

# Environmental Effects on Latex Paint Coatings.

## I. Base Polymer Degradation

D. PATIL, R. D. GILBERT, and R. E. FORNES,\* *Fiber and Polymer Science Program, \*Physics Department, North Carolina State University, Raleigh, North Carolina 27695*

### Synopsis

Films of the base polymer used in a latex paint have been exposed to various combinations of UV/SO<sub>2</sub>/H<sub>2</sub>O/air. The polymer is primarily a terpolymer of butyl acrylate, vinyl acetate, and vinyl chloride. Reported here are results from dynamic mechanical analysis ( $T_g$ ), sol-gel analysis, intrinsic viscosity and contact angle measurements. Exposure without the presence of UV causes virtually no change in the properties of the films. In the presence of UV and clean air containing O<sub>2</sub>, there is evidence of both chain scission and crosslinking. When films are exposed to combinations of either UV/SO<sub>2</sub> or UV/SO<sub>2</sub>/H<sub>2</sub>O, a dramatic increase in the rate of change in the properties is observed, indicating a synergistic interaction between UV and SO<sub>2</sub>. The gel fraction increases from about 20% for the control to about 65% in samples exposed to UV/SO<sub>2</sub> or UV/SO<sub>2</sub>/H<sub>2</sub>O for as little as 24 h. In the latter exposed samples, there is a corresponding precipitous drop in the intrinsic viscosity of the soluble fraction, a significant increase in the surface polarity of the films, and a large increase in the  $T_g$ . Reaction mechanisms for changes resulting from the various exposure conditions are proposed.

### INTRODUCTION

Exposure of polymers to hostile environments may cause a variety of changes in the polymer microstructure and physical properties including chain scission, crosslinking, embrittlement, substituent loss, and discoloration. While the photooxidative degradation of polymers has been studied extensively,<sup>1-8</sup> to date there have only been a few publications regarding the effect on polymers of various air pollutants (SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>, hydrocarbons, etc., alone or in combination) and in the absence or presence of ultraviolet light and/or moisture. We have initiated an investigation on the effect of these pollutants on the microstructure of the base polymer in a latex paint coating.

Here we describe the effect of UV and SO<sub>2</sub> both alone and in combination on a copolymer consisting mainly of approximately equal molar ratios butyl acrylate, vinyl acetate, and vinyl chloride with minor amounts of methyl methacrylate and acrylic acid. The effect of moisture in combination with UV and/or SO<sub>2</sub> is also reported here.

Studies have appeared recently in the literature on compounded paints having the same base polymer as used in our investigations.<sup>9-11</sup> Those reports deal with the leaching of CaCO<sub>3</sub> from thin films by aqueous sulfur dioxide,<sup>9</sup> the porosity of thin films,<sup>10</sup> and the solubility and diffusivity of SO<sub>2</sub> into thin films.<sup>11</sup> However, no reports have appeared in the literature regarding chemical struc-

tural and mechanical property changes in the base polymer of a latex coating as a function of exposure to environmental pollutants.

## EXPERIMENTAL

The copolymer in latex form was kindly supplied by Union Carbide Corp. It was stored in opaque polyolefin containers under  $N_2$  prior to film preparation. Thin, uniform films were cast on release paper using standard draw-down bars. The films were separated from the release paper, dried under vacuum for 24 h, and stored in a desiccator under  $N_2$  until use.

Portions of the films were used to determine the gel content and the intrinsic viscosity  $[\eta]$  of the soluble portion. In each case, tetrahydrofuran (Fisher Scientific) was used as the solvent. Flow times were measured to 0.1 sec using a Ubbelohde viscometer. Contact angles of distilled  $H_2O$  were measured with an NRL goniometer (Ramé-Hart). Dynamic mechanical measurements were made with an Autovibron (I Mass) DDV-II-C, at a frequency of 11 Hz and a scanning speed of  $2.5^\circ C/min$  over the temperature range  $-50-100^\circ C$ .

The cast films were exposed to UV and/or  $SO_2$  in the absence and presence of moisture in quartz tubes fitted with inlet and outlet tubes. A glass frame was used to support the films. The quartz tubes and films were placed in a Rayonet Photochemical Reactor (Southern New England UV Co.) equipped with 16 UV lamps (350 nm) located around its interior circumference. Samples were exposed to gasses in the dark and in the presence of UV, and under both wet and dry conditions at ambient temperature (c.  $44^\circ C$ ) and pressure. The gas was either pure  $SO_2$  (Union Carbide), or purified air (Sunox Corp.). The gas was bubbled through distilled water just before passing across the films to study the effect of moisture.

To assure the data were reproducible, the experimental results reported are typically the average of at least several measurements on four separately prepared samples. Comparisons were generally made between samples tested within a batch of samples prepared at the same time, between batches made at different times, and selected measurements between different latex lots.

## RESULTS AND DISCUSSION

The change in gel content, intrinsic viscosity,  $T_g$ , and contact angle upon exposure of the polymer films for various times to UV/ $SO_2$ / $H_2O$  combinations are summarized in Table I and plotted in Figures 1-3. In the absence of UV, exposure to  $SO_2$ ,  $O_2$ , and moisture has little or no effect on polymer properties.

Exposure to UV and air containing  $O_2$  results in a relatively slow decrease in molecular weight of the soluble portion of the copolymer due to chain scission and an increase in the gel content resulting from crosslinking. However, under these exposure conditions, there is only a minor increase in the copolymer  $T_g$ , which suggests a relatively slow rate of oxidative degradation and that both chain scission and crosslinking are occurring at comparable rates, and the contact angle is virtually unchanged.

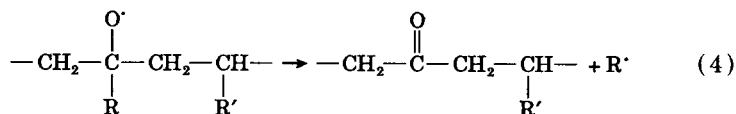
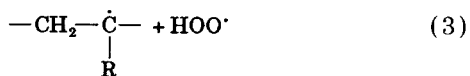
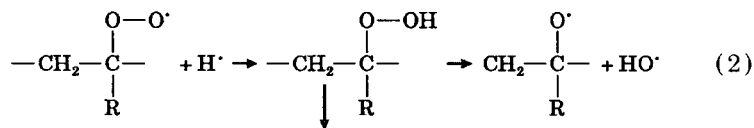
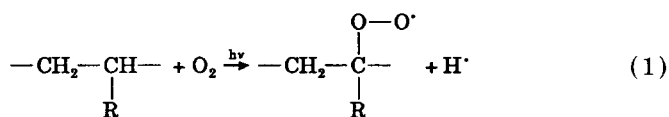
Photooxidation, leading to both chain scission and crosslinking, could occur as follows:

TABLE I  
 Intrinsic Viscosity, Gel Content, Surface Contact Angle, and Glass Transition Temperature of  
 Base Polymer Films Exposed to Combinations of UV, Air, SO<sub>2</sub>, and H<sub>2</sub>O for Varying Times

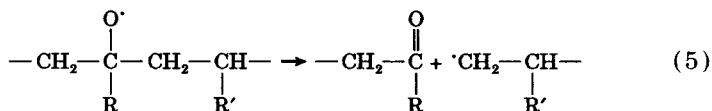
Exposure time (h)	UV (350 nm)	Air	SO <sub>2</sub>	H <sub>2</sub> O	[η] (dL/g)	Gel (%)	Contact angle (°)	T <sub>g</sub> (°C)
0					1.00	22	77	23
24	+	+	-	-	0.98	28	77	15
48	+	+	-	-	0.83	29	78	16
96	+	+	-	-	0.55	36	78	16
24	-	-	+	-				
48	-	-	+	-	1.00	22	74	25
96	-	-	+	-	1.00	21	76	23
24	+	-	+	-	0.15	65	45	NM <sup>b</sup>
48	+	-	+	-	0.13	64	50	78
96	+	-	+	-	0.12	65	<sup>a</sup>	87
24	+	+	-	+	1.00	19	78	NM <sup>b</sup>
48	+	+	-	+	1.00	21	72	24
96	+	+	-	+	0.90	23	83	NM <sup>b</sup>
24	+	-	+	+	0.19	61	45	NM <sup>b</sup>
48	+	-	+	+	0.05	60	40	49
96	+	-	+	+	0.08	58	<sup>a</sup>	60

<sup>a</sup> Drop spread immediately.

<sup>b</sup> NM = not measured.



or



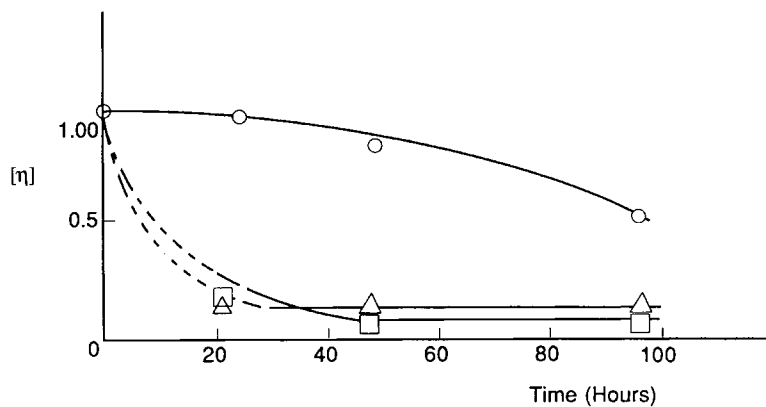


Fig. 1. Intrinsic viscosity vs. exposure time: (○) UV/air; (Δ) UV/SO<sub>2</sub>; (□) UV/SO<sub>2</sub>/H<sub>2</sub>O.

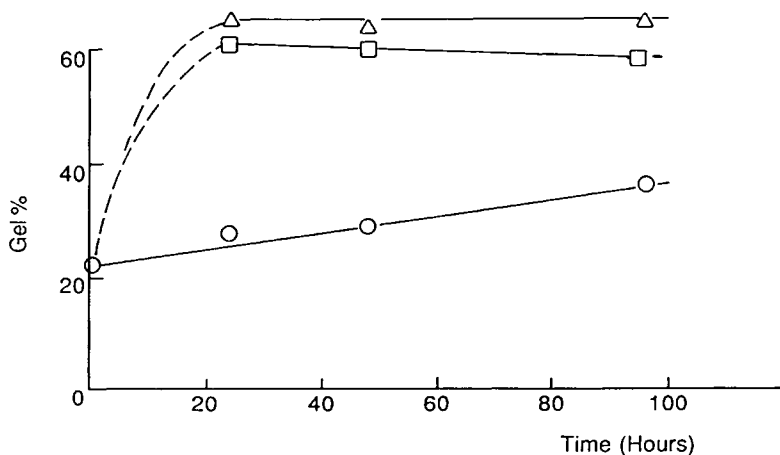
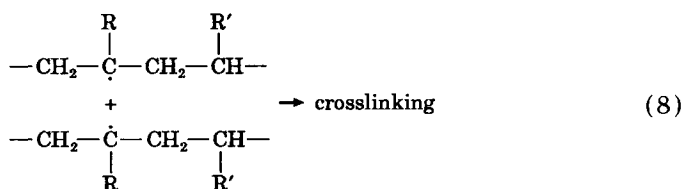
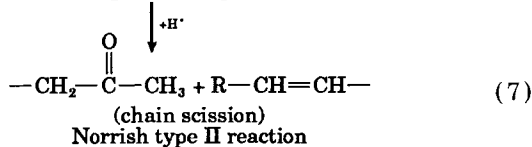
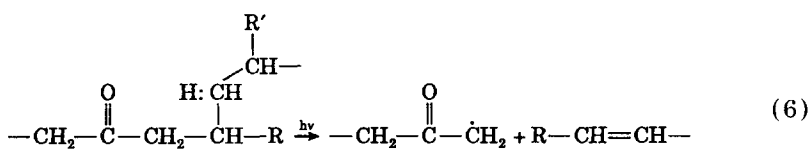
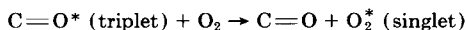


Fig. 2. Gel fraction vs. exposure time: (○) UV/air; (Δ) UV/SO<sub>2</sub>; (□) UV/SO<sub>2</sub>/H<sub>2</sub>O.

The relatively small amount of degradation would probably not significantly increase the number of carbonyl groups, compared to the amount originally present, accounting for the contact angle being virtually unchanged.

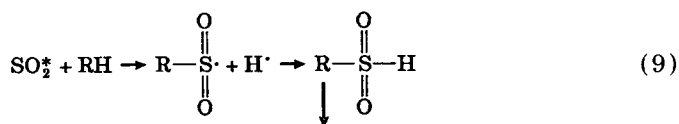
Little or no photoactivation of  $O_2$  occurs at 350 nm. However, the carbonyl groups in the side groups of the copolymer will act as photosensitizers. Irradiation of carbonyl groups produces a triplet (of life time c.1 sec) which could transfer energy to  $O_2$  and photoactivate it.



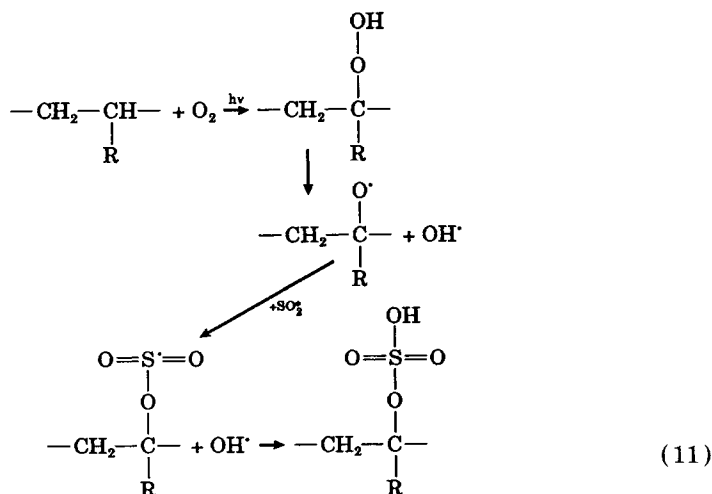
Then reactions 1-5 result leading to both chain scission and crosslinking. The carbonyl groups could similarly function as photosensitizers in the photoactivation of  $SO_2$  in the presence of 350 nm UV light.

In the presence of both UV,  $O_2$ , and  $SO_2$  there is a rapid decrease in the molecular weight of the soluble portion, and significant increases in surface polarity, gel content, and  $T_g$ . The significant increase in the  $T_g$  suggests that in the presence of  $SO_2$ , UV, and  $O_2$  crosslinking predominates. (NB: It is assumed that  $O_2$  was not completely removed from the polymer films.)

Dainton and Ivin<sup>2</sup> demonstrated that photoactivated  $SO_2$  ( $SO_2^*$ ) reacts with hydrocarbons to form sulfinic acids:

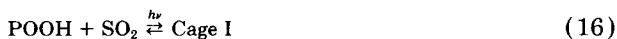


In the presence of UV,  $O_2$ , and  $SO_2$ , the following reactions have been postulated by Jellinek and Pavlinec<sup>8</sup> and by Richters<sup>12</sup> to occur in polystyrene and polypropylene, respectively:



Similar groups have been proposed in thermal and photooxidation studies of polysulfone.<sup>13</sup>

Jellinek and Kryman<sup>3</sup> report the combination of UV, SO<sub>2</sub>, and O<sub>2</sub> causes chain scission in polymethyl methacrylate. They also reported<sup>7</sup> that SO<sub>2</sub> is essential for effecting or enhancing chain scission of isotactic polystyrene in the presence of near UV light, and that UV irradiation or SO<sub>2</sub> alone does not cause degradation. They suggest the large quantum yields for SO<sub>2</sub> (14 times larger than that for O<sub>2</sub>) accounts for the synergistic effect of SO<sub>2</sub> in causing chain scission. They offered the following mechanism:



That is, chain scission in highly viscous media proceeds via ion cages but they did not provide an exact mechanism. Later Jellinek<sup>5</sup> suggested the following reactions:

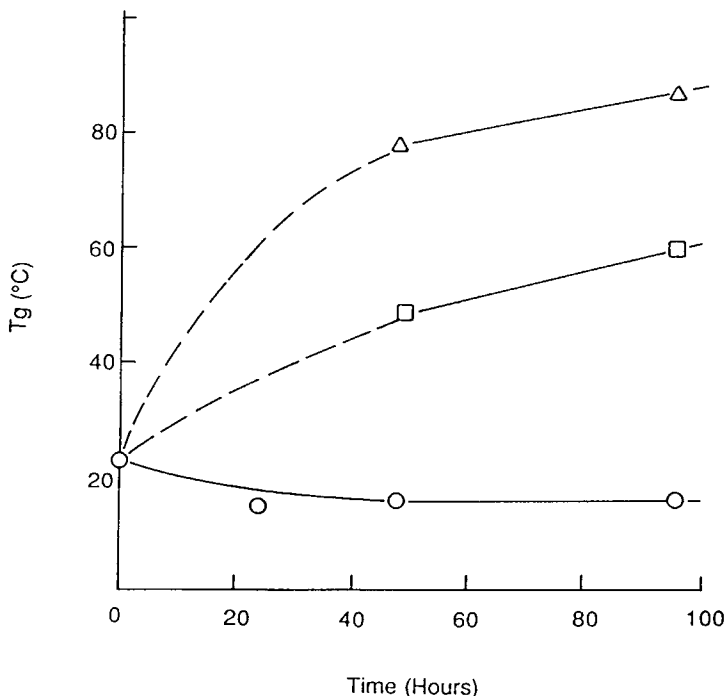
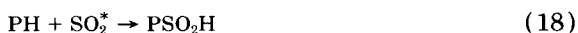
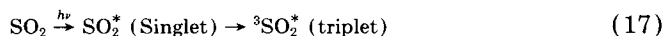


Fig. 3. Glass transition temperature ( $T_g$ ) vs. exposure time: (○) UV/air; (△) UV/SO<sub>2</sub>; (□) UV/SO<sub>2</sub>/H<sub>2</sub>O.



and  $\text{PSO}_2\text{H}$  "performs a similar function as hydroperoxides in causing chain scission." Thus



I

The high quantum yield of  $\text{SO}_2$  results in a higher yield of species I than in the presence of  $\text{O}_2$  alone. Chain scission and crosslinking via reactions 2–6 then occur at a faster rate, accounting for the synergistic effect of UV and  $\text{SO}_2$  (in the presence of  $\text{O}_2$ ) in causing polymer degradation and embrittlement.

In the presence of UV, air, and moisture, both chain scission and crosslinking are virtually suppressed. Presumably,  $\text{H}_2\text{O}$  interferes with the photoactivation of  $\text{O}_2$ . This is confirmed by the data in Table II. Polymer films were exposed to UV, air, and  $\text{H}_2\text{O}$  for 96 h, and were then dried and exposed to UV and air only for 48 and 96 h. The change in  $[\eta]$  of the soluble portion and the gel fraction are virtually identical to those for films exposed in the absence of moisture for 48 and 96 h. (Table I).

In the presence of UV,  $\text{SO}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$ , chain scission occurs very rapidly (Table I). Presumably, the attack by photoactivated  $\text{SO}_2$  is augmented by the presence of  $\cdot\text{OOH}$  radicals.



TABLE II  
Intrinsic Viscosity and Gel Contents for Films Exposed Sequentially  
under Wet and Dry Conditions to UV and Air

Exposure time (h)		[ $\eta$ ] (dL/g)	Gel (%)
UV (350 nm) + $\text{H}_2\text{O}$	UV (350 nm)		
96	48	0.86	31
96	96	0.46	42

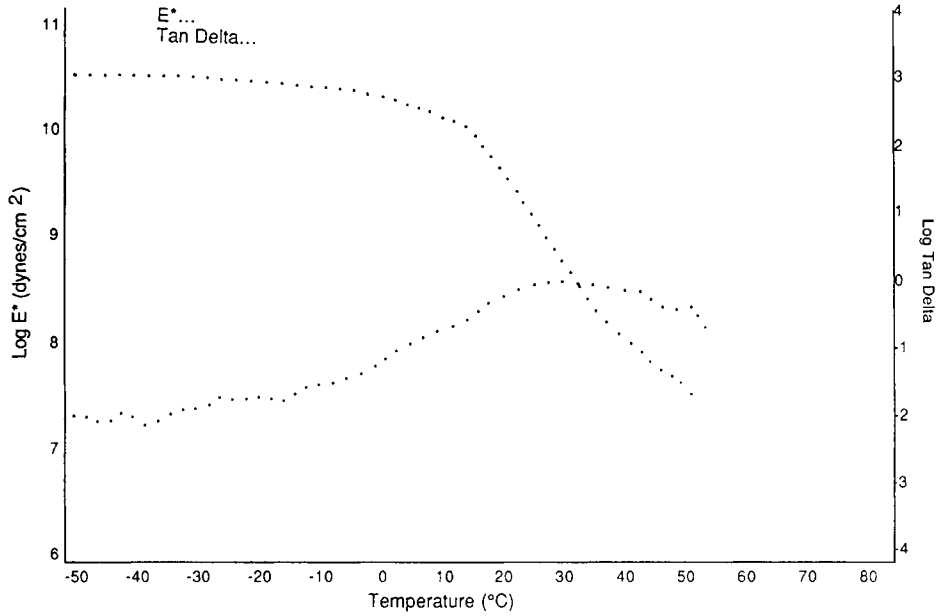


Fig. 4. Dynamic mechanical analysis of a thin film (control) of the copolymer.

The  $T_g$  increases due to crosslinking but the increase is lower than in the absence of  $H_2O$ , reflecting increased plasticization due to the very low molecular weight of the chain scission products.

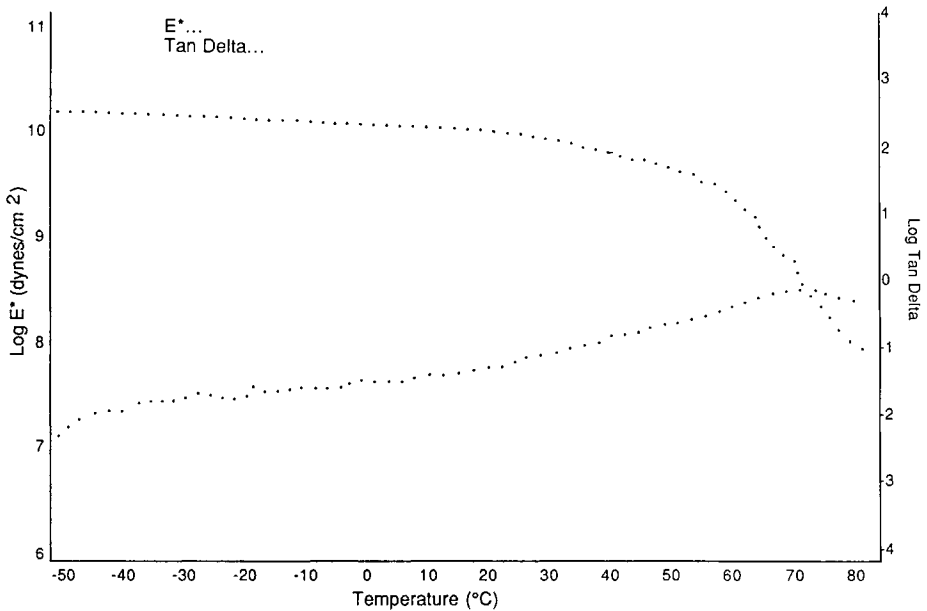
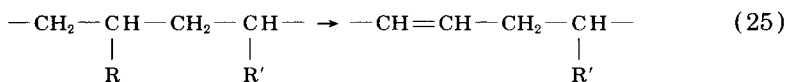


Fig. 5. Dynamic mechanical analysis of a thin film of the copolymer exposed to UV and  $SO_2$  for 48 h.



In Part II it will be shown that significant dehydrohalogenation and loss of acetate groups occur on exposure to UV, O<sub>2</sub>, and SO<sub>2</sub>, with and without the presence of H<sub>2</sub>O.



The allylic methylene groups would be susceptible to photooxidation, increasing the possibility for chain scission and crosslinking. The films exposed to UV, SO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O show color changes which could be attributed to conjugation resulting from the loss of substituents.

Exposure to SO<sub>2</sub> and UV under dry or wet conditions causes dramatic changes in the properties of the system. There are rapid increases in the gel content and T<sub>g</sub>s, indicating the effects of crosslinking. Within approximately 24 h, the gel content increases from about 20 to 60–70% (Table I). At the same time the [η] of the soluble fraction rapidly decreases showing that significant chain scission is also occurring. Under this exposure, the mechanical properties of the system are dominated by the crosslinking reactions. This is illustrated in Figures 4 and 5, which show DMA plots of the control and 48 h SO<sub>2</sub>/UV exposed samples. This plot clearly demonstrates the dramatic shift in the T<sub>g</sub>. The DMA plots of SO<sub>2</sub>/UV/H<sub>2</sub>O treated samples show similar behavior to SO<sub>2</sub>/UV treated samples, whereas UV/air samples show very little change (Fig. 6) in the dynamic mechanical behavior. Films exposed to UV/air/H<sub>2</sub>O for 96 h were very tacky, and the DMA data are not reported.

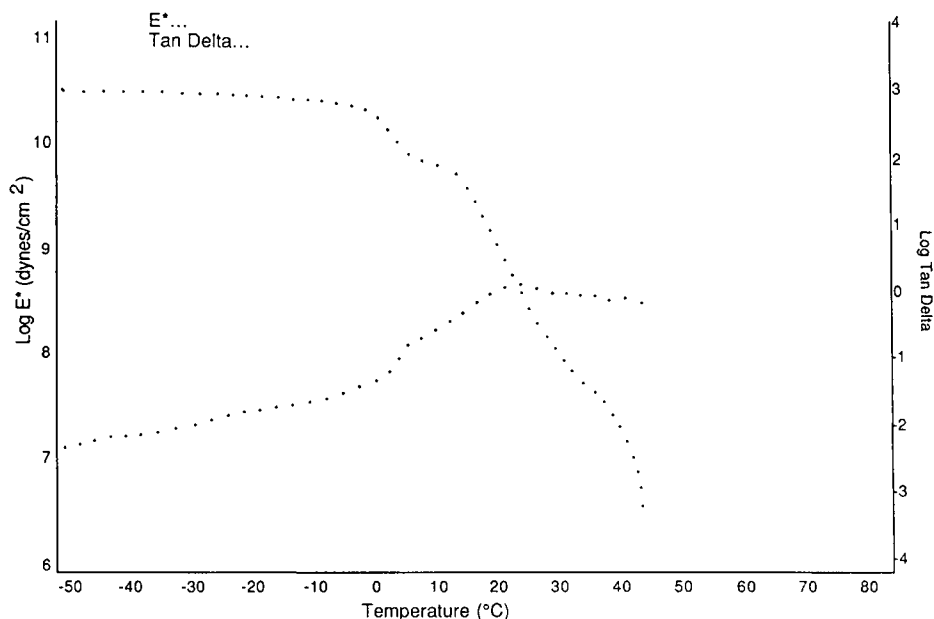


Fig. 6. Dynamic mechanical analysis of a thin film of the copolymer exposed to UV and air for 96 h.

In summary, there is a synergistic effect of UV and SO<sub>2</sub> on polymer degradation which is magnified both with and without the presence of moisture. These results are of significance in view of present-day increased levels of atmospheric pollutants.

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