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Techniques for Predicting the Weathering Performance of Rigid PVC

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ABSTRACT

A range of techniques has been applied to the assessment of resistance to weathering of rigid PVC. Of the techniques evaluated, only ATR spectroscopy appears to satisfy the requirements of sensitivity and reliability to justify its use for the prediction, based on short periods of weathering, of the likely long-term stability of PVC compounds. However, confirmation of this potential use depends on more extensive correlations between predictions and practical observations.

INTRODUCTION

In common with virtually all materials, PVC compounds suffer changes on weathering. For many applications, the two most significant changes which occur in rigid PVC compounds are discoloration and deterioration of impact resistance. Unfortunately, it is difficult to characterize these properties with sufficient precision to enable useful data to be collected unless many replicate samples can be aged simultaneously. Since materials for outdoor applications should have a useful life in excess of ten years or so, the problems of assessing weathering resistance assume unacceptably large proportions. In any event, it is usually impracticable to have to wait for several years before being able to demonstrate an improvement in product quality. For these reasons methods must be sought to enable grade development to take place at sensible rates.

Two approaches are usually adopted to overcome these problems. The first approach is to adopt "accelerated" forms of weathering. However, little reliance can be placed upon most conventional artificial weathering techniques which seldom produce reasonable correlation with natural weathering data. A variant of this approach is to expose samples in climatically extreme areas such as Arizona or Madras. It is unlikely, however, that this style of accelerated natural weathering gives a reliable indication of the suitability of a PVC composition for use in temperate climates. Although it is not the subject of this paper, it is worth noting that artificial forms of weathering have been developed [1] which correlate closely with natural aging. However, they offer little acceleration of weathering.

The second approach towards obtaining weathering data within acceptably short time spans is to develop much more sensitive analytical techniques with which to detect the onset of degradation at an earlier stage. This paper is concerned with this type of approach and describes an investigation into the effects of weathering on a wide range of material properties.

EXPERIMENTAL

Materials

Three white rigid PVC compounds were selected, all having known weathering performance based upon several years experience: compound A, a lead-stabilized, impact-modified, calcium carbonate-filled compound not designed for outdoor applications and known to have poor resistance to weathering; compound B, a tin-stabilized compound designed for outdoor applications over 20 years ago and used successfully during this period; compound C, a lead-stabilized, calcium carbonate-filled compound designed for outdoor applications over 5 years ago and used successfully during this period.

These compounds were milled and compression-molded into 0.76 mm and 1.52 mm sheet.

Based on several criteria, it is believed that compound B may be slightly more resistant to weathering than is compound C. Compound A is relatively much less stable than compounds B or C.

Weathering

Samples in sheet and tensile dumbbell (as defined in British Standard 2782, 301G) forms were aged near to the coast at Hayes Farm, South Wales, U. K. for up to three years. All samples were located on unbacked racks facing south and inclined at 45°.

Assessment Techniques

Color. Changes in color were assessed by eye. Additionally, attempts were made to quantify these changes by use of ultraviolet and visible reflectance spectroscopy (all materials are optically opaque). A Unicam SP 1800 spectrometer fitted with diffuse and spectral reflectance attachments was used.

Gloss. A 60° Sheen Specular meter and a 45° EEL Gloss meter were used to measure changes in gloss.

Surface Structure. The surfaces of samples before and during weathering were examined by using a Cambridge scanning electron microscope.

Tensile Properties. Tensile strength at break, tensile stress at yield, and elongation at break were determined on weathered samples and on controls aged in the dark. The tests were carried out in triplicate, basically in accord with British Standard 2782,301G by using an Instron testing machine at 23 ± 2°C at crosshead speeds of 5 and 50 mm/min.

Flexural Properties. Specimens measuring 76 mm × 12 mm were cut from both thicknesses of sheet after weathering and were subjected to three-point bending tests by using an Instron testing machine. The load was applied to the unweathered surface and testing was also carried out on controls aged in the dark. The tests were conducted at 23 ± 2°C at a crosshead speed of 100 mm/min with the specimens resting on supports 51 mm apart. The flexural strength and flexural modulus were determined in this way.

Creep Properties. A similar three-point bending test was applied to measure the 100-sec isochronous stress-strain curve in flexure according to British Standard 4618 1.1.2. Stress was applied for 100 sec and the resultant deflection measured. The stress was removed for 400 sec before the application of a higher stress. This was repeated several times up to a maximum stress of 25 MPa.

Impact Performance. Impact performance was measured on all samples by using a special test rig [2]. This rig was designed to enable many tests to be performed on one small sample of sheet. A striker was dropped onto a tup with a rounded base in contact with the weathered surface of the sheet. The sheet was supported over a hole 0.2 mm greater than the tup diameter (12.5 mm). The striker was dropped to give a constant high energy level at impact of 3.62 joules. Fifty tests were performed on each sample and the number of brittle failures recorded.

This technique has been established after considerable previous work. The incidence of brittle failure has been found to be a more critical aspect of impact performance on which to judge the effects of weathering than either notched pendulum impact tests or drop weight staircase methods in which the 50% failure level is established with little concern for the type of failure occurring.

Rheological Properties. Melt rheological properties of all the materials including the controls aged in the dark were determined on the Sieglaff McKelvey rheometer with a capillary of 1 mm diameter and a length of 25.4 mm. The melt was taken to a temperature of 170°C and the melt viscosity determined at several rates of shear within the range 1-1000 sec^{-1}.

Residual Thermal Stability. The Agrement Board-recommended procedure [3] for monitoring dehydrochlorination induction period at 200°C was evaluated by using a Radiometer Automatic Titrimeter. Samples were ground before use to about 1 mm diameter.

Infrared Analysis. Chemical changes occurring at the surfaces of weathered samples were assessed by using a Specac ATR (attenuated total reflectance) attachment fitted to a Perkin-Elmer 457 spectrometer. By using KRS 5 crystals designed to give 25 reflections and angles of incidence ranging from 30° to 50°, high quality spectra were obtained which closely resembled conventional transmission spectra. To eliminate variability due to imperfect sample/crystal contacts, all absorptions were normalized with respect to the C–H absorption at 2920 cm^{-1}. It is estimated that the effective depth of material accessible for ATR analysis is of the order 1 to 2 μm.

RESULTS AND DISCUSSION

Color

Only material A showed significant yellowing after weathering for 3 yr. No significant changes could be detected in compounds B and C. UV and visible reflectance spectroscopy proved no more sensitive than visual assessment. The qualitative nature of this assessment obviates its use as a sensitive predictive test.

Gloss

All compounds showed a progressive loss in gloss on weathered surfaces. Compound A was the least stable, followed by compound C.

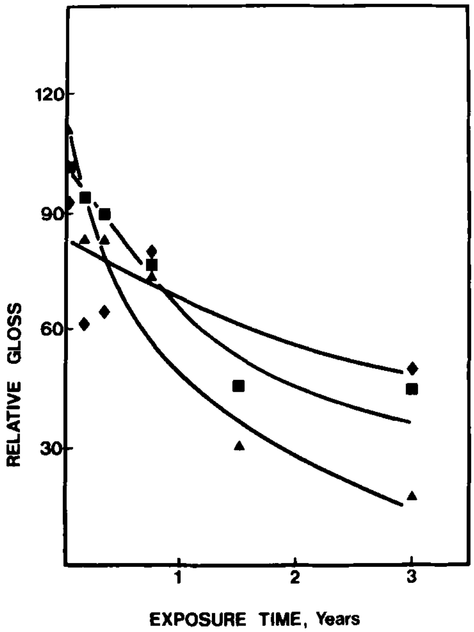

FIG. 1. Variation of gloss (45 EEL) with weathering for 0.76 mm thick sheet: (▲) compound A; (◆) compound B; (■) compound C.

Figure 1 illustrates typical data. This technique rates the materials in the expected order after long periods of exposure, but the results for short periods are too scattered for prediction.

Surface Structure

Typical SEM micrographs are reproduced in Figs. 2-4. These micrographs show a progressive development of microcracks on exposed surfaces, most noticeably with material A. These changes in surface structure are presumed to be the cause of the observed losses in gloss. Significantly, no changes in surface structure could be detected on the unexposed surfaces (backs) of aged samples. This technique is possibly sufficiently sensitive to detect at an early stage the onset of more significant degradation. However, SEM analysis does not lead readily to quantitative treatment.

Tensile Properties

Table 1 shows tensile strength at break results (average of three specimens). As is usual with the measurement of ultimate strength

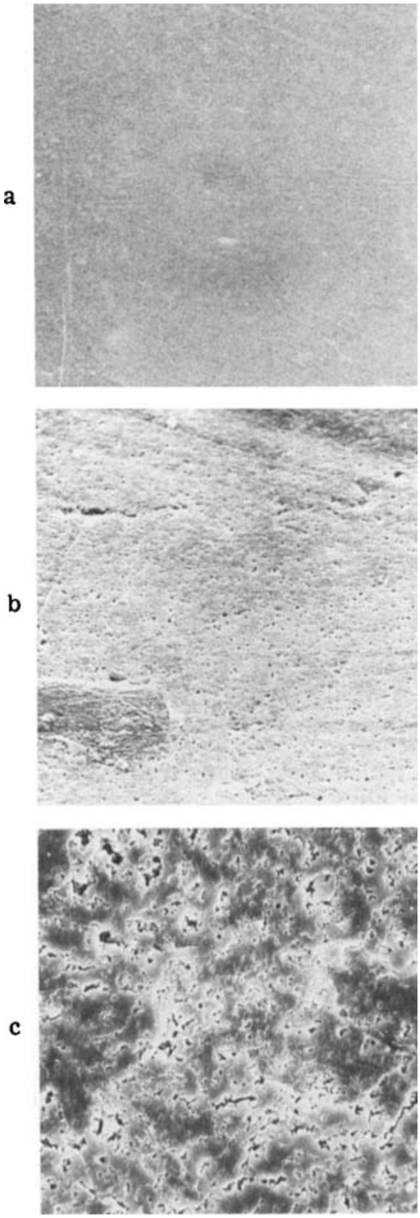

FIG. 2. Scanning electron micrographs of weathered samples at 1000× magnification for compound A: (a) control, (b) 18 months weathering; (c) 36 months weathering.

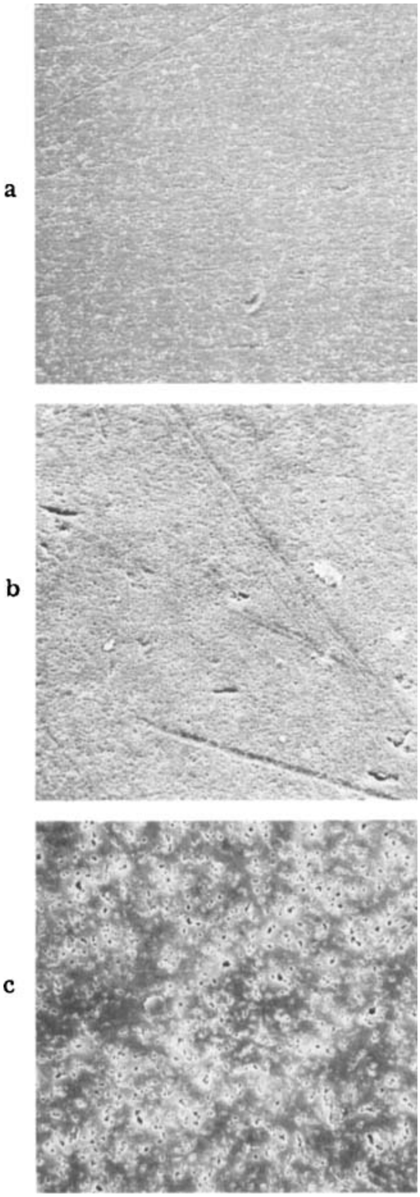

FIG. 3. Scanning electron micrographs of weathered samples at 1000× magnification for compound B: (a) control; (b) 18 months weathering; (c) 36 months weathering.

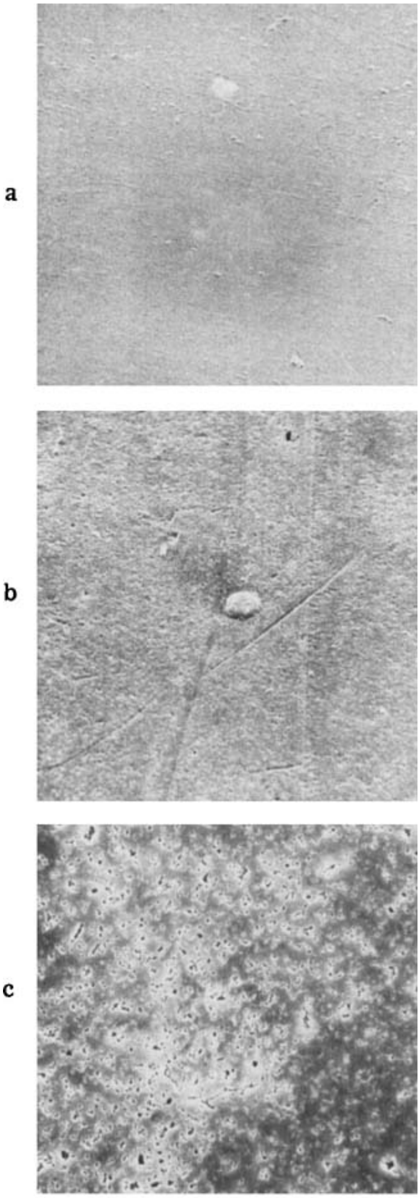

FIG. 4. Scanning electron micrographs of weathered samples at 1000× magnification for compound C: (a) control; (b) 18 months weathering; (c) 36 months weathering.

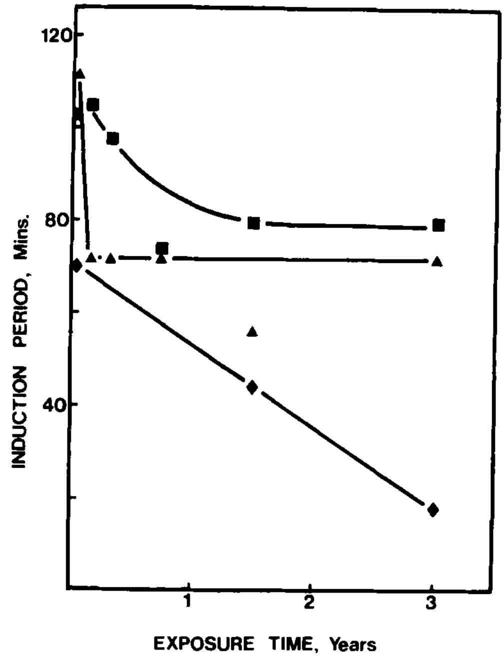

FIG. 5. Variation of dehydrochlorination induction period with weathering for 0.76 mm thick samples: (▲) compound A; (◆) compound B; (■) compound C.

TABLE 1. Variation of Tensile Strength at Break with Weathering for 1.52 mm Thick Samples

Age (months)	Tensile strength at break (MPa)					
	Compound A		Compound B		Compound C	
	Control	Weathered	Control	Weathered	Control	Weathered
0	39		42		41	
9	35	34	49	44	38	38
18	35	31	45	39	37	35
36	34	32	43	41	38	34

characteristics, there is a fair amount of scatter in the results making all but dramatic changes difficult to establish with confidence. Nonetheless, the tendency to decrease with time of storage or exposure shows up for compounds A and C though possibly not for compound B, and there is a suggestion that this decrease is greater for the weathered specimens.

As would be expected, elongation at break results gave wide scatter, but it would be reasonable to say that compounds A and C showed a reduction (in elongation at break) from about 120% to about 30% after 36 months. The controls showed a smaller reduction to about 70%. Compound B showed much less change, only the weathered samples dropping significantly from about 150% to about 135% after 36 months.

All samples showed an increase in tensile stress at yield, but there was little significant difference between the weathered samples and the controls aged in the dark. This is probably a reflection of the increase of stiffness under storage expected and shown also in creep properties but of little relevance to weathering.

These changes in tensile properties were not sufficient to be of value in predicting weathering performance at an early stage.

Flexural Properties

It was thought that bending tests might be more sensitive to the effects of weathering, as the surface in tension has a greater effect on the results than has the bulk of the material. However, flexural strength and flexural modulus results showed no correlation with weathering.

Creep Properties

100 second isochronous creep modulus in bending measurements showed a slight stiffening of all materials including the controls aged in the dark as would be expected. The weathered samples showed more stiffening than the controls, and this was most pronounced in the case of compound A. The magnitude of the additional stiffening in the weathered materials was insufficient for this test to be of value in predicting weathering.

Impact Performance

Table 2 shows the percentage of brittle failures observed on 50 tests on each sample. Included in Table 2 are the 95% confidence limits of the results, had an infinite number of impacts been performed.

TABLE 2. Variarion of Impact Properties with Weathering[a]

	Material A		Material B		Material C	
Exposure time (months)	Brittle failures (%)	95% confidence limits of real value	Brittle failures (%)	95% confidence limits of real value	Brittle failures (%)	95% confidence limits of real value
0	0	7.5	0	7.5	0	7.5
		0		0		0
2	4	13.5	0	7.5	0	7.5
		1.5		0		0
4	4	13.5	0	7.5	2	10.0
		1.5		0		0.5
9	30	44.5	4	13.5	8	20.0
		18.0		1.5		3.0
18	22	35.0	0	7.5	0	7.5
		11.5		0		0
36	100	100	40	55.0	0	7.5
		93		26.0		0

[a] Percentage brittle failures for 0.76 mm thick samples based on test populations of 50. 95% Confidence limits are those estimated had an infinite number of samples been tested.

Although a progressive increase in brittle failures is observed it is evident that this test is unsuitable as a basis for predicting weather resistance. Nevertheless the results demonstrate clearly the known inferiority of compound A compared with compounds B and C. The increase in brittle failures with weathering is believed to be due to the microcracking of the surface. Similar impact results on both thicknesses of samples indicate that the microcracks are equally effective in promoting brittle failures over a range of thicknesses.

Rheological Properties

The melt viscosities of all samples, including controls aged in the dark, showed a progressive reduction, possibly due to chain scission. The extent of these changes was less marked for the weathered samples, which may indicate a degree of crosslinking in these cases. However, the scope of these changes is generally much too small for this technique to be of value in predicting resistance to weathering.

Residual Thermal Stability (Agrement Board Procedure)

Typical results of this test are indicated in Fig. 5. Similar results were obtained with both thicknesses of sheet but with the thinner sheet producing changes of greater magnitude. According to the Agrement Board this test should yield linear plots of induction period versus exposure time, from which weathering "lifetimes" can be determined by extrapolation to zero induction period. It is evident from Fig. 5 that the data for compounds A and C do not exhibit the predicted pattern of behavior. For this reason, together with the apparent inversion of stability predicted by this test, it cannot be regarded as a useful means for assessing or predicting weather resistance. It is not surprising that this technique is unreliable, since it seeks to assess surface changes caused by weathering by monitoring a bulk property. Perhaps the technique may be of limited value for very thin specimens.

ATR

Figures 6 and 7 illustrate typical spectra of weathered PVC. These spectra show several chemical changes taking place on the surfaces of weathered samples. Virtually identical spectra are obtained for both thicknesses of each sample indicating strongly

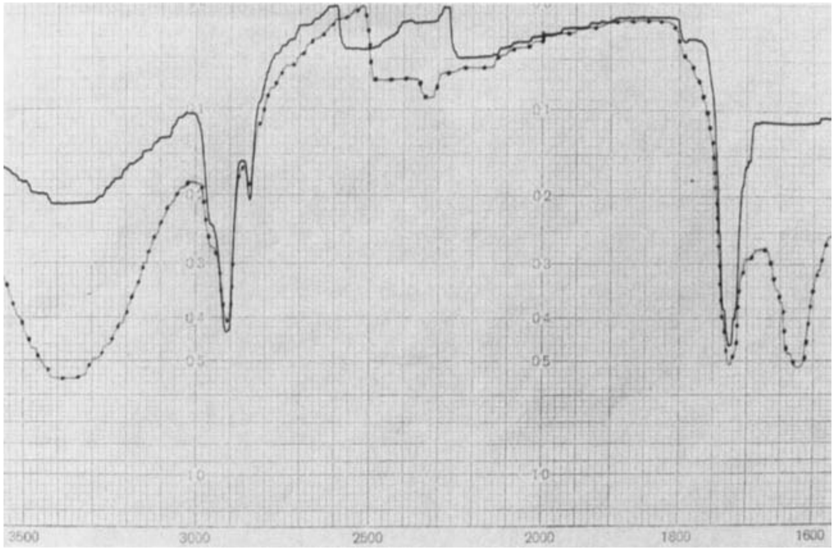

FIG. 6. Typical ATR spectra of weathered PVC: (--) weathered surface; (—) back of same sample.

that weathering is restricted to the surface layers. Two of these changes are of obvious interest in the development of techniques for the early prediction of weathering performance.

Reductions in absorptions at 875 and 1455 cm^{-1} are due to loss of inorganic carbonate (present as filler in A and C). Loss of carbonate on aging is presumed to be a result of interaction with HCl formed during the degradation process. The results given in Fig. 8 show that the rate of loss of carbonate correlates well with the known practical weathering performance of compounds A and C. Generally carbonate absorption can be assessed with a reproducibility better than ±10%. It is felt that some partially overlapping background absorption occurs in the region of 875 cm^{-1}, which contributes to the relatively poor reproducibility. Nevertheless, the magnitudes of the changes in carbonate content shown in Fig. 8 are substantially greater than experimental inaccuracy and provide a clear illustration of the greater stability of compound C relative to compound A.

Increased absorption at 1730 cm^{-1} is due to an increase in carbonyl group concentration. The relatively large peak from the unexposed surface is due to carbonyl-containing additives. Again, the results obtained (Fig. 9) are broadly in accord with the known weathering performances of compounds A, B and C. Compound A, having the worst weathering performance, shows the fastest rate of carbonyl

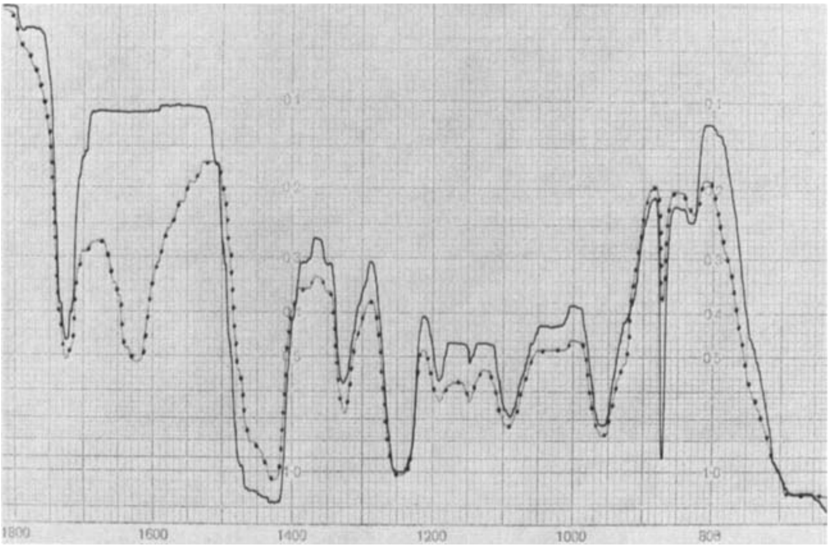

FIG. 7. Typical ATR spectra of weathered PVC: (--) weathered surface; (—) back of same sample.

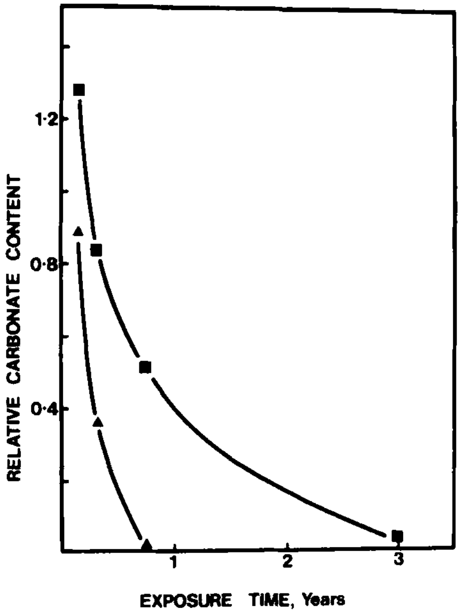

FIG. 8. Variation of relative carbonate content with weathering. ATR angle of incidence 45°: (▲) compound A; (■) compound C.

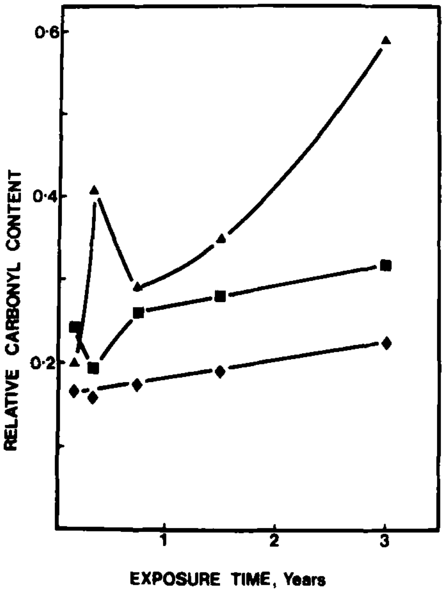

FIG. 9. Variation of relative carbonyl contact with weathering, ATR angle of incidence 45 : (▲) compound A; (◆) compound B; (■) compound C.

group formation with an interesting peaking effect after only about 4 months exposure, an effect not shown by the other compounds. The reproducibility of carbonyl content assessment is usually much better than ±5%, but this figure is influenced slightly by the pressure applied to the sample on the ATR crystal. As contact pressure is increased, the carbonyl content appears to be reduced. It is suggested that this effect occurs as a result of slight sample distortion with increasing contact pressure, giving greater proportions of less degraded lower layers in contact with the crystal. Significantly, this effect is not observed in relation to the carbonate peak, possibly because the effective penetration of the infrared beam is directly proportional to its wavelength and should therefore be about twice as great for the carbonate as it is for the carbonyl.

Although changes in carbonyl and carbonate contents appear to give adequately sensitive results for the compounds covered by this paper, it is envisaged that limitations could apply in some circumstances. For example, not all compounds contain carbonates. Additionally if a compound contains a high initial level of carbonyl-containing additives, small increases in carbonyl content may prove difficult to assess accurately. Consequently it would be useful to identify other absorption bands which could be used to assess weathering.

One change which is judged to be worthy of further study is the broad band absorption centered at about 3360 cm^{-1}. Based on studies with simple hydroperoxides, this peak is most likely attributable to –OOH groups, but it is likely that water contributes. The increased absorption at 1770 cm^{-1} is probably due to α,α'-dichloroketo group formation, but the peak lacks sufficient definition to be of value in predicting weathering performance.

Significant peak development at 1625 cm^{-1} is also evident in many samples, and this peak may provide additional data for assessing changes occurring during weathering. However, at present no firm identification can be offered for this peak. Initially it was thought that relatively short conjugated carbon-carbon sequences could be responsible. This explanation cannot be ruled out, but it seems unlikely since short, say less than 5, conjugated sequences are unlikely to exist without some slightly longer sequences (8 to 10) coexisting, and resonance Raman spectroscopy failed to detect these slightly longer sequences. The sensitivity of the Raman technique [4] is sufficiently great to detect very much lower levels of conjugated sequences than can be observed by ATR. A further possibility is that the 1625 cm^{-1} absorption is due to water, but several experiments involving PVC compounds and water failed to provide firm evidence for this hypothesis. This suggestion is also seemingly inconsistent with the frequent observation that more extensive development of this peak occurs during artificial (indoor) aging, where the contact with water is much less than during natural aging. Perhaps the most likely explanation is that the 1625 cm^{-1} absorption is caused by water of hydration associated with inorganic chlorides formed during weathering. This suggestion could account for the observation that the 1625 cm^{-1} peak is most frequently found in samples containing calcium carbonate. It is suggested that the carbonate is converted to the chloride which absorbs water to form the hydrate. On this basis, the lower level of the 1625 cm^{-1} peak on outdoor aging is accounted for by leaching out of the chloride by rainwater. Evidence for substantially reduced levels of calcium at the surfaces of aged samples has been acquired by x-ray microanalysis.

In passing, attention must be drawn to a quite unexpected observation that the changes which are observed on the exposed surfaces invariably take place at a slower rate on the unexposed back of the sample. Since the samples are all relatively thick, it is virtually impossible that degradation has occurred throughout the thickness of the samples. The only satisfactory explanation is that the low level of scattered radiation falling on the reverse of the samples has caused degradation. This conclusion is supported by evidence from experiments in which the surfaces of aged samples have been very mildly abraded to remove an exceedingly small amount of the surface layer. It is impossible to measure accurately the depth of the material removed, but it is estimated that this amount does not exceed 10 μm.

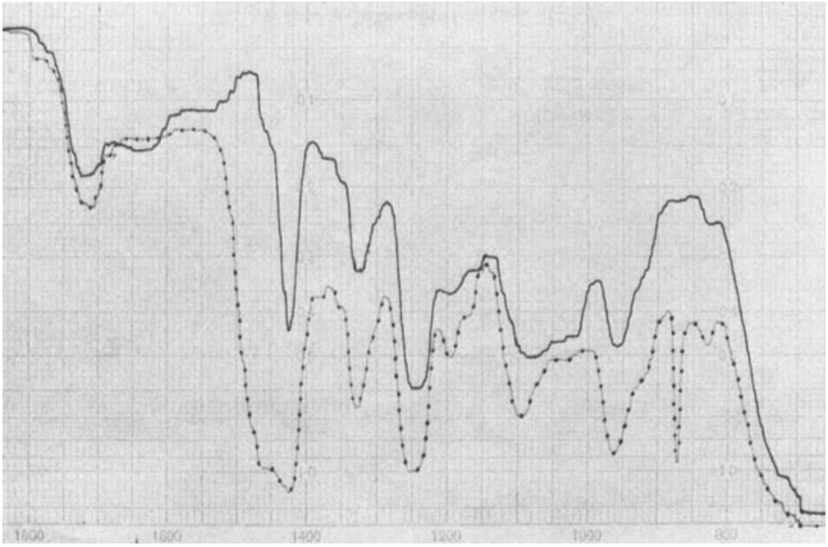

FIG. 10. Effect of mild abrasion on ATR spectrum of weathered PVC: (—) weathered surface after 9 months exposure; (--) same surface after mild abrasion. Compound A, 0.76 mm thick; ATR angle of incidence 45°.

Figure 10 shows the effect of such a treatment, from which it can be seen that a "normal" spectrum is regenerated by this treatment, i.e., degradation is restricted to very thin surface layers. The significance of this observation remains to be confirmed.

Generally the magnitudes of the changes observed by ATR are relatively great and can be measured with good reproducibility. Furthermore, ATR can detect changes within a few months of weathering whereas significant changes in other properties require much longer time scales. It is concluded, therefore, that this technique, particularly the monitoring of changes in carbonyl group and carbonate group concentrations at the exposed surfaces, offers much potential for the early prediction of weathering performance. Certainly, this technique offers more potential in this connection than the various other measurements discussed in this paper. However, it must be stressed that firm conclusions regarding the suitability of ATR for this purpose must await detailed correlations with long-term weathering.

ACKNOWLEDGMENTS

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REFERENCES

[1] G. C. Marks, unpublished data.
[2] R. C. Neumann, Polym. Eng. Sci., 6, 124 (1966).
[3] D. Fougea, et al., Cahiers CSTB, 124, 1070 (November 1971), Agrement Board Translation No. 232.
[4] D. L. Gerrard and W. F. Maddams, Macromolecules, 8, 54 (1975).

DISCUSSION

Dr. J. C. Chauffoureaux (Solvay, Brussels, Belgium): If I understood correctly, the main difference between the three products, A, B, and C was the processing conditions. I agree completely with Dr. Marks that processing conditions exert an extremely great influence on aging. Can he tell us what was the difference in the processing conditions used to produce his three products?

Dr. Marks: The three compounds were of completely different formulations. There is clearly a problem here in relating the differences in processing three different formulations. My final point was that, even with a single formulation, large differences can be seen in photostability. As far as the three compounds A, B, and C were concerned, they had very different formulations but each of them was processed near to what we believe to be its optimum conditions.