MONITORING SHORT-TERM WEATHERING EFFECTS
ON uPVC PIPES
BY GEL PERMEATION CHROMATOGRAPHY

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1. INTRODUCTION

Methods of monitoring weathering effects, of predicting service life, and of providing an early warning of oncoming failure are of interest in many areas of polymer application. Such is the case with unplasticized poly(vinyl chloride) (uPVC) pipe produced and used in Saudi Arabia, an application which has received considerable attention during the past decade. The majority of uPVC pipes, used for transporting potable water, domestic and industrial wastes, and treated sewage effluent, have an acceptable standard of quality and performance. However, early failures of uPVC pipes have occurred, particularly during the initial months of operation of these pipes in the industrial city of Al-Jubail in the Eastern Province in Saudi Arabia.

Considerable literature is devoted to the nature of brittle failures [1−4], and significant progress has been made in that area. However, answers to many questions have still not been found. A current literature survey shows that one method of evaluation, loss in mechanical properties, particularly a 50% loss in elongation, is an indicator of the serviceability of the product in use. This method of evaluating degradation requires exposure periods ranging from several months to several years and is not economically feasible in most cases. It was therefore, highly desirable to look into an alternative technique to provide the desired information in a short time. Hence, this work using gel permeation chromatography (GPC) was undertaken.

The shortest wavelengths of solar radiation reaching the surface of the earth begin at about 300−310 nm. The molecular structure of poly(vinyl chloride) suggests that no absorption should take place, but, in fact, it is well established that sunlight is detrimental to poly(vinyl chloride), making it unusable without proper stabilization. Carbonyl groups or short polyene sequences are considered as known light absorbers. These are formed during the thermal processing of PVC. In addition, impurities such as catalyst residues with an absorbance range of 310 to 350 nm may act as sensitizers. Some of the thermal stabilizers and their conversion products have also shown analogous effects [5].

Photodegradation of PVC is usually associated with oxidative attack. Poly(vinyl chloride) becomes more susceptible to thermal degradation after exposure to light. This suggests that oxidative photodegradation causes an increase in the number of thermally labile groups in the polymer.

This implies that the overall mechanism for oxidative photodegradation involves two processes: dehydrochlorination by a radical chain process; and oxidation resulting in hydroperoxides and ultimately carbonyl groups. Both these processes can become autocatalytic. The double bonds activating adjacent chlorine atoms are removed by oxidation, but

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photolysis of an oxidation product may produce intermediates that initiate dehydrochlorination. That oxidation of unsaturated sites is an important factor in the total reaction is evidenced by the bleaching of discolored samples by oxygen, with the final color depending on the balance of dehydrochlorination and bleaching [6–10].

The objective of this work was to evaluate the combined effects of high temperature (above 40°C), humidity, UV-radiation, and airborne particles which uniquely characterize the environment of the Arabian Gulf region.

2. EXPERIMENTAL

2.1. Specimen Preparation and Weathering

The results presented here were obtained by exposing the two locally manufactured uPVC pipes stabilized with lead-based additives designated Saudi Co. # 1 and Saudi Co. # 2 in Dhahran (latitude 26°13′N longitude 50°00′E) for a period of six weeks during the summer months of June and July.

The average meteorological parameters at this location are shown in Table 1.

Scrapings from these pipes, from different areas of the exposed pipes, were taken periodically on a weekly basis for six weeks and were analyzed for changes in molecular weight and its distribution, using Waters Association Model 150 C gel permeation chromatograph interfaced with a printer–plotter–integrator Data module 730.

2.2. Apparatus: Waters 150 C Gel Permeation Chromatograph

Gel permeation chromatography is a type of liquid-solid elution chromatography which separates polydisperse polymers into fractions by means of the sieving action of a cross-linked polystyrene gel. The polystyrene gel, which serves as a stationary phase, is commercially available in a wide range of pore sizes

(1 to 10^6 Å). Since the smaller molecules permeate the gel particles preferentially, the highest molecular weight fractions are eluted first. The fractions are therefore separated on the basis of polymer size. Some of the operating conditions and experimental details of the instrument used for the analysis of exposed and unexposed pipe samples are given below in Table 2.

2.3. Materials

Solvent

The solvent used was GPC grade tetrahydrofuran (Burdick and Jackson, Michigan, USA).

PVC Calibration Standards

The system was calibrated with four PVC standards (Polymer Laboratory Ltd., UK) of known peak molecular weights. The number average molecular weight and retention times of these standards are shown in Table 3.

The retention time of these standards was employed for the direct calculation of that for the PVC pipe samples, using a Waters 730 data module.

3. RESULTS AND DISCUSSION

The GPC traces of the unexposed and exposed polyvinyl chloride pipe samples from the two Saudi companies are given in Figures 1 and 2. Table 4 gives the number average molecular weight of the unexposed and exposed PVC pipe samples.

The GPC traces of the two unexposed pipe samples in Figure 1 have nearly similar molecular weight and molecular weight distribution. A comparison of the GPC traces of the unexposed and exposed samples in Figures 1 and 2 indicate that, as the exposure period goes up, the molecular weight distribution gradually broadens. The broadening accompanies a gradual decrease in the molecular weight with increasing sample exposure as given in Table 4.

Table 1.

Months	UV Dosage (kly)	Relative Humidity (%)	Temperature (°C)	Wind Velocity (mps)
June	23	40.4	34	5.8 NNW
July	22	34.0	39.5	0.5 NNW

One kilolangeley (kly)=4187 joules per square centimeter
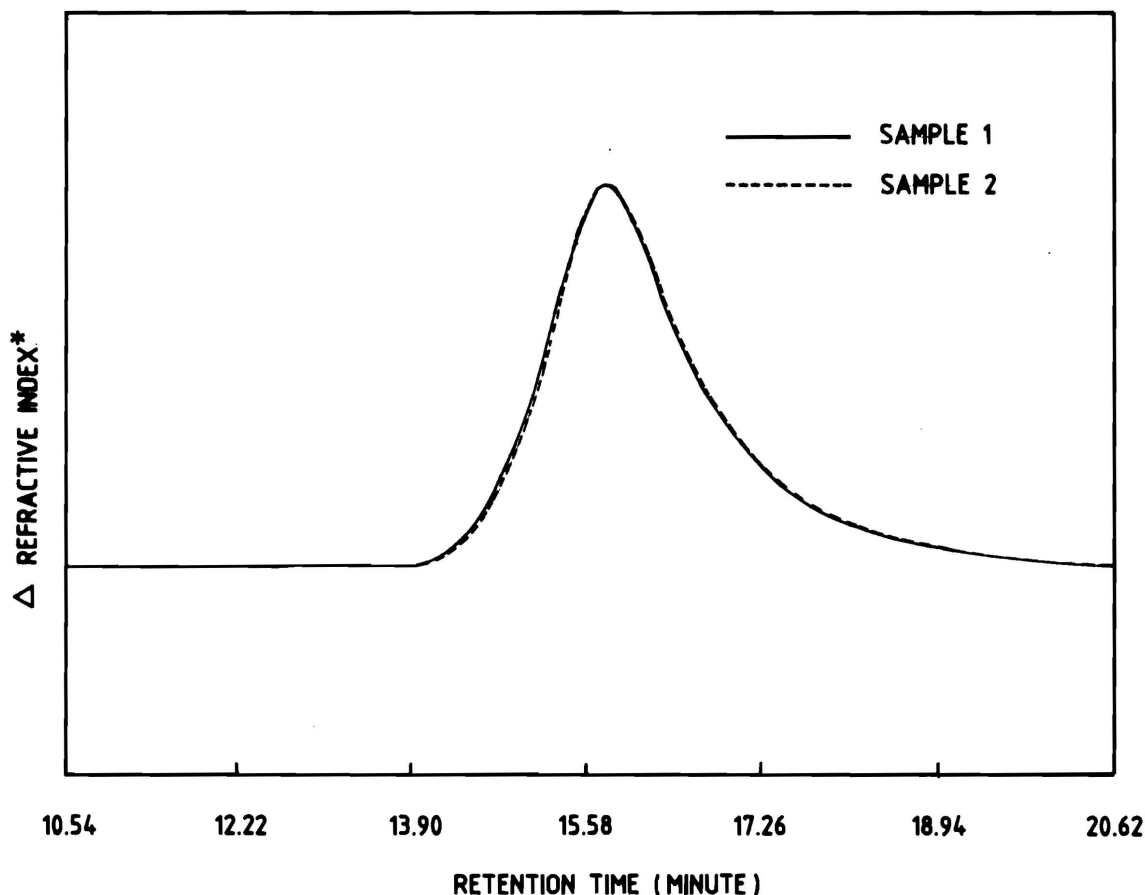
Figure 1. GPC Traces of Two Unexposed uPVC Pipes from Local Manufacturers.

The lowering of the number average molecular weight and the broadening of its distribution may be attributed to the combined effect of thermal and photooxidative degradation. This combination leads to chain scission and cross-linking in nearly all outdoor exposure of plastics materials. However, the predominant reaction in the present investigation seems to involve chain scission, as evidenced by the decrease in the number average molecular weight. In addition to the above degradation effects, color was observed to change slightly from the original gray to pale yellow without the appearance of any visible cracks or cavities, suggesting that the .effects of polyene sequence formation were being countered by oxidation of unsaturated bonds. This may be attributed to dehydrochlorination and bond scission as shown by slight changes in color of the surface of the exposed pipe samples. Although the locally produced uPVC pipes showed an acceptable stan-dard of quality and performance, premature failures of pipes in service, caused by brittle fracture, have been observed.

4. CONCLUSIONS

The degradation of PVC pipe samples exposed at Dhahran was found to be quite severe. This correlates with the harsh climatic factors: the strong windborne particles hazard, the high UV-dosage, the elevated temperatures, and the many hours of sunshine during summer.

It is not possible to draw firm conclusions based on this short-term study. However, the following trends were noted:

1. The number average molecular weight decreases with exposure time.

2. Broadening of the molecular weight distribution increases with exposure time.
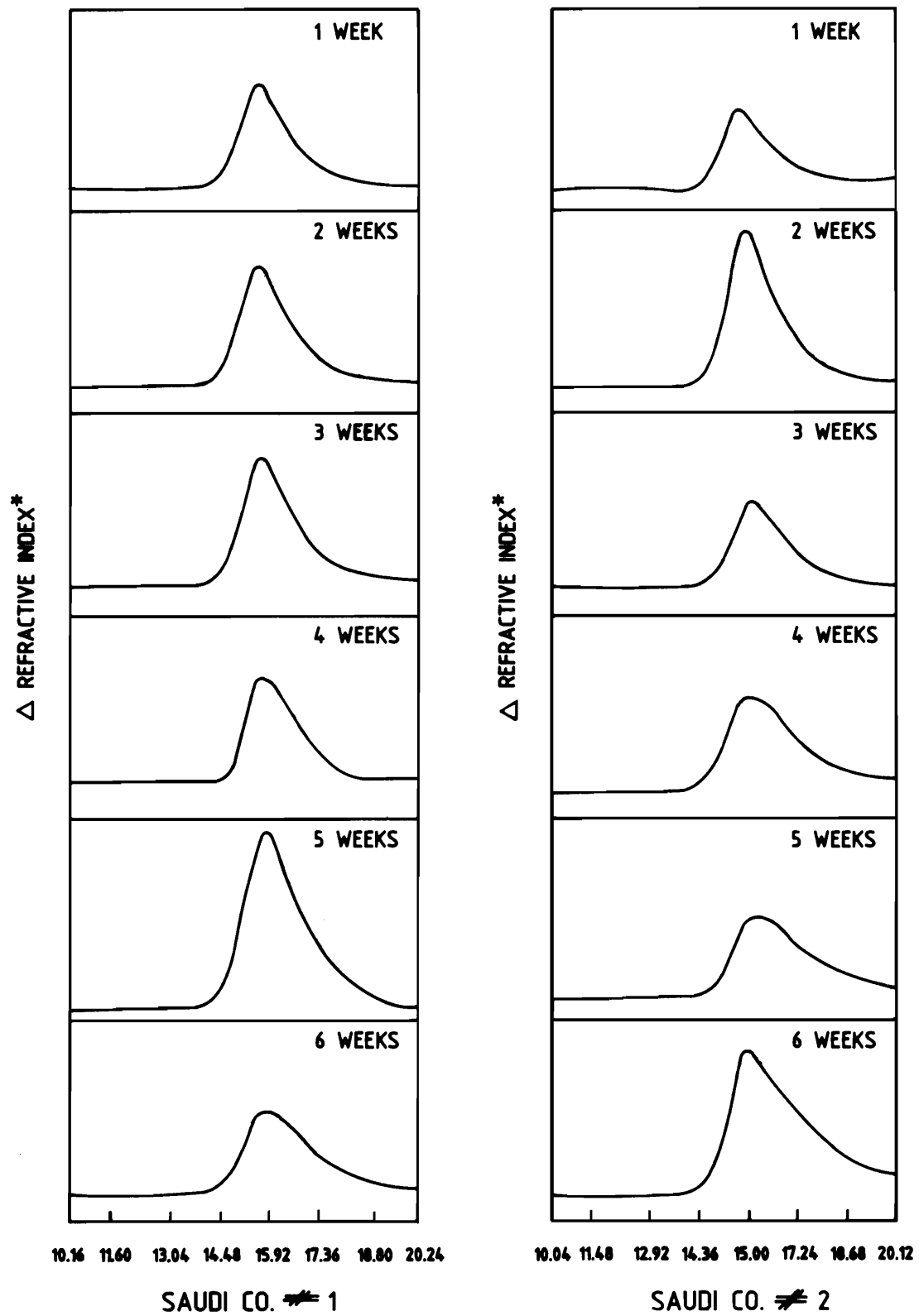
Figure 2. GPC Traces of Exposed uPVC Pipes from Local Manufacturers.

Table 2.

Column Type:	Ultrastyragel
Column exclusion limits:	500, 10^3, 10^4, and 10^5 Å
Solvent:	Tetrahydrofuran
Flow rate:	2 ml min^{-1}
Solution concentration:	0.125% mass/volume (m/v)
Sample size:	50 μl
Operating temperature:	35°C
Sample solution preparation:	Allowed to stand overnight at 35°C, filtered through stainless steel filter (0.5 micron) prior to injection.

Table 3.

Peak retention time (minutes)	Peak molecular weight ($\overline{M}_p$)	Polydispersity ($\overline{M}_w/\overline{M}_n$)
16.63	23 900	1.21
15.36	38 750	1.20
14.76	92 100	1.25
13.86	202 000	1.34

Table 4. Molecular Weight ($\overline{M}_n$) of Exposed PVC Pipe Samples by Gel Permeation Chromatography

Sample Identification	Number Average Molecular Weight ($\overline{M}_n$)	Exposure Duration (weeks)
Saudi Co. # 1		
Unexposed PVC Pipe	64 590	0
Exposed Pipe Sample # 1	63 588	1
Exposed Pipe Sample # 2	59 994	2
Exposed Pipe Sample # 3	57 990	3
Exposed Pipe Sample # 4	53 186	4
Exposed Pipe Sample # 5	52 350	5
Exposed Pipe Sample # 6	46 833	6
Saudi Co. # 2		
Unexposed PVC Pipe	61 961	0
Exposed Pipe Sample # 1	61 389	1
Exposed Pipe Sample # 2	58 776	2
Exposed Pipe Sample # 3	55 205	3
Exposed Pipe Sample # 4	51 815	4
Exposed Pipe Sample # 5	47 569	5
Exposed Pipe Sample # 6	45 792	6

3. The color change of the exposed pipe surface is dependent upon the extents of both thermal and photooxidative degradation. The final color change is due to both polyene sequence formation and oxidation of unsaturated bonds arising from dehydrochlorination of PVC.

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