JOURNAL OF MATERIALS SCIENCE 20 (1985) 3574–3580

Accelerated ageing of cement sheets containing polypropylene networks

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Oven ageing experiments are described which have been used to accelerate the thermal oxidation of networks made of polypropylene films when embedded in cement mortar. The composite is intended to be used in approximately 6 mm thick sheets as an alternative to asbestos cement, the required in-service lifetime for which may be more than 30 years. The accelerated ageing data were obtained from direct tensile tests on the composite, the predictive criteria being strength of the film and strain to failure of the composite. It is shown that 0.25% of commercial antioxidants by weight of the film should give resistance to degradation of the films for well in excess of the required lifetimes when contained in the composite. The performance of the networks with these antioxidants at the lowest test temperature of 80° C is so good that the tests at this temperature will probably take more than five years to complete, and therefore the data presented mostly relate to temperatures between 100 and 140° C.

1. Introduction

Any fibre-reinforced, cement-based, thin sheeting which is offered as an alternative to asbestos cement sheeting has to be able to demonstrate a predicted life in excess of 30 years when subjected to natural weathering conditions in most parts of the world. The particular composite now known as Netcem* which is the subject of this paper relates to the use of layers of networks of opened fibrillated polyalkene films embedded in cement mortar. Typically, ten layers of 50 to 80 μm thick nets per mm thickness of composite are used, and the technology has already been extensively described in the literature [1, 2].

Although real-time durability tests of five years' duration have already been completed [3, 4], experiments of 30 years duration are impossible to carry out before the commencement of marketing and therefore accelerated test procedures on the critical component of the composite are required. The appropriate test procedure will vary with the type of composite; for instance, for glass-reinforced cement, storage at normal or elevated temperatures under water is a critical condition whereas this test has been found [4, 5] to have little effect on the strength or ductility of polypropylene-reinforced cement. The appropriate accelerated test in the latter case may therefore be to use the techniques developed in the plastics industry to test stabilizers for polymers as used, for instance, in textile fibres and in car bodies, except that no protection against ultra-violet light is necessary when the nets are embedded in cement [5]. These techniques are designed to accelerate the oxidation of the polymer.

2. Oxidation and stabilization of polypropylenes

All alkenes react with oxygen at ambient temperatures. The general reaction mechanisms of alkene oxidation were established for simple hydrocarbons before polypropylene was commercially available. The oxidation and

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stabilization of simple hydrocarbons have been extensively reviewed by Ingold [6]. It has later been established that during the oxidation of polypropylene

(a) hydroperoxides are formed;
(b) the decomposition of hydroperoxides into free radicals catalyses the oxidation; and
(c) the oxidation is autocatalytic.

Consideration of the autoxidation mechanism suggests two ways in which the chain reaction can be interrupted or inhibited. The alternatives are suppression of either (a) the initiation, or (b) the propagation process. Suppression of the initiation process means preventing the formation of free radicals. As the decomposition of hydroperoxides is the main source of free radicals, this can be achieved by using an additive which decomposes the hydroperoxide into non-radical species, or which prevents the decomposition of the hydroperoxide by complex formation. Stabilizers which act by suppressing intiation are generally classified as peroxide decomposers. Propagation is suppressed by additives, known as free-radical scavengers, which react with peroxy radicals thereby preventing the radical from extracting another hydrogen atom from the polymer and continuing the chain reaction.

Two commercial stabilizers were chosen for this study, one being basically a free-radical scavenger and the other basically a peroxide decomposer. However, a stabilizer may act by several different mechanisms, and the dominant mechanism may change with temperature due to the different activation energies of the reactions involved. One mechanism may be completely effective in retarding oxidation, preventing any significant degradation until the stabilizer is severely depleted, while another mechanism may slow down the oxidation without completely preventing degradation.

3. Theory of accelerated testing

Reaction rates are temperature-dependent and can be represented by the standard Arrhenius equation

$$K = Ae^{-E/RT} \tag{1}$$

where K is reaction rate, A is the pre-exponential factor, E is activation energy, R is the gas constant and T is the absolute temperature. Equation 1 can be expressed in the form

$$\ln K = \ln A - \frac{E}{RT} \tag{2}$$

Hence a plot of $\ln K$ against $1/T$ for a single reaction should yield a straight line. However, the oxidation of polypropylene is a complex reaction and the inhibited oxidation of polypropylene is more complex. Therefore an Arrhenius plot of our reaction rates is unlikely to be a straight line but if sufficient points are obtained to define a curve, then an extrapolation to lower temperatures can be made although Gysling [7] found that this procedure predicted longer lifetimes than were actually obtained. The accuracy of prediction will be increased, the lower the temperature used in the accelerated tests.

However, there are a number of additional complicating factors in the prediction of in-service lifetime when films are contained in a cement matrix. The diffusion of oxygen through the matrix may affect the rate of oxidation of the polypropylene and any direct reaction between the stabilizer and oxygen. In these cases the presence of the matrix would be beneficial. However, the matrix could catalyse the formation of hydroperoxides or have an adverse effect on the chemical depletion of the stabilizer by preventing the rapid removal of small, volatile radicals which can catalyse the oxidation reactions. Also, in natural weathering the composite may be saturated with water for a significant time. In such a case, the water could reduce the amount of oxygen reaching the polymer but it could have an adverse effect if the stabilizers used are able to be leached out.

Due to the complexity of the reactions involved, and the differences in the composition and moisture content of the matrix between oven-aged laboratory samples and naturally weathered commercial composites, the assumption of an Arrhenius plot may not be valid for predictive purposes. Therefore, it is impossible to obtain an absolute value for the life of the composite at ambient temperatures under natural weathering conditions, and any values obtained by extrapolation should be treated with caution.

Notwithstanding the above remarks, oven-ageing in the presence of oxygen is the only available accelerated test at the present time, and

TABLE I Mix proportions of the matrix

Material	Ratio by weight
Ordinary Portland cement	1.0
Water	0.34
Pulverized fuel ash	0.25
Silica sand	0.19
Melment L10 (Hoechst)*	0.024
Total	1.804

*A sulphonated melamine formaldehyde resin which reduces the viscosity of the matrix.

with the use of safety factors an indication of the effectiveness of commercial stabilizers may be obtained.

4. Materials

Fibrillated nets were specially produced for the investigation by the Lambeg Industrial Research Association (LIRA) to the specification of the authors.

Two separate commercial stabilizers were used. For Film A we used Arbestab Z[†] produced by Robinson Brothers Ltd. This is a higher dialkyl dithiocarbamate of zinc specially recommended as a thermal antioxidant for polyalkenes and acts mainly as a peroxide decomposer. For Films B and C we used Chimassorb 944[‡] produced by Ciba-Geigy. This is of the hindered amine class and is a highly effective heat stabilizer as well as being an excellent light stabilizer. It is of a type which partly acts as a free radical scavenger. Both stabilizers for Films A and B were specified to be included at a nominal 0.25% by weight of polymer, and subsequent analysis of the films by the suppliers of the stabilizers showed that 0.23% of Arbestab Z had been retained and 0.28% of Chimassorb 944 had been retained.

In addition, a nominal 0.5 wt % of Chimassorb 944 was included in a third film (Film C), but the results are not directly comparable because it was discovered later that a larger quantity of fine chalk filler had been included in the film in this case which could have affected the stabilization by additional absorption of additive on the filler surface [8]. Analysis showed that Film C actually contained 0.46% of Chimassorb 944.

The thicknesses of the films were as follows: Film A 78 μm; Film B 68 μm; Film C 62 μm. The films were effectively aligned in the direction of tensile stress, the film volume ranging between 5 and 8% of the volume of the composite depending on the position of each specimen in the sheet and the sheet number. The mix proportions of the matrix are shown in Table I.

5. Design of the experiment

5.1. Temperature conditions

In order to construct the Arrhenius plot, four ageing temperatures were chosen after consideration of ASTM Standard procedure for the heat ageing of plastics without load [9]. After preliminary trials, appropriate temperatures were decided to be 140, 120, 100 and 80° C even though the 80° C temperature was not expected to produce failure within one or two years. For each temperature, a series of times was chosen and six specimens of composite were aged for each time, the properties being compared with those of six similar unaged specimens used as controls. Continuous temperature records were kept of each oven.

A total of 770 specimens were prepared from 22 separate sheets and the samples were randomized to ensure a representative sample at each ageing condition.

5.2. Tensile testing

The test specimens were nominally 300 mm long, 25 mm wide and 6 mm thick. Samples were loaded in uniaxial tension, using an Instron tensile testing machine, at a constant crosshead speed of 10 mm min^{-1}. Strain was measured using linear variable differential transformers (LVDT) attached to a clip-on extensometer. The extensometer had a gauge length of 100 mm and a range of 0 to 8% strain. The strains from the LVDTs on each side of the specimen were electrically averaged and a single load–strain plot obtained on an X–Y recorder. The techniques have been described in more detail elsewhere [2, 3]. Fibre volume (V_f) was determined for each specimen before placing in the oven by dissolving the matrix from a small sample of known volume by submersion in dilute hydrochloric acid for 10 days. The film was then washed clean, dried and weighed.

A typical tensile stress–strain curve for the

[†] Registered trade mark of Robinson Brothers Ltd.

[‡] Registered trade mark of Ciba-Geigy.

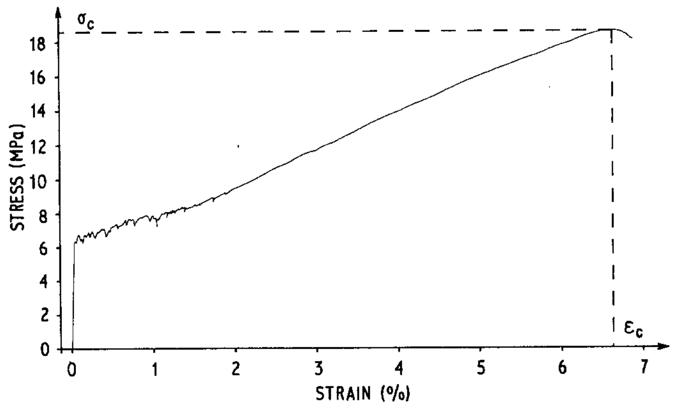

Figure 1 Typical tensile stress–strain curve for unaged composite.

unaged composite which has considerable multiple cracking is shown in Fig. 1 and from this can be determined the strength (σ_c) and strain to failure (ε_c).

These are important parameters for composite performance and they can be linked directly to film strength (σ_f) which can be determined from the following equation provided that the critical fibre volume [10] for tensile strengthening is exceeded

$$\sigma_f = \frac{\sigma_c}{V_f} \tag{3}$$

When $\sigma_f V_f$ is below the cracking stress of the composite, only one crack will occur and the composite strain to failure will reduce drastically. The ASTM procedure [9] recommends that for the purpose of the Arrhenius plot the time should be selected at which the property of interest is reduced to 50% of its original value, and hence this time was determined for film strength and for composite failure strain. A reduction of only 50% in the strain to failure would also ensure that the volume of film remains above the critical value.

6. Results and discussion

The procedure used to assess the results for the purpose of predicting lifetime at 25° C was that recommended by the ASTM standard [9].

6.1. Results for Film A

Fig. 2 shows film strength plotted against time for the four chosen temperatures, the abscissa being a logarithmic time scale. The data are not yet complete because it is expected to be about five years before the samples at 80° C have reduced their strength to 50% of the unaged strength. Values of standard deviation for the film strength for batches of six specimens were typically 30 MPa, but varied between 10 MPa and 50 MPa. This range of variability could explain the apparently high strength at 80° C. A typical real-time plot for one temperature level (100° C) which shows 95% confidence limits on the mean strength is shown in Fig. 3.

Fig. 4 shows the failure strain of the composite plotted against log (time) as for Fig. 2 for the four temperatures, the cut-off for 50% strain reduction being shown as a dashed line. Standard deviations for the strain values varied between 0.4 and 1.4%, which could give coefficients of variation as high as 50% at low strain values.

The times at which the property of interest was reduced to 50% of its original numerical value are shown on Figs. 2 and 4, and these were combined to give the Arrhenius plot in Fig. 5. The specific times were obtained from least-squares plots of all the data including the zero-time points as shown in Fig. 3.

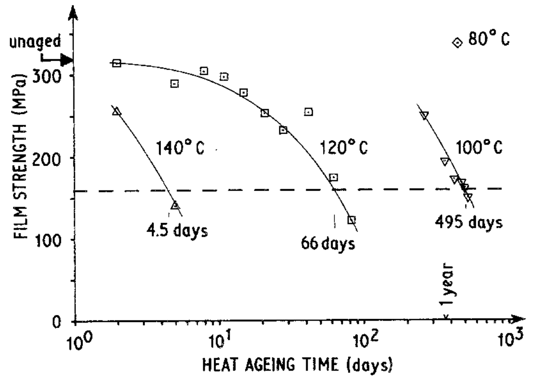

Figure 2 Results for Film A (0.25% Arbestab Z). Dashed line corresponds to 50% reduction.

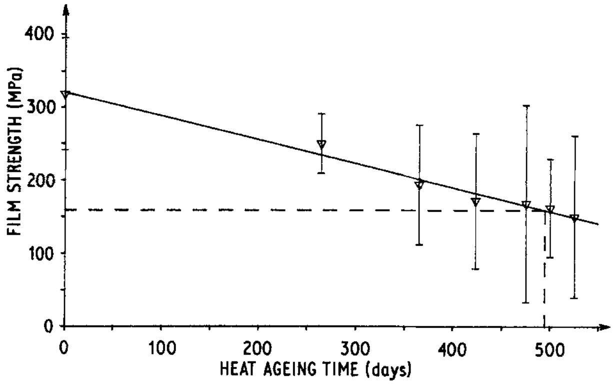

Figure 3 Results for Film A at 100° C. Bars indicate 95% confidence limits of the mean. A 50% reduction is reached at 495 days. Dashed line corresponds to 50% reduction.

Extrapolation of the three available temperatures to 25° C is obviously going to lead to considerable errors. However, a general guide, widely used for estimating the rates of chemical reactions including the degradation rates of polymers is that raising the temperature by 10° C doubles the rate of reaction or degradation. Conversely, lowering the temperature by 10° C would double the life of the polymer.

The dashed line shown in Fig. 5 uses the above rule of thumb from the last available data point (100° C) for a 50% reduction in film strength; and it can be seen that initially, at least, this dashed line is less steep and hence would predict shorter lifetimes than a true extrapolation of the actual data points. On this basis the time to 50% reduction in film strength at 80, 50 and 25° C would be 5.42 years, 43.4 years and in excess of 170 years, respectively.

No great precision can be attached to these predictions, but even if the predictions are divided by a considerable safety factor the lifetimes will be more than adequate.

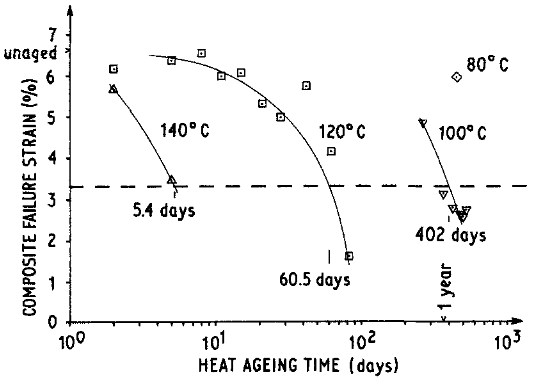

Figure 4 Results for composite containing Film A. Dashed line corresponds to 50% reduction.

6.2. Results for Film B

Figs. 6 and 7 show the oven-ageing results for film strength and composite strain to failure respectively. The stabilization is so good that even after nearly a year at 120° C the reduction in film strength or composite strain to failure has not reached 50%, and more than one year at 80 and 100° C have had virtually no effect. Hence a complete curve is only available for the 140° C samples, and these took 160 and 126 days for a 50% reduction in film strength and composite strain to failure respectively. It is not possible to construct an Arrhenius plot with such limited data, but when it is considered that Film A took only 4.5 days at 140° C and 66 days at 120° C to reduce the film strength by 50% it will be appreciated that Film B would be expected to have a lifetime far in excess of Film A.

6.3. Results for Film C

It might have been expected that twice the quantity of stabilizers would considerably improve the oven-ageing properties. However, the times to 50% reduction properties at 140° C were similar to those for Film B, and at 120° C little change was apparent after 240 days. Likewise there was no change after over one year at 100 and 80° C. As explained in Section 4, differences in film manufacture between Types B and C may limit the comparability of the tests.

6.4. General comments

It is well known that a number of different factors may affect the lifetime of polymers. These factors include irradiation by ultraviolet light, the effects of tensile stress and the resistance to leaching of the stabilizing agent when subjected to wetting and drying. The cement paste acts as an excellent screen against ultraviolet [5] and the

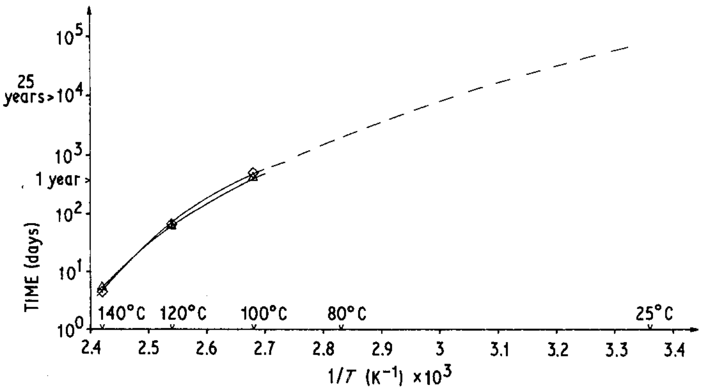

Figure 5 Arrhenius plot for Film A and its composite, for 50% property reduction: ◇ time to 50% film strength, △ time to 50% composite failure strain. The dashed line assumes that lowering the temperature by 10° C doubles the life of the polymer.

stabilizers were chosen to have a high resistance to leaching. Other tests by heating under water for one year with different stabilizers have not shown any significant problem due to leaching [5].

Several investigators [11, 12] have looked at the effect of stress on the time to fracture of polymers and have shown that tensile stress can cause appreciable acceleration of the embrittlement of polymers. However, the major end-uses of the Netcem composite are in roofing and cladding where the long-term tensile stresses are very low, and the bulk of the polypropylene is likely to be in compression because the shrinkage of the matrix is considerably in excess of the matrix tensile failure strain. Even in the cracked state, the tensile stress in the film due to the self-weight of the sheet at the standard span of a corrugated sheet is likely to be only about 3.5 MPa [1] compared with a film strength in excess of 300 MPa.

A more severe test may be in some parts of Europe where snow loads on roofs of 1 to 2 kN m^{-2} may exist for periods of three months, and these loads could result in film stresses in a cracked sheet of 47 MPa. However, these stresses would occur at temperatures below 0° C where the effects of creep and oxidation are greatly reduced, and a simulative test at these temperatures would probably take many years to achieve a result. Other tests in the laboratory at 20° C have applied continuous tensile stresses to the films of up to 50 MPa for more than three years in cracked composites without failure.

More significant stresses from the point of view of satisfactory composite performance are likely to be stresses due to installation, wind load and daily thermal and moisture gradients, but as these are only transient the effect on embrittlement of the film may be small.

7. Conclusions

(a) Oven-ageing at temperatures of up to 140° C can be used to accelerate the oxidation of polypropylene networks in cement. A temperature at least as low as 80° C is required to enable the construction of an appropriate Arrhenius plot.

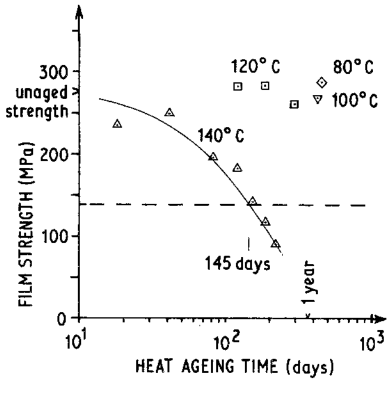

Figure 6 Results for Film B (0.25% Chimassorb 944). Dashed line corresponds to 50% reduction.

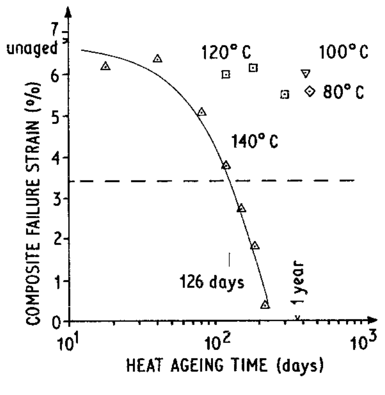

Figure 7 Results for composite containing Film B. Dashed line corresponds to 50% reduction.

(b) The two commercial stabilizers used at approximately 0.25% by weight of film were so effective that five years or more of accelerated testing at 80° C is expected to be required to give a 50% reduction in film strength or composite strain to failure.

(c) On the basis of current data, it is expected that lifetimes of the film well in excess of 30 years at 25° C can be obtained with commercial stabilizers.

Acknowledgements

The advice and assistance of Mr J. J. Zonsveld, visiting Reader in the Department of Civil Engineering, have been greatly appreciated.

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Received 15 October
and accepted 6 November 1984