Accelerated Aging of EPDM And Butyl Elastomers

Federal Manufacturing & Technologies

M. H. Wilson

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Final Report

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ACCELERATED AGING OF EPDM AND BUTYL ELASTOMERS

M. H. Wilson

Published June 1996

Final Report
M. H. Wilson, Project Leader

Project Team:
A. V. May
H. C. May
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ABSTRACT

This study was composed of three parts: a postcure study to optimize final properties of an ethylene-propylene-diene (EPDM) formulation, an accelerated aging study to compare the stress relaxation behavior of a butyl and an EPDM elastomer under compression, and a cursory evaluation of a new 70 Shore A EPDM. The optimum postcure for the EPDM was found to be 2 to 4 hours at 182°C in a vacuum. The EPDM was also shown to have superior aging characteristics compared to the butyl and is recommended for use instead of the butyl material. The physical properties for new 70 Shore A EPDM are satisfactory, and the stress relaxation behavior was only slightly inferior to the other EPDM.

SUMMARY

This study was composed of three parts: a postcure study to optimize final properties, an accelerated aging study to compare the stress relaxation behavior of two elastomers under compression, and a cursory evaluation of a new 70 Shore A ethylene-propylene-diene (EPDM) supplied by the University of Akron (Akron, OH). The materials tested for the postcure and accelerated aging studies were a butyl and an EPDM elastomer to be used for O-rings on a weapon assembly. The butyl compound was B612-70, which is a proprietary formulation from Parker Seal Group, O-Ring Division, and the EPDM formulation tested was SS384725. The optimum postcure for the EPDM was found to be 2 to 4 hours at 182°C in a vacuum, and accelerated compression stress relaxation testing showed the EPDM to be far superior when compared with the butyl material.

The postcure study evaluated changes in certain physical properties, solvent swell, and extractables after an air or vacuum postcure at 182°C. Postcuring is recommended because of the improvement in compression set to values lower than 10 percent after 70 hours at 125°C. Postcure times longer than 4 hours did not improve properties and may be detrimental, especially in air. Also, postcuring in a vacuum is preferred in order to achieve optimum properties.

Comparing the accelerated compression stress relaxation behavior is the most appropriate method to determine which material will better meet the O-ring service life requirement of 20 to 25 years. Stress relaxation testing was performed at 70 and 80°C for a maximum of 616 days. To determine whether the method of removing the samples from the oven for measurement adversely affected the stress relaxation behavior, some samples were only measured at the end of the aging period. Removing the samples from the oven for measurement caused no significant difference in stress relaxation behavior from samples that were allowed to remain in the oven continuously. The EPDM was shown to have superior aging characteristics compared to the butyl and is recommended for use instead of the butyl material.

A 70 Shore A durometer EPDM originally requested from the University of Akron was finally supplied for evaluation. The lower durometer was achieved by adding a small amount of polybutadiene rubber and by reducing the level of curatives. Physical properties for this compound are satisfactory, and cursory stress relaxation results are only slightly inferior to SS384725. This new formulation represents a promising lower durometer rubber that would require further characterization before use.

DISCUSSION

SCOPE AND PURPOSE

The purpose of this project was to optimize postcure conditions on a new ethylene-propylene-diene (EPDM) elastomer formulation, SS384725, and to compare the accelerated compression stress relaxation behavior between the new EPDM and a butyl elastomer that is specified for O-rings on a weapon assembly. A new 70 Shore A EPDM from the University of Akron also required a cursory evaluation for comparison with the other EPDMs jointly developed with them. Butyl has been historically specified because of its low permeability; however, excessive compression set measurements from field return units show the butyl to have poor aging characteristics. Accelerated compression stress relaxation testing is the most appropriate method to determine which material will better meet the O-ring service life requirement of 20 to 25 years.

PRIOR WORK

The EPDM elastomer tested in this study was developed under another project: Improved EPDM Elastomer Seal Formulation.

ACTIVITY

This study was composed of three parts: a postcure study to optimize final properties, an accelerated aging study to compare the stress relaxation behavior of two elastomers under compression, and a cursory evaluation of a new 70 Shore A EPDM supplied by the University of Akron. The materials tested for the postcure and accelerated aging studies were a butyl and an EPDM elastomer. The butyl compound was B612-70, which is a proprietary formulation from Parker Seal Group, O-Ring Division. Table 1 contains the EPDM formulation tested, SS384725, which was developed and mixed at the University of Akron (given in parts per hundred of rubber [PHR]).

Postcure Optimization Study

The EPDM batch was mixed at Akron and was molded 10 minutes at 177°C at Allied-Signal Inc., Kansas City Division (KCD), into approximately 6 by 6 by 0.075 inch test slabs. The press-cure conditions were established after running an oscillating disc rheometer (ODR) analysis for the EPDM from the prior work. Slabs that were press-cured 30 minutes at 160°C by the University of Akron were also received and were used for a comparison of

Table 1. EPDM Formulation, SS384725

Ingredient	PHR
Nordel 1440	100
Zinc Oxide	5
N-990 Carbon Black	40
N-539 Carbon Black	25
DiCup 40C	12
Vanox ZMTI	2
Rocryl 910	10

extractables by Soxhlet extraction. These slabs were then postcured in either air or a vacuum for 2, 4, or 6 hours at 182°C. The Akron slabs were also postcured for 8 and 24 hours to determine the magnitude of any damage caused from postcuring for longer times by using Soxhlet extraction.

Table 2 contains some of the properties analyzed to optimize postcure time and to determine whether an air or vacuum postcure was preferred. The hardness value is slightly increased because of postcuring, but this property shows no significant difference between an air or a vacuum postcure for up to 6 hours. The values for t_g from the rheometrics mechanical spectrometer (RMS) are also not significantly affected by either air or vacuum postcure.

Table 2 contains the individual compression set values after aging 70 hours at 125°C, and Figure 1 plots the average of these compression set values. Compression set was performed at 25-percent compression according to ASTM-D-395, Method B. Postcuring causes a beneficial decrease in compression set; however, both vacuum and air postcuring improve the compression set to approximately the same range of 4 to 7 percent after 2 to 4 hours of postcure. This is generally a very low compression set for EPDM formulations, and postcuring is recommended on this basis alone.

Figure 2 contains the weight percent extractables after Soxhlet extraction in toluene for 24 hours. Again, postcuring in air and vacuum produced approximately the same change. The Akron molded slabs appear to be slightly more undercured than the KCD molded slabs, as indicated by the larger amount of unbound material extracted. Also, postcure times longer than 6 hours in air can be seen to cause degradation in the EPDM, based on the data for the Akron slab.

Table 2. Effects of Air Versus Vacuum Postcure

Property	No Postcure	Air Postcure, Hours at 182°C			Vacuum Postcure, Hours at 182°C		
		2	4	6	2	4	6
Hardness (Shore A)	78	80	80	81	79	80	79
Compression Set, 70 h at 125°C (%)	10.7, 10.7	6.9, 6.4	4.1, 4.0	--	4.1, 3.3	4.9, 4.9	--
T_g by RMS at max. G" (°C)	-53	-52	-52	-52	-51	-54	-51

Lastly, Figure 3 contains the weight percent swell after immersion for 3 days in toluene. The error bars represent the 95-percent confidence limits about the mean. As expected, postcuring reduces the swell because of additional crosslinking. There is essentially no difference after postcuring 2 hours in air or vacuum, and the vacuum postcuring shows very little change for up to 6 hours in the oven. However, postcuring in air shows a slight degradation after 4 hours; after 6 hours, the divergence between air and vacuum postcuring is statistically significant.

The data indicate that a postcure is warranted and that postcure times should be limited to 2 to 4 hours. Longer postcure times do not produce any significant improvement in properties and may be detrimental to the performance of the rubber. Vacuum postcure is preferred where practical because of the degradation in air shown by solvent swell and also because of visual effects. Air postcured slabs had a dull matte appearance and surface pitting after postcure, whereas the vacuum postcured slabs had no such areas. The surface blemishes were very evident in areas of finger contact. However, based on subsequent physical property and stress relaxation testing, the degradation appeared limited only to the surface.

The surface attack during air postcure was traced to the antioxidant being used: zinc 2-mercaptotolylimidazole (Vanox ZMTI). Replacing this antioxidant with polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (Flectol H) eliminated this problem. Even though vacuum postcuring produced no visual defects, the surface attack from air postcuring warranted a change because of potential applications where vacuum postcure would be impractical or unnecessary. Therefore, the EPDM

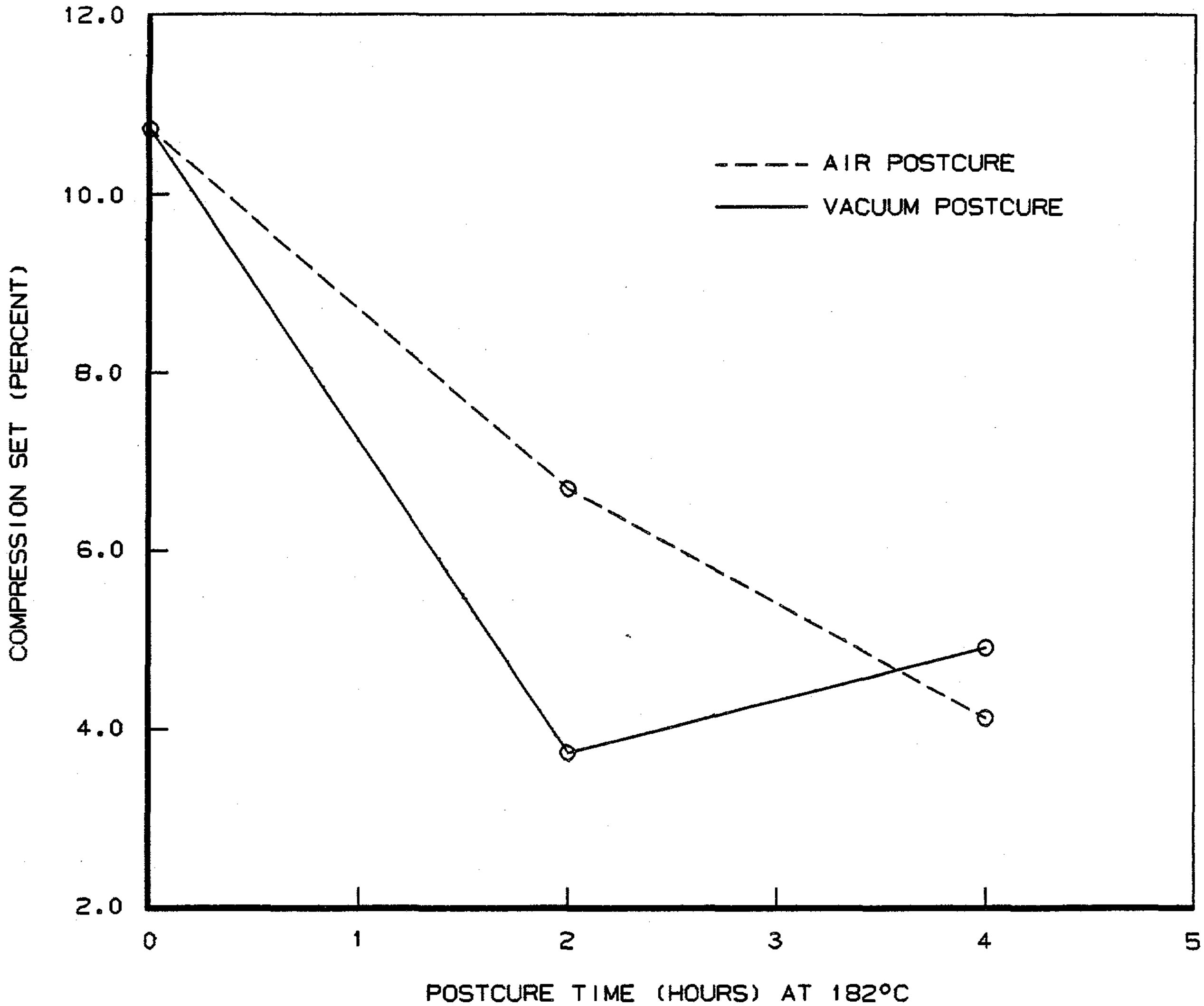


Figure 1. Compression Set Percent Versus Postcure Time of Slabs Press-Cured 10 Minutes at 177°C

formulation has been changed to call out the new antioxidant. The effects of Flectol H on the EPDM formulation have been evaluated in other projects. Generally, Flectol H causes a slight retardation of cure by consuming some of the free radicals generated when the peroxide decomposes. The main effect is a slightly lower hardness value; however, this change is unimportant when compared with the improvement Flectol H imparts in aging behavior and visual appearance after postcure.

Table 3 shows the change in properties for a 2-hour postcure in air at 182°C. All the EPDM batches to date have been vacuum postcured. This table is provided for reference if an air postcure would be used.

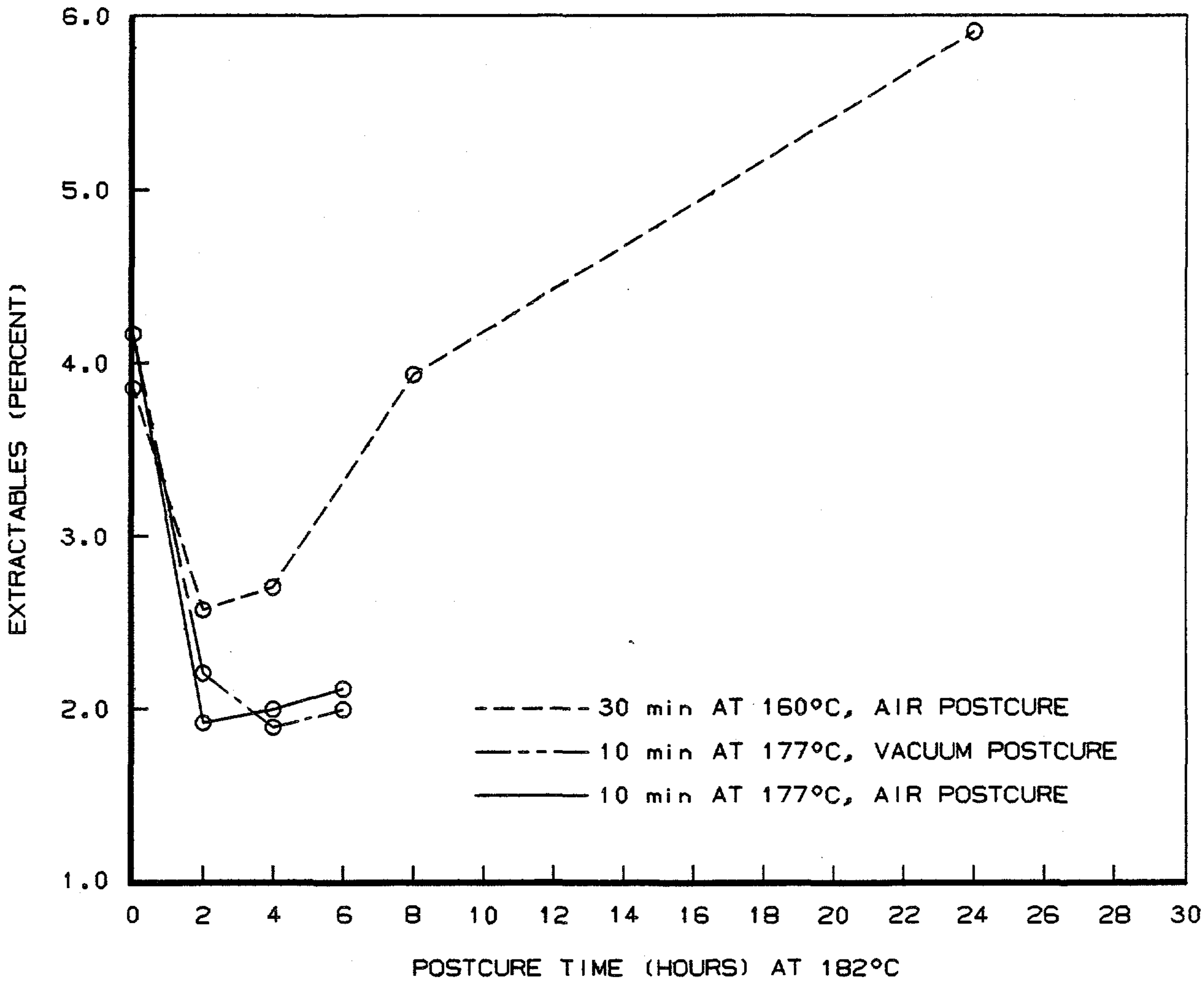


Figure 2. Effect on Extractables With Press-Cure and Postcure Conditions

Stress Relaxation Study

The stress relaxation behavior test of the butyl and EPDM was performed under compression and was used to compare the relative aging behavior between the two materials. The stress relaxation test procedure consists of stacking three disks (approximately 1.575 mm thick by 12.7 mm diameter) for each of three stress relaxation fixtures and then compressing the stacked samples within the fixtures by approximately 25 percent. One to 2 minutes after compressing the samples, the initial resultant compressive force is measured. The fixtures are then placed in an oven at the desired aging temperature. Periodically, the fixtures are removed from the oven and allowed to cool to room

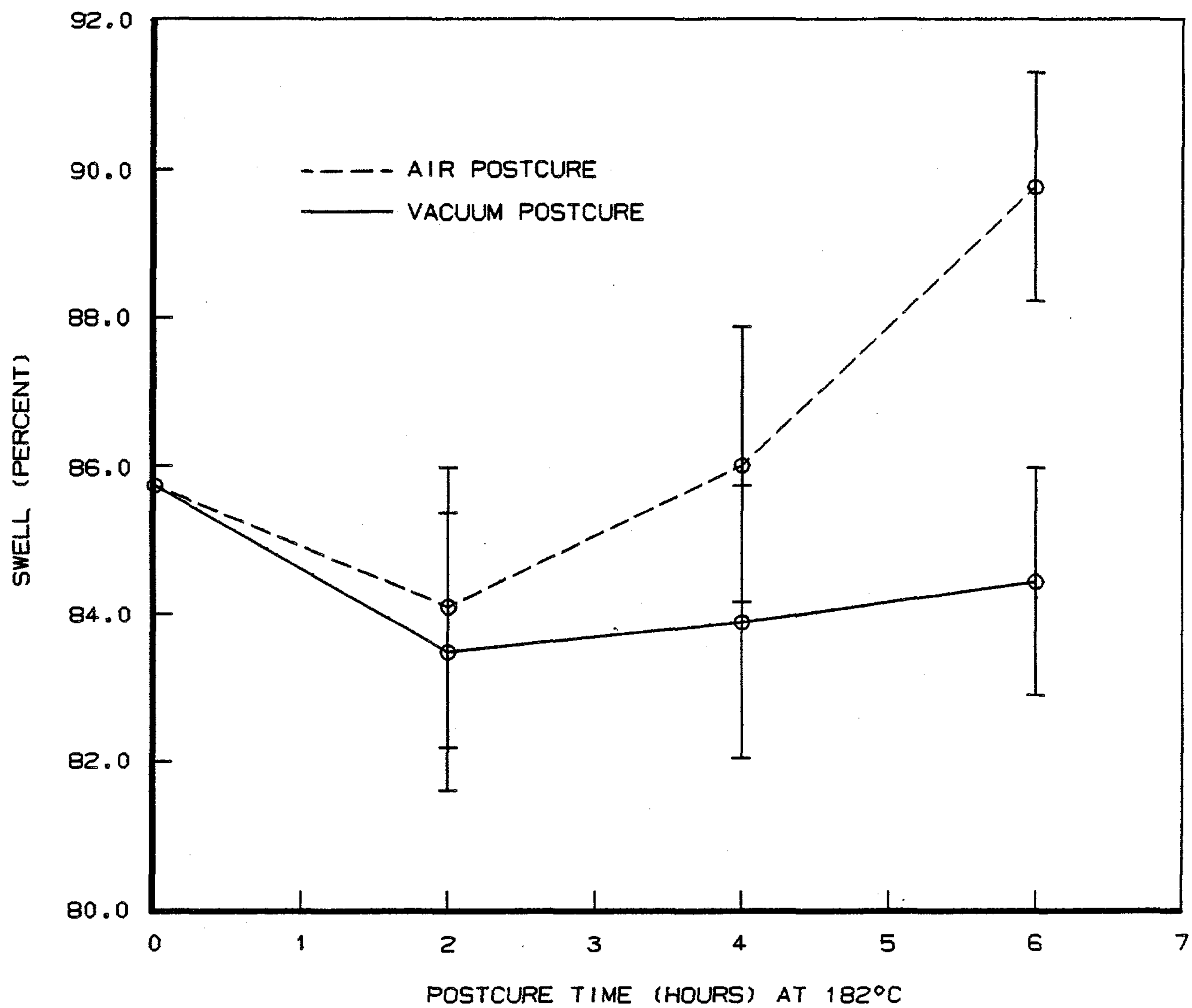


Figure 3. Weight Percent Swell in Toluene Versus Postcure Time of Slabs Press-Cured 10 Minutes at 177°C

temperature for approximately 3 to 4 hours, after which the resultant compressive force is again measured. The amount of decay in force is the stress relaxation, and any permanent decrease from original sample height is the compression set. At the completion of the test, the compression set for the three samples is measured 30 minutes after the material is removed from the fixtures.

Figure 4 shows a stress relaxation fixture, and Figure 5 shows the force measuring instrument with a fixture in place ready to

Table 3. Physical Properties Before and After a Postcure of 2 Hours at 182°C in Air

Property	No Postcure	Postcure
Hardness (Shore A)	78	80
100% Modulus (psi)	1370	1400
Tensile Strength (psi)	1780	1500
Elongation (%)	124	108
Compression Set, 70 h at 125°C (%)	10.7, 10.7	6.9, 6.4

be measured. This equipment is manufactured by H. W. Wallace & Co. Ltd., Croydon, England. The force measurement is automatically displayed after an electrical contact is broken within the fixture, signifying that the applied force is equal to the force exerted by the test sample. This method results in negligible sample deformation during measurement.

Originally, the materials were to be aged for 1 year at 60°C, 6 months at 70°C, and 3 months at 80°C. However, there was so little difference in stress relaxation of the EPDM between 70 and 80°C, it was decided not to run stress relaxation at 60°C. Instead, the stress relaxation data for 70 and 80°C were collected beyond the original time periods of 6 and 3 months, respectively.

The EPDM formulation tested for stress relaxation used Vanox ZMTI as the antioxidant and was postcured in air. The stress relaxation testing was begun before the antioxidant was changed to Flectol H. Even though vacuum postcure is preferred, the air postcure was chosen to represent a worst case condition for the EPDM. The postcure optimization data from the previous section indicate that the stress relaxation behavior for a vacuum postcure should be equivalent to superior for an air postcure. The use of Flectol H should also provide stress relaxation behavior that is equivalent or superior to a formulation using Vanox ZMTI. These conclusions are supported by aging behavior performed in other projects.

Figures 6 and 7 compare the stress relaxation behavior between butyl and the EPDM at 70 and 80°C, respectively. The stress relaxation curves are expressed as a ratio of the stress remaining, F(t), divided by the initial closure force, F(0).

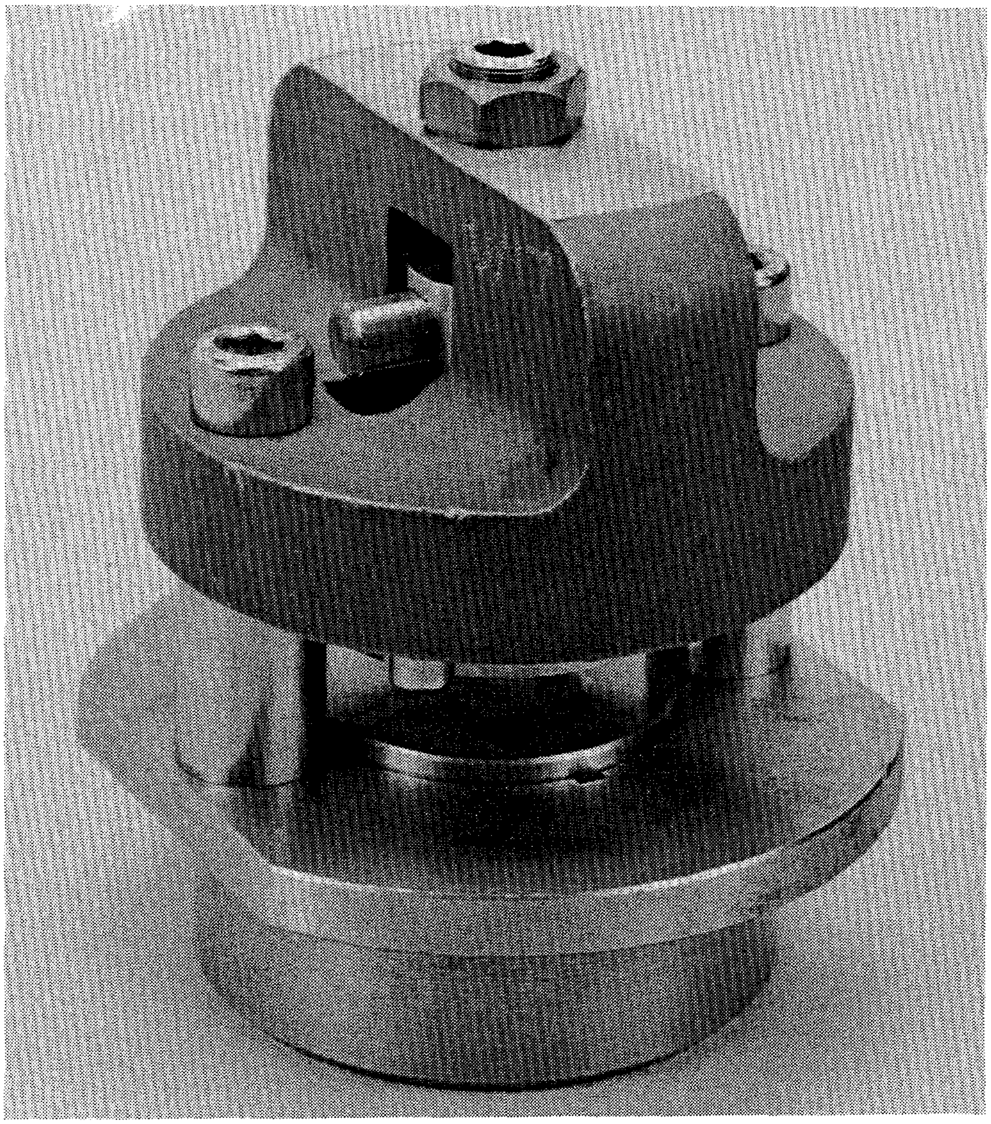


Figure 4. Compression Stress Relaxation Fixture

Both figures show that the EPDM has outstanding stress relaxation behavior when compared with the butyl. The stress relaxation for the EPDM is very stable and exhibits essentially linear decay that indicates only physical relaxation processes are predominant for the 616-day time period of the test. Butyl, on the other hand, shows chemical relaxation effects by the nonlinear behavior of the stress relaxation.

The EPDM-1 curve (Figure 7) represents material tested in new fixtures. The standard deviation among the three fixtures was felt to be higher than preferred; therefore, a second set of

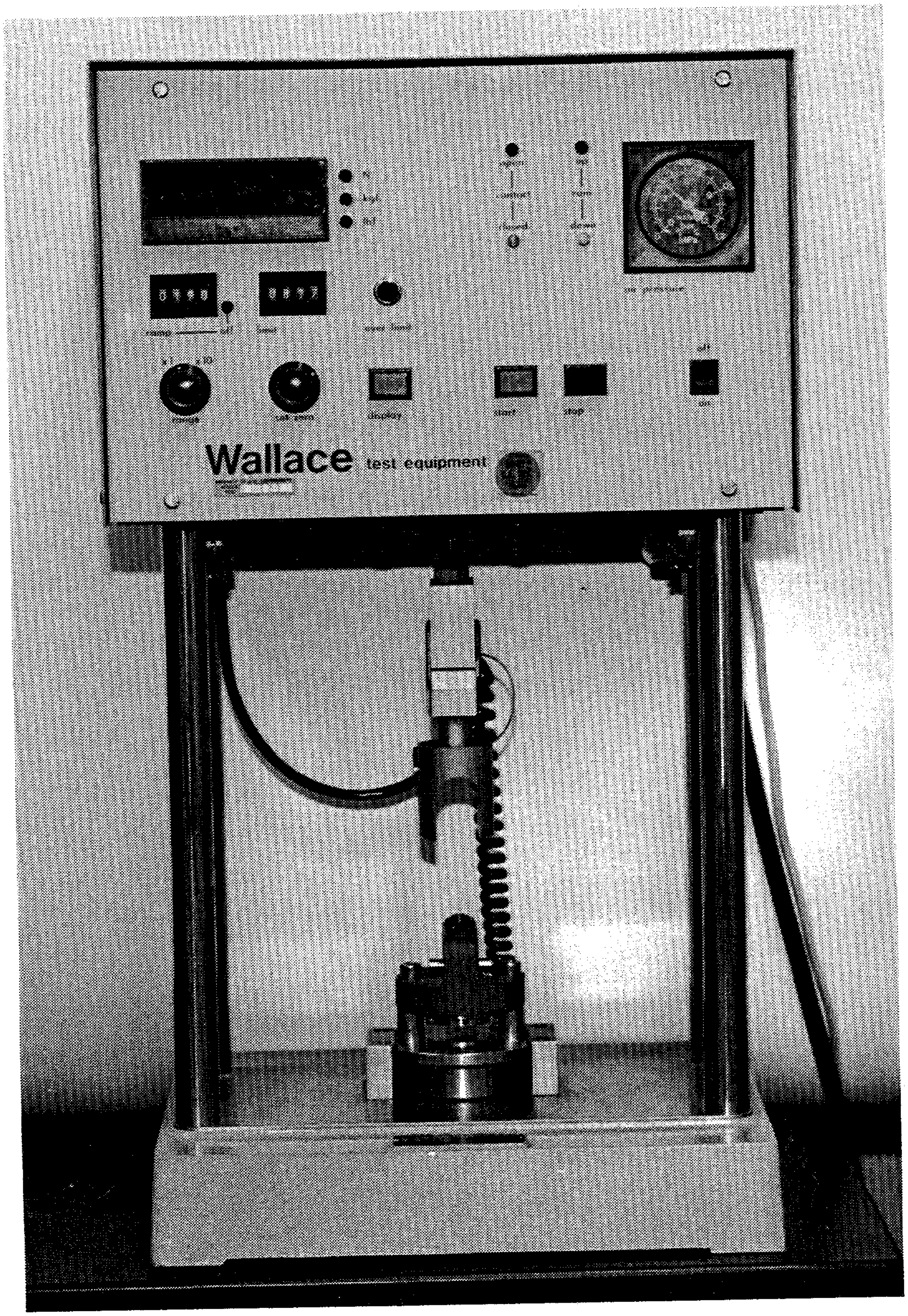


Figure 5. Force Measuring Instrument With Fixture Ready to Be Measured

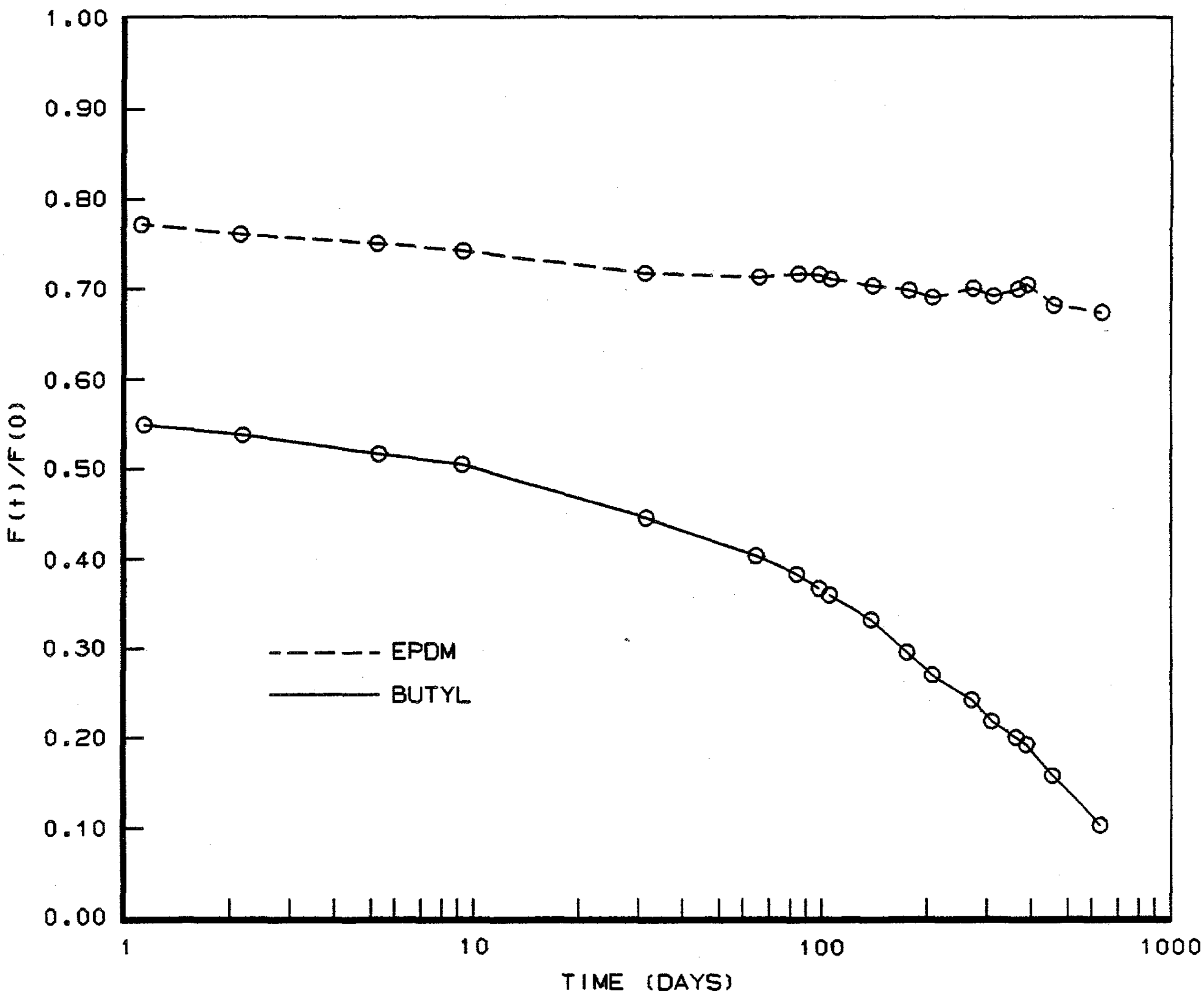


Figure 6. Stress Relaxation of Butyl and EPDM After Aging at 70°C [F(0) = initial closure force; F(t) = closure force at time (t)]

samples, EPDM-2, was begun to improve the accuracy by using fixtures that had produced successful results in the past. Although the standard deviation did improve from 4.1 to 2.3% for the first day, the average initial closure force decreased from 537 to 437 newtons for material out of the same slab and compressed by the same amount. The cause of this difference was never determined. Nevertheless, the two EPDM stress relaxation curves are essentially equivalent and are decaying at the same rate. It should also be noted that the initial modulus of the EPDM was twice as large as for the butyl. The average initial closure force for EPDM-1 was 537 newtons, whereas the closure

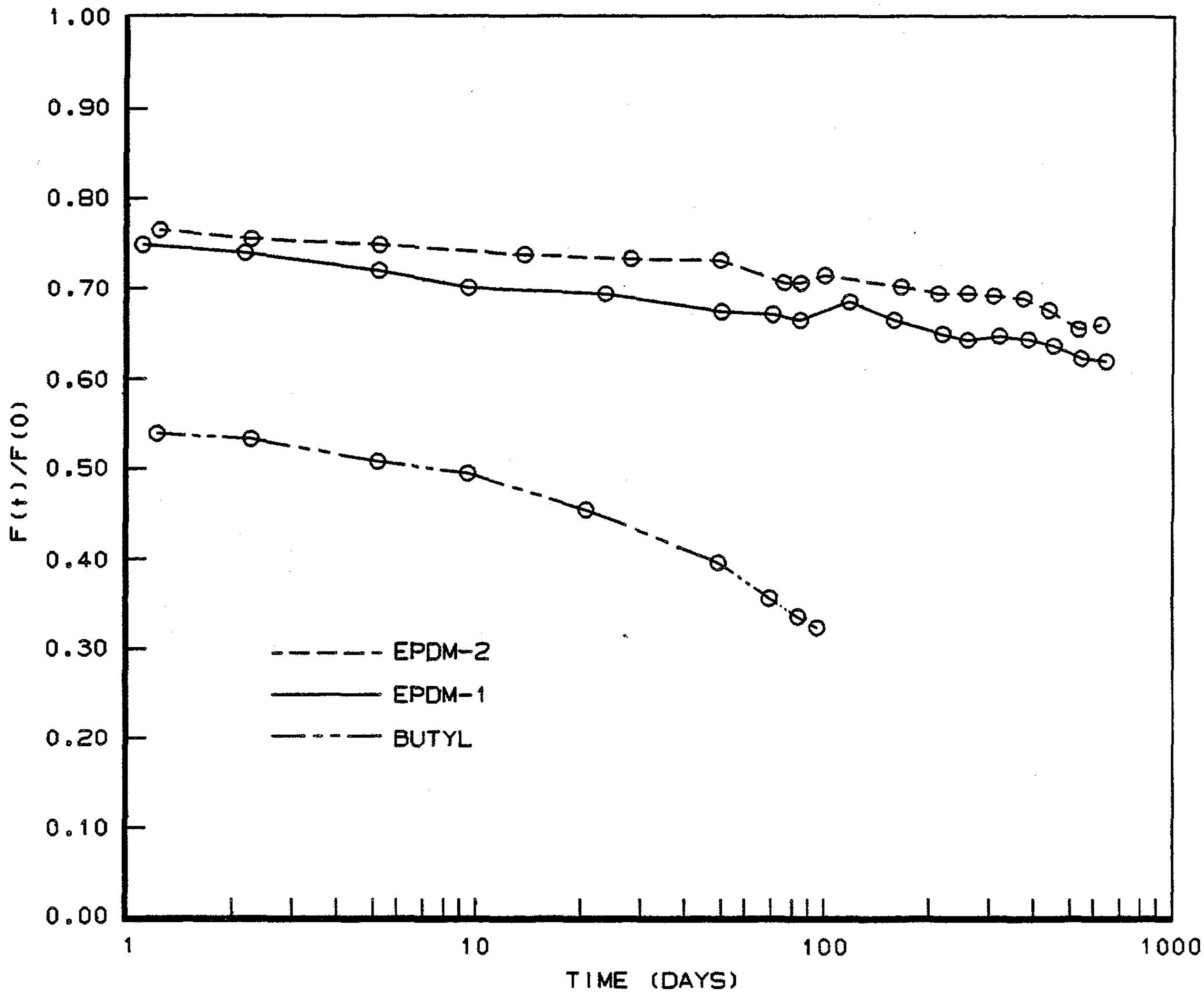


Figure 7. Stress Relaxation of Butyl and EPDM After Aging at 80°C [F(0) = initial closure force; F(t) = closure force at time (t)]

force for the butyl material was 256 newtons. Consequently, the force necessary to squeeze an EPDM O-ring will be greater than for a butyl O-ring.

Because the fixtures are removed from the oven and allowed to cool at room temperature before measurement, there was concern that this periodic thermal cycling would affect the stress relaxation behavior. Therefore, three additional fixtures each for the butyl and EPDM-1 materials aged at 80°C were allowed to remain in the oven continuously and were only removed for measurement at the end of the aging period. Table 4 contains the

Table 4. Stress Relaxation of Intermittent and Continuously Aged Butyl and EPDM Expressed as a Percent of Initial Stress

Aging Temperature (°C)	Material	Aging Time (days)	Average Stress Relaxation ±Sigma	
			Intermittent	Continuous
70	Butyl	616	10.6 ±0.9	---
70	EPDM	616	67.6 ±1.7	---
80	Butyl	93	32.4 ±2.6	32.6 ±2.1
80	EPDM-1	616	61.4 ±3.3	64.3 ±1.7
80	EPDM-2	616	66.0 ±2.5	---

stress relaxation values plus or minus the standard deviation measured at the end of the aging period for the intermittent and continuously aged materials. The data indicate that removing the fixtures for measurement had no effect on the stress relaxation behavior.

Table 5 contains the compression set values plus or minus the standard deviation measured at the completion of the stress relaxation testing. As with the stress relaxation data, these results show that there is no difference between the intermittent and continuously aged samples. As expected, the EPDM is also shown to have much better compression set resistance than the butyl material.

Analysis of variance at the $\alpha = 0.05$ level indicates that the compression set value for EPDM-2 is slightly larger than for EPDM-1 but that the values for stress relaxation are indistinguishable. As with the difference in initial closure force for EPDM-1 and EPDM-2, the cause of this difference in compression set resistance is unknown; however, the overall aging behavior of the EPDM is clearly superior to the butyl.

Based on its superior stress relaxation behavior, the EPDM is recommended for use instead of the butyl. The EPDM also has a higher permeability than the butyl. For sealing applications where permeability is important, this higher permeability should be taken into consideration when the EPDM is used to replace O-rings that were made with butyl.

Table 5. Compression Set of Intermittent and Continuously Aged Butyl and EPDM After Stress Relaxation Testing

Aging Temperature (°C)	Material	Aging Time (days)	Average Compression Set ±Sigma	
			Intermittent	Continuous
70	Butyl	616	80.3 ±0.6	---
70	EPDM	616	23.3 ±0.3	---
80	Butyl	93	35.8 ±2.6	37.2 ±0.9
80	EPDM-1	616	29.9 ±1.0	29.9 ±1.3
80	EPDM-2	616	33.3 ±3.1	---

70 Shore A EPDM Evaluation

A condition of the original contract with Dr. David Winkler, Institute of Polymer Science, The University of Akron, was to provide an EPDM formulation with a nominal hardness value of 70 Shore A. The actual hardness was closer to 80 Shore A because he was using an out-of-calibration durometer. Dr. Winkler reformulated the EPDM to achieve a 70 Shore A hardness and provided test slabs and uncured material for testing. Table 6 contains the new formulation, and the full report from Akron is contained in the appendix of this report. The original EPDM formulation was modified slightly by reducing the level of curatives (Varox 40C and Rocryl 910) and by adding a small amount of polybutadiene polymer.

Table 7 shows a comparison of the physical properties for different cure conditions. The KCD value of 74 for hardness is lower than the original EPDM formulation but higher than the hardness reported by the University of Akron. By replacing the antioxidant, Vanox ZMTI, with the new antioxidant, Flectol H, the hardness should be reduced a few more points. More lots would be needed to determine if the natural hardness is in the 65 to 75 Shore A range as desired. The compression set after postcure is slightly higher than the original EPDM formulation but is still felt to be an excellent value.

Stress Relaxation of the 70 Shore A EPDM

Figure 8 adds the new 70 Shore A EPDM formulation's stress relaxation behavior to Figure 7 for comparison with the other materials. The compression set measured after the stress

Table 6. 70 Shore A EPDM Formulation

Ingredient	PHR
Nordel 1440	100
Cis-1,4-polybutadiene	5
Zinc Oxide	5
N-990 Carbon Black	40
N-539 Carbon Black	25
Vanox 40C	8
Vanox ZMTI	2
Rocryl 910	5

relaxation testing was as follows: time, 306 days; temperature, 80°C; and average compression set (±sigma), 33.1 ±0.3. The new EPDM formulation was also postcured in air to represent a worst case condition. The stress relaxation behavior of the new EPDM is slightly worse than the original formulation. The new formulation represents a promising lower durometer rubber that would require further characterization before use.

ACCOMPLISHMENTS

This study was composed of three parts: a postcure study to optimize final properties, an accelerated aging study to compare the stress relaxation behavior of two elastomers under compression, and a cursory evaluation of a new 70 Shore A EPDM supplied by the University of Akron. The materials tested for the postcure and accelerated aging studies were a butyl and an EPDM elastomer to be used for O-rings on a weapon assembly. The butyl compound was B612-70, which is a proprietary formulation from Parker Seal Group, O-Ring Division, and the EPDM formulation tested was SS384725.

The postcure study evaluated changes in certain physical properties, solvent swell, and extractables after an air or vacuum postcure at 182°C. Postcuring is recommended because of the improvement in compression set to values lower than 10% after 70 hours at 125°C. The optimum postcure for the EPDM was found to be 2 to 4 hours at 182°C in a vacuum.

Stress relaxation testing was performed at 70 and 80°C for a maximum of 616 days. Removing the samples from the oven for measurement caused no significant difference in stress relaxation behavior from samples that were allowed to remain in the oven continuously. The EPDM was shown to have superior aging

Table 7. Physical Properties of 70 Shore A EPDM Rubber

Property	Akron	KCD	KCD
Press-Cure	31.5 min. at 160°C	15 min at 166°C	15 min at 166°C
Postcure	None	None	4 h at 182°C in a vacuum
Hardness (Shore A)	70	73	74
100% Modulus (psi)	975	759	892
Tensile Strength			
(psi)	1890	1820	1850
(MPa)	13.0	12.6	12.8
Elongation (%)	155	198	192
Compression Set, 70 h at 125°C (%)	8.0	20.5, 23.0	12.5, 7.9

characteristics compared to the butyl and is recommended for use instead of the butyl material.

The original request for a 70 Shore A durometer EPDM from the University of Akron was received for evaluation. The lower durometer was achieved by adding a small amount of polybutadiene rubber and by reducing the level of curatives. Physical properties for this compound are satisfactory, and the stress relaxation results at 70°C are only slightly inferior to SS384725.

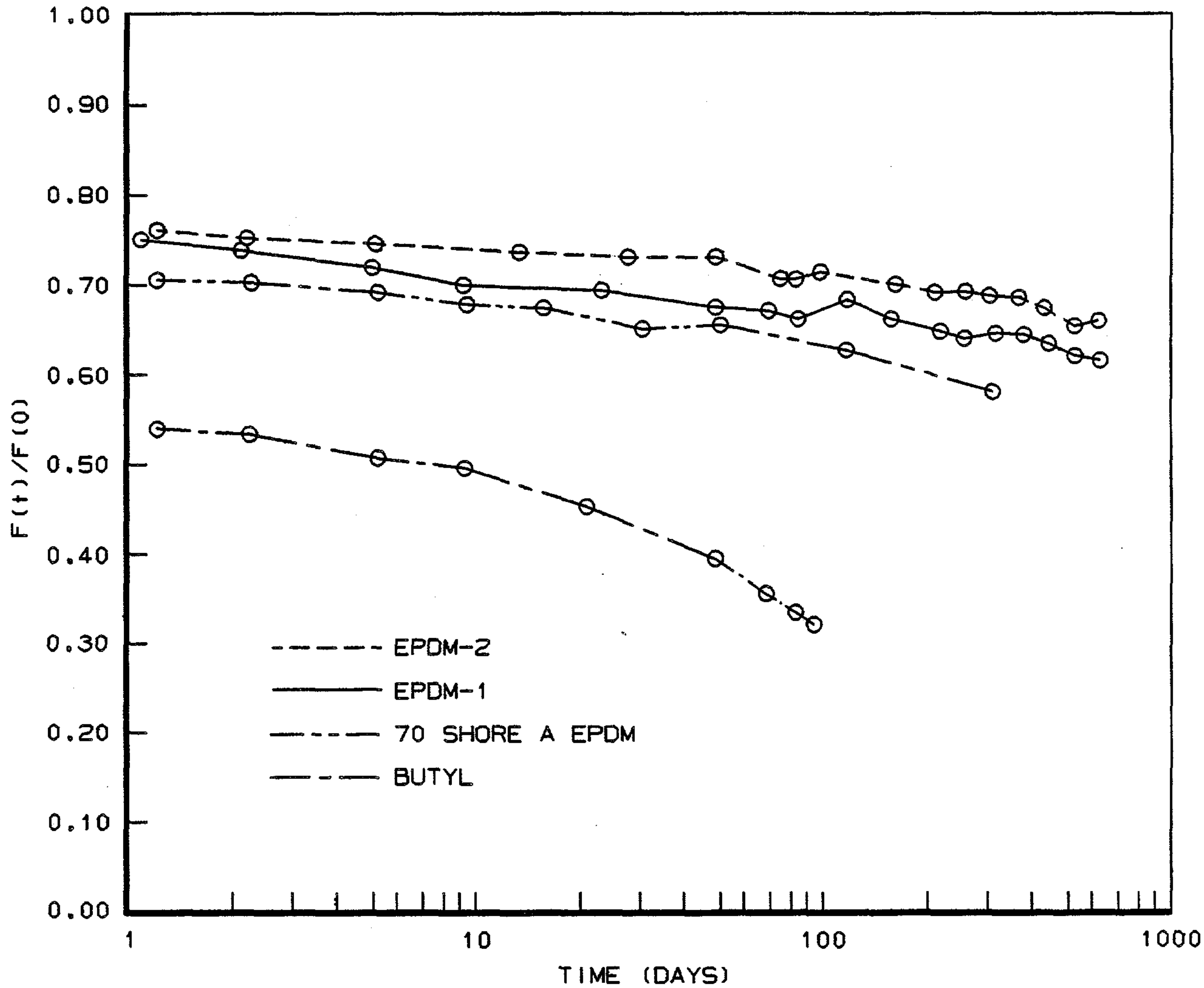


Figure 8. Stress Relaxation of Butyl, the Original EPDM Formulation, and the 70 Shore A EPDM Formulation After Aging at 80°C [F(0) = initial closure force; F(t) = closure force at time (t)]

Appendix

DEVELOPMENT OF EPDM COMPOUND
BY THE UNIVERSITY OF AKRON

Epic

EDISON POLYMER INNOVATION CORPORATION

In Cooperation With The University of Akron.

Institute of Polymer Science
Applied Research
Phone (216) 375-7513

January 5, 1988

Allied Bendix Aerospace
Bendix Kansas City Division
2100 East 95th Street
Kansas City, Missouri 64131

Attn: Mr. Mark Wilson
Dept. 814W-XD44
Reference: P. O. 017D 218068

Dear Mr. Wilson:

The development of an EPDM compound to meet your specifications has been completed. The formulation for this compound is shown below.

Ingredient	PHR	Supplier
Nordel 1440	100	du Pont
Cis-1,4 polybutadiene	5	Goodyear (1208)
N-990 Carbon Black	40	
N-539 Carbon Black	25	
Varox 40C	8	Vanderbilt
Vanox ZMTI	2	Vanderbilt
Zinc Oxide	5	
Rocryl 910	5	Rohm & Haas
	190	

Ingredient	Chemical Name
Varox 40C	40% Decumyl Peroxide on $CaCo_3$
Vanox ZMTI	Zinc 2-mercaptotolylimidazole
Rocryl 910	Trimethylolpropane trimethacrylate

The compound was formulated on a two roll rubber mill. A cure temperature of 320°F was employed. The cure characteristics were obtained with an oscillating disc rheometer (ODR) at 320°F. The cure time obtained was 31.5 minutes. Please find enclosed the rheograph of this compound at 320°F.

The ethylene/propylene ratio was studied by NMR using a Varian 400 megahertz instrument. The ethylene content observed was 94.26% and the propylene content was 5.74%.

Toluene extractions were found to be 7.3% on an unaged sample. After a post cure of 2 hours at 360°F, this value was found to be 4.6%.

The specific gravity was observed to be 1.121 g/cc.

The compression set obtained in accordance with ASTM D-395, Method B was 8.0%. This test was conducted at 257°F for 70 hours.

The Shore A hardness observed on vulcanizates of this compound was 70.

A strip cut from a cured tensile slab was immersed in a dry ice/methanol bath at -80°C and left there for 1 hour. The test strip was grasped with a pair of tongs and then bent back on itself without cracking or breaking. The Tg of this compound appears to be below -80°C thus meeting your requirement.

The physical properties of this vulcanizate are shown below.

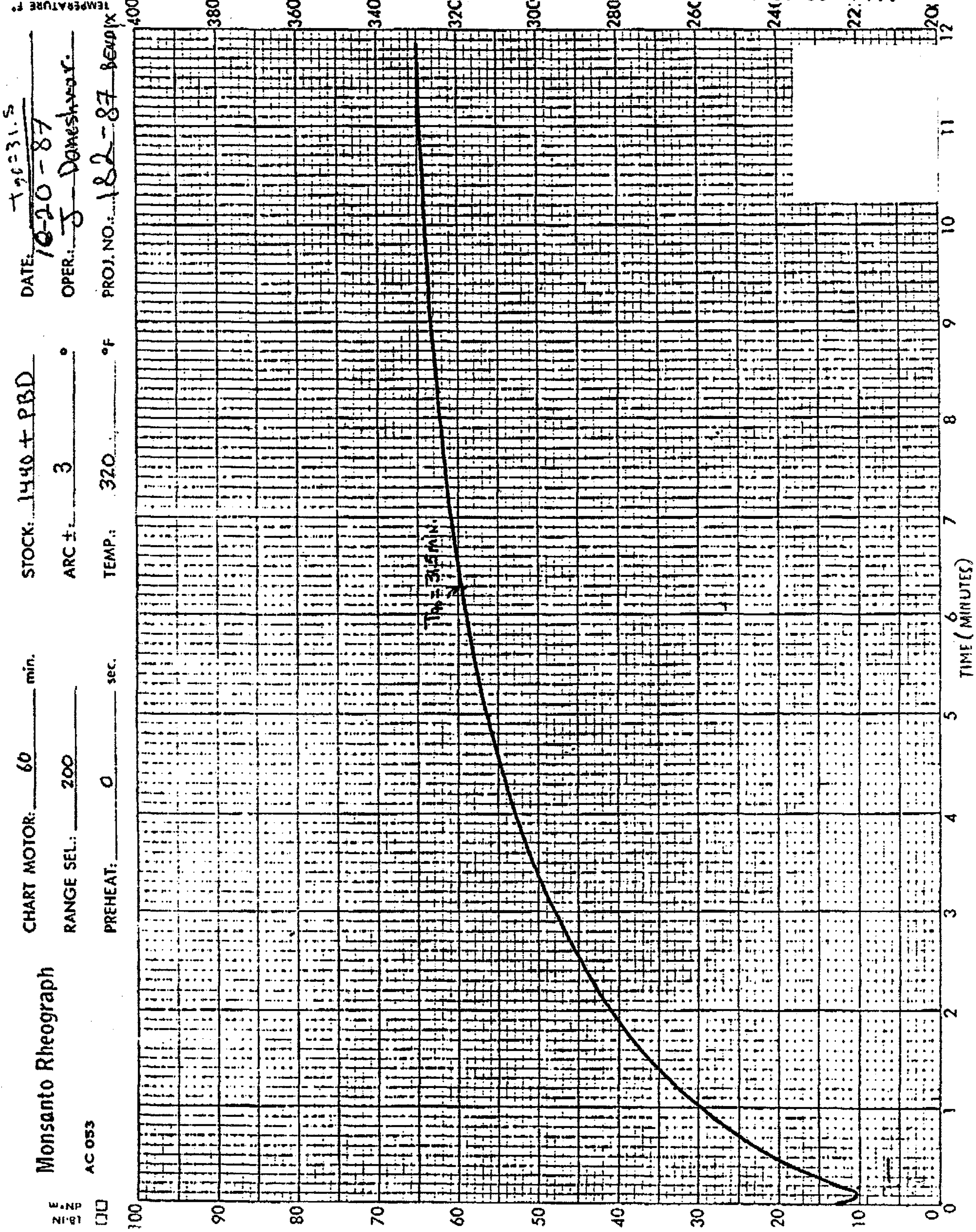
Tensile Strength, psi	1890
100% Modulus, psi	975
Elongation, %	155
Die C Tear Strength, lbs/in	160

Should you have any questions concerning the above, please feel free to contact me at your convenience.

Yours very truly,

David S. Winkler
Manager Applied Research

lb


Monsanto Rheograph
AC 053
CHART MOTOR: 60 min.
RANGE SEL.: 200
PREHEAT: 0 sec.
STOCK: 1440 + PBD
ARC ±: 3 °
TEMP.: 320 °F
DATE: 10-20-87
OPER.: J. Daneshvar
PROJ. NO.: 182-87 BEAD
TEMPERATURE °F
TIME (MINUTES)