

Poly(vinyl Chloride): Effect of Molecular Weight and Vapor Environment on Viscoelastic and Fatigue Properties

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Synopsis

Viscoelastic and fatigue studies were made on polyvinyl chloride films using oscillatory loading on prestressed samples in dry nitrogen and nitrogen saturated with both water and ethanol vapor. Samples included unfractionated PVC, narrow molecular weight distribution fractions and blends made from the fractions. A combination of SEM photomicrographs and the viscoelastic data showed differences in crazing and plasticization in the different environments. Failure time, loss factor, creep and elastic modulus were all affected by some of the environments. Molecular weight was also a major factor in determining fatigue life as well as the mode of failure. For example rupture times were increased by four orders of magnitude when M_w was raised by a factor of five.

INTRODUCTION

In part II of this series,¹ the previous fatigue studies on poly(vinyl chloride) were tabulated and discussed briefly. This study continues that reported in part II and extends it to different vapor environments in addition to examining the effect of molecular weight and molecular weight distribution on viscoelastic and fatigue properties.

EXPERIMENTAL

All of the viscoelastic tests were conducted on a modified Rheovibron Model DDV II. The modifications to the apparatus are discussed in reference 1. All of the samples tested were cast from a tetrahydrofuran solution onto mercury using a technique described in detail elsewhere.² Unless otherwise stated, the tests were run at $25^\circ \pm 1^\circ\text{C}$, a stress level of 1 kg/mm^2 , and a frequency of 3.5 Hz. Strain amplitude was ± 0.0030 .

The vapor tests were conducted at saturation conditions using nitrogen as the carrier gas. Preliminary measurements with a variety of vapors and test conditions indicated that sample stiffness and loss factor were noticeably affected in some cases by the per cent of vapor saturation. It was possible to alternately soften and stiffen a sample by perturbations in per

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cent saturation so close control of nitrogen flow rate through the pre-saturator column was important.

The poly(vinyl chloride) used in this study was purified and fractionated from B. F. Goodrich product Geon 110 X 265. It was fractionated on a large-scale gel permeation chromatograph. Molecular weights were determined using GPC. The results were corrected for band broadening. Characterization of the test materials is given in reference 1.

The SEM photomicrographs were made using the Cambridge Stereoscan Mark II.

RESULTS AND DISCUSSION

When the dumbbell-shaped PVC films were fatigued in water vapor at 40°C and a stress level of 1.2 kg/mm², they quickly plasticized. This is quite evident from the data shown in Figure 1 where the modulus rapidly fell to less than 1/3 of its initial value while the loss factor increased from 0.046 to 0.11 after 20 min of fatigue loading. The test was terminated at an elongation of 120% owing to the limited travel available on the test instrument. Photomicrographs of the surface of this sample are given in

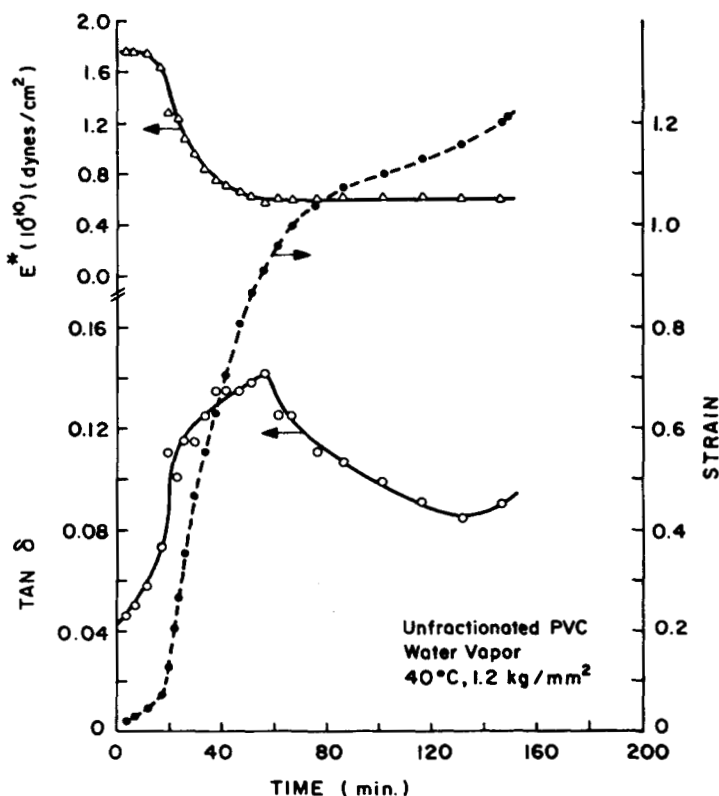
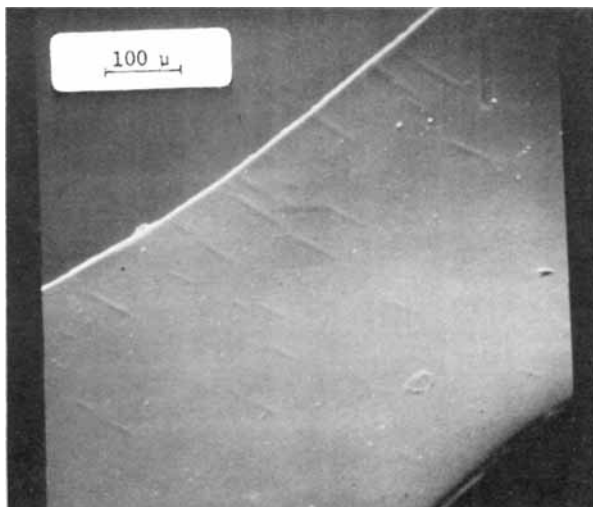
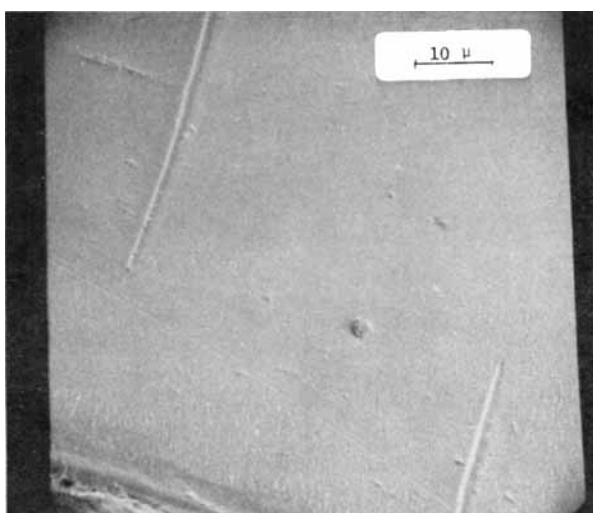


Fig. 1. Complex modulus, loss factor, and strain for unfractionated PVC ($M_w = 92,200$; $M_w/M_n = 1.67$).

Figure 2. Although there were crazes scattered over this surface, it is obviously quite different from the heavily crazed surface shown in Figure 3. The latter photos show a PVC fraction which had been tested in ethanol vapor at 25°C. It, too, elongated to 120% without rupturing. As indicated in Figures 4, 5, and 6, the ability to attain high strains in the ethanol test was limited to the highest MW fraction. This is discussed further in reference 3.

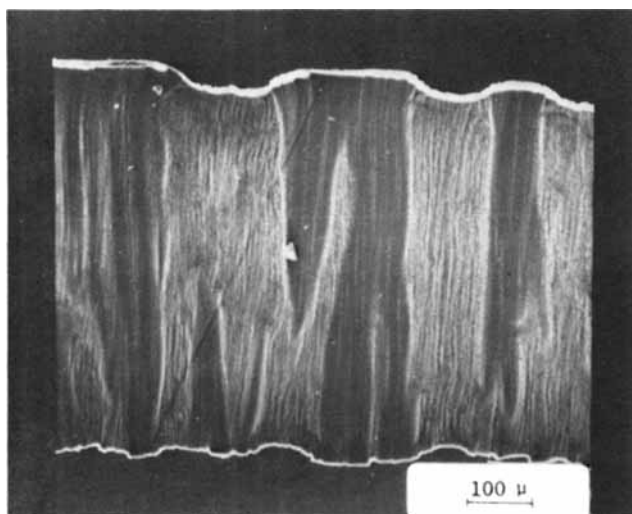


(a)

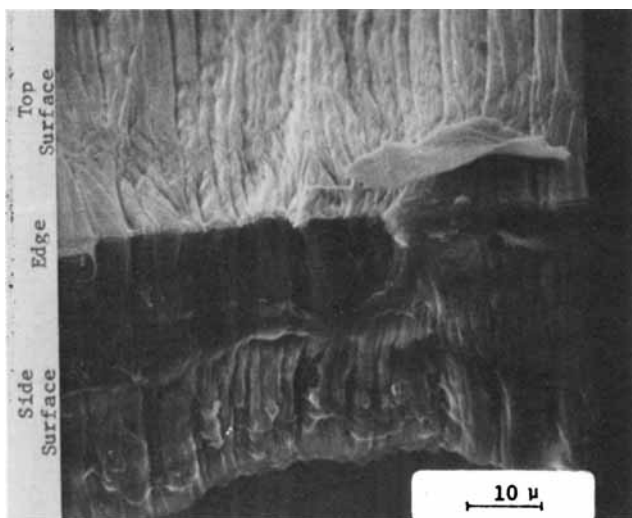


(b)

Fig. 2. Surface of unfractionated PVC after elongating 120% in water vapor at 40°C.
(a) original magnification 135 \times ; (b) original magnification 1400 \times .



(a)



(b)

Fig. 3. Surface of fraction 1 ($M_w = 228,000$; $M_w/M_n = 1.11$) after yielding in EtOH vapor. (a) original magnification 115 \times ; (b) original magnification 1300 \times .

Thus, the two sets of test conditions caused gross deformation by two different mechanisms. Ethanol, at 25°C, did not significantly plasticize the specimen. Rather, it induced crazes which could propagate through high molecular weight specimens without causing rupture. In contrast, water vapor at 40°C gave a uniform plasticization and left a relatively featureless surface.

The mode of deformation is, of course, dependent on test conditions as well as molecular weight. For example, the unfractionated PVC in-

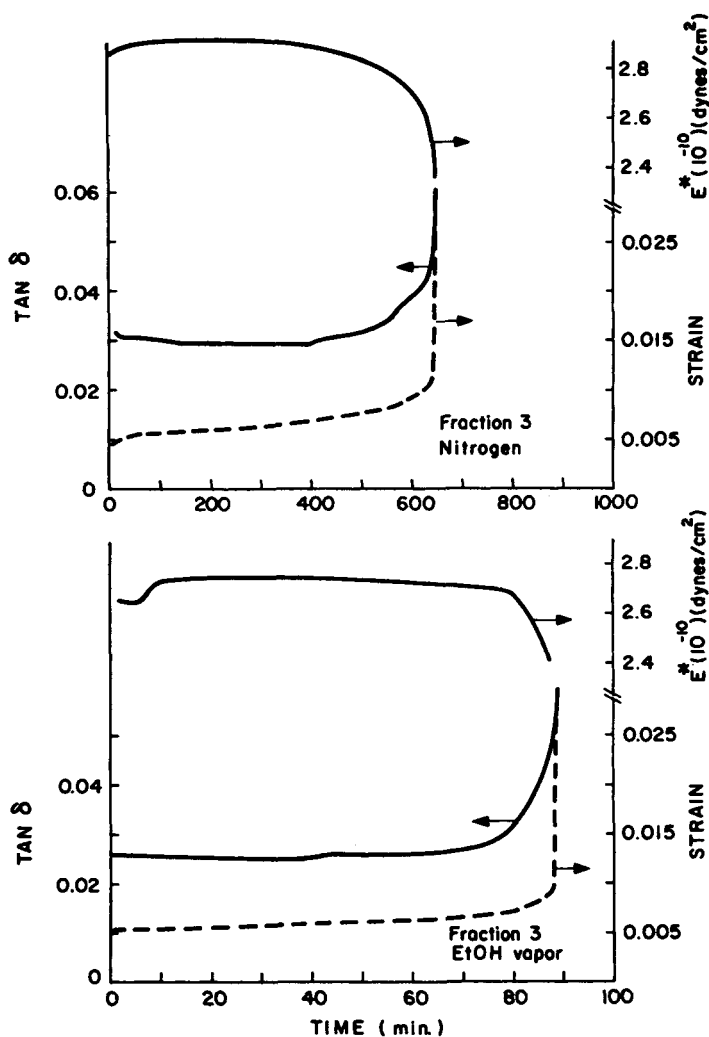


Fig. 4. Complex modulus, loss factor, and strain for fraction 3 ($M_w = 144,000$; $M_w/M_n = 1.13$).

variably fractured at low strains when tested in dry nitrogen, ethanol vapor, or Freon PCA vapor at 25°C. Yet the same films readily plasticized and/or crazed when tested at lower dynamic strain amplitudes in other vapors such as methanol (25–30°C) or ethanol at 48°C.

Typical plots of complex modulus, $\tan \delta$, and strain for samples of different molecular weights and molecular weight distributions are presented as a function of time in Figures 4, 5, and 6. Note the difference in time scales between the nitrogen tests and those conducted in ethanol vapor. In both of these environments, modulus remained essentially constant until rupture or crazing was initiated. $\tan \delta$ also remained almost invariant until this time. This is in sharp contrast to the water vapor test cited above.

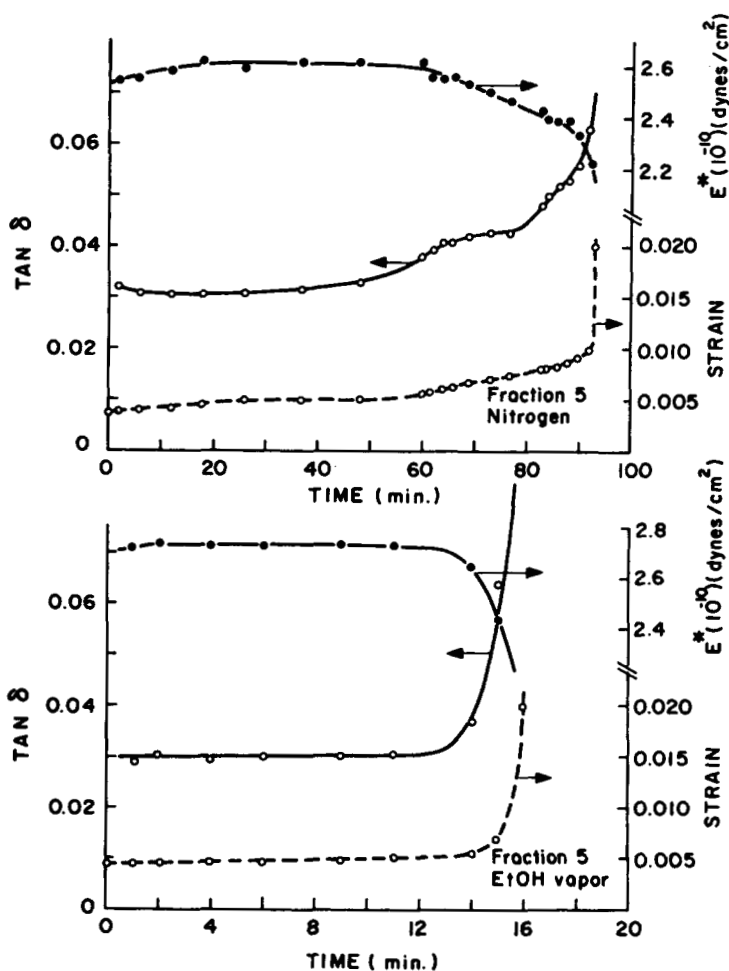


Fig. 5. Complex modulus, loss factor, and strain for fraction 5 ($M_w = 91,400$; $M_w/M_n = 1.25$).

Although it is evident from Figures 4, 5, and 6 that the presence of ethanol vapor greatly reduced fatigue life, these figures also show the dramatic effects of molecular weight. When plots of rupture time versus molecular weight were made, the significance of M_n , M_w , and M_z was examined by comparing the results of fractions, blends, and unfractionated material. It is evident in Figure 7 that when rupture time was plotted as a function of M_n , the broad MWD materials tended to have longer failure times than comparable fractions of the same M_n . However, in the plots based on M_w , superposition of the fractions and broad MWD samples is much more satisfactory. This comparison was also made using plots based on M_z (not shown). As might be expected, the fractions tended to have longer rupture times in this plot. Thus, M_w appears to give the best fit for these tests. In examining Figures 7 and 8, we see relatively few data points for the nitrogen test, so this conclusion is more tentative for this environment.

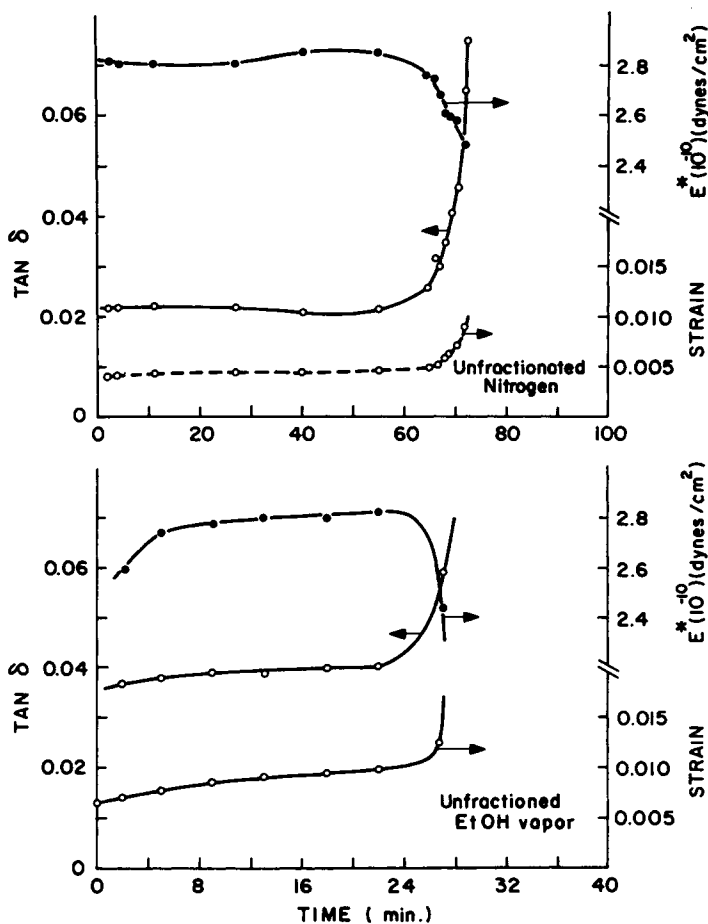


Fig. 6. Complex modulus, loss factor, and strain for unfractionated PVC.

The figures also indicate that the differences between the ethanol and nitrogen tests are greatest at low molecular weights. One is tempted to relate this observation and the overall molecular weight effect to flaws caused by chain ends. However, the lack of a correlation between rupture time and M_n strongly suggests a more complex relationship.

There is a change in failure mode as MW is increased: brittle fracture in low MW samples, ductile yielding in high MW specimens. SEM photographs of these specimens³ indicate that the thickness of the ductile walls which formed around the sample edges increased with MW. However, many aspects of the fracture surfaces of high MW but broad MWD specimens still resembled those of low MW materials. It is not unreasonable, therefore, to link long range extensibility to the high MW tail of the molecular weight distribution while the rupture path would be controlled by the low MW tail. Ethanol apparently aids local rearrangement of chain segments to conform to the applied stresses. If the material has a high

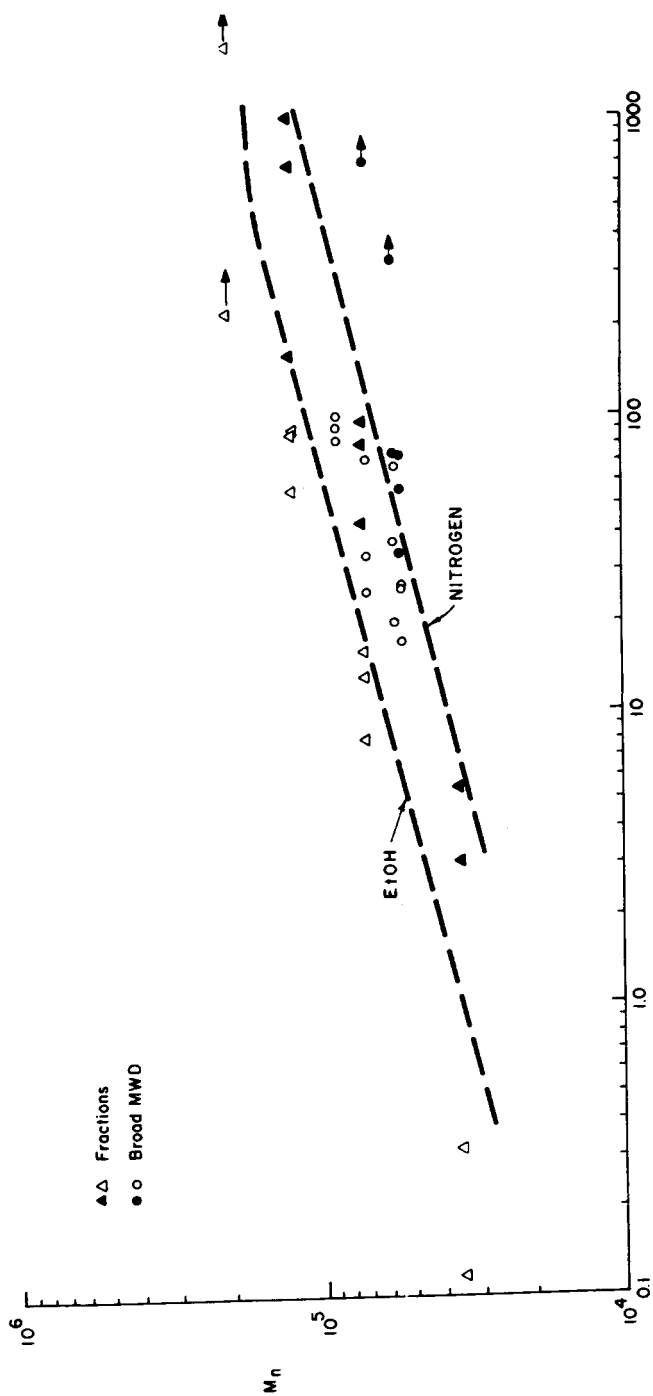


Fig. 7. Rupture time vs. M_n in nitrogen and ethanol vapor: open symbols, ethanol; closed symbols, nitrogen.

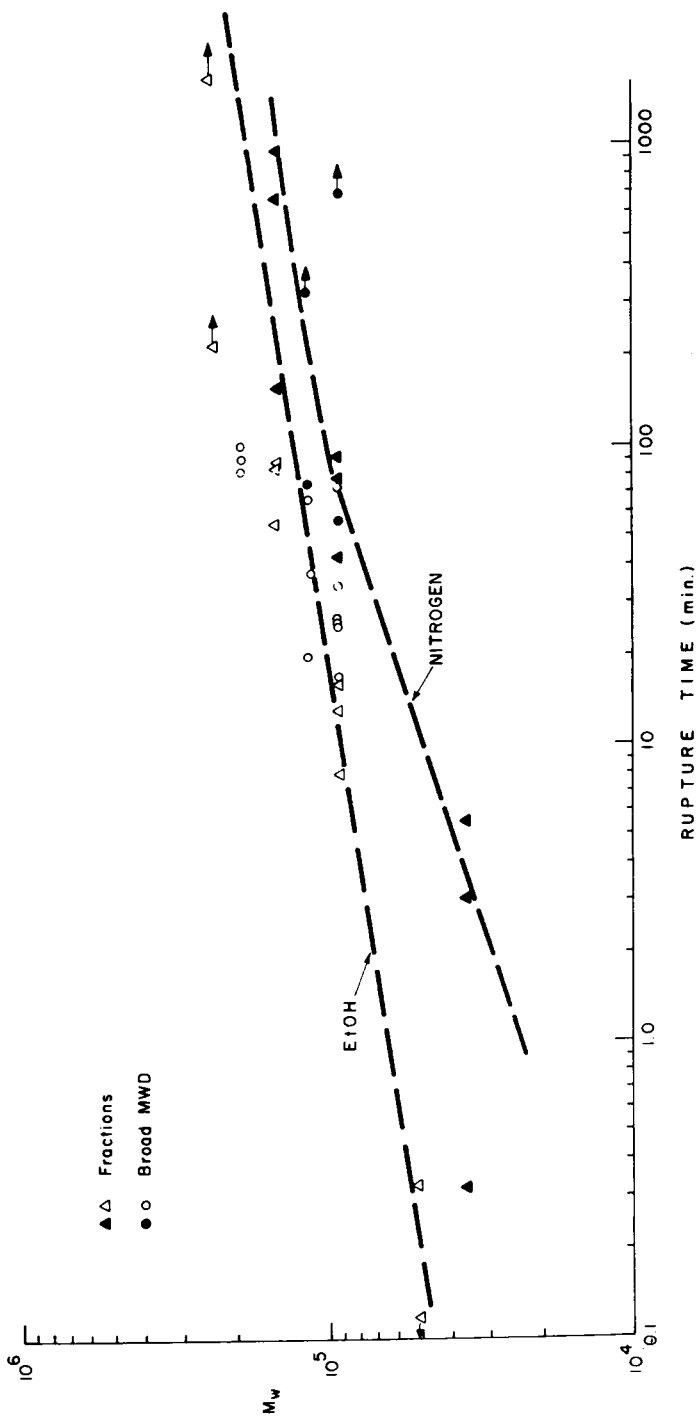


Fig. 8. Rupture time vs. M_w in nitrogen and ethanol vapor: open symbols, ethanol; closed symbols, nitrogen.

M_w , the result is enhanced ductility and yielding which increases rupture time. On low M_w samples, some of the rearranged molecules are unable to bridge the forming crazes. By accelerating molecular rearrangements, the ethanol increases both the rate of craze formation and the rate at which the short-chain molecules reach their maximum extensibility. Thus, while the actual fracture path may be governed by the local density of short chains (an M_n parameter), rupture times were also affected by ductility, a phenomenon related to the higher moment averages such as M_w or M_z . These were apparently controlling, since the M_w plots have the best fit to the data.

In principle, this explanation should also be valid for the nitrogen tests since ductile wall formation was observed in these samples, and the M_w plot gave the best fit to the rupture time data. Without ethanol, the rates of chain segment rearrangement and craze formation are much lower so rupture times are longer.

At 40°C, water vapor does more than aid in reordering chain segments. Judging from the evidence in Figures 1 and 2, substantial plasticization and shear flow must also occur. Indeed, there was substantial optical orientation in the water vapor sample shown in Figure 2. Orientation in the crazed sample shown in Figure 3 was limited to the craze regions. Without the flow and softening effects of a plasticizer, the interior regions of the nitrogen and ethanol specimens were subjected to a dilatational loading. This led to the observed craze formation which in turn caused either brittle fracture or ductile yielding. Dilatational stresses in the warmer, water vapor-plasticized samples would be much lower. To some extent, this is a temperature effect and would be true even without water vapor because Poisson's ratio of glassy polymers comes closer to 0.5 as the glass transition temperature is approached. This value, of course, corresponds to an incompressible or nondilatable condition.

In summary, then, we find that the presence of ethanol vapor reduced fatigue life of prestressed PVC by about an order of magnitude while changes in molecular weight by a factor of 5 led to rupture time variations of four orders of magnitude. The effects of ethanol vapor would seem to be rather surprising since ethanol is a nonsolvent for PVC. The other significant item demonstrated here was the substantial effect of water vapor on PVC when it is under a stress. Unlike ethanol, the water vapor plasticized PVC instead of crazing it.

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References

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2. J. R. Martin and J. F. Johnson, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 579 (1974).
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