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Characterization of artificially weathered foils of polyvinyl chloride by means of thermal methods of analysis

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Abstract

Two types of polyvinyl chloride, one having glass transition temperature $T_g \approx 20°C$, the other $\approx 70°C$, have been artificially weathered at $T_w = 60°C$. The samples were characterized by means of thermal methods of analysis. The results of measurements show that the induced changes in the physical structure of the material are mainly determined by the position of the weathering temperature T_w with respect to the T_g of the sample in question. On the other hand, the extent of changes occurring in the chemical structure is shown to depend on the PVC content, i.e. on the content of additives, in the given sample.

INTRODUCTION

Physical aging takes place in glassy materials due to the relaxation of non-equilibrium states which are frozen into the material during the manufacturing process, or more precisely during the cooling of the material from above to below the glass transition temperature T_g. The faster a melt of an amorphous material is cooled down to a glassy, solid body, the higher is the temperature at which the glass transition occurs and the higher is the enthalpy in the solid state of the material. This increased enthalpy subsequently decreases as the frozen-in metastable state undergoes relaxation. The time and the temperature of any treatment the material experiences after processing determine the degree and the type of relaxation occurring after processing. Illers [1] has shown that the thermal and mechanical properties of quench-cooled samples of polyvinyl chloride (PVC) change considerably upon annealing. Weitz and Wunderlich [2] produced densified glasses of polystyrene (PS), polymethyl-methacrylate (PMMA), phenolphthalein, sucrose and of a 1 : 1 mixture of potassium and calcium nitrate by slow cooling of the corresponding melt under elevated hydrostatic pressure. They found that under such conditions, the enthalpies of the glasses are

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2–6 J g^{-1} higher than the enthalpies of corresponding glasses which are formed by cooling at the same rate but under atmospheric pressure.

Berens and Hodge [3] showed that PVC samples with an increased enthalpy can be obtained not only by rapid cooling of the melt or by cooling of the melt under pressure, but also by cold-drawing or by methyl chloride vapor treatment of PVC in the solid state.

During weathering, physical aging and changes in chemical structure (e.g. chain-breaking, crosslinking and in the case of PVC also elimination of hydrogen chloride, resulting in the formation of polyene sequences) occur simultaneously. For a better understanding of weathering it is thus essential that the effects of physical aging and degradation can be clearly distinguished from one another. The purpose of this paper is to show how thermal analysis can be used to reveal structural changes occurring in PVC samples during weathering.

EXPERIMENTAL

Weathering chamber

The weathering of the samples was carried out using a Q-U-V Accelerated Weathering Tester, manufactured by the Q-Panel Company, Cleveland, OH, USA. This chamber is equipped with a water spray system to approximate rainfall, and it contains a series of UVA-340 lamps which provide an excellent simulation of sunlight in the critical, short wavelength region, i.e. at wavelengths between 360 nm and the solar cutoff at 295 nm [4]. The lamps were in operation for about 80% of the total weathering time. During weathering the temperature in the chamber varied between 40 and 70°C, the mean value was about 60°C. The relative humidity varied between 10 and 70%; the mean value was about 25%. The conductivity of the spray water was less than 5 μS cm^{-1} at 25°C.

Materials

The PVC samples investigated were two commercial, suspension-polymerized, transparent calander-foils of 150 μm thickness. Foil 1 has a PVC content of 80% and a *K*-value (German Standard DIN 53726) of 70 and is used as a graphics foil; foil 2 has a PVC content of 92% and a *K*-value of 57 and is used for packaging, after further processing by thermoforming. It is known [5] that a *K*-value of 57 corresponds to a mean molar mass $M_w \approx 54000$ g mol^{-1}, and $K = 70$ corresponds to $M_w \approx 88000$ g mol^{-1}.

Thermal analysis

The thermal analysis was carried out on samples of 4–5 mg by means of a Perkin-Elmer 7 Series Thermal Analysis System, consisting of a PE 7700 computer, a differential scanning calorimeter DSC 7, a thermo-balance TGA 7 and a thermomechanical analyzer TMA 7.

For DSC measurements, the cell was purged with 75 ml min^{-1} of dry nitrogen, the heating rate was 40°C min^{-1}, and the cooling rate was 100°C min^{-1}. The first scans were run from −60 to 200°C, the second series from −60 to 250°C. For thermogravimetric measurements, the sample tube was purged with 80 ml min^{-1} of dry nitrogen; the heating rate was 40°C min^{-1}. The thermomechanical measurements were performed with a compression probe with hemispherical tip (0.02 inch) which pushed on the sample surface with a force of 0.2 N (i.e. 20 g). The cell was purged with 100 ml min^{-1} of dry helium, and the heating rate was 10°C min^{-1}.

RESULTS AND DISCUSSION

Differential scanning calorimetry

Figure 1 shows the first and second recordings of the heat flow from 0 to 150°C for the PVC foil 1 in the unweathered state (a), after 5 days (b), and after 20 days (c) of artificial weathering. According to ref. 6 the glass

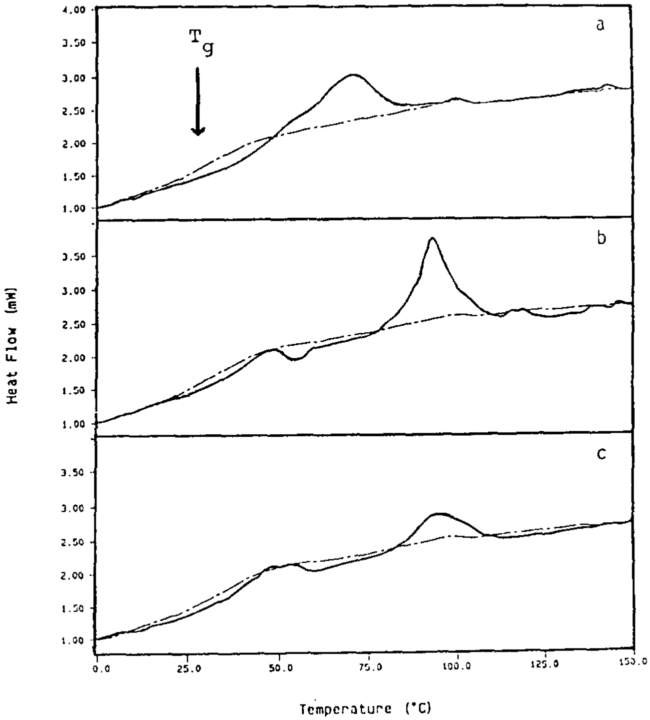

Fig. 1. DSC plots for PVC foil 1. First run, ———; second run ·—·—·—: (a) unweathered, (b) after 5 days of artificial weathering, (c) after 20 days of artificial weathering.

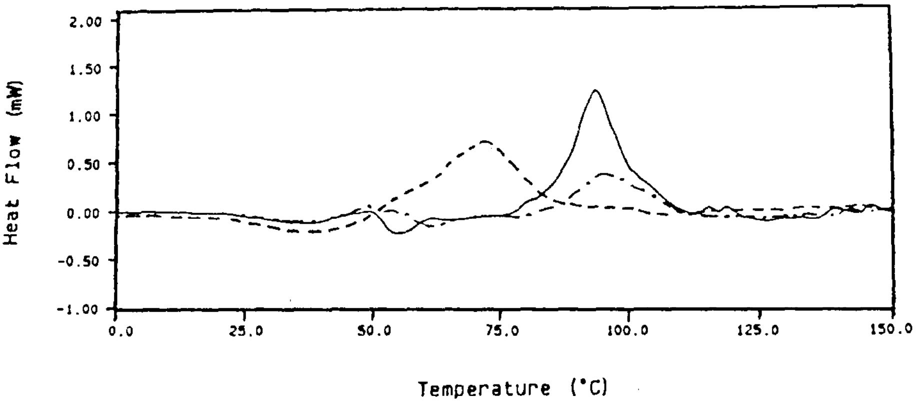

Fig. 2. Difference in heat flow between first and second scan for PVC foil 1. Unweathered, - - - - - -; 5 days weathered, ———; 20 days weathered, ·–·–·–.

transition temperature T_g of pure PVC increases with increasing content of syndiotactic sequences from ≈ 81 to ≈ 98°C. From the low T_g values, depicted in Fig. 1, it follows that the foil 1 contains a rather high amount of plasticizer (the PVC content of this foil is only ≈ 80%). In plasticized PVC the flexibility of the chain molecules is enhanced, so conformational changes do not need elevated temperatures. This makes possible the increase of crystallinity of plasticized PVC during storage at room temperature [7]. The endothermic heat-flow event which is seen in all first scans well above T_g is thus interpreted as a melting process of the crystallites which were formed during storage or weathering. Taking into account that the crystallites in PVC act as crosslinks (which are known to reduce the segment mobility), then our interpretation is further supported by the fact that in all second scans the T_g is shifted to lower temperatures and at the same time the melting peak has disappeared.

The differences in heat flow between the first and second runs for the PVC foil 1, unweathered and after 5 and 20 days of weathering, are presented in Fig. 2. This picture shows that during weathering, the enthalpy due to the melting of the crystallites narrows and shifts. For the first 5 days the shift of the peak is very pronounced (from 71.1 to 93.5°C) and accompanied by a significant increase of peak area (integration from 50–100°C provides, for the unweathered PVC, a heat of fusion of 3.9 J g^{-1}, and integration from 70–110°C yields for the sample after 5 days of weathering an enthalpy of 5.1 J g^{-1}). From the 5th to the 20th day of weathering, the shift of the peak is very small (from 93.5 to 94.6°C) and the heat of fusion decreases markedly from 5.1 to 2.7 J g^{-1} (this value was obtained by integration from 75–115°C). These results, together with the corresponding weathering times t_w, are summarized in Table 1. The fact that the enthalpy of fusion at the end of the test is definitely smaller than it was at the beginning clearly shows that the long term effect of weathering

TABLE 1

Effect of weathering on position and magnitude of melting peak of PVC foil 1

t_w (h)	log t_w	T_{max} (°C)	ΔH_{cryst} (J g^{-1})
0		71.1	3.9
120	2.079	93.5	5.1
480	2.681	94.6	2.7

on the foil 1 is to degrade its physical structure, i.e. to decrease the crystallinity.

However, as the second scans of Fig. 1 are very similar to one another, the chemical structure of the foil 1 seems to be rather unaffected by the weathering over 20 days. Figure 3 shows the second scans of Fig. 1 from 20–80°C in enlarged form. The T_g-shift which is seen in this figure might well be a consequence of crosslinking which occurs under the influence of irradiation.

Figure 4 shows the DSC scans from 50–150°C for the PVC foil 2 in the initial state (a), after 5 days (b) and after 20 days (c) of artificial weathering. It should be noted here that the scaling of the heat flow in the Figs. 4(b)–4(c) has been doubled with respect to Fig. 4(a). The endothermal events which are seen in the first scans of the foil 2 are easily recognized as enthalpy relaxation peaks (T_g overshoot peaks). As Illers already noted [1], these peaks are – unlike those which are shown in Fig. 1 – not due to an increase of crystallinity or order, but to a decrease of the hole concentration in the amorphous phase. Furthermore they provide a quantitative

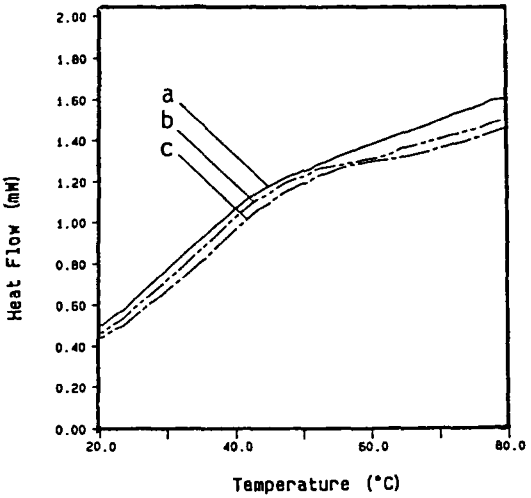

Fig. 3. Second scans of Fig. 1. Labels as in Fig. 1.

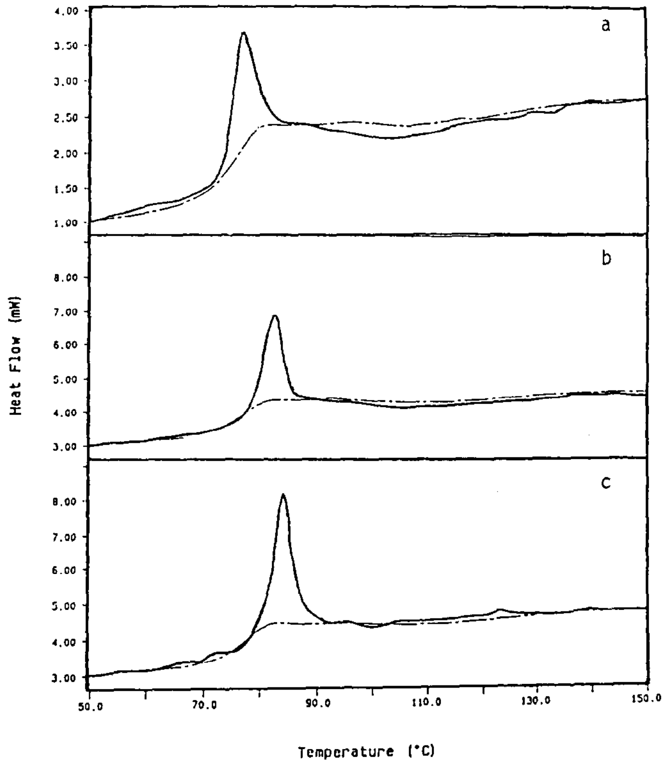

Fig. 4. DSC plots for PVC foil 2. First run ———, second run ·–·–·–: (a) unweathered, (b) after 5 days of artificial weathering, (c) after 20 days of artificial weathering.

measure of the change of state which occurred in the samples in the course of weathering or storage. Figure 5 shows the difference in heat flow between the first and second scans for the PVC foil 2. It can be seen from this figure that the enthalpy relaxation peak increases, narrows and shifts

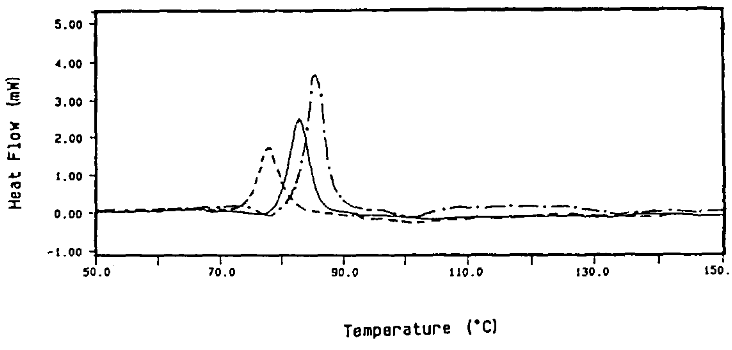

Fig. 5. Difference in heat flow between first and second scan for PVC foil 2. Unweathered - - - - - -, 5 days weathered ——— and 20 days weathered ·–·–·–.

TABLE 2

Effect of weathering on position and magnitude of enthalpy relaxation peak of PVC foil 2

t_w (h)	log t_w	T_{max} (°C)	ΔH_{relax} (J g^{-1})
0		77.3	3.1
120	2.079	82.7	4.1
480	2.681	84.9	5.1

to higher temperatures with increasing weathering time. The experimental findings of Fig. 5 are summarized in Table 2. In this table the values of ΔH_{relax} have been obtained by integration of each curve of Fig. 5 from 50–95°C.

From Table 2 it follows that the ratio $\Delta(T_{max})/\Delta(\log t_w)$ equals 3.7°C per time-decade. For an S-PVC ($M_w \approx 205\,000$ g mol^{-1} and $M_w/M_n \approx 3$) which had experienced different treatments and subsequently been aged at 20, 40 and 60°C, the same ratio is given by Berens and Hodge [3] with a value of ≈ 5°C per time-decade for each of the temperatures mentioned. From the measurements of Illers [1] which were performed on foils of S-PVC, annealed at 65°C, one obtains a ratio of ≈ 2.2°C per time-decade. Figure 6 shows the second scans of Fig. 4 from 60–90°C in enlarged form. As in Fig. 3, a clear shift of the T_g with increasing weathering time is evident; again this shift might well be due to crosslinking. The effect of weathering on the position of the T_g, determined as onset in the second scan, is presented in Table 3 for both foils. It can be seen from Figs. 1 and 4 that the second runs are not affected by effects which are due to the physical structure. As each was taken immediately after the first run, each

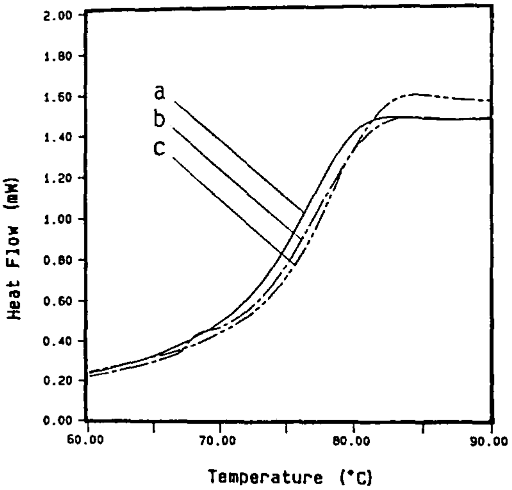

Fig. 6. Second scans of Fig. 4. Labels as in Fig. 4.

TABLE 3

Effect of weathering on position of T_g (°C)

t_w (h)	0	120	480
PVC 1	20.6	21.0	22.1
PVC 2	71.1	71.5	73.0

is determined only by the chemical structure of the corresponding sample. From Table 3 it follows that the weathering induces in both PVC foils a T_g shift which can be represented as a linear function of the weathering time t_w. It should be added here, that T_g was measured at the onset point. The ratio $\Delta T_g/\Delta t_w$ of foil 1 has a value of 3.13×10^{-3}°C h^{-1}, and for foil 2 $\approx 3.96 \times 10^{-3}$°C h^{-1}. If crosslinking indeed is the reason causing the T_g to shift, then the above values suggest that foil 2 has a somewhat higher yield for the crosslinking reaction than foil 1. This in turn could easily be understood as a dilution effect: the probability that a photochemically activated site of a chain finds another chain in its neighborhood to produce a crosslink is reduced in foil 1 because of the presence of a considerable amount of additives, e.g. plasticizer.

Thermogravimetric analysis

Figure 7 shows the weight change of PVC foil 1 in the unweathered state and after 20 days of weathering during heating from 25 to 800°C. Obviously, the decrease of mass which foil 1 undergoes during pyrolysis is not affected by the given treatment, i.e. plasticizer and other low-molecular additives did not evaporate and have not been washed out significantly

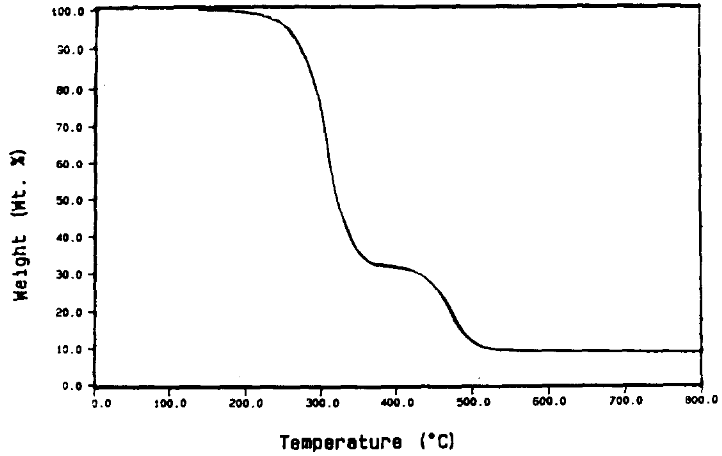

Fig. 7. TGA plots for PVC foil 1 before ——— and after ·–·–·– 20 days of weathering.

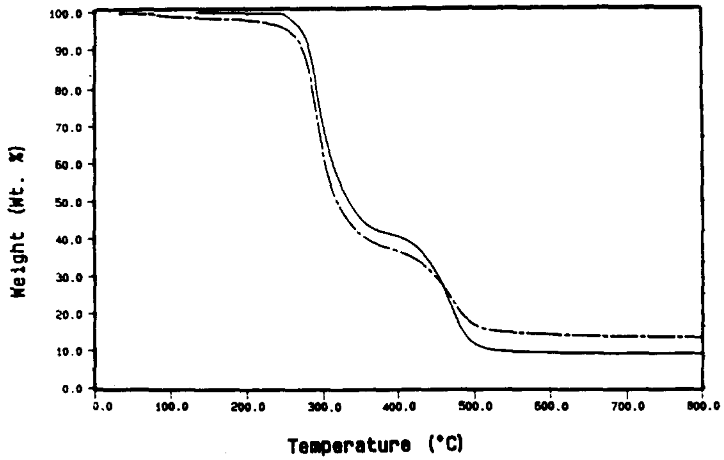

Fig. 8. TGA plots for PVC foil 2 before ———; and after ·–·–·– 20 days of weathering.

during weathering. The thermal degradation, as shown in Fig. 7, proceeds in two distinct stages. It is known that in the first stage (in Fig. 7 from ≈ 150 to ≈ 380°C; weight loss ≈ 70%) PVC releases low-molecular components such as H_2O, plasticizer, HCl, benzene and traces of other products. In the second stage (in Fig. 7 from ≈ 380 to ≈ 550°C; weight loss ≈ 22%) different hydrocarbons are evolved. A list containing about ten major products (in weight %) formed during pyrolysis of PVC has been published in ref. 8.

The TGA results of PVC foil 2 before and after 20 days of weathering are shown in Fig. 8. Here, in contrast to Fig. 7, the effects of weathering can be clearly seen. The drop in weight of the weathered foil 2 starts well below 100°C. At ≈ 250°C it has lost about 4% of its weight, whereas the unweathered foil has lost only about 1%. This weight difference of ≈ 3% remains nearly constant throughout the first stage of decomposition. In the second stage the situation is reversed, while the unweathered foil loses ($t_w = 0$) 41% − 9% = 32% of its weight, the weathered foil loses only ($t_w = 480$) 37% − 13% = 24%. The effects of weathering on the weight loss during pyrolysis are summarized in Table 4 for both foils. In this table, w_0 and w designate the initial and actual weights of the sample, respectively.

Thermomechanical analysis (TMA)

The TMA plot depicted in Fig. 9 shows the penetration of the measuring probe into the PVC foil 1 during heating from ≈ 20–200°C. This provides information on the softening of the sample. In the case of the PVC foil 1, the rigidity decreases right from the beginning of the test and shows three distinct steps, at approximately 35, 75 and 110°C. The corresponding molecular processes are the onset of the segment mobility at T_g, the

TABLE 4

Effect of weathering on weight loss during pyrolysis

$w(T=250°\mathrm{C})/w_0$	$w(T=380°\mathrm{C}/w_0)$	$w(T=800°\mathrm{C})/w_0$	
PVC foil 1			
$t_w=0$	96%	30%	8%
$t_w=480$	96%	30%	8%
PVC foil 2			
$t_w=0$	99%	41%	9%
$t_w=480$	96%	37%	13%

melting of the crystallites and, finally, a dramatic decrease of cohesion. A comparison between the three curves shows that after 5 days of weathering the foil 1 has become slightly more rigid in the temperature range from ≈ 60 to 100°C (due to an increase of crystallinity). However, after 20 days of weathering the resistance of the material towards the applied load of 20 g is definitely reduced (due to a decrease of crystallinity). It is interesting to note that this reduction of rigidity is already fully displayed at $T = 100°\mathrm{C}$ and remains nearly constant until the end of the test. This fact suggests that in our tests (which were performed with a heating rate of 10°C min^{-1}) the network linked by crystallites can still strengthen the unweathered and the 5-days weathered sample even in the flow region when the crystallites are already molten.

Figure 10 shows the softening of the PVC foil 1 in the unweathered state and after 20 days of weathering. Here, prior to the measurements, the

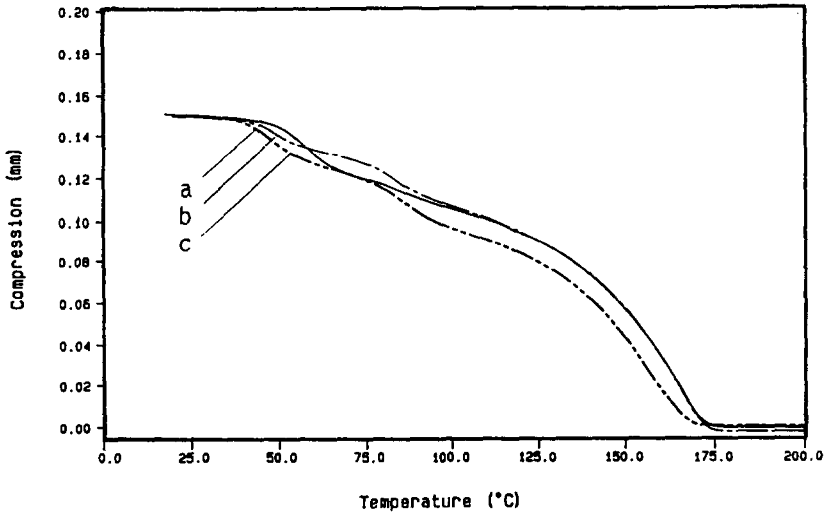

Fig. 9. TMA plots for PVC foil 1: (a) unweathered, (b) after 5 days of weathering, (c) after 20 days of weathering.

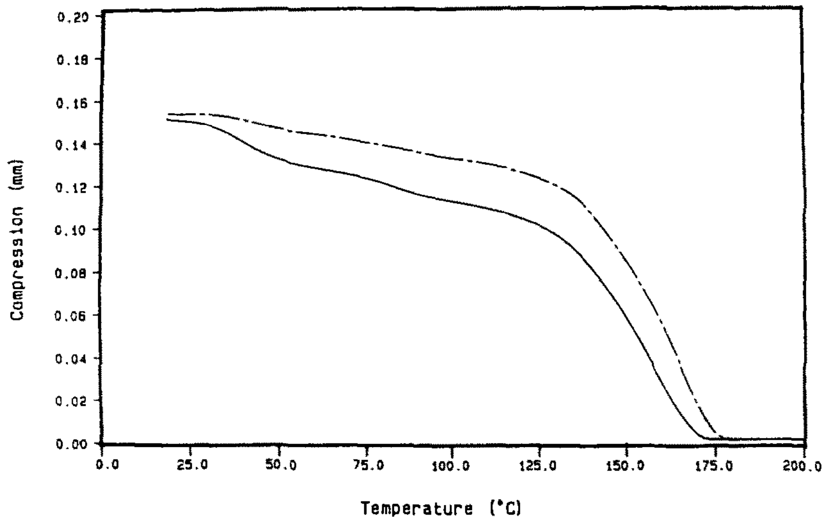

Fig. 10. TMA plots for PVC foil 1: unweathered ——— and weathered for 20 days ·–·–·–, after heating to 140°C at 40°C min^{-1} and immediate cooling to 20°C at 100°C min^{-1}.

physical structure of the sample has been deleted by heating to 140°C at 40°C min^{-1} and immediate cooling to 20°C at 100°C min^{-1}. The data obtained show (in full agreement with the results of the DSC measurements which are shown in Fig. 3) that weathering causes the T_g of the PVC foil 1 to shift to higher values. According to Fig. 10 the ratio $\Delta T_g/\Delta t_w$ is $\approx 5.2 \times 10^{-3}$°C h^{-1} which is about 65% higher than the corresponding value previously determined from DSC measurements (see Table 3). Furthermore, the figure shows that weathering of 20 days shifts the whole TMA plot to higher temperatures, i.e. it induces a marked embrittlement of the chemical structure of the PVC foil 1. This again can be considered as the result of crosslinking reactions occurring during irradiation.

Figure 11 shows the results of TMA for the PVC foil 2. For the following discussion it is convenient to subdivide the temperature range displayed into two domains, one below and one above T_g. In the sub-T_g range of Fig. 11 the effect of weathering manifests itself in a marked shift of the T_g of PVC to higher temperatures (due to a decrease of the hole concentration in the amorphous phase) and additionally in the disappearance of the drop of rigidity at $T \approx 32$°C which is exhibited only by the unweathered foil. Considering that the T_g of polyvinylacetate (PVAC) is located at $T = 32$°C [9], these results seems to indicate that the foil 2 is a copolymer containing some PVAC which, for some unknown reasons, suppresses the display of its glass transition in the weathered state. In the temperature domain above T_g, it can be seen that weathering of 5 days creates a definite embrittlement of the foil 2, however, after 20 days of weathering the brittle behavior has disappeared and the softening of the foil is even slightly

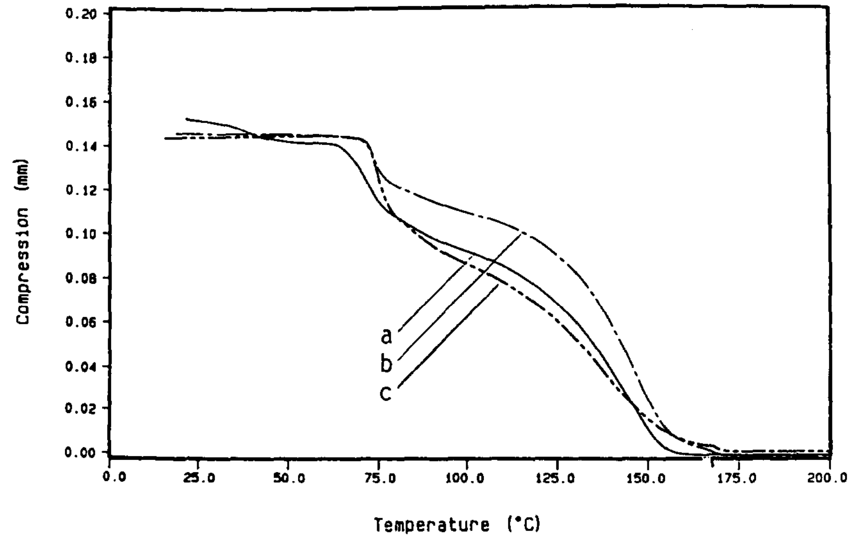

Fig. 11. TMA plots for PVC foil 2: (a) unweathered, (b) after 5 days of weathering, (c) after 20 days of weathering.

enhanced. In addition, at high temperature both weathered foils exhibit a retarded softening which leads to a final drop of penetration resistance at ≈ 170°C. The plateau just before the drop might indicate again a rubber-like behavior due to crosslinking.

Figure 12 shows the softening of the foil 2 in the unweathered state and after 20 days of weathering, both recorded after thermal treatment to

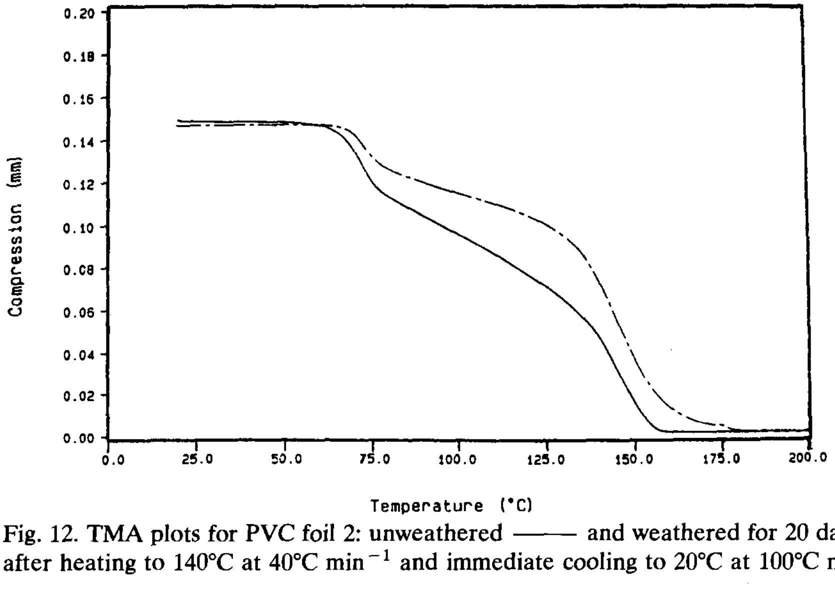

Fig. 12. TMA plots for PVC foil 2: unweathered ——— and weathered for 20 days -·-·-, after heating to 140°C at 40°C min^{-1} and immediate cooling to 20°C at 100°C min^{-1}.

delete their physical structures. First of all, Fig. 12 clearly shows that the overall effect of weathering on the foil 2 is – as in the case of the PVC foil 1 – a marked embrittlement of the material. Furthermore, the recordings show that due to weathering, the foil 2 displays a pronounced shift of the T_g of PVC when the influence of the physical structure is absent. This confirms the results of the DSC measurements presented in Fig. 6. According to Fig. 12 the ratio $\Delta T_g/\Delta t_w$ is $\approx 6.2 \times 10^{-3}$°C h^{-1}, which is about 57% higher than the corresponding value, previously determined from DSC measurements.

It is interesting to note that the ratio $\Delta T_g/\Delta t_w$ provided by the TMA measurements is, for both foils, definitely (i.e. ≈ 60°C) higher than the corresponding ratio from DSC measurements. This indicates that TMA is somewhat more sensitive in detecting such shifts than DSC. Furthermore, the rate of the T_g shift occurring during weathering is again found to be definitely higher for foil 2 than for foil 1 (according to the DSC measurements it is 19% higher, according to the TMA measurements it is 26% higher). This confirms that foil 2 has indeed a higher yield for the crosslinking reaction than foil 1.

Concerning Figs. 9–12, two final remarks are noteworthy. First, a comparison between Figs. 11 and 12 shows that the thermal treatment mentioned above shifts the plateau, which is displayed by the weathered foils before the final drop, by an amount of ≈ 5°C. Second, it is interesting to note that the TMA curves of the two unweathered foils 1 and 2, presented in Figs. 9 and 11, end at definitely different temperatures. The temperature at which a complete penetration has been achieved is ≈ 170°C in the case of the foil 1, and ≈ 160°C in the case of the foil 2. As the two foils have different K-values (foil 1 has $K = 70$, foil 2 has $K = 57$), it seems likely that the end point of a TMA curve of a non-crosslinked material (the two foils are supposed to be free of crosslinks in the unweathered state) is somehow related to the mean molar mass or the zero shear viscosity of the material in question.

SUMMARY AND CONCLUSIONS

The information obtained from a complete thermal analysis (consisting of DSC, TGA, TMA and with the advantage also of dynamic mechanical analysis) provides a sound basis for the efficient planning of further investigations (e.g. gel permeation chromatography, mechanical testing and spectroscopy) which might be necessary to answer some more specific questions. It should be emphasized that all of the results here presented required only about 20 mg of each sample. Furthermore, it should be added that all tests were performed in less than 15 h.

Weathering studies should always include the aspect of physical aging. This is important because, during weathering improvements of certain material properties due to aging may well be cancelled due to degradation which occurs at the same time; the overall effect will then be compensated to a zero-effect. It should be mentioned that beside the simple, monotonic changes of material properties induced by isothermal physical aging, more complex changes may occur too, involving effects of de-aging, under non-isothermal conditions [10].

Physical aging of PVC results in an increase of crystallinity, if the material has been exposed to a temperature $T_w > T_g$, or in a decrease of free volume if $T_w < T_g$. Similar results have previously been reported by Illers [1] who studied the annealing of one type of PVC at different temperatures.

During weathering the two investigated PVC samples experience different changes, with respect to both chemical and physical structures. The induced changes in the physical structure are determined by the position of the weathering temperature T_w with respect to the T_g. In the chemical structure, however, the effects of crosslinking are evident (by means of DSC and TMA). The extent of crosslinking is shown to depend on the actual content of PVC, or PVC and PVAC. By means of TMA it was possible to identify foil 2 as a copolymer PVC/PVAC. It is further interesting to note that TGA clearly showed that foil 1 does not lose any significant amount of plasticizer during weathering.

There still remain some open questions which cannot be answered yet. This concerns mainly the release of hydrogen chloride and acetic acid, and the extent of chain-breaking taking place in the samples during weathering. Furthermore, the results obtained do not give any evidence as to why foil 2 took on a brownish-violet color during weathering, while foil 1 remained visually unchanged.

For further investigations, it is of great advantage to use specially prepared samples with known composition and sample history instead of the commercial samples used here.

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