Poly(vinyl Chloride): Viscoelastic and Fatigue Properties as a Function of Molecular Weight in Ethanol Vapor*

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Synopsis

Viscoelastic fatigue studies were made on poly(vinyl chloride) (PVC) films using oscillatory loading on prestressed samples in an ethanol vapor environment. Samples include unfractionated PVC, relatively narrow molecular weight distribution fractions, and blends made from the fractions. Strain, complex modulus, and tan δ were studied as a function of time until rupture occurred. A marked dependence on molecular weight was observed, for example, a fraction with $\bar{M}_w = 51,000$ failed in a few seconds, while one with $\bar{M}_w = 228,000$ did not fracture after 1600 min.

INTRODUCTION

There have been several PVC fatigue studies reported in the literature. These include oscillatory loading tests as a function of frequency,[1] fatigue crack growth as a function of time,[2] fracture mechanisms,[3,4] and environmental tests.[5,6,7] This study differs from those reported previously in that oscillatory loading on a prestressed sample in a vapor environment was used. The primary variables studied were molecular weight and molecular weight distribution.

EXPERIMENTAL

A Rheovibron Mode DDV II viscoelastic test apparatus was used. To permit measurement of the total stress on the specimen, as well as the elastic and loss moduli, the signal from the stress gauge of the unit, (T-1), was fed into an operational amplifier (Analog Devices Inc. Model 118) and from there into a potentiometric recorder. The applied stress was then measured from the recorder deflection.

The high-temperature cell of the Rheovibron was modified to permit environmental testing. The heating elements were encapsulated in a
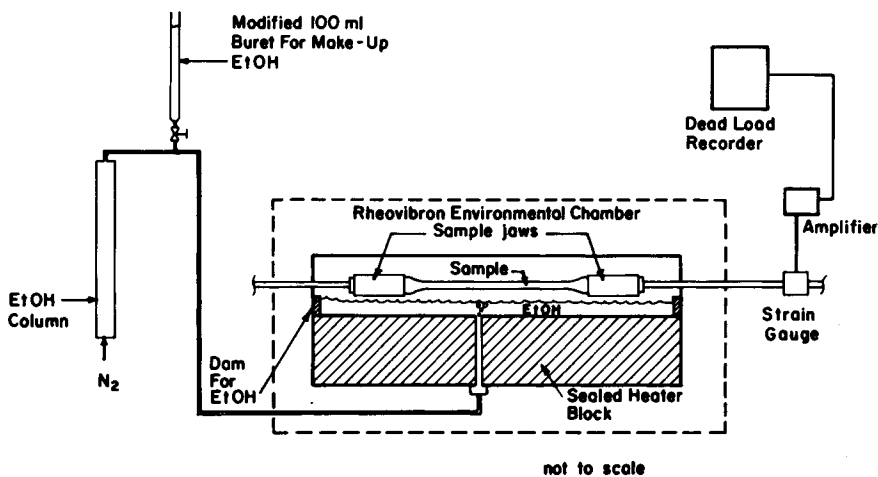
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not to scale

Fig. 1. Dynamic stress cracking apparatus.

silicate cement sealed with an epoxy resin. All joints around the heating block were sealed with an epoxy or silicone rubber where disassembly was necessary. Both ends of the cavity were sealed so a small liquid bath could be maintained within the test chamber. Figure 1 shows a sketch of the apparatus. The column, packed with $^1/_8$-in. Intalox samples and the environmental test liquid, served as a presaturator. Ethanol was selected as the test fluid because the vapor did not significantly plasticize PVC at the test temperature, although a nonsolvent for PVC ethanol vapors did affect fatigue life. The effects of vapor environment on fatigue life will be discussed in a later communication.

Sample films were cast on mercury using a technique described in detail elsewhere.[8] Samples were punched from the films using a small guillotine made by mounting razor blades in a jig. The samples had a constant cross section, except at the ends where the sample width broadened into end tabs. The sample was placed in the jaws and exposed to the environment for a minimum of 15 min before testing. After this initial conditioning, stress was applied to the sample and the cycling begun.

The strain gauge–amplifier–recorder system was calibrated using a small coil spring with a known stress–strain curve. The stress–strain curve was determined using a table-model Instron tester with a type A cell. Periodic checks over a three-month period showed that the coil spring calibration changed by no more than 1%.

All tests were run at a stress level of 1 kg/mm^2 unless otherwise noted. The frequency was 3.5 Hz and the temperature, 25 ± 1°C. Strain amplitude was ±0.0030. Elastic and loss moduli, tan δ, creep, dynamic strain amplitude, and time to failure were measured.

The poly(vinyl chloride) used in this study was Geon 110 X 265 manufactured by B. F. Goodrich. Fractionation was carried out using a large-scale automated gel permeation chromatograph (Waters Associates,

TABLE I
Molecular Weight Averages and Initial Complex Moduli
of Poly(vinyl Chloride) Films

Sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	Complex modulus in ethanol vapor, dynes/cm^2 $\times 10^{-10}$
Unfractionated	5.53	9.22	1.67	2.6
Fraction 1	20.5	22.8	1.11	2.7
Fraction 3	12.7	14.4	1.13	2.7
Fraction 5	7.34	9.14	1.25	2.7
Fraction 7	3.54	5.11	1.44	—[a]
Blend: Fr. 1 + 7 (2:1 by wt.)	9.12	18.9	2.08	2.75
Blend: Fr. 1 + 7 (1:2 by wt.)	5.84	11.5	1.96	2.75
Blend: Fr. 3 + 5 (1:1 by wt.)	7.23	9.14	1.26	2.8

[a] Fracture occurred before readings could be made.

Anaprep) with tetrahydrofuran as solvent. Gel was removed from all samples by solution filtration and subsequent precipitation. This treatment narrowed the molecular weight distribution of the unfractionated polymer somewhat. Molecular weights were measured by gel permeation chromatography using a computer program to correct for peak broadening. Table I lists the $\bar{M}_w$, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ for the films studied. The molecular weight characteristics of the blended samples are based on actual GPC measurements rather than calculated values because some of the material used in the mixtures was fractionated and recovered in another batch.

RESULTS AND DISCUSSION

Table I also lists the initial value of the complex modulus E^* for fractionated, unfractionated, and blends of fractionated poly(vinyl chloride). These are averaged values based on three specimens. As expected, all of the samples, regardless of molecular weight or molecular weight distribution, show similar initial values of E^*.

Figures 2–5 show plots of tan δ, E^*, and strain versus time for film of fractions 1, 3, and 5 and unfractionated PVC.

A substantial increase in the dynamic modulus of fatigue-tested fibers during the first few minutes of testing has been reported.[9] Constant stress tests on nylon fibers also indicated that there was a high rate of free-radical generation during this period.[10] Therefore, one point of interest in this research was to determine whether structural changes in unoriented PVC, as measured by E^* and tan δ, would occur during the early portions of the fatigue tests. However, examination of the test data shows changes that are just marginally significant. Usually a small increase in E^* was observed, but this rarely exceeded 3%. Tan δ values
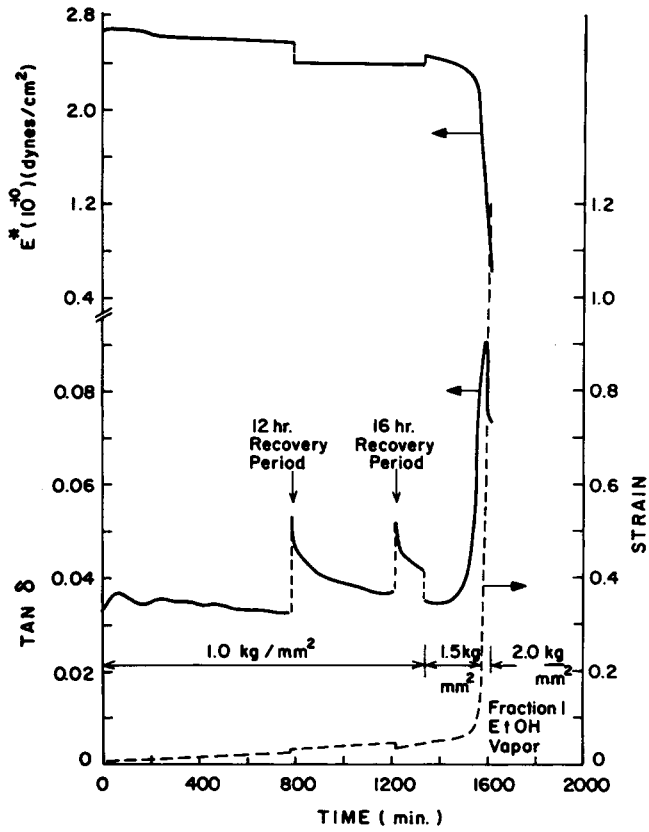
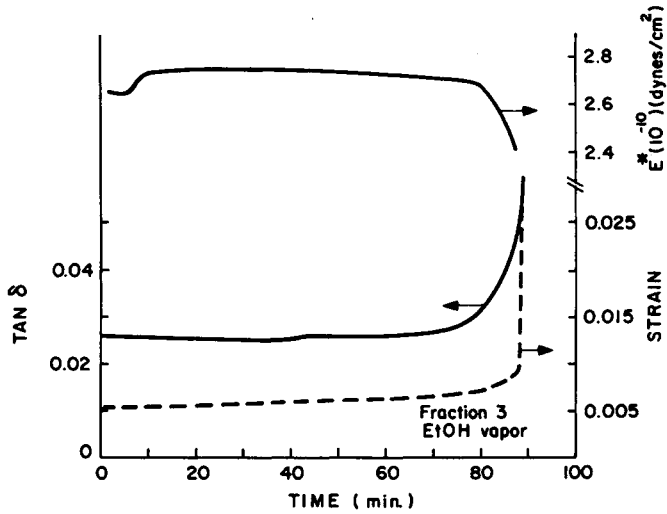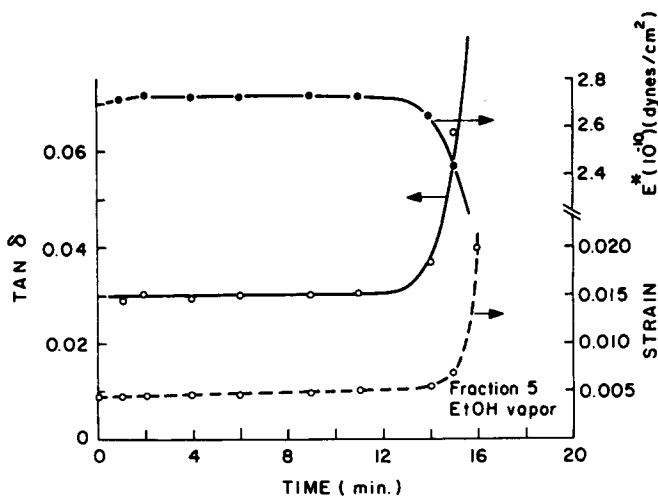Fig. 2. E^*, tan δ, and ϵ for fraction 1.

Fig. 3. E^*, tan δ, and ϵ for fraction 3.

Fig. 4. E^*, tan δ, and ϵ for fraction 5.
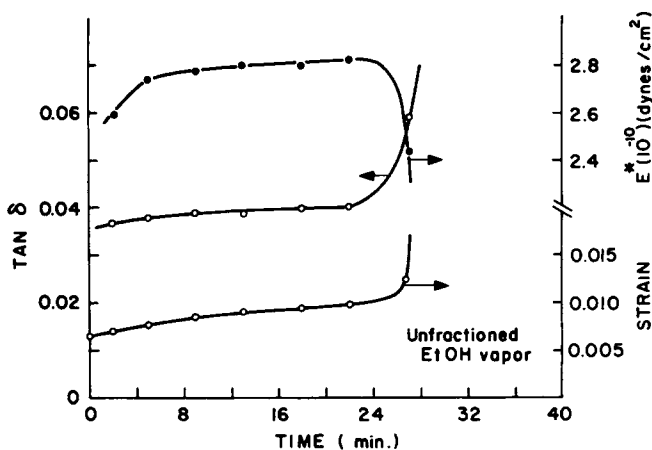
Fig. 5. E^*, tan δ, and ϵ for unfractionated PVC.

often showed a small initial decrease, especially in the fractionated material, but this, too, was usually no more than 3%. Such results are not un-expected because the changes reported in the fiber tests were presumably due to reorientation and rearrangement of crystalline regions. These movements would be of no great import in slightly crystalline PVC films.

Aside from these minor perturbations, the modulus and tan δ values remained constant until, at some point, tan δ began to increase. Depend-ing on the environment and molecular weight, the sample would then either fail quickly or else show progressively greater increases in tan δ and strain. Modulus remained invarient until a growing crack or craze was large enough to affect the overall sample stiffness.
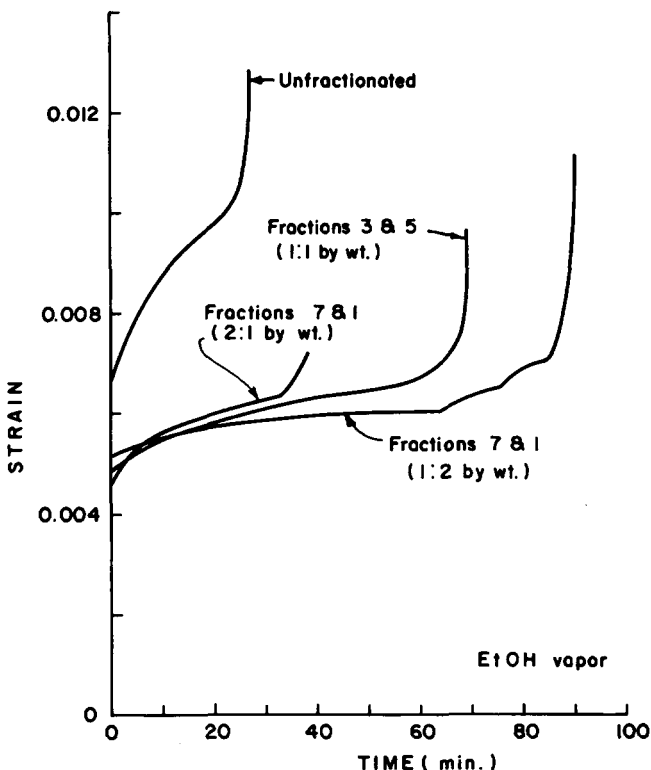
Fig. 6. Strain vs. time for broad-distribution specimens.

One example of the change in tan δ is the small perturbation in the tan δ curve of Figure 3 at 40 min. Another is the increase in the tan δ reading of fraction 1 during the first 2 hr as shown in Figure 2. This probably corresponded to a local stress whitening which was observed at the time. The tan δ shifts were small compared to the scale of the figures presented here but are readily observable in the raw data or on larger scale plots.

Tan δ appeared to be reasonably sensitive to craze formation and crack propagation in these samples. A good example of this is given in Figure 6 and 7 where the plots of strain and tan δ of the 1:2 blend of fractions 7 and 1 go through similar stages during the final half-hour of the test. Craze formation and crack propagation were not monitored directly but sample strain should be an indirect measure of these parameters since the average load was constant and creep in the uncrazed portions was relatively insignificant.

With few exceptions, cracks and crazes in the sample were limited to a narrow region; often only one macroscopic crack was formed. No starter crack was made in the specimens. However, the cross-sectional area did vary slightly along the sample axis because the mercury-cast films tended
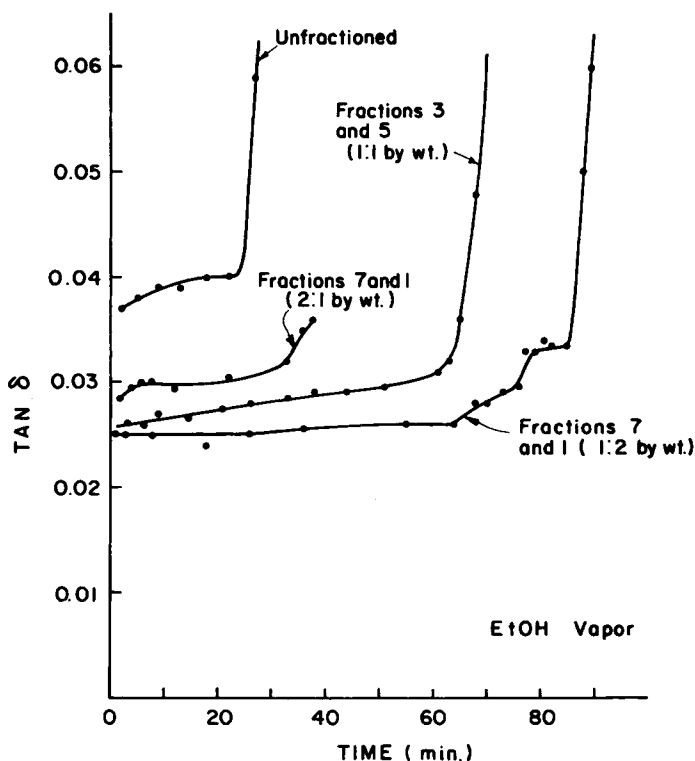
Fig. 7. Tan δ vs. time for broad-distribution specimens.

to be slightly thinner around the periphery. As a result of this gradient, the minimum cross-sectional area of a typical sample was 5% or 10% below the average cross-sectional area. Rupture normally occurred near the minimum so the 1.0 kg/mm² preload was based on this area. Values of E^* were calculated using the average cross-sectional area.

Perhaps the major feature evident in Figures 2–7 is the effect of molecular weight on failure time. Plots showing the relationship between these parameters in EtOH vapor are included in Figures 8 and 9. Figure 8 gives rupture time as a function of $\bar{M}_n$. It is clear from this plot that relatively small increases in the $\bar{M}_n$ of the fractions drastically improved sample durability. However, molecular weight distribution effects are also apparent because the test points representing the broad-distribution blends and the unfractionated material all fell outside of the failure envelope. This suggests that use of another molecular weight average might give a better correlation. Replotting the data as a function of $\bar{M}_w$, Figure 9, gave much better agreement between the fractions and the broad-distribution samples. Molecular weight effects are quite obvious since the fraction 7 samples ($\bar{M}_w = 51,100$) failed in a few seconds while those made from fraction 1 ($\bar{M}_w = 228,000$) had not fractured after 1600 min. Although further testing would be required to statistically confirm the
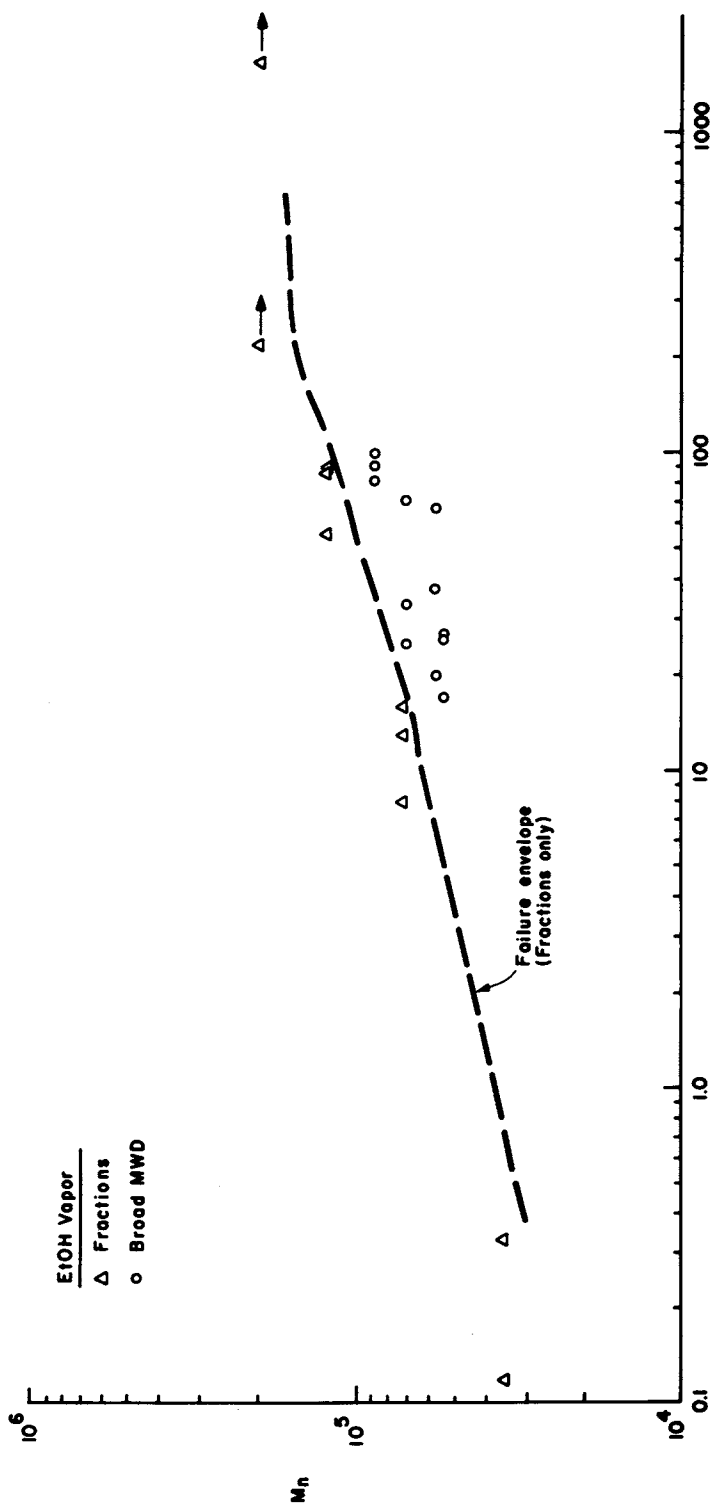
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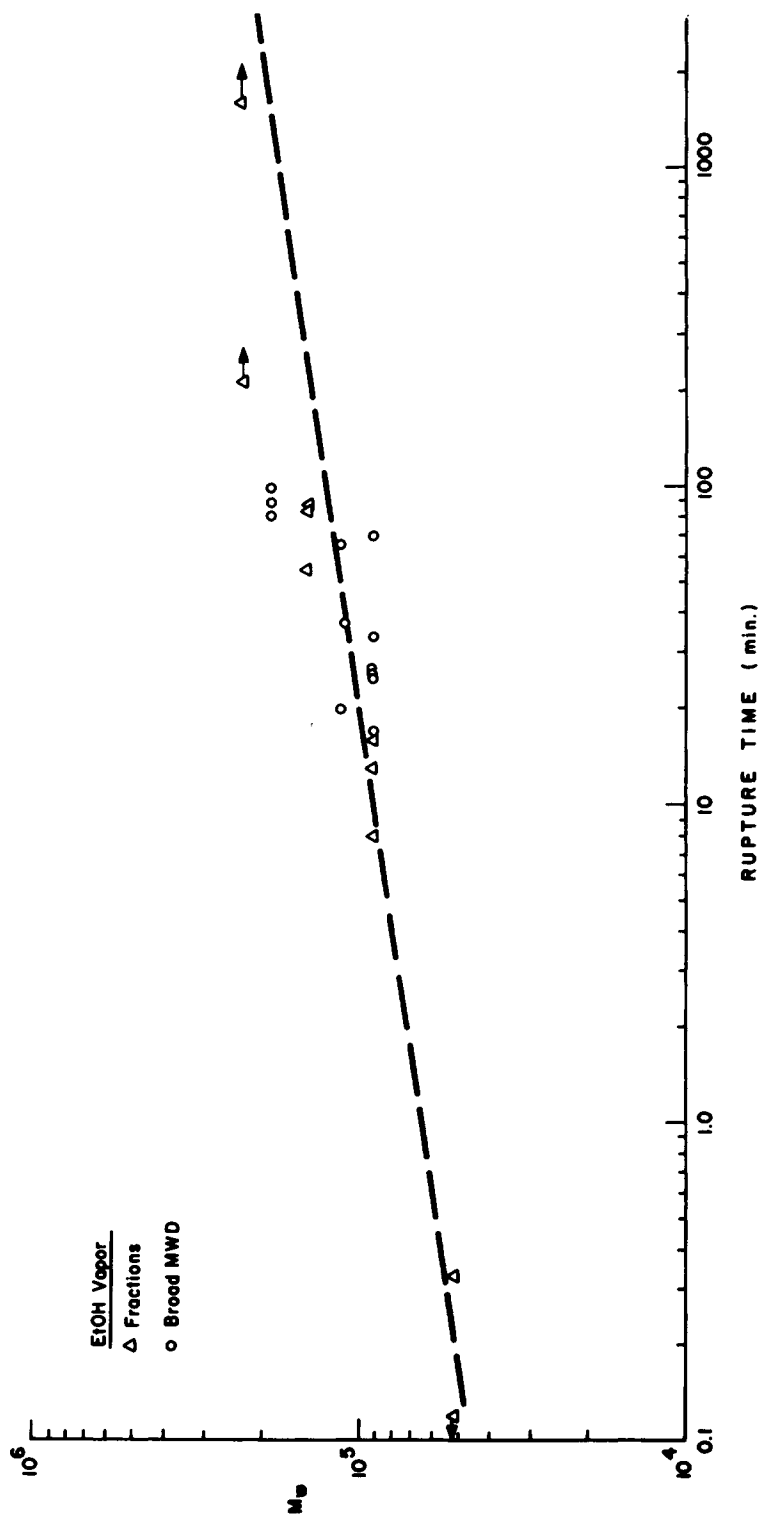Fig. 8. Rupture time vs. $\bar{M}_n$ in ethanol vapor.

Fig. 9. Rupture time vs. $\bar{M}_w$ in ethanol vapor.

rupture time relationships shown here, it is evident that molecular weight has a major effect on this parameter.

References

1. P. P. Benham and S. J. Hutchinson, *Plast. Polym.*, **38**(136), 259 (1970).

2. J. P. Elinck, J. C. Bauwens, and G. Homes, *Int. Fracture Mech.*, **7**, 277 (1971).

3. S. J. Hutchinson and P. P. Benham, *Plast. Polym.*, **38**(134), 10102 (1970).

4. M. Suzuki, S. Yada, N. Mabuchi, Y. Saviche, and Y. Matsuya, *Kobunshi Kagaku,* **28**(319), 915 (1971).

5. S. Okuda and S. Nishina, *Proc. Jap. Congr. Testing Mater.*, **9**, 109 (1966).

6. F. Fischer, *Centre Belge Etude Doc. Eaux*, **21**(294), 243 (1968); *Gummi Asbest Kunstst.*, **21**(2), 112 (1968).

7. P. G. Faulkner and J. R. Atkinson, *Plast. Polym.*, **40**(147), 109 (1972).

8. J. R. Martin and J. F. Johnson, *J. Polym. Sci., Polym. Phys. Ed.*, submitted for publication.

9. D. C. Prevorsek and W. J. Lyons, *Polym. Preprints*, **5**(2), 427 (1964).

10. K. L. Devries et al., *Int. J. Fracture Mech.*, **7**, 197 (1971).