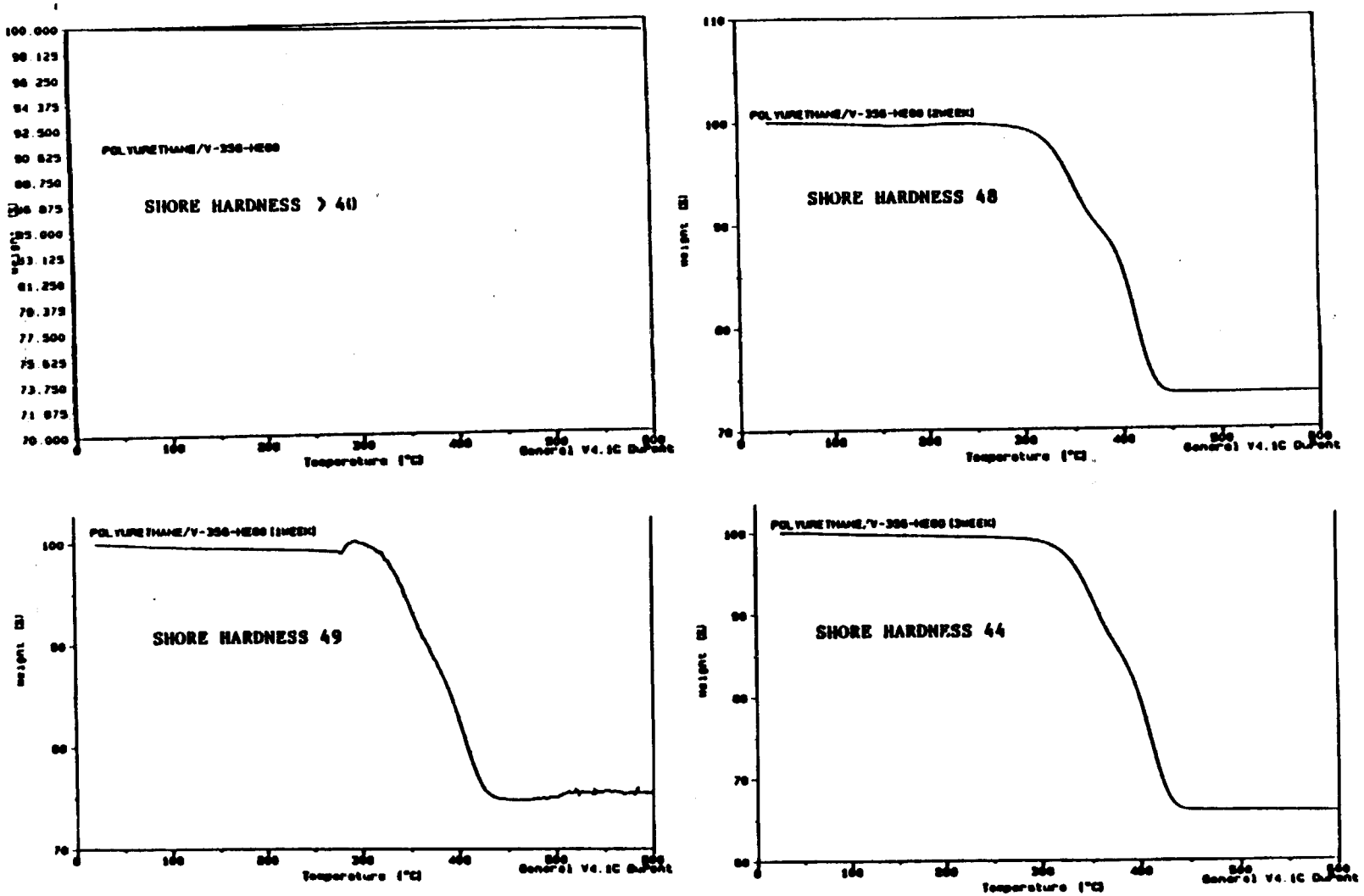

Figure 5. Thermogravimetric Curves of Polyurethane V-356-HE80

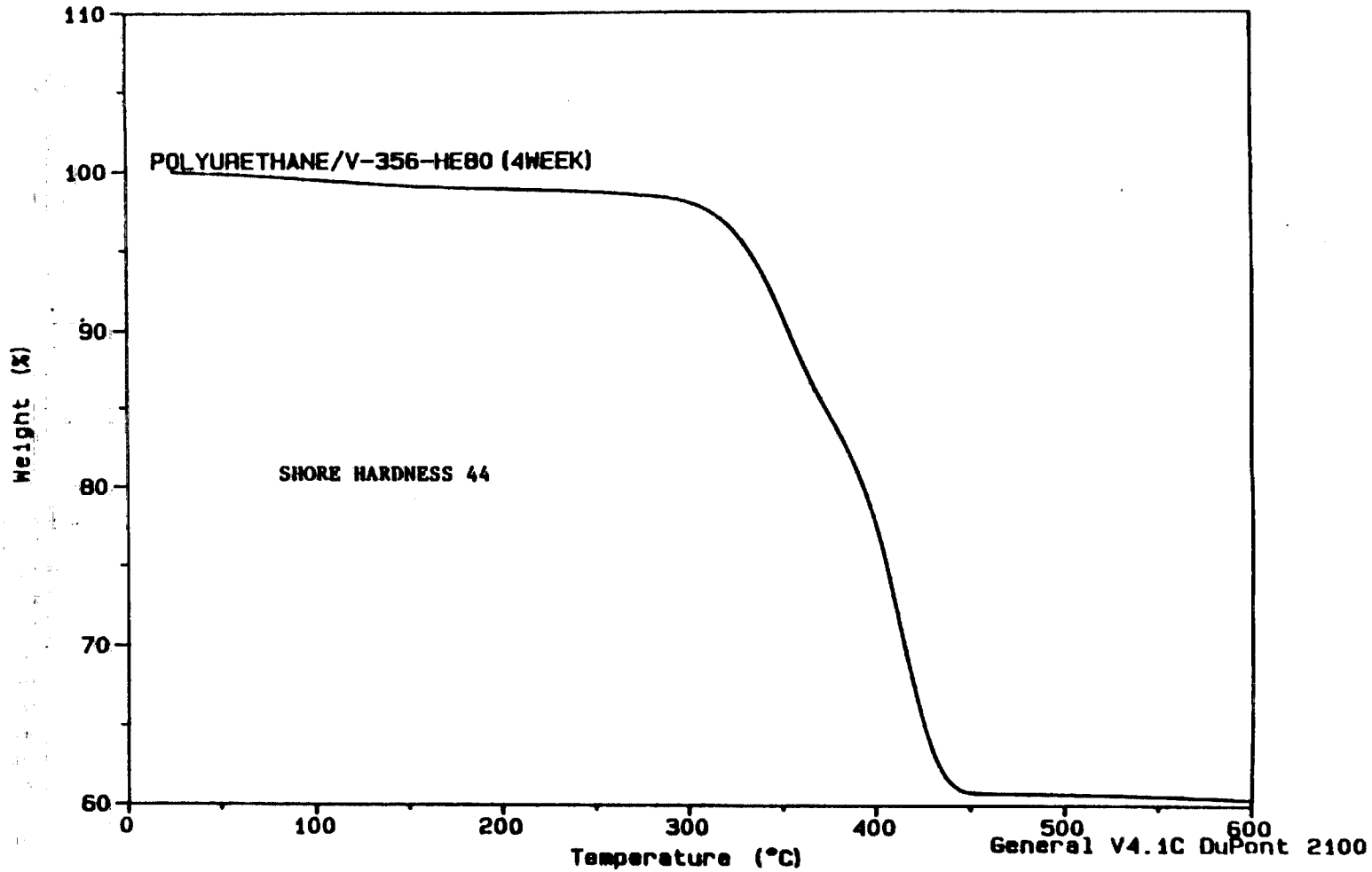

Figure 6. Thermogravimetric Curve For Polyurethane V-356-HE80 (Week 4)

The TGA data for the compound V-356-HE80 (figure 5) is consistent with the hardness versus time exposed data; that is, the incipient temperature of weight loss is practically independent of the weeks of exposure, except the first week when most of the degradation seemed to occur. This is supported by vendor data (figure 2) which shows hydrolytic degradation to occur within the first week (3). The thermal environment used by the vendor was some 30 °C lower than that used in this study, with relative humidity being the same at 95 percent.

3.2.2 Thermomechanical Analysis

Since the TGA study did not show meaningful correlation between the hardness and incipient temperature of weight loss, the TMA study was conducted. The depth of penetration of a quartz probe on the surface of the samples was measured as a function of temperature. Figures 7 and 8 show the results of this study. The sharp decrease in dimension indicates the softening of the sample as it is subjected to programmed temperature increase. This softening temperature decreased for the sample PR-1535 as the exposure time increased (figure 6) signifying polymer degradation. The data for the unexposed (zero week) sample are inconclusive because of the slippage of the probe on the small sample at about 150 °C. This trend correlates with the loss of hardness with an increase of exposure time. The data for the sample V-356-HE80 are shown in figure 8. The softening temperature decreased by about only 10 °C for the entire hydrolytic exposure of four weeks. The data for the first, second, and third weeks were inconclusive because of the slippage of the probe caused by the smallness of the samples available. Because of the limitation of samples provided, samples of adequate shape and size for the TMA study were not always available. The softening temperatures were measured using the double-tangent-intersection method.

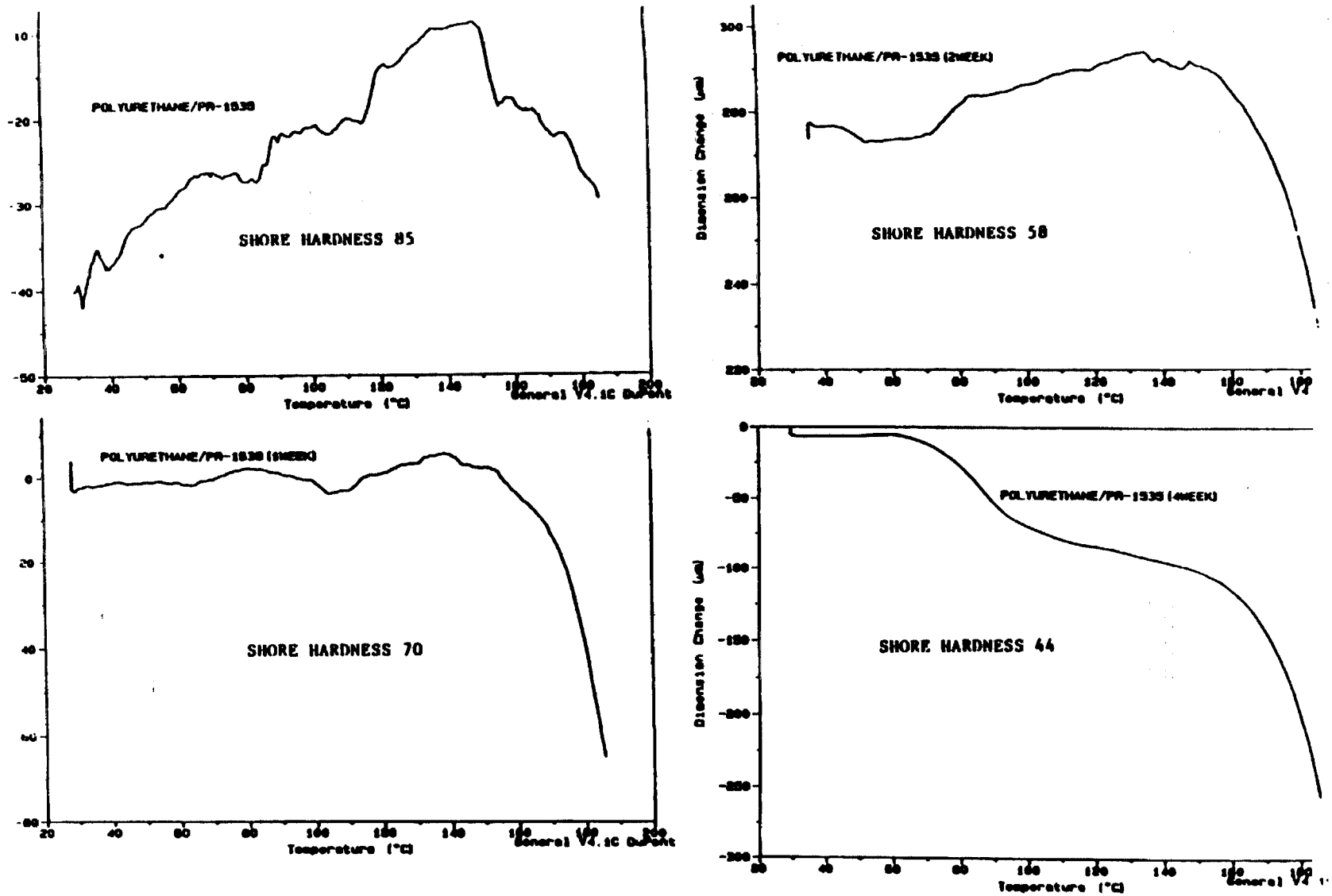

Figure 7. Thermomechanical Curves For Polyurethane PR-1535

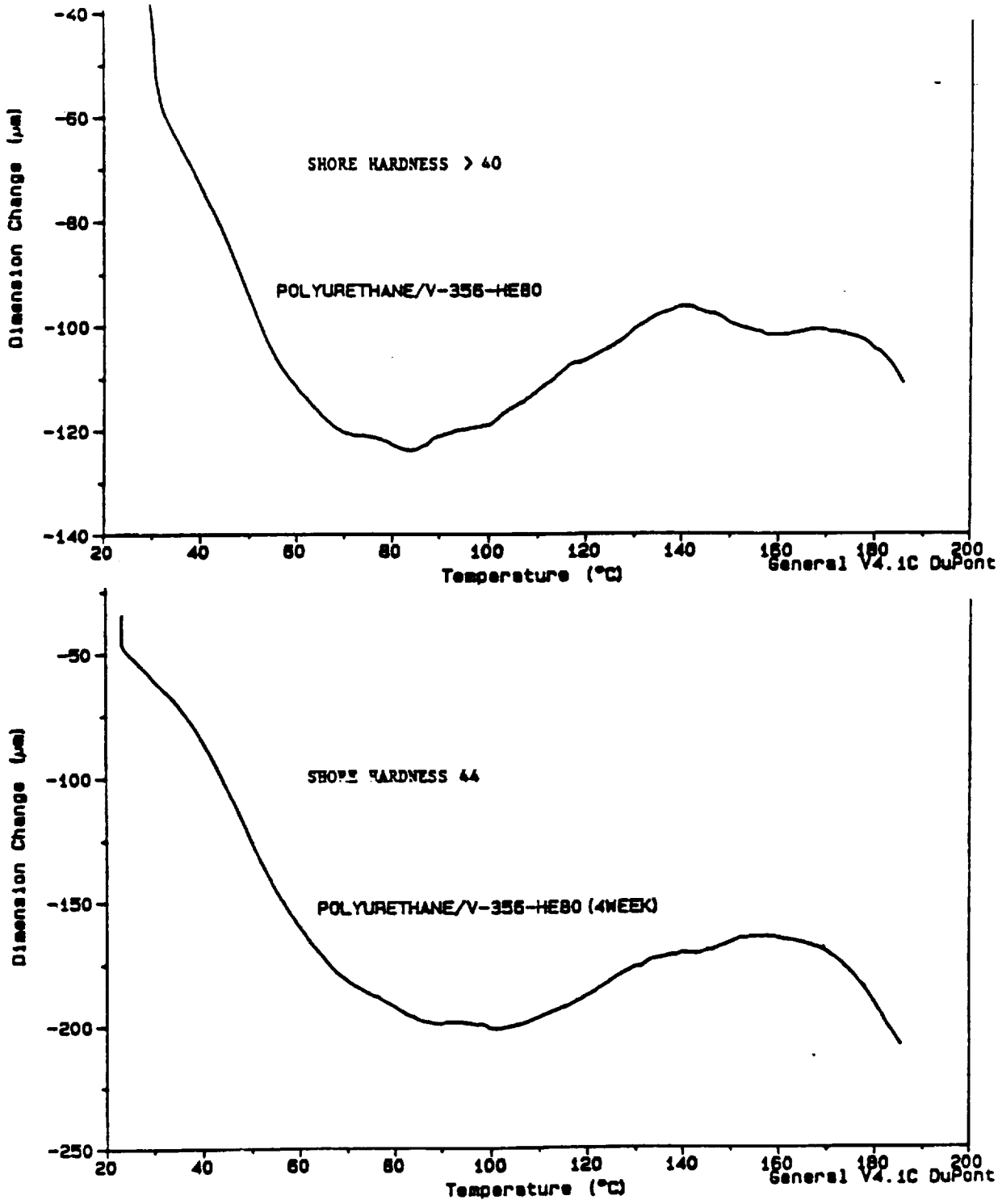

Figure 8. Thermomechanical Curves For Polyurethane V-356-HE80

3.2.3 Differential Scanning Calorimetry Analysis

Figures 9, 10, 11, and 12 show the thermograms of the compounds PR-1535 and V-356-HE80. The sample PR-1535 gave two small endotherms at 240 °C and 220 °C at zero and two weeks of exposure respectively (figures 9 and 10). Similar transitions, but less pronounced, were evident for the one, three, and four weeks of exposed samples. As the exposed time increased, the thermograms showed increased exotherm between 50 to 220 °C. These exotherms are most probably due to the curing effect.

J. Mead, et al, reported similar high temperature transitions for the polyether polyurethane system prepared from an aromatic glycol and TDI with a diamine curative (4).

The thermograms for the compound V-356-HE80 show practically no difference between the unexposed, one, two, and three weeks of exposed samples.

The four-week exposed sample shows a transition at about 70 °C. This change does not correlate to the hardness data. Further work is needed to resolve this anomaly.

4.0 CONCLUSIONS

Of the eight polyurethane compounds [current product (PR-1535) and seven candidates], only four compounds (PR-1535, PR-1574, EN-9, and V-356-HE80) passed the hydrolytic stability (weatherability) test. Of these four compounds, only two (PR-1535 and V-356-HE80) passed the NASA flammability test.

TMA gave softening points of the unexposed and exposed samples, which correlated with residual hardness data. DSC data showed some correlation with residual hardness data and increased curing effect with weeks exposed. TGA data showed practically no correlation with the residual hardness data.

5.0 RECOMMENDATIONS

Based on the accelerated hydrolytic stability and flammability tests, the compound V-356-HE80 is recommended to replace the current product PR-1535 which contains MOCA, provided it passes the hypergolic compatibility test.

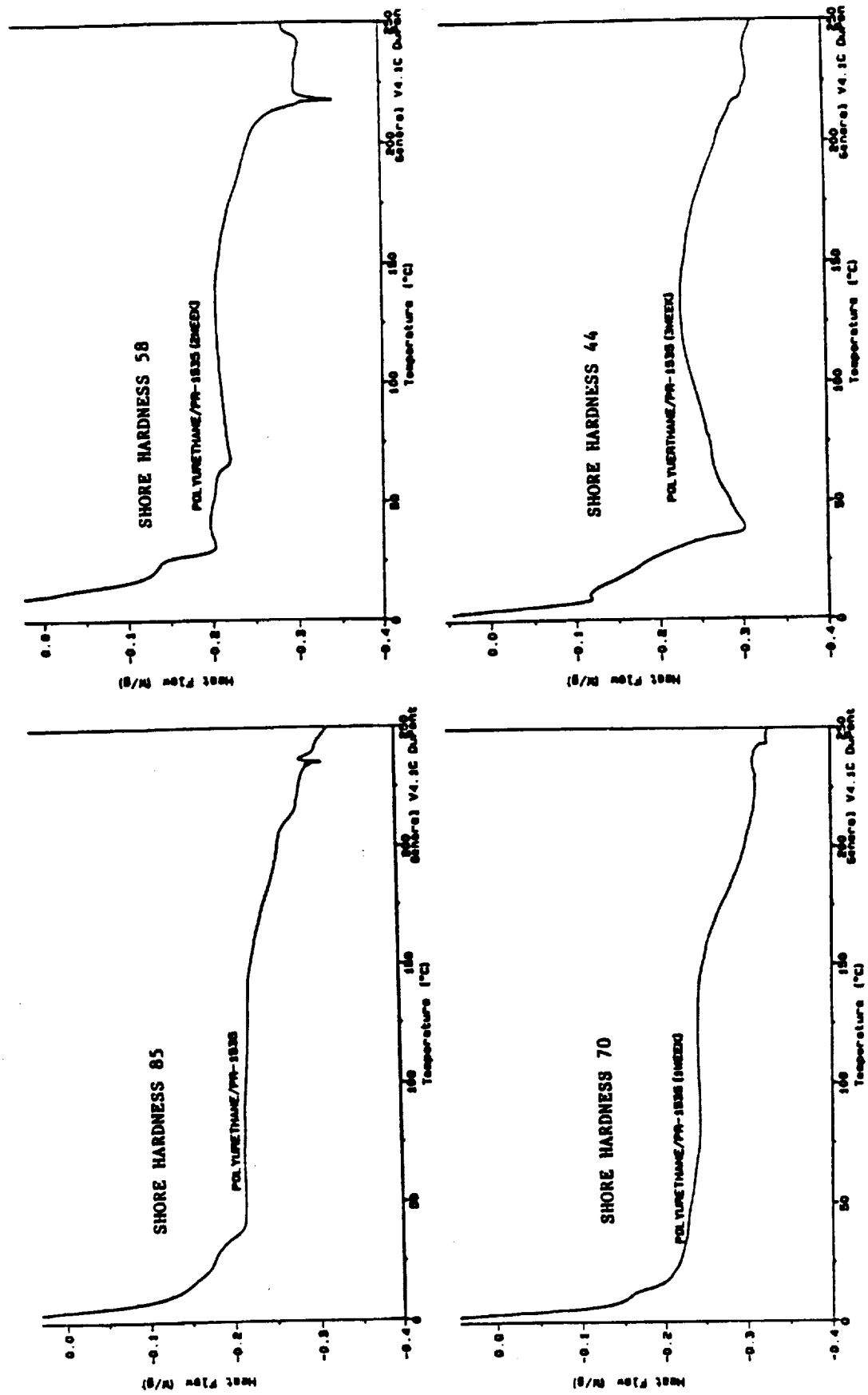

Figure 9. Differential Scanning Calorimeter Curves For Polyurethane PR-1535

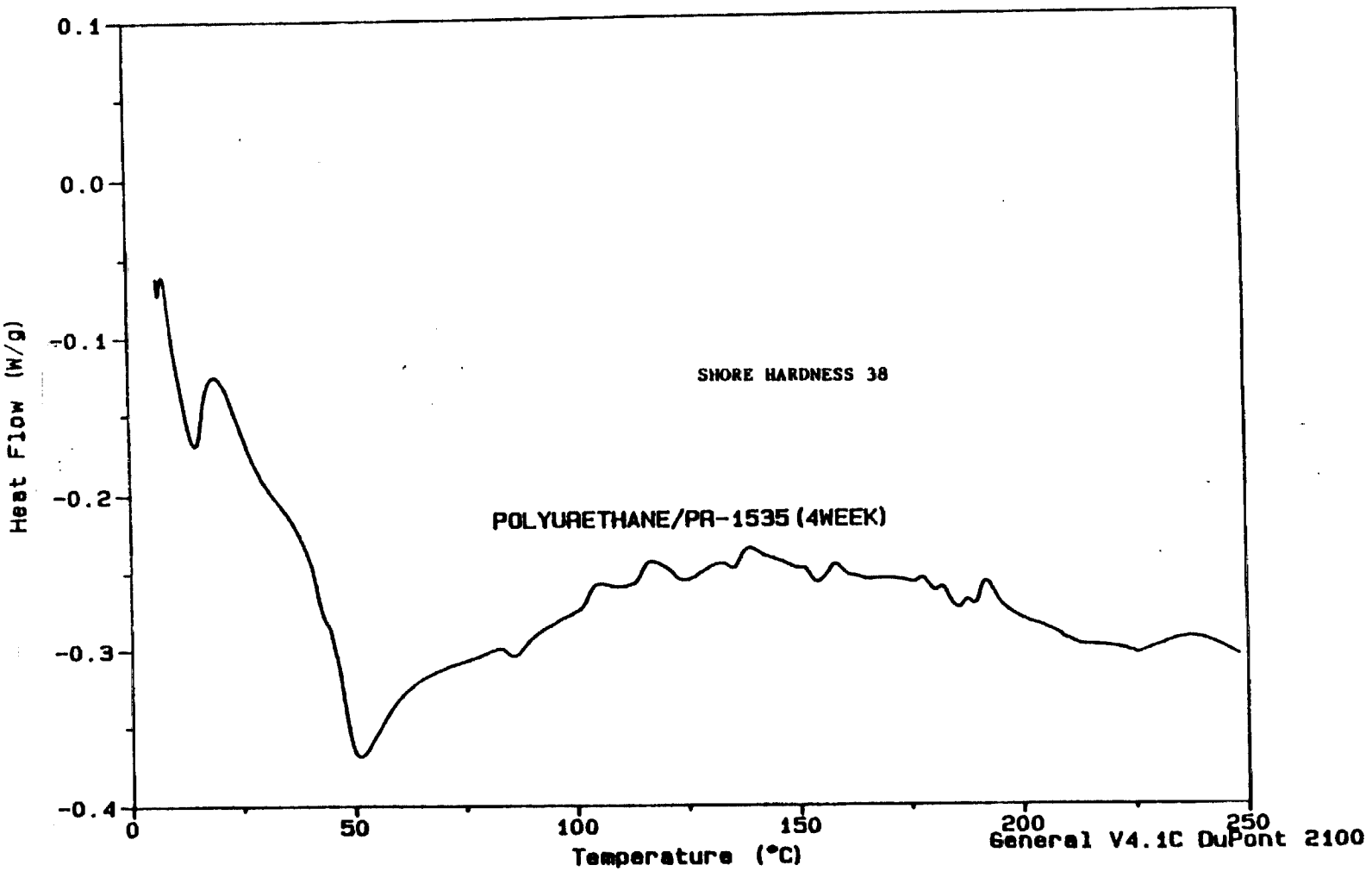

Figure 10. Differential Scanning Calorimeter Curves For Polyurethane PR-1535 (Week 4)

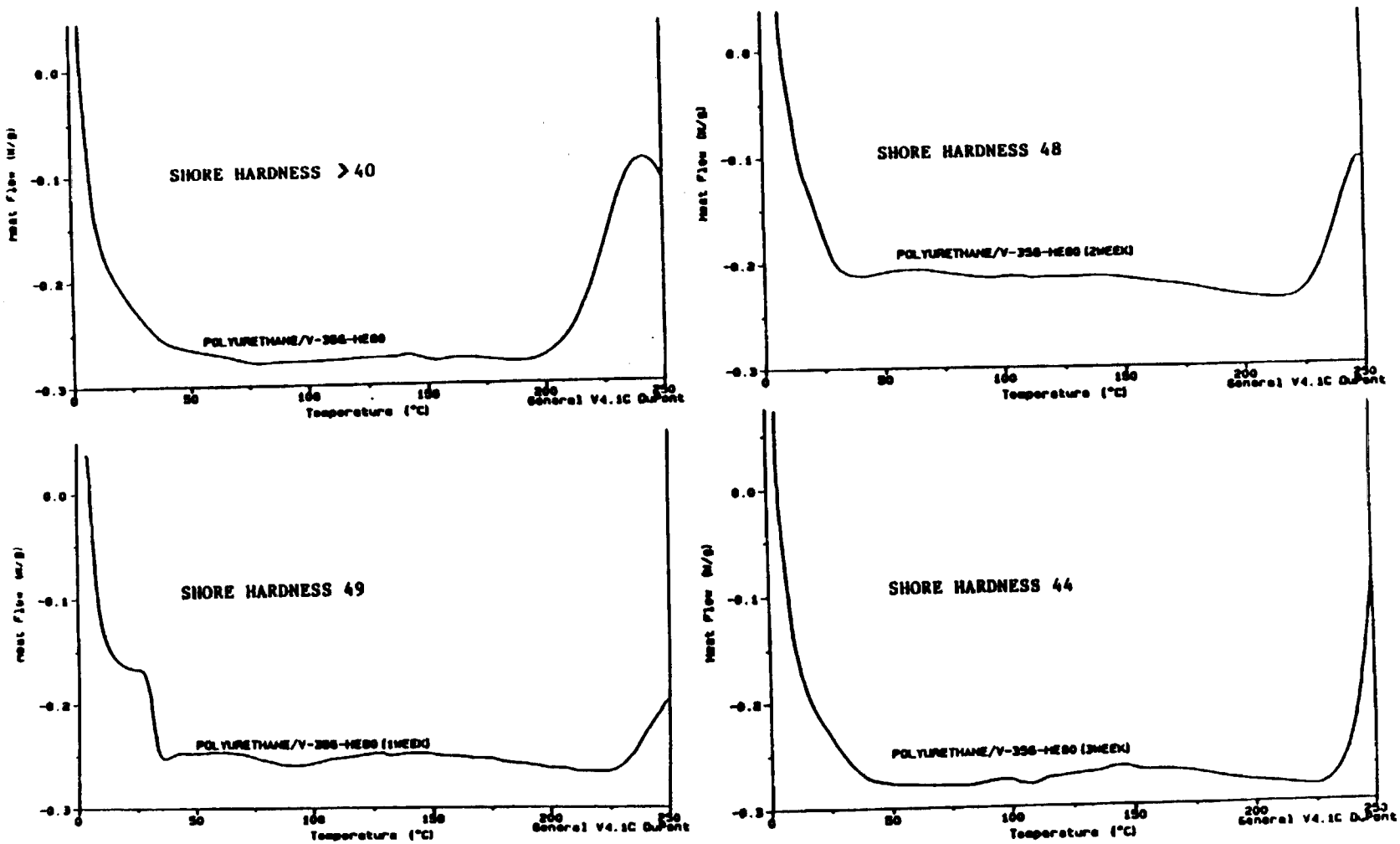

Figure 11. Differential Scanning Calorimeter Curves For Polyurethane V-356-HE80

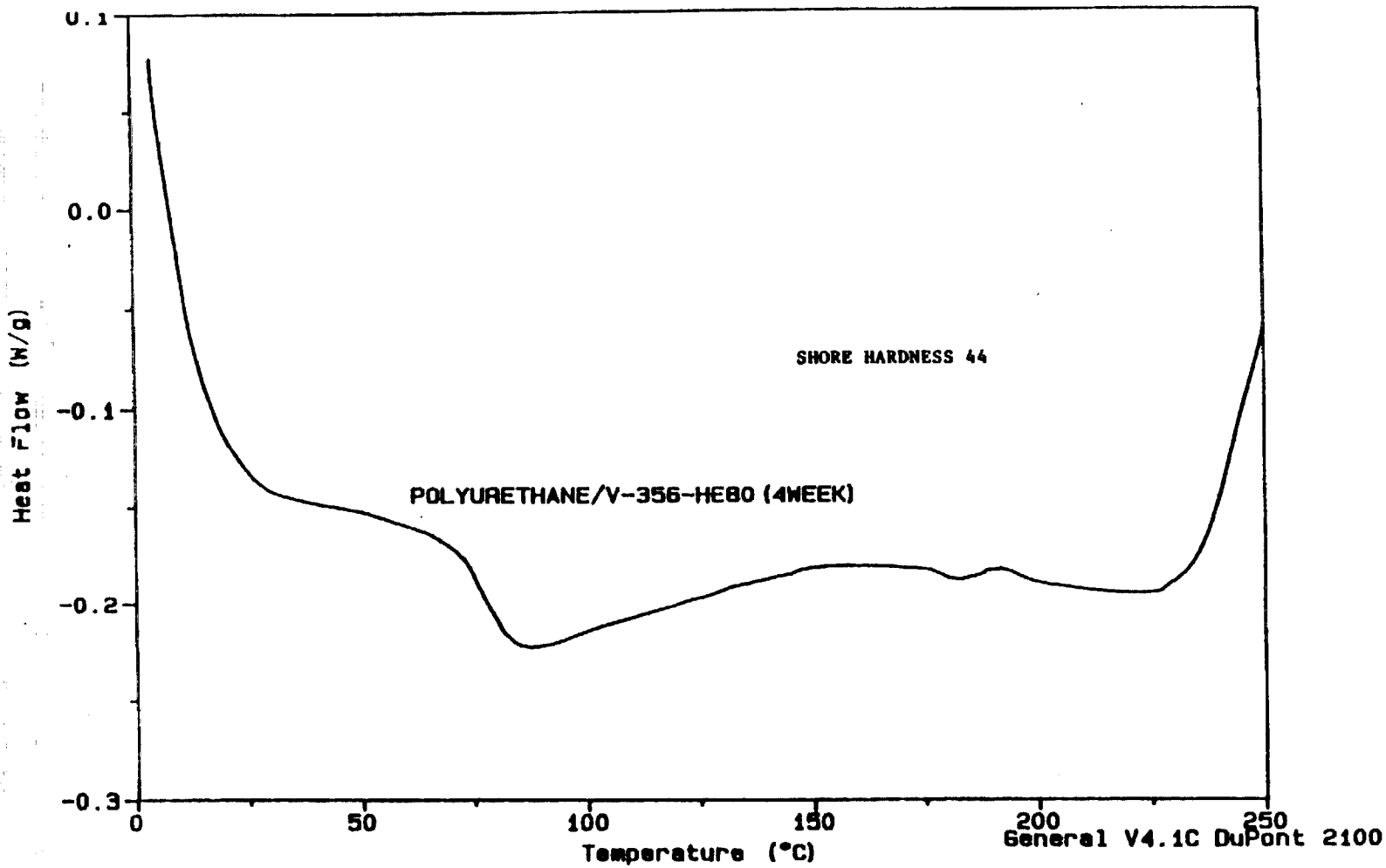

Figure 12. Differential Scanning Calorimeter Curves For Polyurethane V-356-HE80 (Week 4)

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