AD A063049

DDC FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
1

2. GOVT ACCESSION NO.
(11)

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
(6) Crystallinity in Hydrolytically Aged Polyester Polyurethane Elastomers,

5. TYPE OF REPORT & PERIOD COVERED
Technical; 1-78 to 9-78

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
D. W. Brown, R. E. Lowry and L. E. Smith

8. CONTRACT OR GRANT NUMBER(s)
NR 356-647

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Polymer Science and Standards Division
National Bureau of Standards
Gaithersburg, Md 20234

(9) Technical rept. no. 1, Jan-Sep 78,

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research
800 N. Quincy St.
Arlington, Va. 22217

12. REPORT DATE
(11) Sep[redacted]78

13. NUMBER OF PAGES
15

14. MONITORING AGENCY NA[redacted] (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
(12) 15p.

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Approved for Public Release; Distribution Unlimited

(10) Daniel W. /Brown, Robert E. /Lowry
Leslie E. / Smith

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DDC
JAN 8 1979

18. SUPPLEMENTARY NOTES
To be published in ACS Symposium Series

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Aging of polymers; degradation of polymers; elastomers; lifetime prediction; hydrolytic stability; polyurethane; polyester; service life.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Several experimental and two commercial polyurethanes were aged in wet air. Polyester types suffered molecular weight degradation but became more crystallizable at 25° C than unaged specimens. Crystallinity contributes to modulus and hardness, and, if measured at 25° C, these properties appear to have been increased by aging. However, at 60° C, 10° C above the crystalline melting point, the moduli of the wet-aged polyester types are less than those of unaged counterparts, showing the effect of the decreased molecular weight. Earlier

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6601

410 345

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

79 01 05 043

Block 20, Continued

assessments of polyurethane stability were based on the mechanical properties of reconditioned samples at room temperature, and this probably caused an overestimate of the lifetime of polyester types. Polyether types showed little change in molecular weight on aging, and remained uncrystallizable. Consequently, aged and unaged polyether types show the same relative moduli at 25 and 60° C.

The commercial polyester type underwent about ten times as many scissions as the polyether type when aged under the same conditions.

Crystallinity in Hydrolytically-Aged Polyester Polyurethane Elastomers

Daniel W. Brown, Robert E. Lowry, and Leslie E. Smith
National Bureau of Standards
Washington, D. C., 20234

Abstract

Several experimental and two commercial polyurethanes were aged in wet air. Polyester types suffered molecular weight degradation but became more crystallizable at 25° C than unaged specimens. Crystallinity contributes to modulus and hardness, and, if measured at 25° C, these properties appear to have been increased by aging. However, at 60° C, 10° C above the crystalline melting point, the moduli of the wet-aged polyester types are less than those of unaged counterparts, showing the effect of the decreased molecular weight. Earlier assessments of polyurethane stability were based on the mechanical properties of reconditioned samples at room temperature, and this probably caused an overestimate of the lifetime of polyester types. Polyether types showed little change in molecular weight on aging, and remained uncrystallizable. Consequently, aged and unaged polyether types show the same relative moduli at 25 and 60° C.

The commercial polyester type underwent about ten times as many scissions as the polyether type when aged under the same conditions.

Crystallinity in Hydrolytically-Aged Polyester Polyurethane Elastomers

Daniel W. Brown, Robert E. Lowry, and Leslie E. Smith
National Bureau of Standards
Washington, D. C. 20234

Polyester polyurethanes degrade in humid environments. The expected lifetime of five years for the best polyester polyurethanes at 25° C [1] is frequently not achieved [2,3]. The ordinary degradation is due to hydrolysis of the polyester component [4]. Acid produced catalyzes additional hydrolysis, thus increasing the rate autocatalytically [5]. Larger acid numbers in the polyester diol from which the polyurethane is made increase the degradation rate of the polyurethane [5]. Polyester polyurethanes can also be attacked by fungi [2].

We have found that aged polyester polyurethanes can be more crystallizable than their unaged counterparts. The crystallinity affects the modulus, whose change has been used to estimate the lifetime [1].

Experimental

Polyurethanes were prepared by both prepolymer and one-shot methods. Our polymers were molded at about 190° C into 0.3 mm thick sheets. A commercial supplier provided 0.25 mm sheets of polyester based and polyether based polyurethanes. These were used as received, except for cutting.

Strips were aged in sealed tubes containing 1 atmosphere of air (at 25° C) above liquid water. The tubes were placed in thermostatted water baths or in a circulating air oven. Our polymers were aged for 10 days at 24° C, 11 days at 35° C, 13 days at 42° C, 14 days at 50° C, and 35 days at 58° C. Then the tubes were opened and the samples kept at 25° C and 50% relative humidity for 60 days before further processing. The commercial polyurethanes were aged for 19 days at 42° C, 22 days at 50° C, 113 days at 58° C, and 60 days at 25° C. Then the tubes were opened and the samples kept at 25° C and 50% relative humidity for 3 days before further processing. The complex sequential agings were done as part of a study of creep, which will not be presented at this time.

When the tubes were opened the gasses above the polymers were analyzed for O_2, N_2, and CO_2. The analyses were not significantly different from that of laboratory air. The stress-strain curves of the polymer samples were run to 300% elongation at 25° C and 60° C (on different specimens). Gage marks were initially 2.5 cm apart, jaws were 7.5 cm apart, and crosshead speed was 5 cm/min, unless specified. Sol fractions of insoluble polymers were determined by extraction with tetrahydrofuran at 25° C. Intrinsic viscosities, $[\eta]$, of soluble polymers were determined, also in tetrahydrofuran at 25° C. A differential scanning calorimeter was used to measure the heat of fusion, ΔH_F. Scans were at 10° C/min on 10-20 mg of polymer that had not been subjected to the stress-strain measurements. Samples were rescanned immediately after the first scan, at least 30 days later, and sometimes at intermediate times.

Soluble polymers were run through a gel permeation chromatograph. Polystyrene fractions of known molecular weight were run also and their intrinsic viscosities were measured. The universal calibration technique was used in conjunction with a computer program to calculate the number average molecular weight, M_n, of the polyurethane.

Results and Discussion

Figure 1 shows stress-strain curves for the commercial polyether polyurethane and for PU-13, made from methane diphenyl diisocyanate (MDI), butane diol (BD), and polytetramethylene oxide diol of molecular weight, 2000 (PTMO 2000). There is little difference in stress values for aged and unaged polymers. At 60° C, stress values are about 25 - 35% less than at 25° C.

Figure 2 shows stress-strain curves for the commercial polyester polyurethane and for PU-16, made from MDI, BD, and a polycaprolactone diol of molecular weight 2000 (PCL 2000). At 25° C the stress values for each aged polymer are higher than for the corresponding unaged polymer. The aged commercial polymer broke when drawn at the usual rate so a fourfold slower draw rate was used with all the commercial polyester polyurethane samples. At 60° C even with the slower draw rate the aged sample stretched only 50% before breaking; at 20 and 50 strain the stresses are about half those of the unaged polymer. PU 16 has nearly the same stress values at 60° C, whether aged or unaged. Thus raising the temperature from 25 to 60° C, lowered the stress-strain curves more for aged, than for unaged samples.

Results qualitatively similar to those in Figure 2 were obtained with polyurethanes made from toluende diisocyanate (TDI), BD, and: 1) PCL 2000 2) a polycaprolactone diol of molecular weight 1220 (PCL 1220) 3) a polyethyleneadipate diol of molecular weight 2000 (PEAD 2000). However, all TDI based polymers had very low stress values at 60° C.

Wide angle X-ray patterns of the aged and unaged polymer are in Figure 3. Sharp lines, indicative of crystallinity, occur in the pattern from the former polymer; these are absent from the pattern from the unaged polymer.

When samples were run in a differential scanning calorimeter none of the polyether polyurethanes showed evidence of crystallinity. All the aged polyester polyurethanes showed melting peaks, generally with maxima near 42° C. In all cases melting appeared complete below 51° C. Figure 4 shows the calorimeter plots for the aged commercial polyester based polymer as observed initially and three times thereafter. Recrystallization occurs over a period of days at 25° C. The commercial polyester type did not show a melting transition. Our polyester polyurethanes behaved somewhat differently in that aged and unaged samples both showed melting transitions; those of the aged polymer took up more heat. In addition, for as long as 16 hours after being scanned no melt transitions were detectable in our polymers.

Table 1 lists the heats of fusion found initially and also after the samples had been at 25° C and 50% relative humidity for at least 30 days after the first measurement. Also included in the table are results of solution studies of the polymers - their sol fractions, if not completely soluble, or their intrinsic viscosities.

Our polymers were crosslinked. On molding, sol fractions increased and on aging increased still further, indicating that chain scissions occurred. PU-9 and the commercial polyester type were soluble and showed substantial drops in intrinsic viscosity on aging. The last two polymers in Table 1 are polyether based; for these less scission is indicated by the changes in sol fractions and intrinsic viscosity.

Values of M_n calculated from gel chromatograms of the commercial polymers are: polyester type, Unaged 42400, Aged 11800; polyether type, Unaged 44900, Aged 35800. The difference of the reciprocals of the M_n for aged and unaged samples is the mol of scissions per gram. Values are 6×10^{-5} and 0.6×10^{-5} for the polyester and polyether types, respectively. Thus in our study the overall scission rate of the polyester polyurethane was about 10 times greater than that of the polyether polyurethane.

No crystallinity is detectable in a polymer of MDI, BD, and PCL 1220, that was aged until its M_w had decreased from 64000 to 49000. Thus it appears that it is the molecular weight reached, not the degradation process <u>per se</u>, that results in crystallization.

In Table 2 are shown data relating molecular weight and crystalline content of unaged polymers. These were prepared by using an excess of OH or NCO functionality. If the functionality not in excess is used up, the theoretical M_n (listed) is the weight charged divided by the excess number of mols. Intrinsic viscosities found show that the desired effect was achieved. Heats of fusion decrease as $[\eta]$ increases, becoming zero for the polymers with the two highest $[\eta]$. However, of these the one with the lower $[\eta]$ had slight residual crystallinity after being stretched 300% at 25° C and released. No crystallinity was detected in the sample of highest $[\eta]$ after the same treatment. The stress values listed decrease more between 25 and 60° C for the polymer that crystallized on stretching at 25° C, showing that the crystallization influenced the stress at 25° C.

All hard segment (MDI+BD) and all soft segment (MDI+PCL 1220) polymers have melting peaks with maxima at about 200° C and at about 40° C respectively. Therefore the crystallinity observed in our specimens probably is due to the soft segment.

It is uncertain if earlier lifetime estimates [1] were affected by crystallization of the degraded specimens. An effect so large that the modulus was raised on aging, as found here, must not have occurred. However, the data in Table 2 suggest that stretching might induce crystallinity more readily in aged than in unaged samples, and partially compensate for the molecular weight reduction in the former. This would have affected the lifetime estimates. By comparing moduli of aged and unaged material at high temperature one can detect this effect.

Polyester polyurethanes in service probably crystallize as they age, retaining their usual physical characteristics to casual examination. As the molecular weight decreases the melting temperature will eventually decrease also. Sorbed water may also affect the melting temperature. Eventually ambient temperature will exceed the melting temperature causing a relatively sudden loss of physical properties. Until a more certain lifetime estimate is available, test strips of the polyester polyurethane used might be located near critical applications. These could be tested at intervals, by modulus measurements at elevated temperature or perhaps by acid number determinations. Since each hydrolytic scission of an ester produces an acid group, it is likely that the increase in acid content will equal the increase in the number of polymer molecules, which can be used to calculate the change in molecular weight.

Acknowledgements

The work was supported in part by the Naval Air Systems Command and the Office of Naval Research.

References

(1) G. Magnus, R. A. Dunleavy, and F. E Critchfield, Rubber Chem and Tech., 39, 1328 (1965).

(2) Z. T. Ossefort and F. B. Testroet, Rubber Chem and Tech., 39, 1308 (1965).

(3) C. F. Bersch, Naval Air Systems Command, Private Communication.

(4) R. J. Athey, Rubber Age 96, 705 (1965).

(5) C. S. Shollenberger and F. D. Stewart, J. Elastoplastics, 3, 28 (1971).

Table I

Melting and Solution Behavior of Polyurethanes

Polymer and Treatment	ΔH_F J/g	Sol wt%	$[\eta]$ d/g
PU 9, TDI: 1 PEAD 2000: 0.95 BD			
Before molding		58	
After molding, unaged	28, 29	100	1.15
Aged wet	42, 40	100	0.17
PU 15, 2TDI: 1 PCL 2000: 1 BD			
Before molding		4	
After molding, unaged	36, 32	26	
Aged wet	41, 39	97	
PU 17, S TDI: 1 PCL 1220, 1 BD			
Before molding		2	
After molding, unaged	6, 5	30	
Aged wet	25, 21	90	
PU 16, 2 MDI: PCL 2000: 1 BD			
Before molding		2	
After molding, unaged	2, 2	75	
Aged wet	15, 16	95	
Commercial Polyester Polyurethane			
Unaged	0, 0	100	0.99
Aged wet	7.7, 15	100	0.41
PU 13, 2 MDI: 1 PTMO; 0.95 BD			
Before molding		3.5	
After molding, unaged	0, 0	74	
Aged wet	0, 0	83	
Commercial Polyether Polyurethane			
Unaged	0, 0	100	1.50
Aged wet	0, 0	100	1.36

Table II

Moleculâr Weight Effects in an MDI, PCL 1220, BD Polyurethane

MDI:PCL:BD mol ratio	M_n g/mol	[n] dl/g	ΔH_F[a] J/g	Stress at 200% Strain MPa	
				25° C	60° C
2:1:2	1910	0.19	17	0	0
2:1:1.25	7370	0.28	2.1	b	0
2:1:0.95	36300	0.60	0, 1.3	5.4	2.5
2:1:1	∞	2.1	0, 0	6.0	4.3

a) Melting curve maxima at 41 - 43° C.

b) Broke at 2.1 MPa at less than 100% strain.

Figure Legends

1) Stress vs. strain at 25 and 60° C for polyether polyurethanes. Filled symbols at 25° C, unfilled symbols 60° C. Commercial polymer: Unaged ◆, ◇; Aged wet ▲, △. PU 13: Unaged ●, ○; aged wet ■, □.

2) Stress vs. strain at 25 and 60° C for polyester polyurethanes. Filled symbols 25° C. Unfilled symbols 60° C. Commercial polymer (stretched 0.5 in/min) Unaged ◆, ◇; Aged wet ▲, △. Pu 16: Unaged ●, ○; Aged wet ■, □.

3) X-Ray photographs for commercial polyester polyurethane. Lower, unaged; upper, aged wet.

4) DSC scans, commercial polyester polyurethane, aged wet.

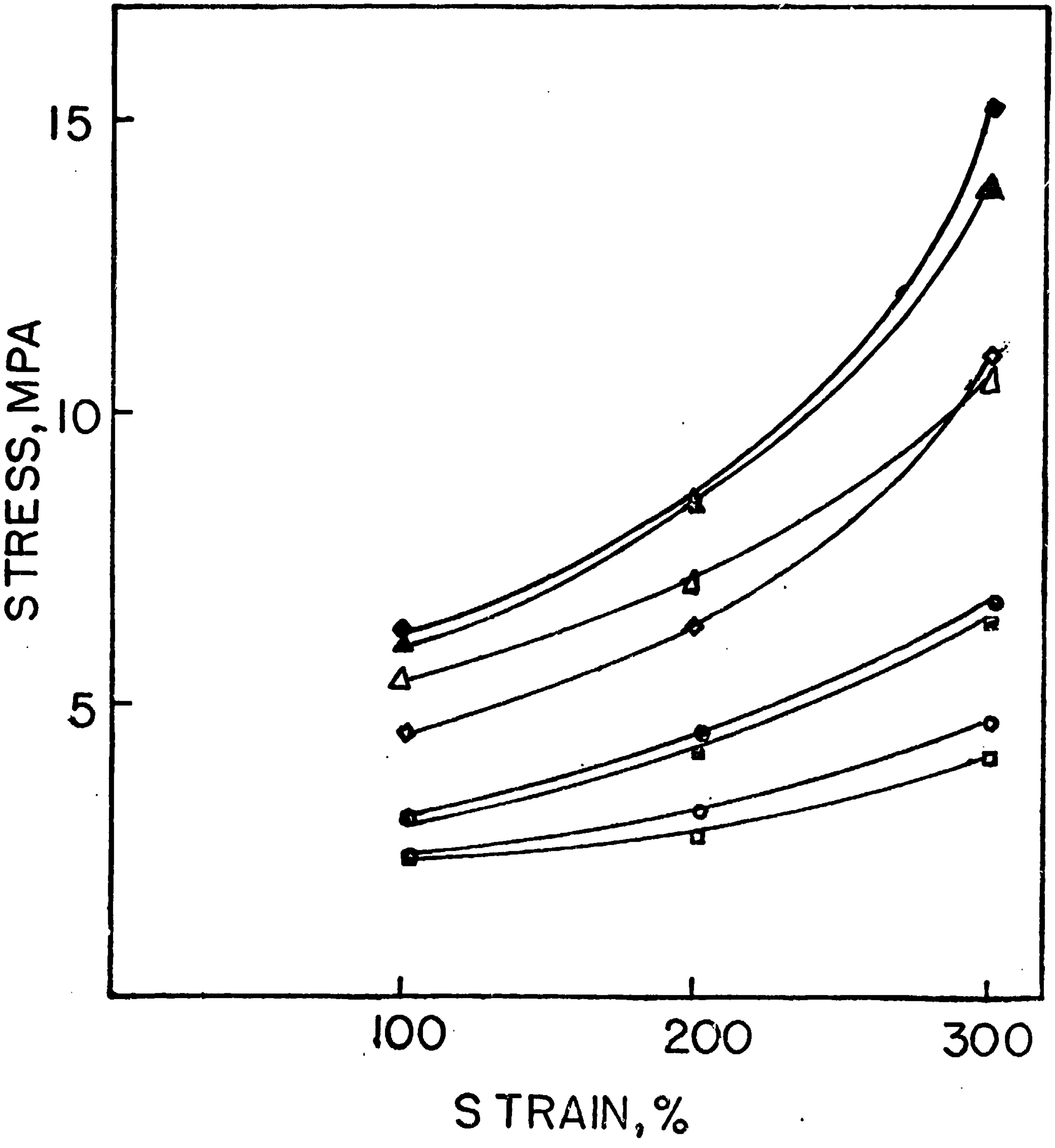
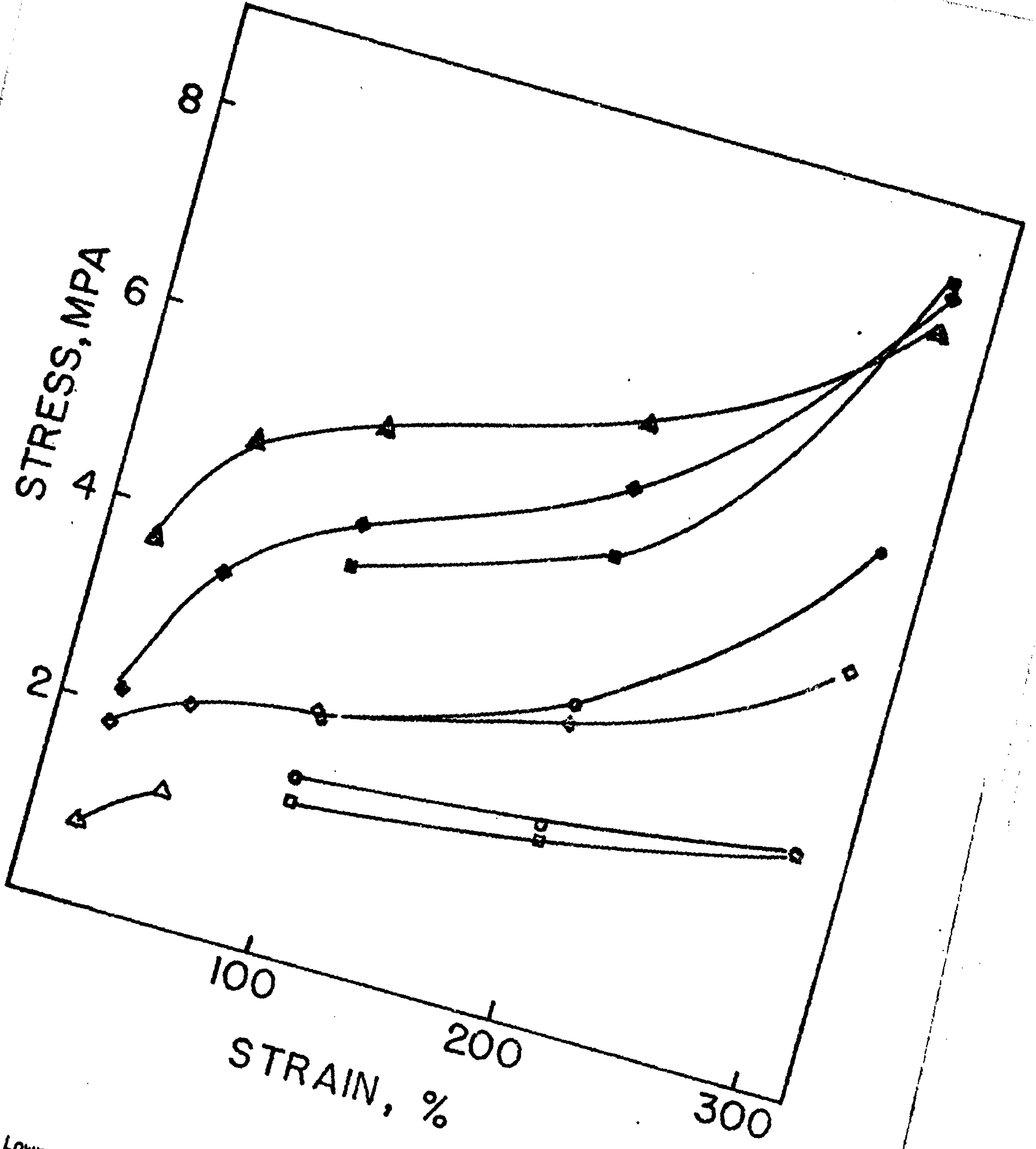


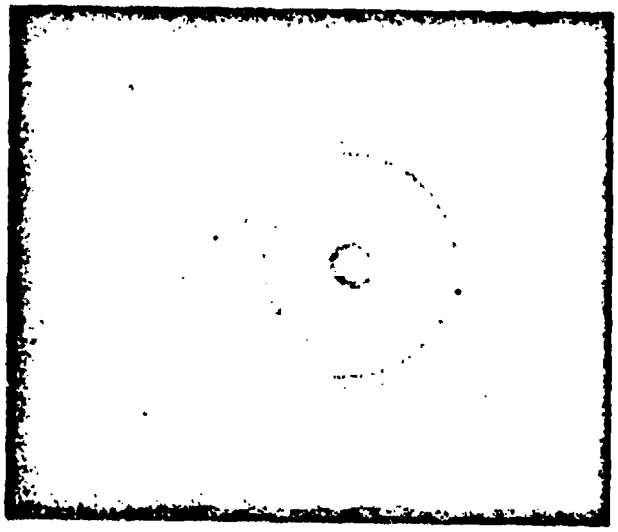
Figure 1

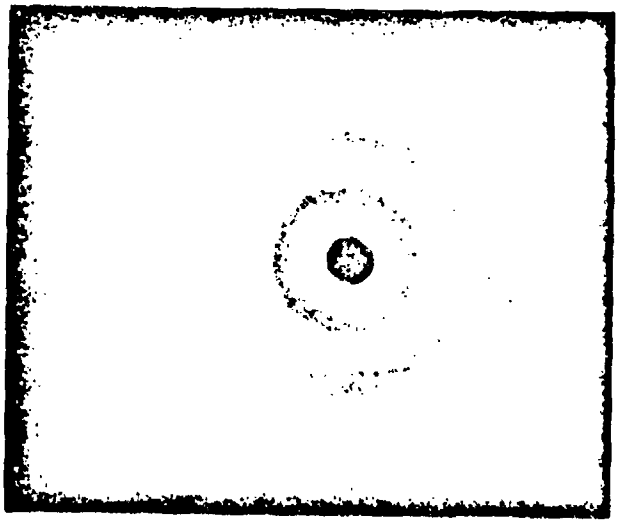
Brown, Lowry, Smith



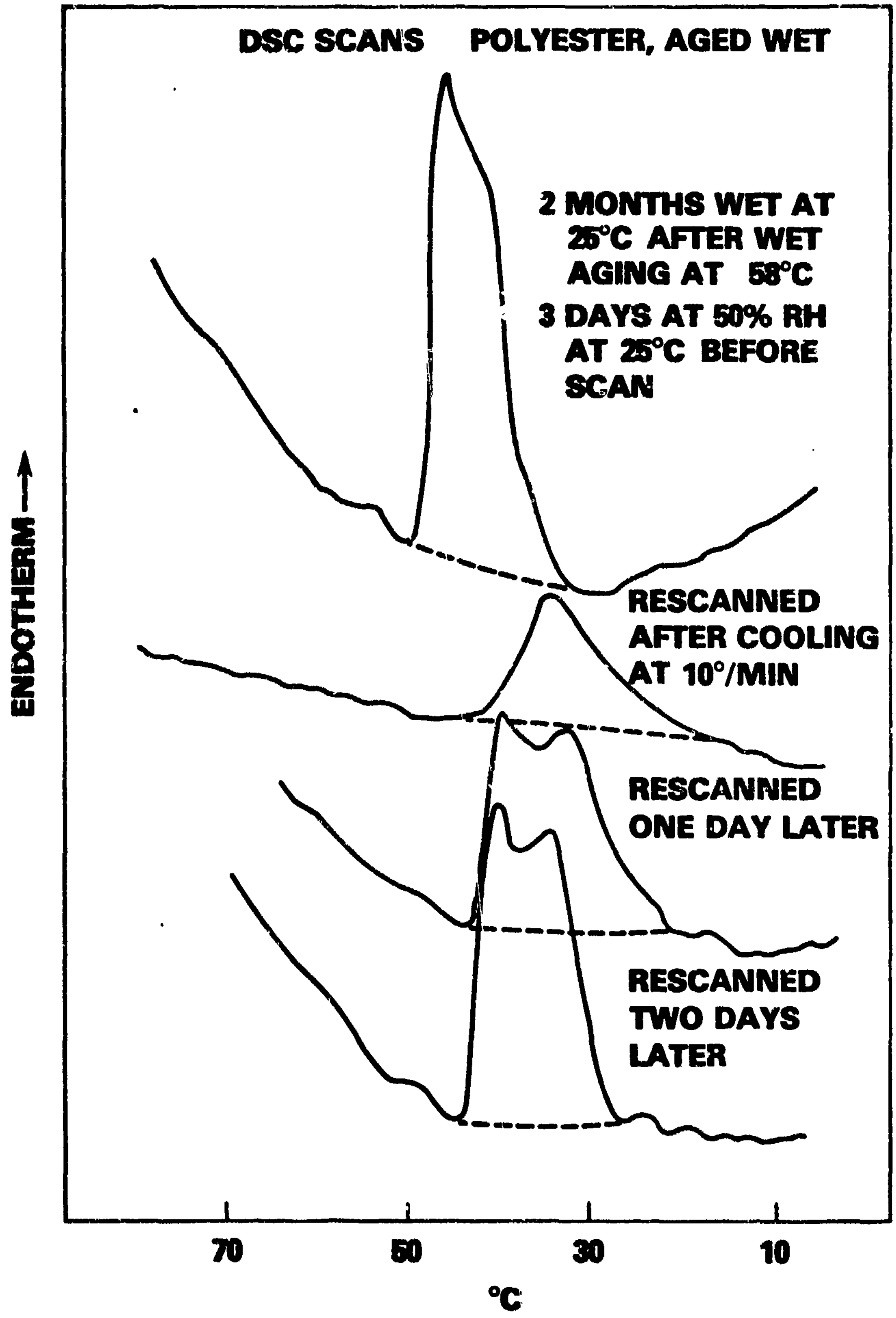
Brown, Lowry, Smith

Figure 2





Brown, Lowry, Smith Figure 3


DSC SCANS POLYESTER, AGED WET
2 MONTHS WET AT 25°C AFTER WET AGING AT 58°C
3 DAYS AT 50% RH AT 25°C BEFORE SCAN
RESCANNED AFTER COOLING AT 10°/MIN
RESCANNED ONE DAY LATER
RESCANNED TWO DAYS LATER
ENDOTHERM →
70
50
30
10
°C