CARILON® Polymer P1000 Molding and Annealing Studies – Screening for UL Testing

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ABSTRACT

Efforts to obtain a UL relative temperature index for CARILON®[1] polymer P1000 has required that molding and annealing studies be carried out to ensure that conditions are chosen which maximize the retention of mechanical properties during long term heat aging. It has been determined that injection molding variables such as a slow injection rate and a low barrel temperature maximize the heat aging performance of molded specimens. The effects of annealing on mechanical properties were determined between temperatures of 70-110°C. Based on UL test criteria of tensile strength and impact strength, annealing will only benefit the retention of impact properties.

Key words: CARILON polymer, injection molding, annealing, oven aging, mechanical properties, impact, tensile, UL

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CARILON® POLYMER P1000 MOLDING AND ANNEALING STUDIES - SCREENING FOR UL TESTING

by

C. E. Ash, M. Londa, R. P. Gingrich, R. E. Garrett, N. E. Peck

INTRODUCTION

A recognized standard in the industry for comparing the long term heat aging characteristics of polymeric materials, especially engineering thermoplastics, is the UL relative temperature index. The long term polymer property evaluation of UL746B establishes a temperature rating below which a "material maintains its characteristics over a reasonable period of time." During the development of CARILON polymers, various estimations for its UL index have been made, but no formal attempts have been made to establish the value.[2] Efforts are underway to establish the UL index for CARILON polymer P1000. However, appropriate molding conditions and an annealing protocol were needed prior to undertaking long term UL testing. This technical information record documents the results of these studies. Critical molding conditions have been identified which should maximize CARILON polymer's ability to age well at elevated temperatures.

The UL746B standard establishes temperature indices based on an Arrhenius method which defines the time of failure when the property being measured falls to 50% of its original value. The standard leaves room in defining the original value since many polymeric materials undergo property changes upon annealing due to stress relaxation and post-crystallization. For CARILON polymer, it has been previously reported that the level of crystallinity and concomitant mechanical properties change quickly during the first stages of oven aging.[3] UL generally allows the window for defining the initial property values by permitting up to 40 hours of preconditioning at the lowest aging temperature. Therefore, the effects that annealing in an inert atmosphere between 70-110°C have on the physical properties of CARILON polymer P1000 were investigated prior to submitting samples for UL testing.

EXPERIMENTAL

CARILON® polymer P1000, lot# 01QMA0021, LVN of 1.84 dL/g, COT of 25 min, and additive package #27 was used in these studies. Standard 1/8 inch ASTM test specimens were prepared by injection molding dried pellets using an Engel 250 ton molding machine and a mold temperature of 200°F. The injection rate and barrel temperature were varied from 0.5-2.5 in/sec and 240-280°C, respectively.

Samples for property analysis were conditioned at 23°C and 50% relative humidity for at least 48 hours prior to testing. An Instron model 1123 with a 1000 lb reversible load cell, crosshead speed of 1.6 in/min, jaw separation of 4.5 in., and type 1 tensile bar was used for tensile testing. For Izod impact strength, a Baldwin impact tester with a 2 lb hammer was utilized.

Specimens were annealed in vacuum ovens under a nitrogen purge at 70°C, 90°C, or 110°C. Samples were withdrawn at 0, 4, 8, 16, 24, 40, and 72 hours. Specimens that were heat aged were placed in a forced air Blue M oven set at 150°C for 24 or 90 hours.

SUMMARY OF RESULTS

Injection Molding / Oven Aging

It was observed that injection molding at injection rates above 0.5 in/sec resulted in specimens which contained very fine surface imperfections in the form of ribs or chatter marks. The texture was not overwhelmingly obvious but occurred regardless of the barrel temperature. Specimens molded at 0.5 in/sec were smooth and free of any texture. Concerns over the effects this surface texture might cause to mechanical properties, as-molded and upon accelerated heat aging, prompted an investigation of specimens molded at injection rates of 0.5 and 2.5 in/sec and barrel temperatures of 240°C, 260°C, or 280°C.

Results tabulated in Appendix 1, demonstrate that as-molded tensile and Izod properties are virtually independent of the barrel temperature, injection speed, and whether the specimens contained any surface texture. CARILON® polymer properties are thus very forgiving when tested as-molded. However, specimens with surface imperfections could be quickly differentiated upon aging at 150°C. After 24 hr at 150°C, specimens containing the ribbed surface texture had less than one half the elongation to break compared to the smooth surface specimens. During elongation of the samples, it was observed that the surface defects provided surface tears to be generated, which ultimately resulted in premature part failure. Surface texture did not influence other tensile properties, however all samples showed upon 24 hr aging an increase in both elongation and stress at yield. Upon further aging for 90 hours, all samples were so extensively degraded that no yield was observed.

It was observed that while as-molded mechanical properties were not influenced by barrel temperature, this variable did affect the retention of tensile strength after aging at 150°C. After 90 hours at 150°C, the specimens molded with lower barrel temperatures exhibited significantly higher strength, Appendix 1. This was most likely the result of somewhat greater melt damage at the higher processing temperatures which accelerates oxidative degradation.

Annealing

To determine the effects of annealing on the mechanical properties of CARILON polymer P1000, one set of molding conditions was chosen (barrel temp = 260°C, injection speed = 0.5 in/sec, mold temp = 200°F). The samples experienced a significant change in mechanical properties upon annealing, Appendix 2. Tensile yield stress increased with both annealing time and temperature. This may be attributed to an increase in overall crystallinity. Consistent with this is a slight decrease in elongation at yield and a reduction in notched Izod impact strength upon annealing. It was also observed that the rates of change with respect to time for Izod and yield properties were very similar, i.e. most of the change occurred within 4 hrs even at the lowest temperature. Due to a large scatter in the data, appropriate trends for tensile break stress and elongation are difficult to distinguish. It is interesting to note that the scatter in break properties for as-molded specimens was extremely tight, however after any annealing the scatter increased dramatically. Although in general, the average values for tensile break stress and elongation decreased compared to the unannealed samples, some samples were able to reach or even exceed the unannealed values, as depicted by the error bars in the appropriate figures in Appendix 2. This may be the result of premature breaks due to stress concentration around molded-in flaws after annealing.

CONCLUSIONS

Failure in UL long term aging is defined as the time when a sample loses 50% of its original value (tensile strength and impact properties) upon accelerated oven aging. Key molding conditions which appear to be beneficial in maintaining CARILON® polymer properties include slow injection rates and low barrel temperatures. These molding conditions have little influence on as-molded properties, but become distinguishing parameters after heat aging. Slow injection speeds (0.5 in/sec) were used to eliminate surface defects, which after heat aging initiated premature failures during tensile elongation. Barrel temperature was varied from 240-280°C, and the lowest barrel temperatures resulted in the greatest retention of mechanical properties after aging.

UL provides for up to 40 hr of preconditioning (annealing) to establish the starting property set before long term heat aging. It is, therefore, beneficial to anneal when lower initial mechanical properties can be obtained. For CARILON polymer, it was observed that Izod impact strength dropped approximately 20-25% upon annealing. Most of the change was within 4 hours and was not strongly dependent on the temperature (70-110°C). Annealing, however, caused a significant increase (11-16%) in tensile strength. This rise was also most dramatic in the first few hours of annealing, but the magnitude of the rise increased with increasing temperature. Therefore, from a UL testing point of view to retain original mechanical properties upon heat aging, annealing CARILON polymer samples will be beneficial for impact properties but detrimental for tensile strength.

ACKNOWLEDGEMENTS

Thanks to John Clasby and Dixie Waters for their collaboration and help with tensile testing.

REFERENCES

1. CARILON is a registered trademark of Shell Oil Company.

2. A UL index of 50°C currently exists for P1000 polymer, but this is only a generic rating given to new polymers without supporting aging data.

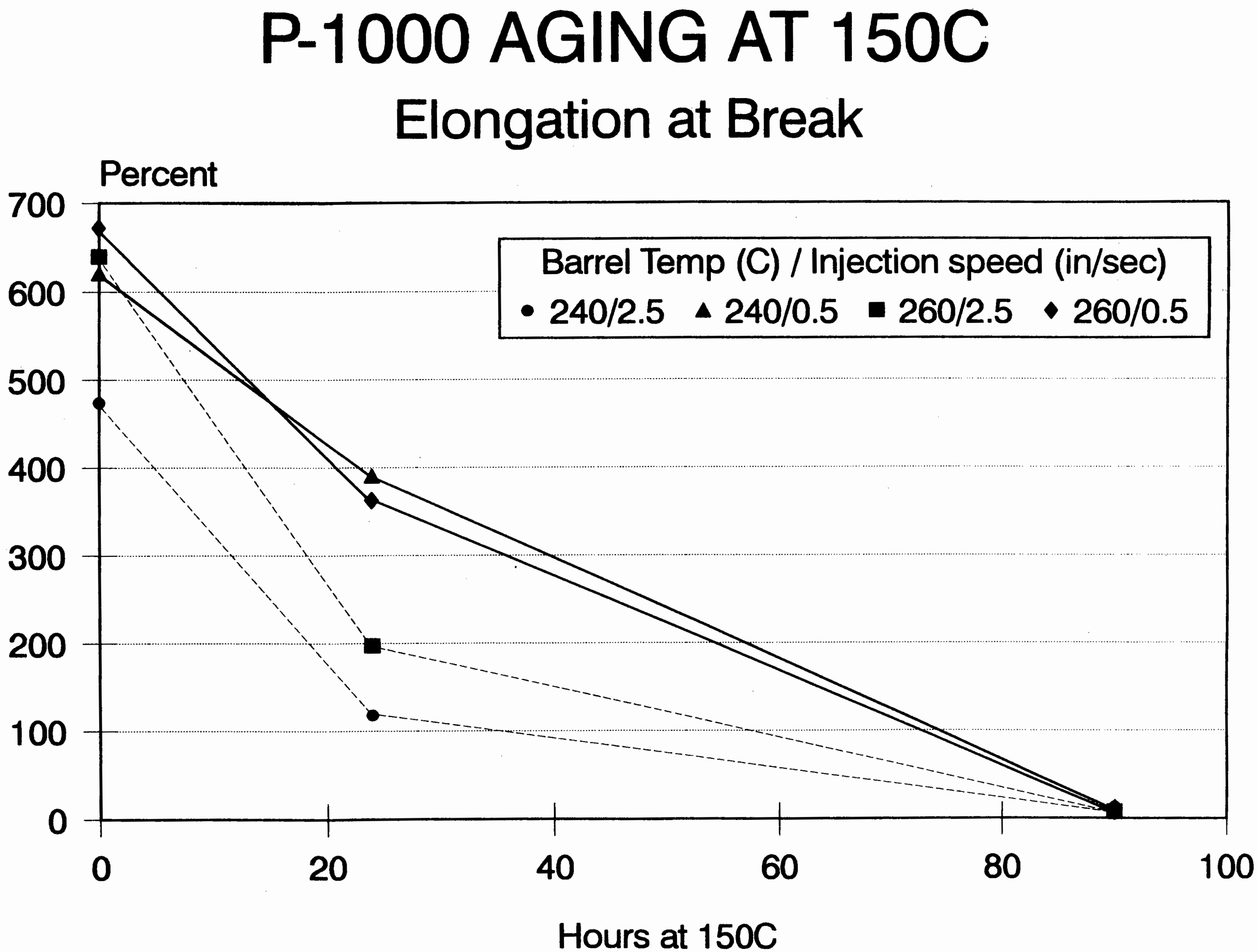
3. J. M. Machado, P. B. Himmelfard, S. C. Tang, R. M. Irwin, J. S. Grebowicz, C. A. McDaniel, M. P. Williams Technical Information Record, WRC-2013, 8/90.

APPENDIX 1

P-1000 Molding / 150C Aging Study - Lot#01QMA0021

SAMPLE							
Barrel Temp (C)	Inj. Speed (in/sec)	Hours @ 150C	ELONG. @ YIELD (%)	STRESS @ YIELD (kpsi)	ELONG. @ BREAK (%)	STRESS @ BREAK (kpsi)	Notched IZOD (ft-lb/in)
240	2.5	0	43.0 +/-1.0	8.82 +/-0.09	474 +/-97	9.20 +/-1.17	5.7 +/-0.4
240	2.5	24	51.1 +/-0.8	9.75 +/-0.05	118 +/-97	7.604 +/-0.11	
240	2.5	90	-	-	13 +/-2	6.90 +/-0.46	1.6 +/-0.2
240	0.5	0	42.0 +/-1.0	8.73 +/-0.08	621 +/-91	10.26 +/-0.94	5.5 +/-0.3
240	0.5	24	50.9 +/-0.4	9.82 +/-0.05	391 +/-189	9.83 +/-1.19	
240	0.5	90	-	-	13 +/-5	6.49 +/-1.33	1.8 +/-0.4
260	2.5	0	40.0 +/-1.0	8.66 +/-0.04	640 +/-40	9.75 +/-0.14	5.2 +/-0.2
260	2.5	24	51.8 +/-0.4	9.96 +/-0.06	197 +/-64	7.67 +/-0.16	
260	2.5	90	-	-	8 +/-1	5.15 +/-0.41	
260	1	0	41.0 +/-1.0	8.67 +/-0.01	616 +/-33	10.48 +/-0.13	5.5 +/-0.2
260	0.5	0	41.0 +/-1.0	8.70 +/-0.08	672 +/-41	10.32 +/-0.04	5.4 +/-0.2
260	0.5	24	52.7 +/-0.6	10.04 +/-0.08	363 +/-156	8.20 +/-0.38	
260	0.5	90	-	-	8 +/-1	5.07 +/-0.44	
280	2.5	0	40.0 +/-0.5	8.65 +/-0.08	649+/-124	9.66 +/-1.26	5.4 +/-0.3
280	0.5	0	41.0 +/-1.0	8.38 +/-0.07	636 +/-7	10.49 +/-0.05	5.4 +/-0.4
280	0.5	24	52.8 +/-0.5	9.94 +/-0.04	246 +/-127	7.82 +/-0.89	
280	0.5	90	-	-	6 +/-1	4.32 +/-0.07	

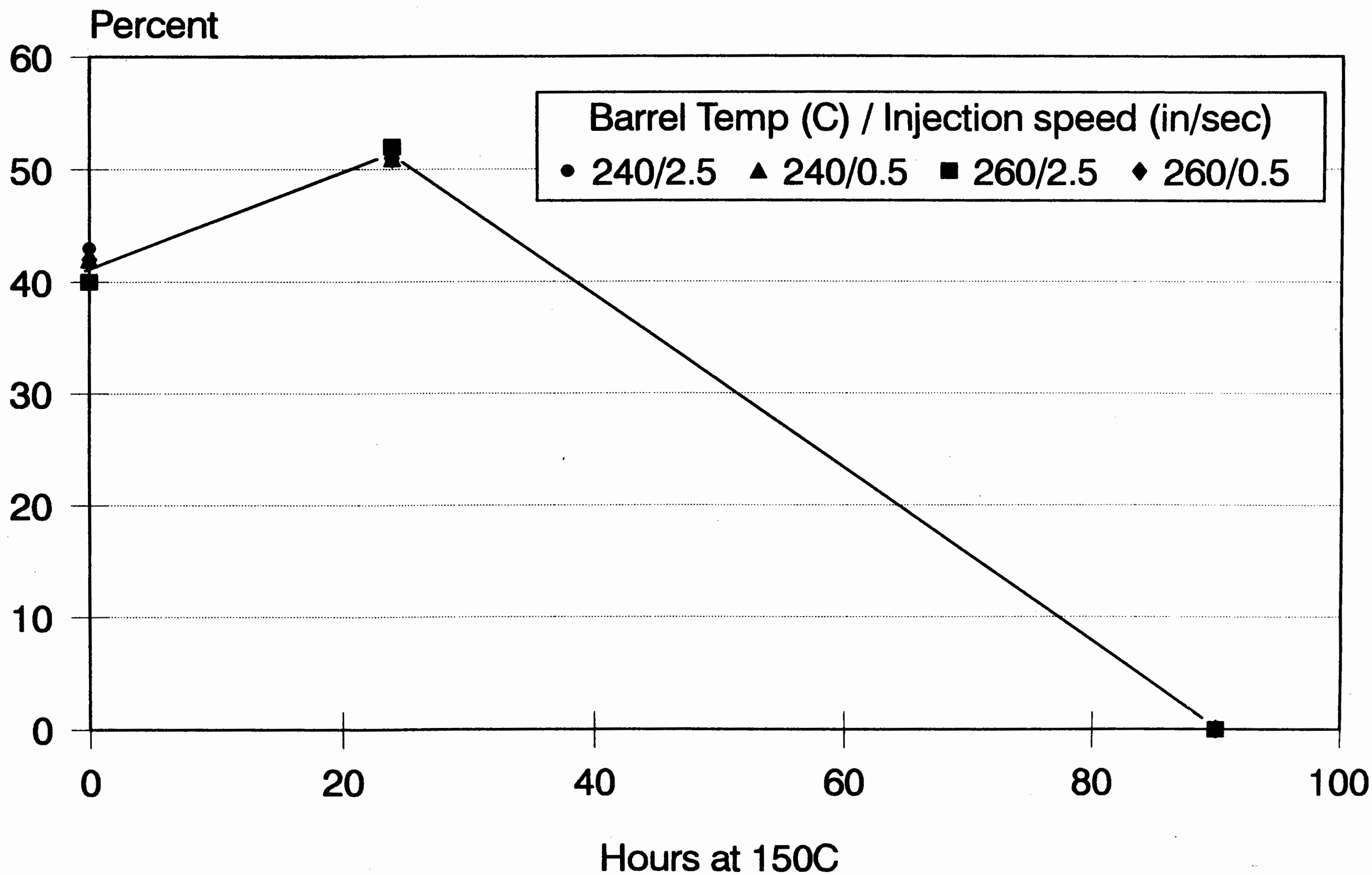
* Injection speed of 0.5 in/sec gave parts of smooth surface finish. Speeds above 0.5 in/sec displayed surface ribs.



Lot#01QMA0021, Mold temp = 200F

P-1000 AGING AT 150C

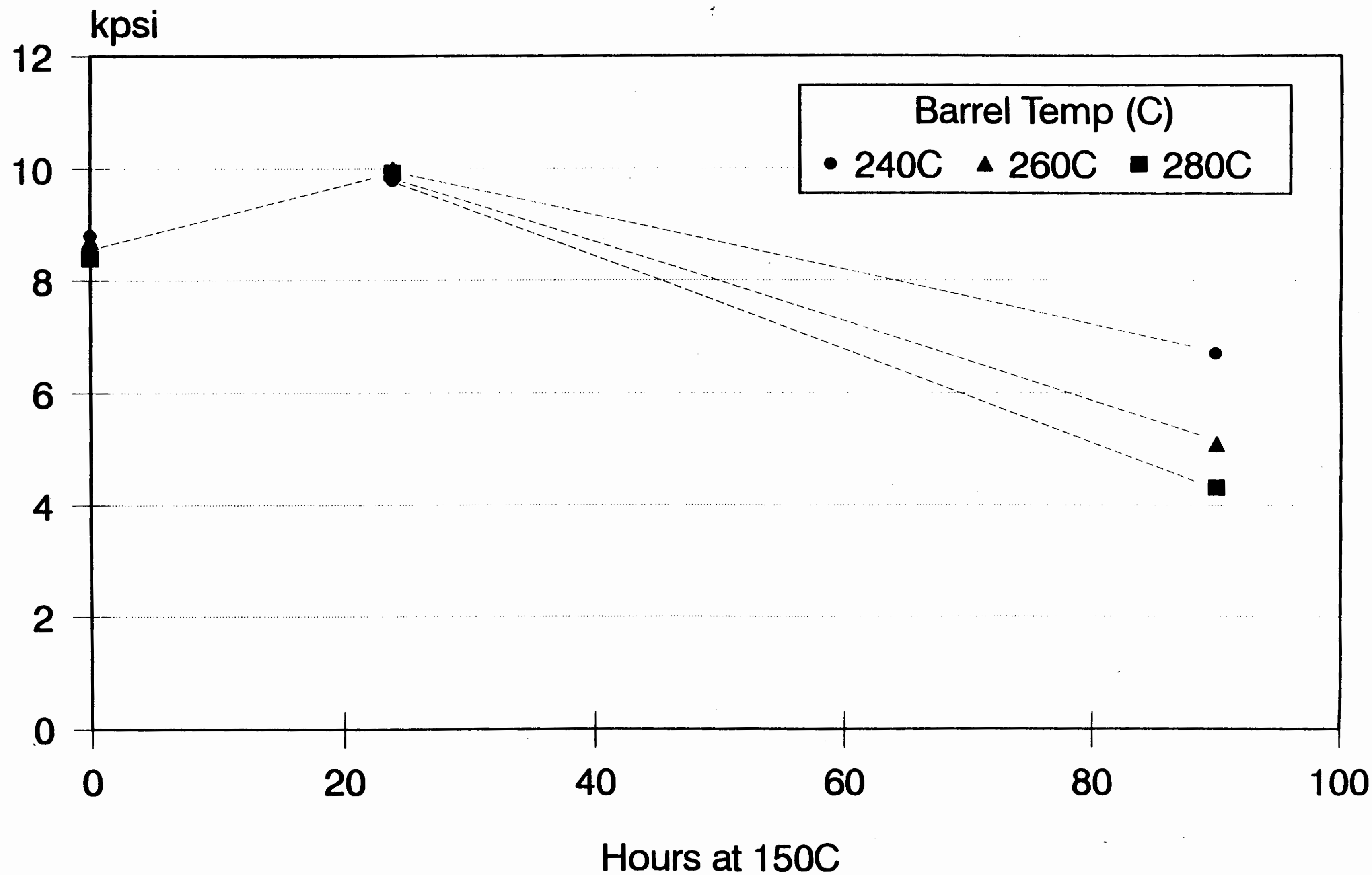
Elongation at Yield



Lot#01QMA0021, Mold temp = 200F

P-1000 AGING AT 150C

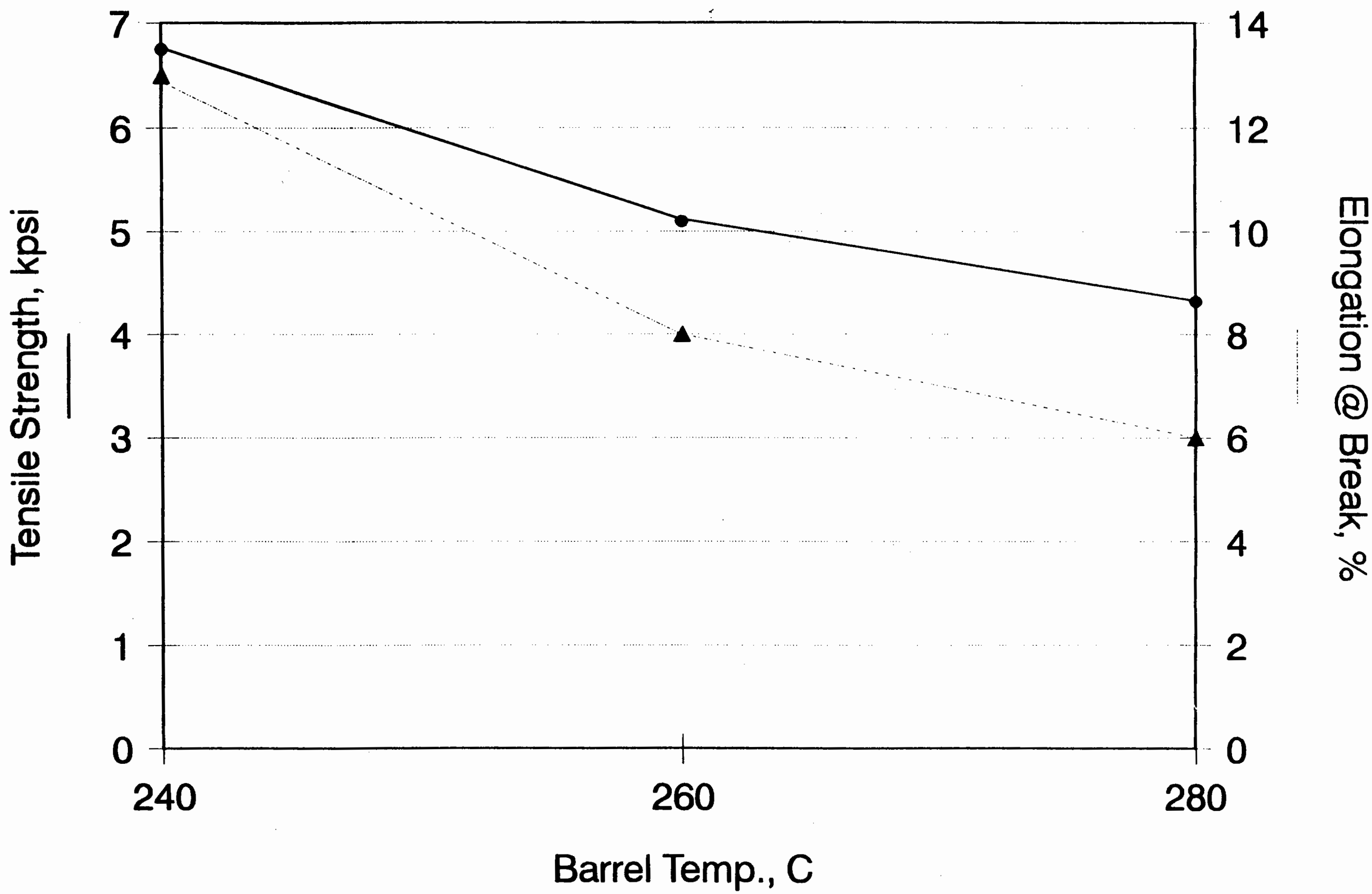
Tensile Strength



Lot#01QMA0021 Mold temp = 200F

P-1000 AGING AT 150C FOR 90 HR

Tensile Properties vs Barrel Temperature



Lot#01QMA0021, Mold temp = 200F

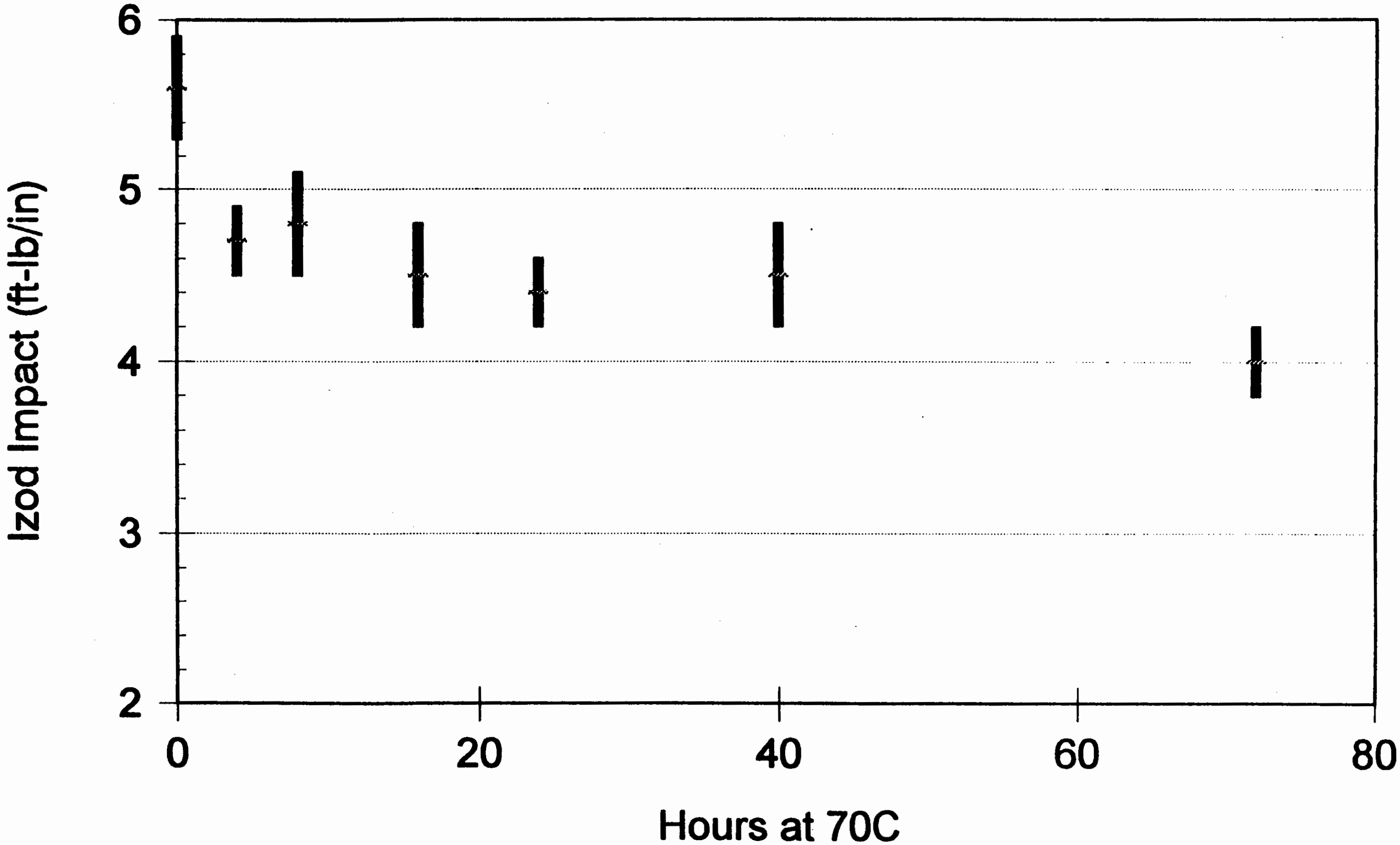
APPENDIX 2

Annealing Study on P-1000, Lot # 01QMA0021
IM Barrel Temp=260C, Inj speed=0.5in/~~min~~ sec, Mold Temp=200F, Conditioned at 23C, 50%RH for at least 48hr

Sample	Notched Izod Impact Strength (ft-lb/in)	Tensile Elongation @ Yield (%)	Tensile Stress @ Yield (kpsi)	Tensile Elongation @ Break (%)	Tensile Stress @ Break (kpsi)
Control	5.61+/-0.26	41.33+/-0.54	8.59+/-0.027	636+/-11.0	10.4+/-0.02
4hr@70C	4.73+/-0.17	38.49+/-0.67	8.86+/-0.086	501+/-104	9.19+/-0.80
8hr@70C	4.78+/-0.28	38.31+/-0.37	9.01+/-0.053	536+/-125	10.0+/-1.2
16hr@70C	4.46+/-0.30	37.2+/-0.37	9.12+/-0.026	604+/-87.5	10.1+/-1.3
24hr@70C	4.35+/-0.17	36.53+/-0.37	9.23+/-0.039	572+/-81.9	10.2+/-0.92
40hr@70C	4.46+/-0.34	37.33+/-0.54	9.30+/-0.091	544+/-111	9.60+/-1.2
72hr@70C	4.02+/-0.16	35.56+/-0	9.61+/-0.021	479+/-60.9	9.15+/-1.0
4hr@90C	4.59+/-0.19	37.60+/-0.51	9.18+/-0.061	479+/-191	8.82+/-1.1
8hr@90C	4.55+/-0.22	37.60+/-0.40	9.32+/-0.047	524+/-55.4	9.42+/-1.4
16hr@90C	4.51+/-0.38	38.04+/-2.1	9.42+/-0.084	440+/-161	8.61+/-0.96
24hr@90C	4.32+/-0.32	39.82+/-0.51	9.59+/-0.056	461+/-103	8.77+/-1.3
40hr@90C	4.39+/-0.09	38.40+/-0.97	9.59+/-0.067	566+/-41.9	10.3+/-1.1
72hr@90C	4.00+/-0.26	36.44+/-0	9.86+/-0.026	356+/-125	8.09+/-0.45
4hr@110C	4.94+/-0.27	39.47+/-0.58	9.40+/-0.064	584+/-79	10.0+/-1.1
8hr@110C	4.70+/-0.52	39.56+/-0.54	9.52+/-0.051	265+/-121	7.50+/-0.74
16hr@110C	4.91+/-0.77	39.11+/-0.44	9.63+/-0.020	420+/-62	8.74+/-0.67
24hr@110C	4.44+/-0.50	39.56+/-0.63	9.80+/-0.043	381+/-118	8.12+/-0.95
40hr@110C	4.11+/-0.13	42.40+/-1.3	9.83+/-0.057	376+/-138	8.35+/-0.44
72hr@110C	4.06+/-0.37	40.53+/-1.0	10.0+/-0.060	288+/-151	8.00+/-0.34

Annealing Study for P-1000

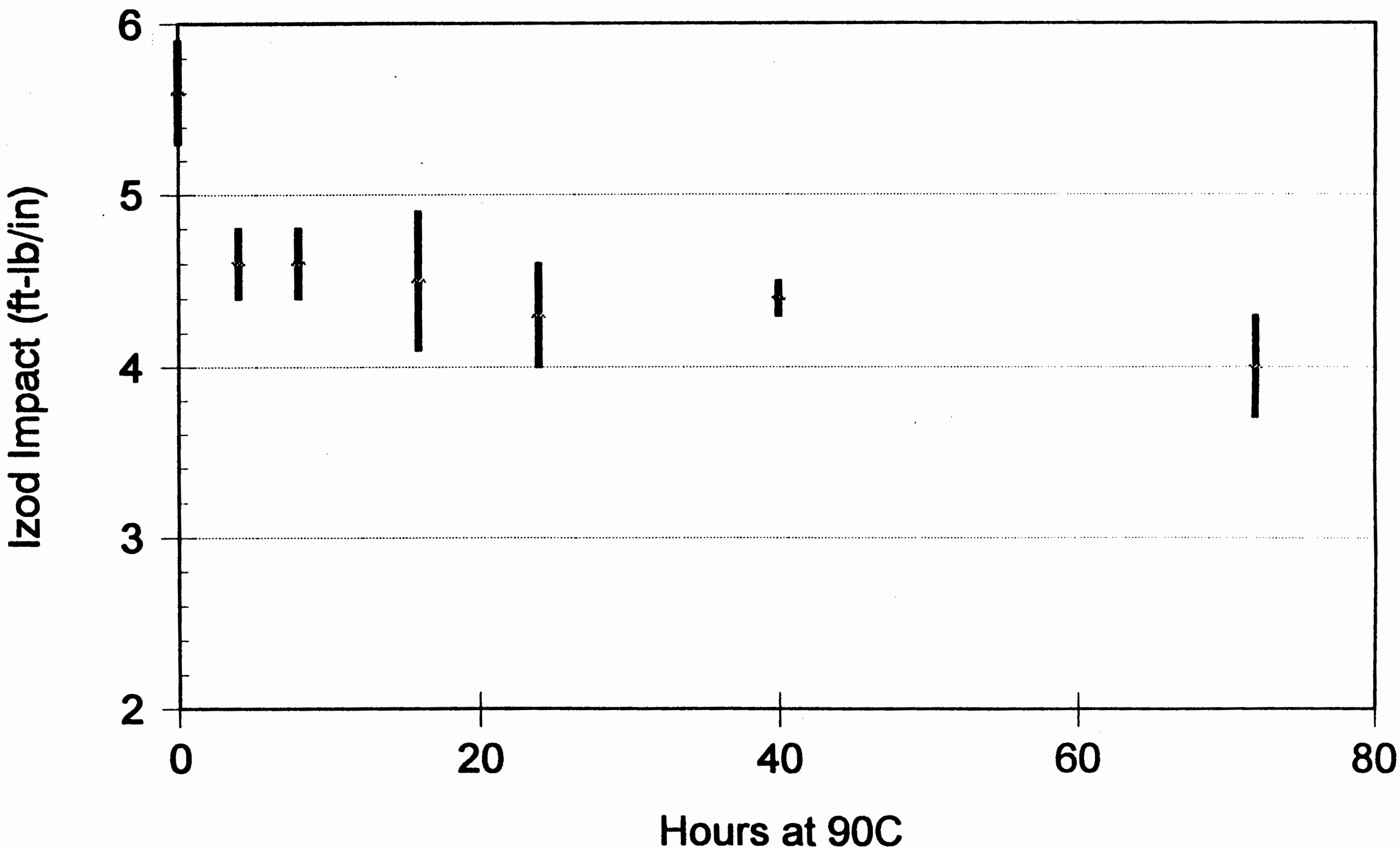
Notched IZOD vs Time @ 70C



Lot#01QMA0021, Barrel = 260C, Inj. = 0.5"/sec, Mold = 200F

Annealing Study for P-1000

Notched IZOD vs Time @ 90C



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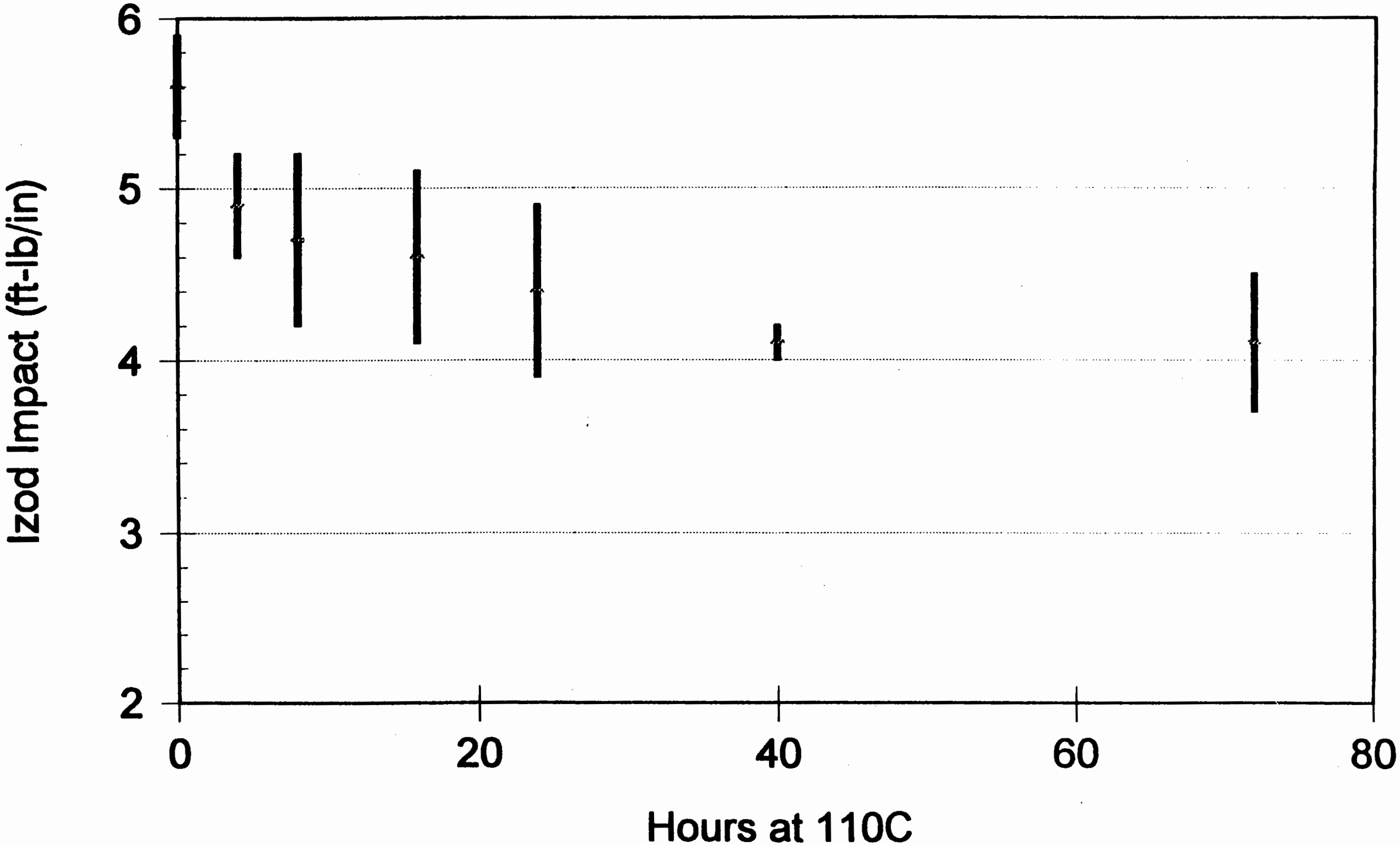
Annealing Study for P-1000

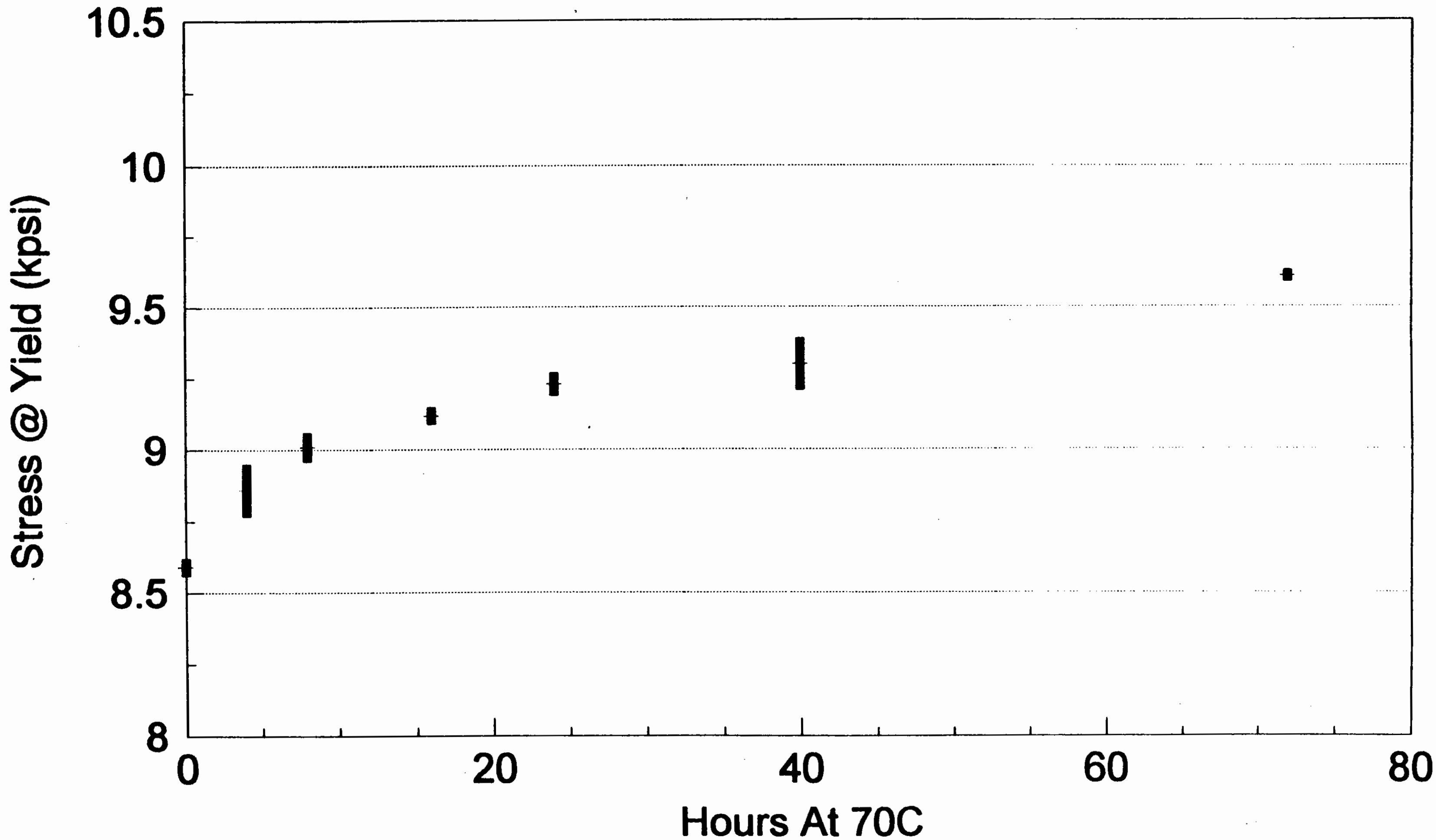
Notched IZOD vs Time @110C



Lot#01QMA0021, Barrel = 260C, Inj. = 0.5"/sec, Mold = 200F

Annealing Study for P-1000

Stress @ Yield vs Time at 70C



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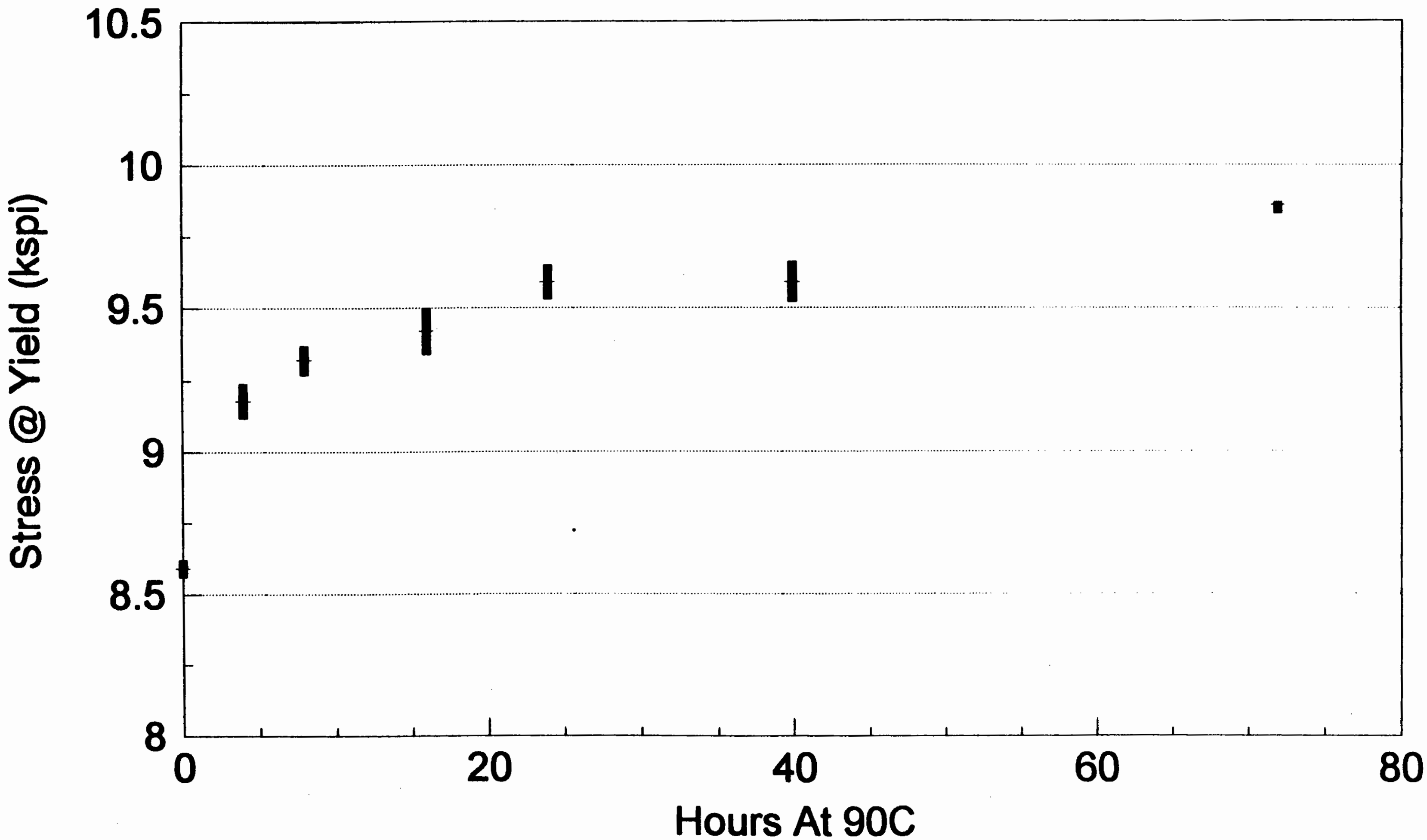
Annealing Study for P-1000

Stress @ Yield vs Time at 90C



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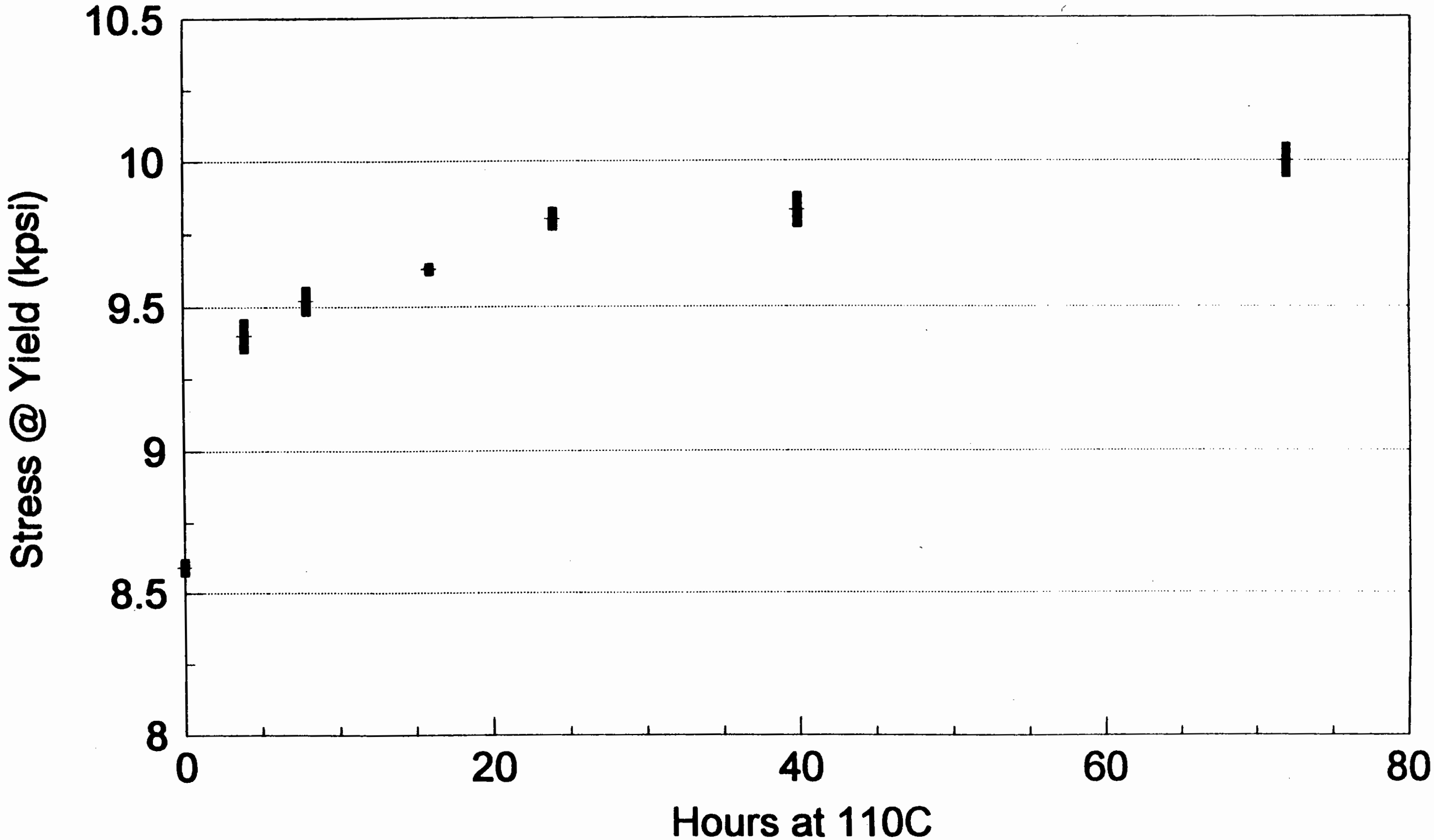
Annealing Study for P-1000

Stress @ Yield vs Time at 110C



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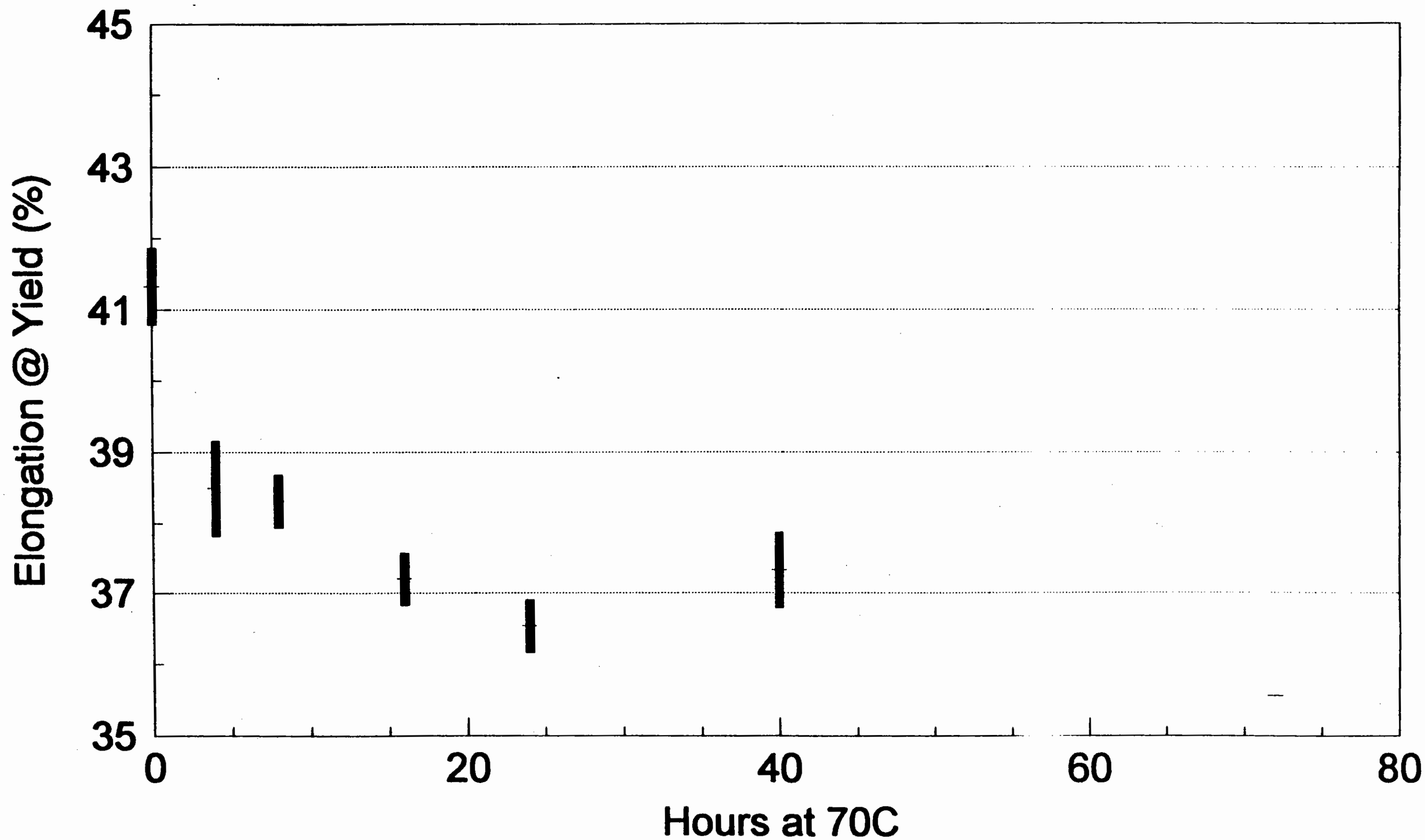
Annealing Study for P-1000

Elongation @ Yield vs Time at 70C



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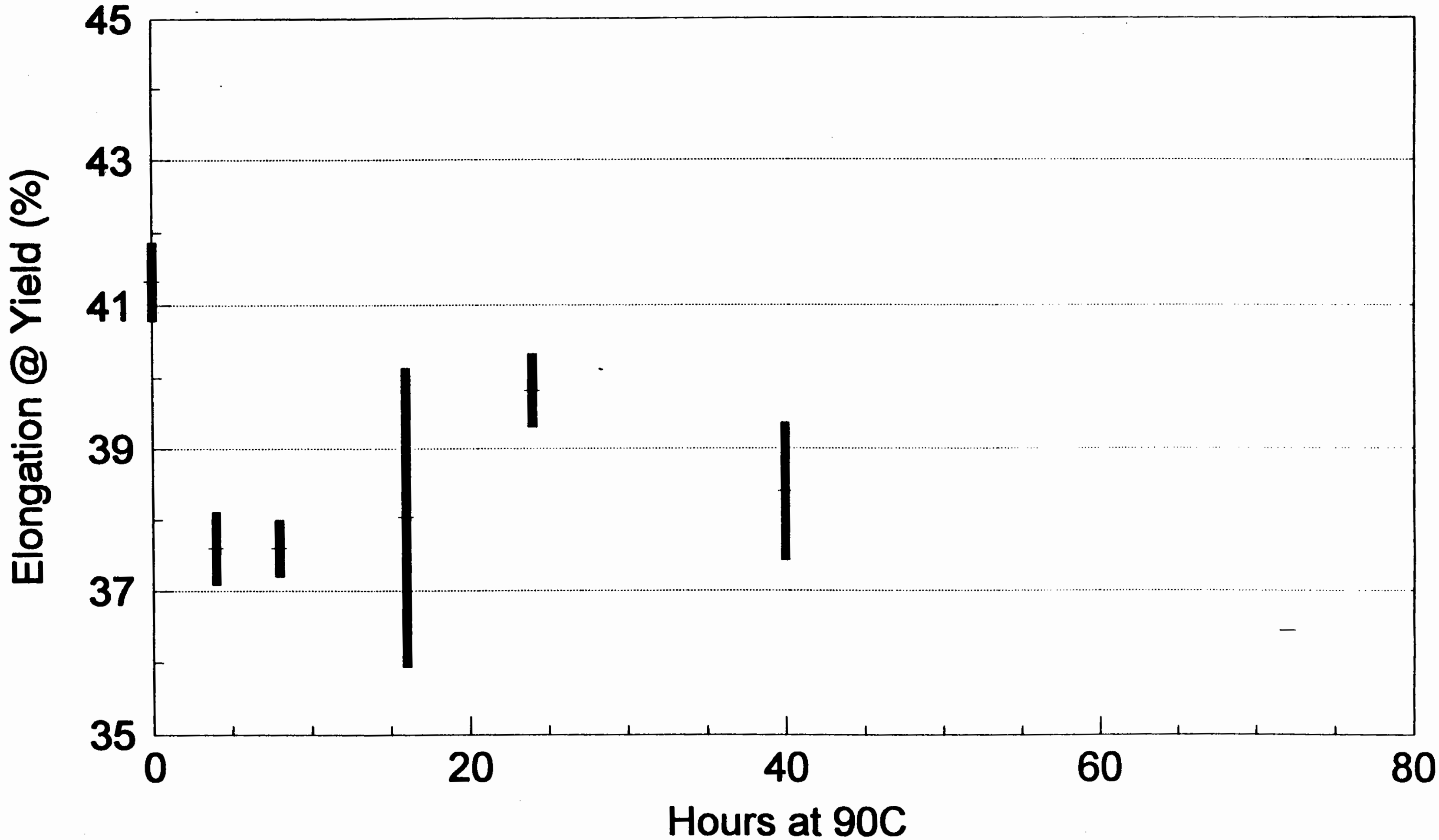
Annealing Study for P-1000

Elongation @ Yield vs Time at 90C



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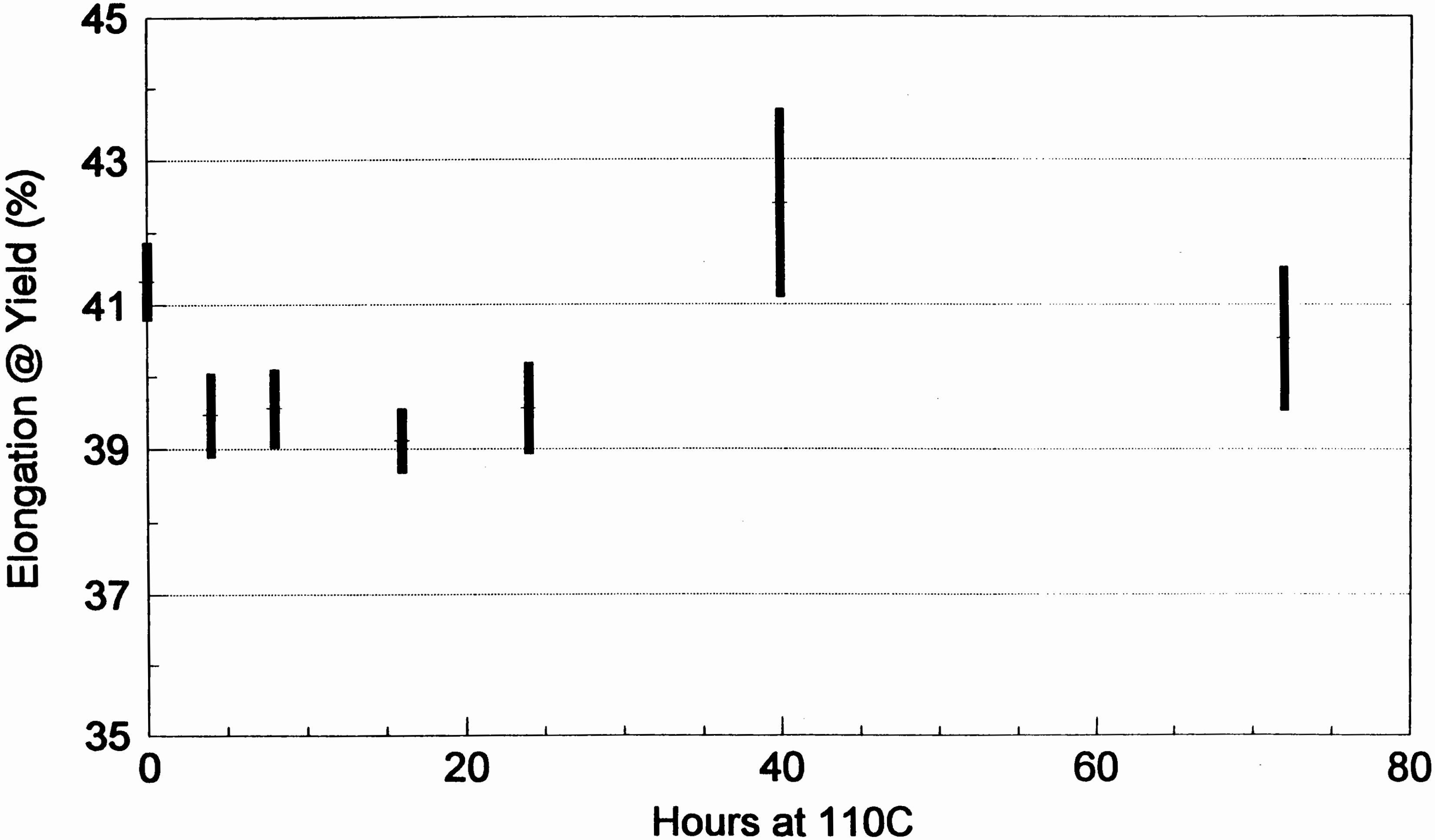
Annealing Study for P-1000

Elongation @ Yield vs Time at 110C



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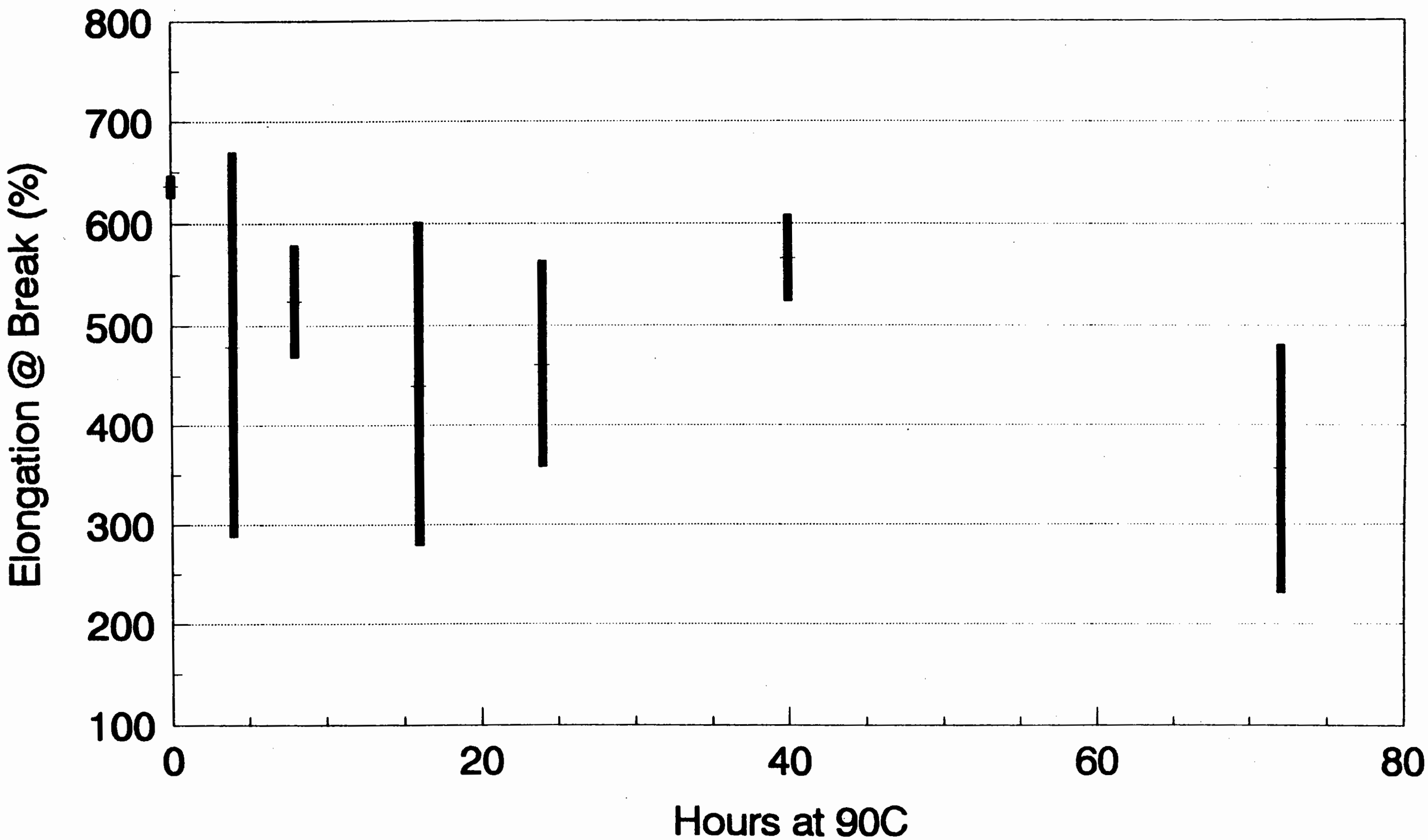
Annealing Study for P-1000

Elongation @ Break vs Time at 90C



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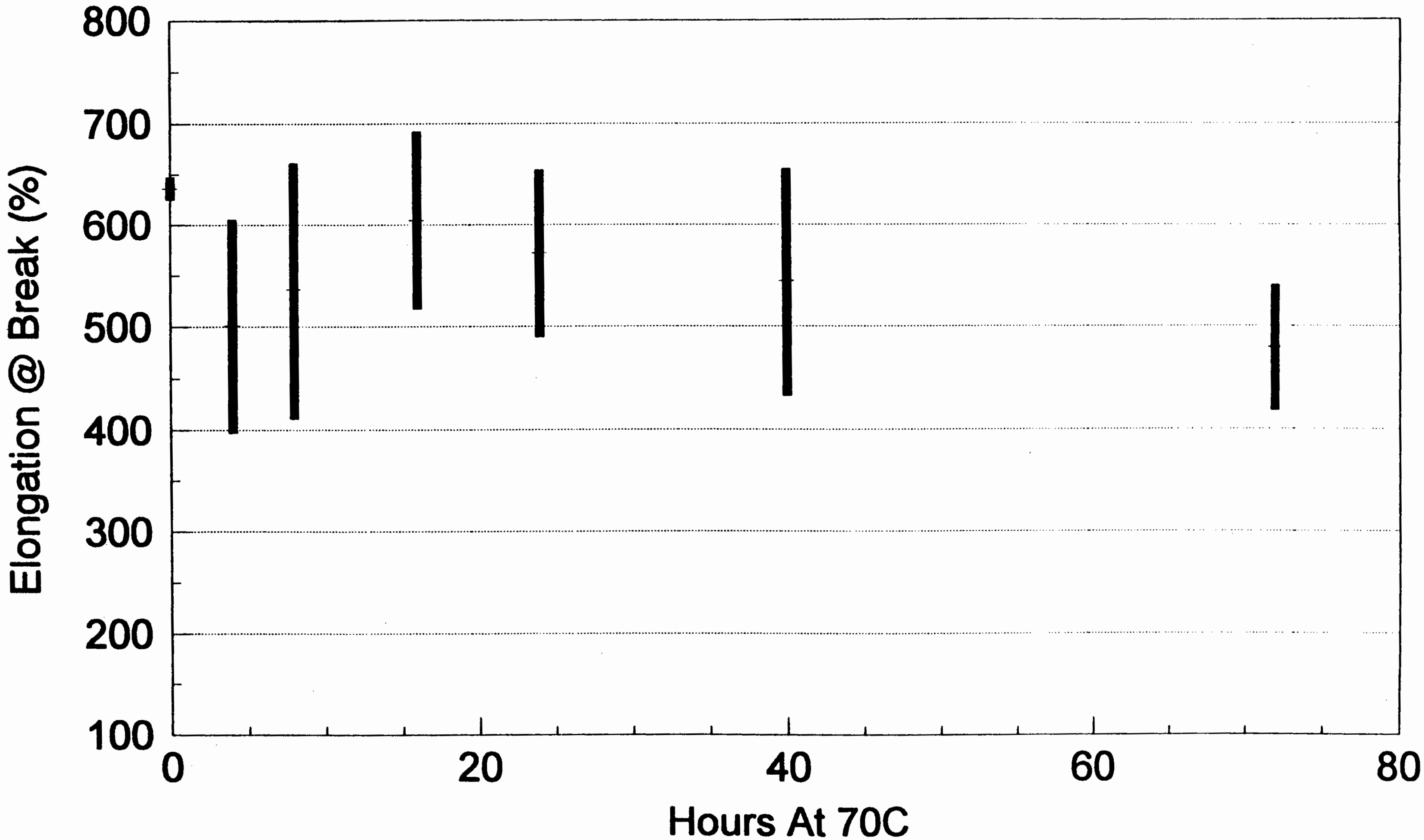
Annealing Study for P-1000

Elongation @ Break vs Time at 70C



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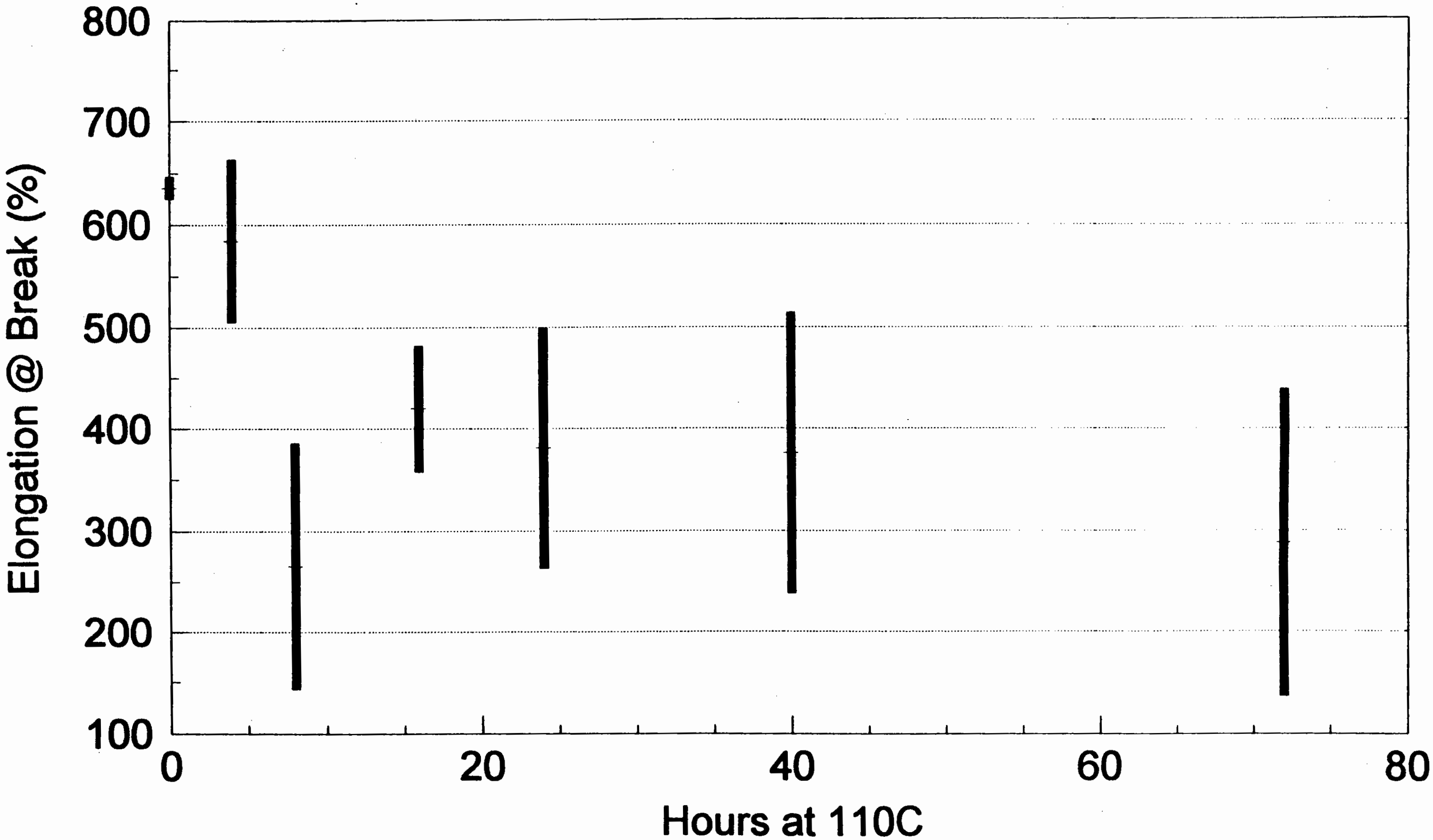
Annealing Study for P-1000

Elongation @ Break vs Time at 110C



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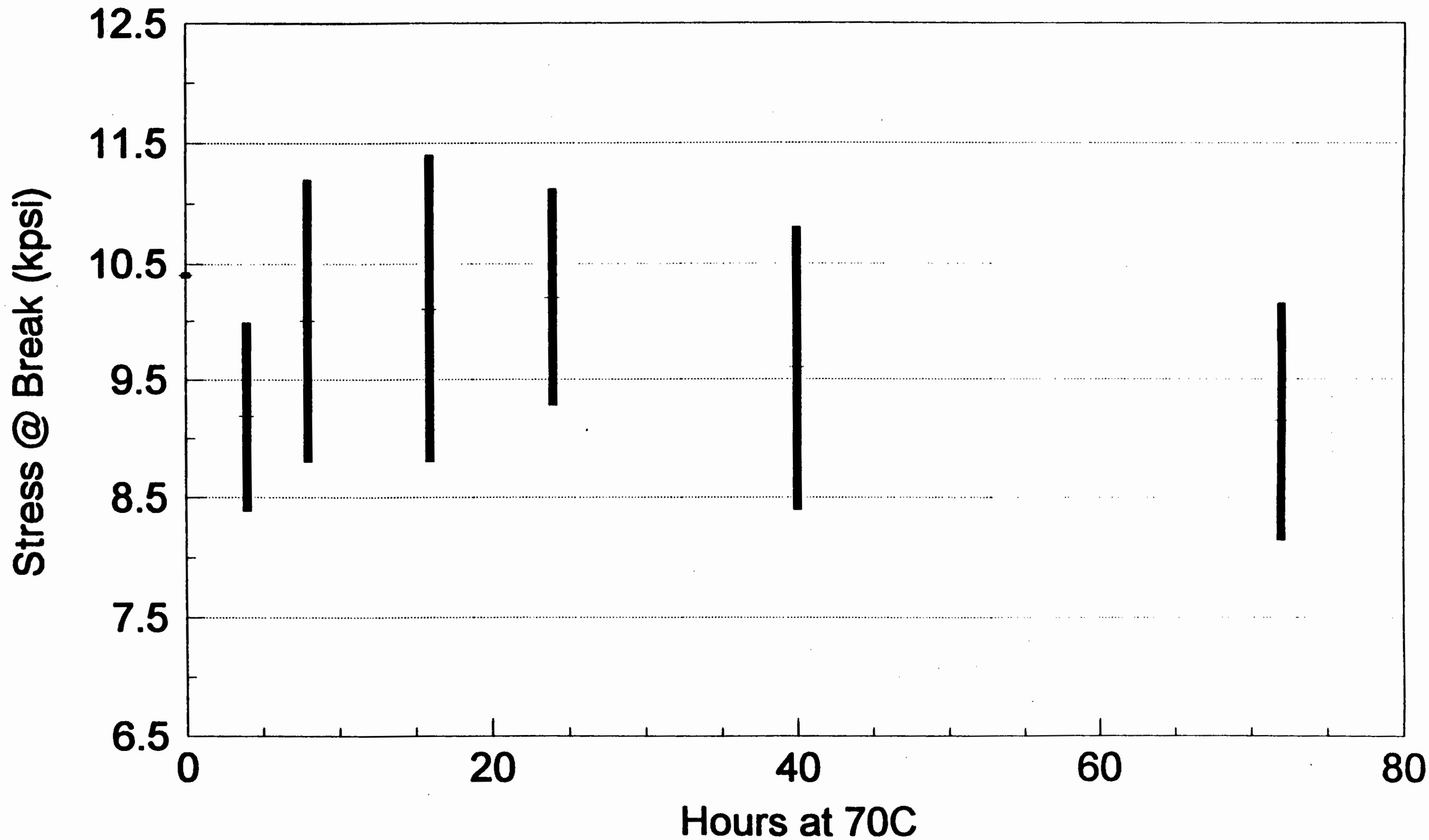
Annealing Study for P-1000

Stress @ Break vs Time at 70C



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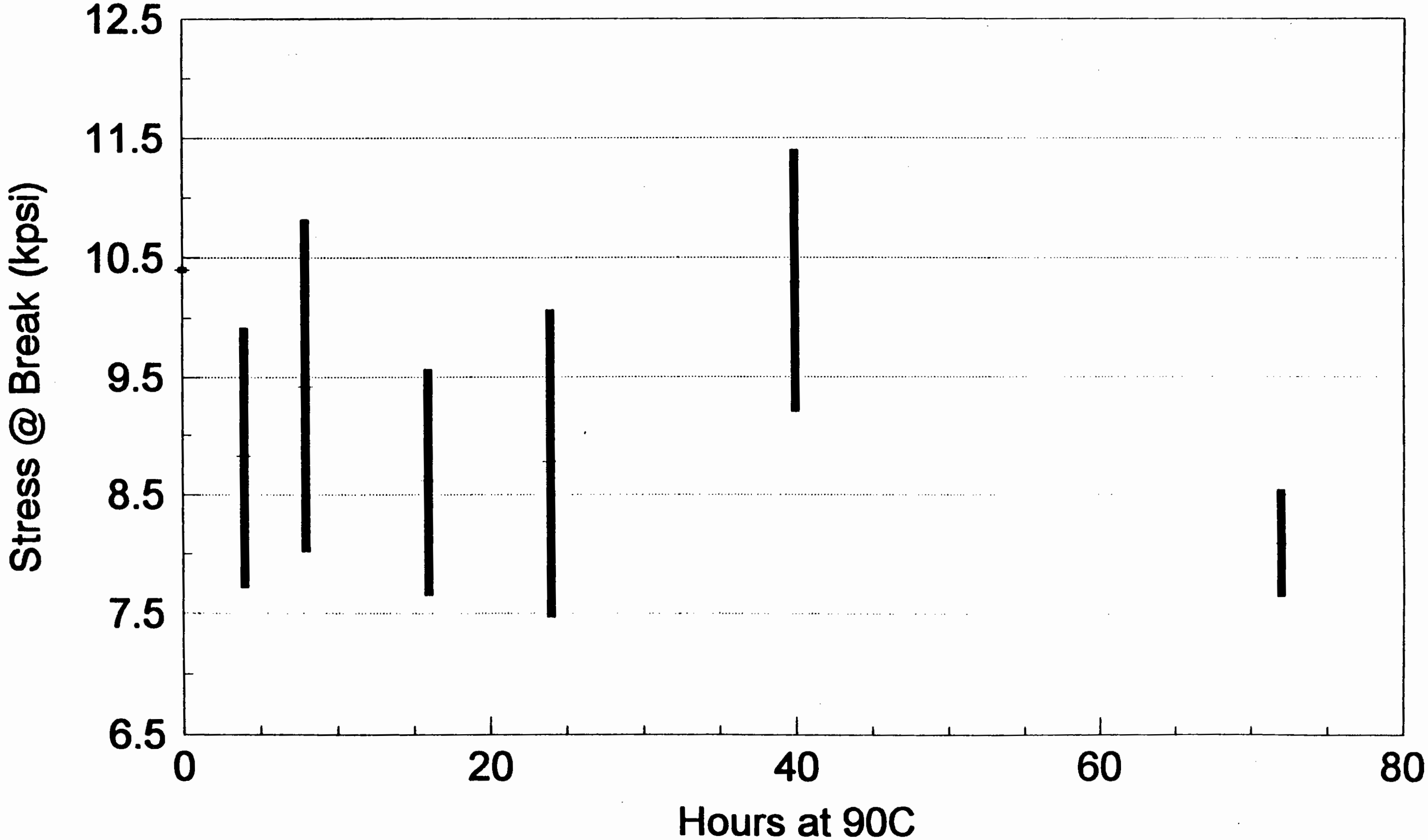
Annealing Study for P-1000

Stress @ Break vs Time at 90C



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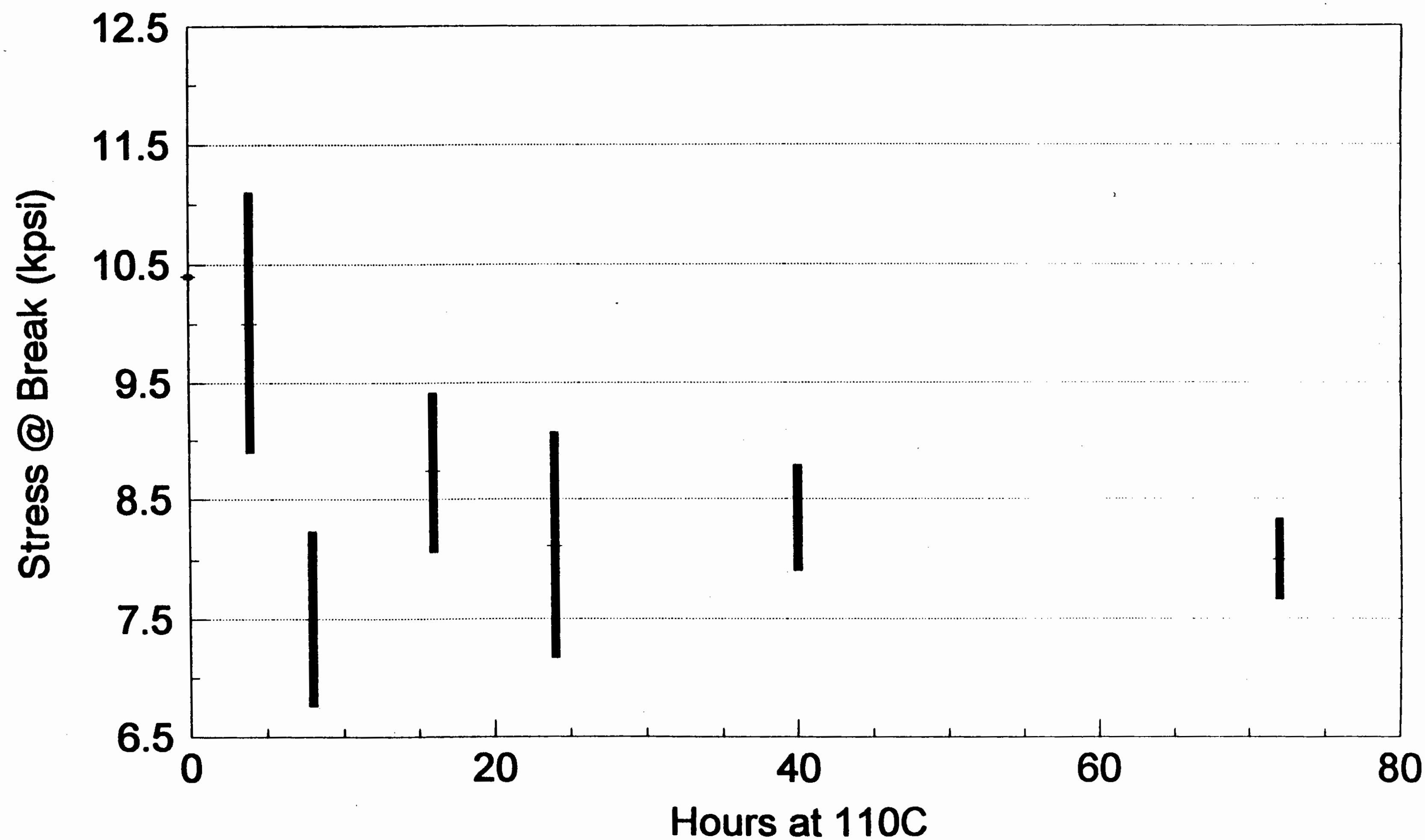
Annealing Study for P-1000

Stress @ Break vs Time at 110C



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