ELSEVIER

PII: S0032-3861(97)00277-2

Polymer Vol. 39 No. 5, pp. 1155–1164, 1998
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00+0.00

Water absorption and leaching effects in cellulose diacetate

M.E.R. Shanahan* and Y. Auriac
Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris, Centre des Matériaux P.M. Fourt, B.P. 87, 91003 Evry Cedex, France
(Received 26 November 1996)

Degradation of polymers caused by water ingress is a recognised problem for the long term strength of structural materials but may be considered too slow for some packaging materials! Following an earlier study of water degradation in an epoxy resin, we here consider effects in cellulose diacetate—a biodegradable material. As before, initial weight increase following exposure to water is followed by weight decrease such that, at sufficiently long times, there is a net weight loss. The overall behaviour has been wholly or partially observed at six temperatures ranging from 10°C to 90°C. A model based conceptually on the initial attachment of water to the polymeric structure (causing weight increase) followed by chain segment separation and subsequent leaching (leading to weight decrease) was developed and explains satisfactorily the overall behaviour. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: absorption; ageing; cellulose diacetate)

INTRODUCTION

The widespread use of polymers in modern society has led to many advantages facilitating everyday life but also considerable disadvantages from the point of view of pollution and ecological damage. As a simple example, the use of polymers for food packaging has brought about easier and cleaner transport and use, with improved hygiene and convenience as principal gains, but unfortunately, the polymeric wrappers and containers are often discarded thoughtlessly in the countryside leading to pollution. Many of the polymers employed degrade exceedingly slowly and so this pollution is relatively permanent unless physically removed. At the other extreme, considerable use is made of speciality polymers which are intended to serve over extended periods as essentially permanent components, but unfortunately these may degrade because of environmental conditions and lose their usefulness prematurely. Thus we are faced with a variety of Murphy's law in which polymers that we wish to degrade rapidly do not, and those intended to be reasonably permanent wither!

In the latter class, recently we have been interested in the degradation of structural adhesives caused by exposure under conditions of elevated temperature and high humidity. Although structural adhesive joints often lose their strength because of a degradation occurring at the interface, or more specifically the interphase[1–3], it is also well known that more or less reversible plasticisation can weaken joints[4]. Moreover, by extended exposure to high humidity conditions, in addition to reversible effects, permanent damage may occur leading eventually to weight loss of the polymer[5,6]. An epoxy structural adhesive of the type diglycidyl ether of bisphenol A (DGEBA) cured with dicyandiamide (DDA) was studied using gravimetric methods, after ageing for various times and at various temperatures in an environment of ca. 100% relative humidity (RH). Initial weight increase of the polymer after humid exposure and subsequent drying was attributed to chemical attachment of some of the diffused water whilst weight loss after more extended periods could be explained by the leaching of low molecular weight chains after scission of the network in two or more places. A mathematical model was developed to account semi-quantitatively for the observed behaviour and, though the model was really more suitable for application to uncross-linked polymers, it was found to give quite a satisfactory explanation for the results.

If we now return to mass-produced polymers used for packaging, it must be noted that efforts are now being made to develop biodegradable materials in order to reduce long term pollution. Although biodegradation involves various processes and bacteriological attack, we thought it would be interesting to consider the behaviour of a biodegradable material under environmental conditions similar to those used for the epoxy adhesive described previously. The material studied is cellulose diacetate.

EXPERIMENTAL

The material studied is a commercial polymer, Bioceta, which the manufacturers (Mazzucchelli, Italy) declare to be cellulose diacetate containing plasticisers capable of accelerating the degradation process by micro-organisms[7]. Given the quoted percentages by weight of the three elements present: 50.5% carbon, 6.4% hydrogen and 43.1% oxygen, it may be reasonably assumed that the percentage of plasticisers is relatively small. We shall therefore assume our material to be essentially cellulose diacetate, of which the formula is $[C_{10}H_{14}O_7]_n$ and the monomeric molecular weight 246 g mole^{-1}. The degree of polymerisation, n, and dispersity are unknown but, as will be seen later, this is of little significance for the present study.

---

* To whom all correspondence should be addressed

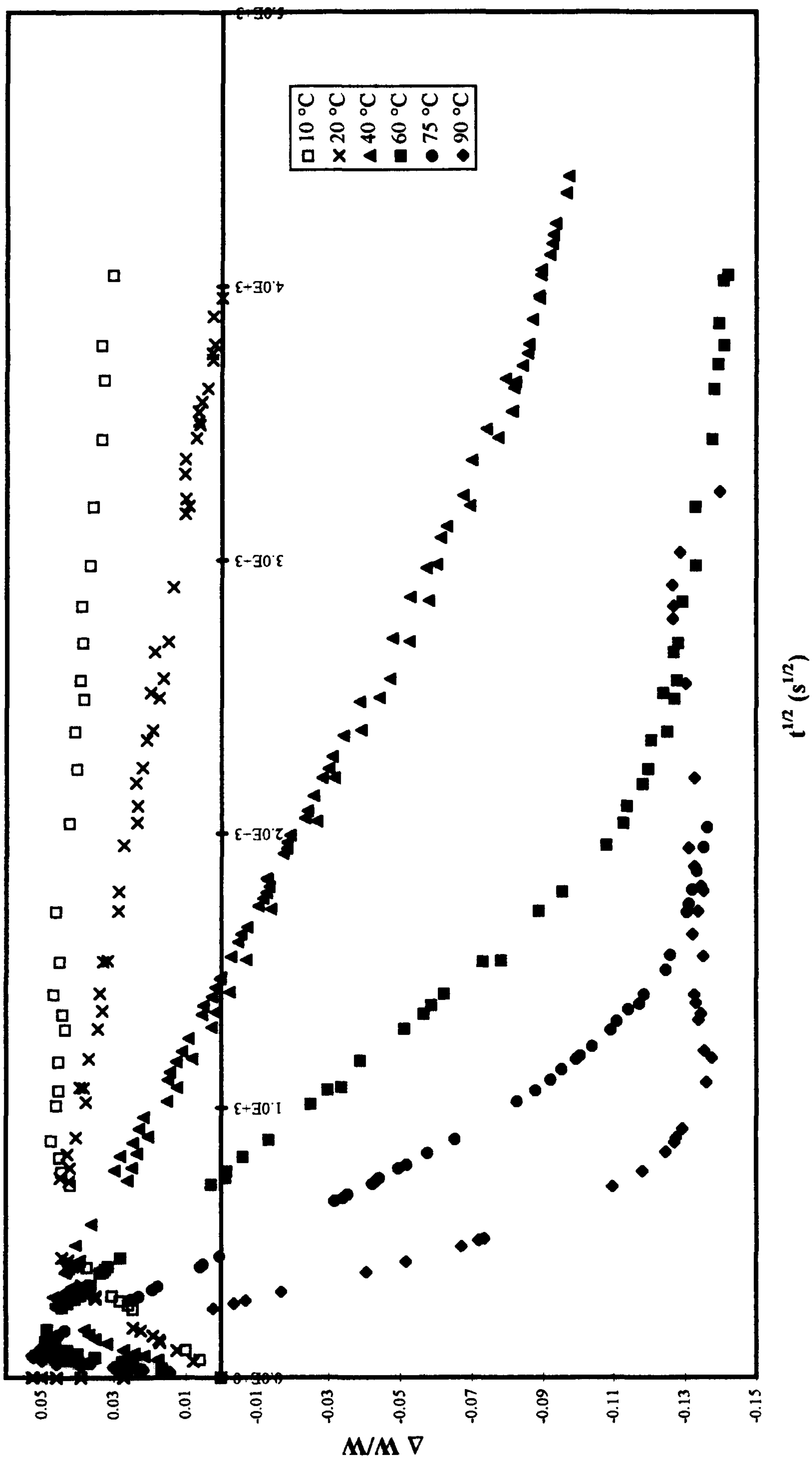

Figure 1 Relative weight change, $\Delta W/W$, of cellulose diacetate immersed in water at 10, 20, 40, 60, 75 and 90°C versus square root of time of immersion, $t^{1/2}$

Small bars of the material, of thickness, *h*, of ca. 1.6 mm, width, *a*, of ca. 7.5 mm and length, *b*, in the approximate range 30–60 mm, were aged in distilled water at temperatures of 10, 20, 40, 60, 75 and 90°C, the first corresponding to ageing in a refrigerator. Periodically, the bars were taken out of their water environment, superficially dried, weighed and then returned to the water. Depending on the temperature studied and the availability of the polymer, one to three samples were studied per temperature. Where applicable, reproducibility of behaviour was found to be good, as will become apparent below.

In the previous work on an epoxy polymer, after exposure to humidity for a given period, the samples were dried to obtain a net weight change after disappearance of physically absorbed water. It should be noted that this was unfortunately not possible in the present case because of the limited quantity of cellulose diacetate available. With the humid exposure/drying procedure, a separate sample is required for each experimental point on a weight change versus time graph, whereas with the present procedure, a given sample is followed giving many readings.

RESULTS

Figure 1 gives the results of gravimetric experiments at the six temperatures studied. Weight increase, or decrease, ΔW, as a fraction of initial weight, *W*, is shown as a function of the square root of time of immersion, $t^{1/2}$, for 10, 20, 40, 60, 75 and 90°C. At some temperatures, there is a narrow, yet apparent, band of results. This is because results from various samples at a given temperature were combined and shows that reproducibility is acceptable.

Several observations may immediately be made. In all cases an initial weight increase is followed by a decrease, and in all cases except at temperatures of 10°C and 20°C, where the kinetics of the processes involved are much slower, the decrease is observed eventually to lead to a net weight loss compared with the unaged material. Presumably, this would also occur at the lowest temperatures given enough time—for 20°C net weight loss is imminent at the halt of experiments (N.B. given that the abscissa is $t^{1/2}$, any desire to see the values of $\Delta W/W$ at 10°C and 20°C go negative would have been rather time-consuming!). This general trend of weight increase followed by decrease will be treated in the next section.

Figure 1 was plotted on a $t^{1/2}$ scale, as is conventional for diffusion data, in order to see if the Fickian model of diffusion seems applicable[8]. Given the satisfactorily linear relationships for water absorption up until at least half of the saturation value, we may indeed take the behaviour to be Fickian. Clearly the initial gradients are a function of temperature with absorption rate increasing with temperature.

Assuming Fickian behaviour, it may be shown, for rectanguloid solids, that[8]:

$$\frac{m(t)}{m(\infty)} = \frac{4}{h}\left(\frac{Dt}{\pi}\right)^{1/2}\beta \qquad (1)$$

where $m(t)$ and $m(\infty)$ represent respectively mass uptake (as a fraction of polymer weight) of water at time *t* and at saturation, *D* is the (constant) coefficient of diffusion and β is a factor correcting for edge effects[9], given by:

$$\beta = 1 + \frac{h}{a} + \frac{h}{b} \qquad (2)$$

in which *h*, *a* and *b* are respectively thickness, width and length of the sample. equation (1) applies in the range $m(t)/m(\infty) \leq 0.6$ and assuming, of course, that $m(\infty)$ may be determined. Since in our case, weight loss also occurs (by leaching, anticipating the next section), it is not clear what the saturation values of water absorption should be. Nevertheless, assimilating $m(t)$ with ΔW for the moment, and treating only the initial part of the absorption curves for which leaching effects will be assumed to be negligible, we may calculate values of *D* if $m(\infty)$ can be estimated. For this, we assume that maximum values of ΔW, before mass loss occurs, correspond to $m(\infty)$, realising that some error may be involved (underestimation if leaching has already commenced, which is probable). Values of $m(\infty)$ and of the coefficient of diffusion calculated from equation (1) at the six temperatures are given in *Table 1*.

Assuming that the coefficient of diffusion of water into cellulose diacetate may be considered to be an Arrhenius type process, we have;

$$D = D_0 \exp\left(-E_D/(RT)\right) \qquad (3)$$

where D_0 is a constant, E_D, an activation energy and *RT* the product of the gas constant and absolute temperature. A regression analysis of ln *D* versus T^{-1} (shown in *Figure 2*) for the six temperatures gives a correlation coefficient of $r = -0.995$ and leads to a value of E_D of 49 kJ mole^{-1}. The good linearity and the relative constancy of $m(\infty)$ suggest that no radical modifications in behaviour occur in the temperature range covered. It should nevertheless be recalled that poor determination of values of $m(\infty)$ necessarily limits the precision of the above simple analysis.

Having ascertained the classic nature of the initial Fickian water uptake and the standard temperature dependence of diffusion in this biodegradable polymer, let us now consider the less well known behaviour leading to marked weight loss.

INTERPRETATION OF MASS GAIN/LOSS BEHAVIOUR

Theory

At all six temperatures it can be clearly seen in *Figure 1* that initial weight increase of the polymer caused by immersion in water is followed by weight loss, the overall behaviour being temperature dependent. As a result of the temperature dependence, the weight loss, although clearly visible, is less marked at the lower temperatures and, in particular, the asymptotes are still far from being attained. As a result, only the data for 60, 75 and 90°C will be analysed statistically and we shall then attempt to extrapolate behaviour at the lower temperatures of 10, 20 and 40°C.

Table 1 Values of the estimated fractional water uptake of the polymer at saturation, $m(\infty)$, and of the coefficient of diffusion, *D*, of water into cellulose diacetate at various temperatures

T(°C)	10	20	40	60	75	90
$m(\infty)$	0.048	0.040	0.047	0.049	0.048	0.053
D(m^{2}s^{-1})	1.15×10^{-12}	2.45×10^{-12}	1.18×10^{-11}	3.10×10^{-11}	7.32×10^{-11}	9.54×10^{-11}

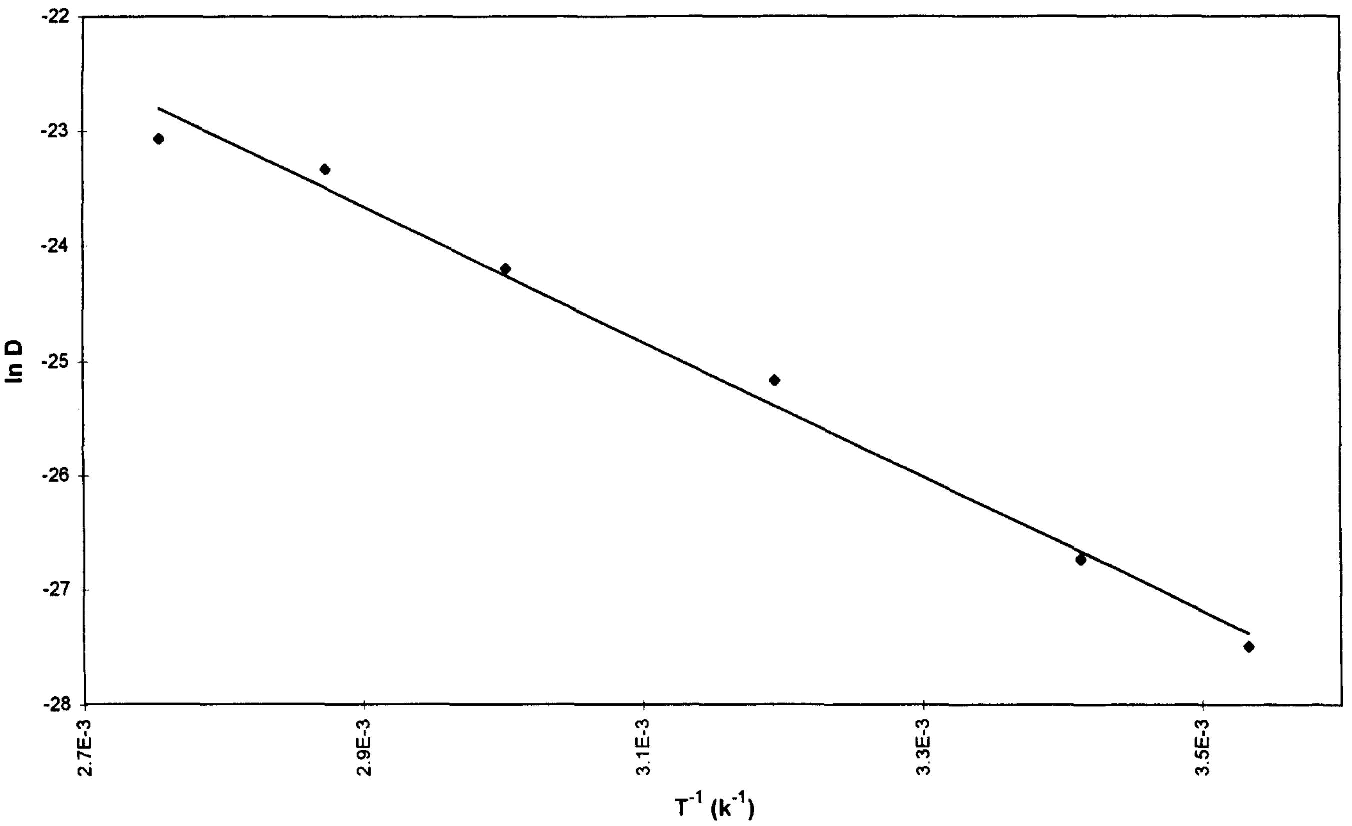

Figure 2 Results of ln D (D is diffusion coefficient of water into cellulose diacetate) vs inverse of absolute temperature, T^{-1}

The basic theory was discussed previously[5,6] as applied to a crosslinked polymer, but will be set out below for its application, with slight modifications, to the present biodegradable material. The basic physical chemistry of the weight gain/weight loss process is assumed to be as follows. As water diffuses into the polymer, a fraction of that having entered will remain physically absorbed but some will lead to the scission of macromolecular chains. We shall denote as θ the fraction reacting chemically with the polymer. It may be expected that $\theta \ll 1$ but this may well depend very much on the system being considered. The type of chemical reaction is also unknown, but its knowledge is unnecessary for the development below. However, hydrolysis of the following scheme may be expected;

$$\sim X - Y \sim + H_2O \rightarrow \sim X - OH + H - Y \sim \qquad (4)$$

where X and Y represent chemical groups in the cellulose diacetate chain.

When water initially diffuses into the polymer, the fraction θ will react and thus combine chemically with the matrix. However, as water continues to diffuse, the likelihood of having two chain scissions close to each other increases, thus leading to the creation of low molecular weight species. These may then leach out of the bulk polymer offsetting, at least to some extent, the weight gain caused by water absorption. When this second process occurs on a large enough scale, weight loss can be significant.

Mathematically, we consider the polymer sample to be one, very long, macromolecule. Clearly this will not be the case in reality but if the degree of polymerisation is sufficiently high, the (relatively) few intrinsic 'cuts' separating large, individual macromolecules will have little effect on the following mathematics. (In fact this could be allowed for but would lead to unnecessary complication of the theory.)

We consider that our 'unique' macromolecule, of mass W, reacts chemically with n molecules of water, of mass a per molecule (18 g mole^{-1}). Assuming the scheme shown by expression (4), there will be n cuts produced leading to a scission frequency, $\lambda = n/W$. The *average* mass of each segment produced will be $\bar{\ell} = W/n$, but the probability of obtaining a segment of mass ℓ, inferior to some given value, ℓ_c, will be given by;

$$P\{\ell < \ell_c\} = P = 1 - \exp(-\lambda \ell_c) \qquad (5)$$

The number of such segments will be nP. The value of ℓ_c which is at present arbitrary will be considered to correspond to the largest segment of cut polymer chain that can leach out of the bulk in a time scale comparable to that of the experiment. Assuming that $\ell_c \ll \lambda^{-1}$, the average weight of a leachable segment will be close to 0.5 ℓ_c.

The n water molecules combine chemically with the polymer and so the mass of segments capable of leaching out of the matrix, $w +$, will be given approximately by;

$$w_+ \approx n\left(a + \frac{\ell_c}{2}\right)(1 - \exp(-\lambda\ell_c)) \qquad (6)$$

We must now consider the kinetics of the various processes. Three distinct phases exist: (i) diffusion of water into the polymer, (ii) chemical interaction between polymer and water and (iii) leaching of low molecular weight species thus formed. We shall assume that (i) occurs following Fickian diffusion, as discussed previously, that (ii) is virtually instantaneous and that (iii) is also a kinetic rate process. Both (i) and (iii) are thus rate determining steps but (ii) is assumed not to be.

Considering (i), the number of 'active' water molecules, n, having diffused into the polymer is supposed to represent a fraction, θ, of the total number absorbed, $m (n = \theta m)$, at a given time. Thus w_+ is a function of exposure time, t. However, as t increases, so does the probability of low molecular weight species, already separated by scission, having leached out. The weight of these will be denoted w_-. At a given time, the number of segments capable of leaching out, and still present is $(w_+ - w_-)$. Taking process (iii) to be controlled by first order kinetics, with rate constant k (similar to a diffusion coefficient), we have;

$$\frac{dw_-}{dt} = k(w_+ - w_-) \tag{7}$$

It is probable that k will be a function of ℓ ($\leq \ell_c$), but anticipating that ℓ_c will be rather small, we assume that an average value will suffice. In addition, equation (7) neglects any effects caused by concentration gradients or orientation. Since $\ell_c \ll \lambda^{-1}$by hypothesis, the combination of equation (6) and (7) leads to;

$$\frac{dw_-}{dt} + kw_- \approx kn\lambda\ell_c\left(a + \frac{\ell_c}{2}\right) \tag{8}$$

We now return to process (i). The elementary analysis suggests that water diffusion is Fickian. Strictly speaking, we may then assume that $n \sim t^{1/2}$ up to something like half saturation ($m(t)/m(\infty) \lesssim 0.6$) and then asymptotic behaviour occurs towards a plateau ($m(t) = m(\infty)$). However, in order not to complicate unduly the mathematics we separate diffusion into two simplified regimes;

$$n \approx bt^{1/2}\ ;\ t \leq t_s \tag{9}$$

$$n \approx bt_s^{1/2} = constant\ ;\ t \geq t_s \tag{10}$$

This will inevitably lead to some inaccuracy, but is deemed to be acceptable.

Using equation (9) and the initial condition that $w_- = 0$ at $t = 0$, equation (8) leads, after integration to;

$$w_- \approx \frac{b^2\ell_c^2}{2kW}(kt - 1 + \exp(-kt)) \tag{11}$$

where it is assumed that $\ell_c \gg 2a$.

Now the net change in the mass of the polymer, ΔW, will be caused by the addition of m molecules of water, allowing also for the $(m - n)$ molecules which were simply absorbed physically, and the extraction of mass w_-. Thus we have;

$$\Delta W = ma - w_- \approx b\left\{\frac{at^{1/2}}{\theta} + \frac{b\ell_c^2}{2kW}(1 - kt - \exp(-kt))\right\};t \leq t_s \tag{12}$$

The theoretical argument until now was based on molecular concepts, but experimental results are based on macroscopic readings and thus some conversion of units will facilitate treatment. In order to convert the mass of the water molecule, a, and the leached segment, ℓ_c, into tangible numbers (g mole^{-1}), we introduce Avogadro's number N and equation (12) becomes;

$$\Delta W \approx b\left\{\frac{at^{1/2}}{\theta N} + \frac{b\ell_c^2}{2kWN^2}(1 - kt - \exp(-kt))\right\}\ ;\ t \leq t_s \tag{13}$$

For the regime corresponding to equation (10), equation (8) may be solved by quadrature using the boundary condition of continuity of ΔW at $t = t_s$. Introducing Avogadro's number again, we obtain the counterpart of equation (13);

$$\Delta W \approx b\left\{\frac{at_s^{1/2}}{\theta N} + \frac{b\ell_c^2}{2kWN^2}([\exp(kt_s) - 1]\exp(-kt) - kt_s)\right\};$$
$$t \geq t_s$$

Application to temperatures of 60, 75, and 90°C

We shall now apply the above theory to experimental results of relative mass increase/decrease, ΔW, as a function of time of immersion, t. Equation (13) and equation (14) may be written in the form;

$$\frac{\Delta W}{W} \approx At^{1/2} + B(1 - kt - \exp(-kt))\ ;\ t \leq t_s \tag{15}$$

$$\frac{\Delta W}{W} \approx At_s^{1/2} + B([\exp(kt_s) - 1]\exp(-kt) - kt_s)\ ;\ t \geq t_s \tag{16}$$

where constants A and B are given by;

$$A = \frac{ab}{\theta NW} \tag{17}$$

$$B = \frac{b^2\ell_c^2}{2kW^2N^2} \tag{18}$$

We thus have two equations, (15) and (16), containing four (unknown) parameters, A, B, k and t_s. These parameters are, in principle, functions of the absorption temperature, T. The sets of experimental data for each of the three higher temperatures were analysed using equations (15) and (16), and non-linear regression analysis. Values obtained for the parameters are given in *Table 2*. Considering equation (1) and equation (15), it may be shown that;

$$D \approx \pi\left[\frac{Ah}{4\beta m(\infty)}\right]^2 \tag{19}$$

Values of D thus calculated are presented in *Table 2* and may be compared with those obtained by direct analysis of the initial parts of the absorption curves in Section Section 3 of this article. Differences between the two evaluations are of the order of 10%, 26% and 15% respectively at 60, 75 and 90°C. This agreement may be considered satisfactory considering that the non-linear regression analysis takes into account the totality of data presented and not just the initial ones pertaining to (approximately) Fickian absorption. The corresponding graphs of $\Delta W/W$ versus log t, calculated from equations (15) and (16) together with experimental data are shown in *Figure 3*. As can be seen, the theoretical curves give a most satisfactory representation of the data. It would

Table 2 Values of the four parameters A, B, k and t_s from equation (15) and equation (16) obtained by non-linear regression analysis of results corresponding to 60, 75 and 90°C. Estimations of the coefficient of diffusion, D, calculated from A and equation (19) are also given and may be compared with those of *Table 1*

T(°C)	60	75	90
A(s$^{-1/2}$)	4.60×10^{-4}	6.55×10^{-4}	8.25×10^{-4}
B	35.8	27.0	10.9
k(s^{-1})	4.83×10^{-7}	1.28×10^{-6}	4.44×10^{-6}
t_s(s)	10500	5200	3850
D(m^{2}s^{-1})	2.78×10^{-11}	5.39×10^{-11}	8.25×10^{-11}

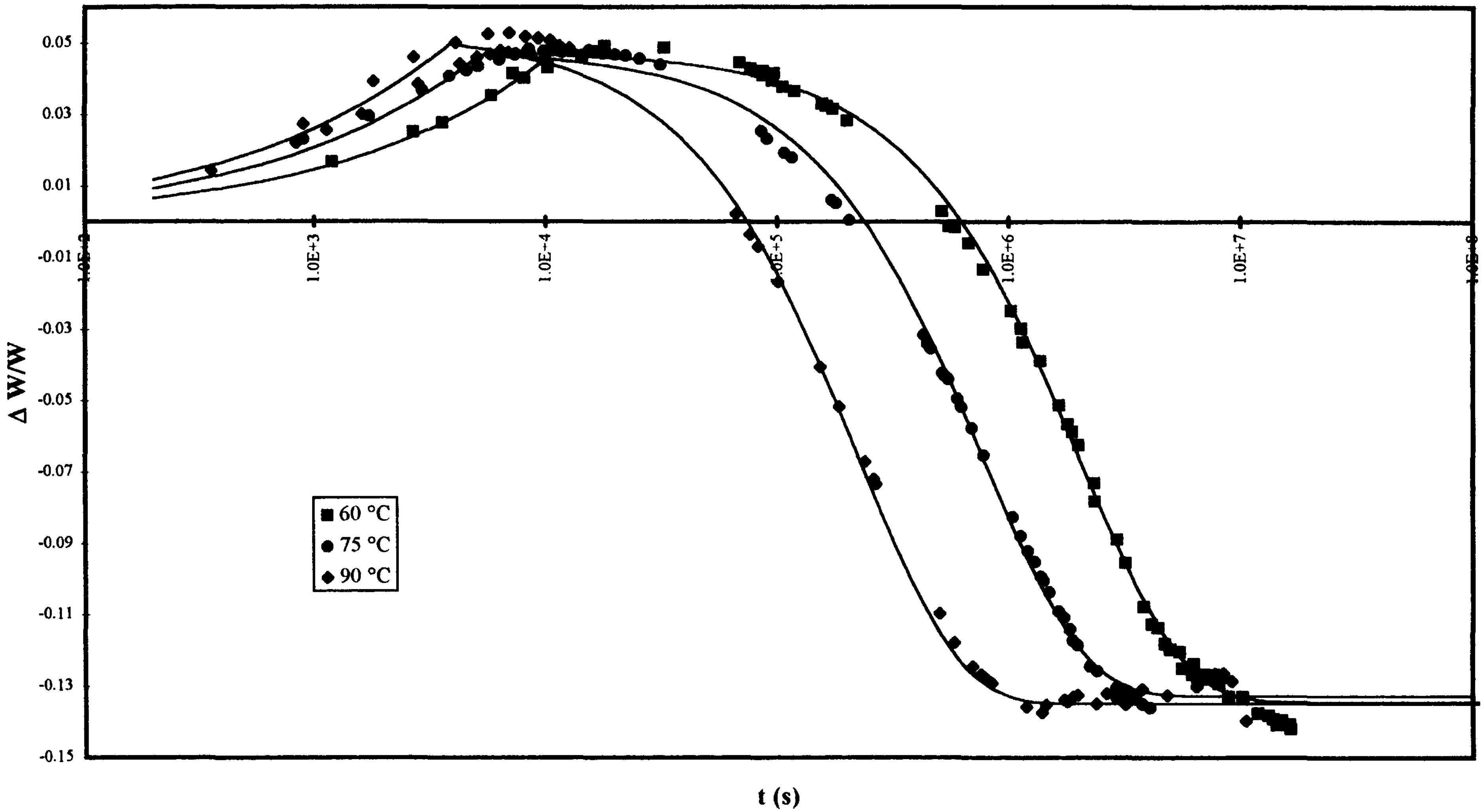

Figure 3 Relative weight change of polymer, $\Delta W/W$, versus t (on a logarithmic scale) at 60, 75 and 90°C and non-linear regression curves

seem that in the three cases, asymptotic behaviour suggests stabilisation at a weight loss of ca. 13%. The parallelism of the curves would also suggest that a time temperature shift mechanism could apply, as in viscoelasticity[10], but there seems to be little point in elaborating an empirical formula for a theoretical model which already works quite satisfactorily.

The term A was dealt with above to quantify initial absorption (coefficients of diffusion, D, and activation energy, E_D). Using the definitions of A and B (equation (17) and (18)) and rearranging we find;

$$\theta \ell_c \approx \frac{a}{A}(2kB)^{1/2} \tag{20}$$

where a is equal to 18 g mole^{-1} and the other values are known from regression analysis. Using equation (20) we find $\theta\ \ell_c$ equal to 230, 230 and 215 g mole^{-1} respectively for results obtained at 60, 75 and 90°C, giving a mean value of $\langle\theta\ell_c\rangle = 225 \pm 10$ g mole^{-1}. We recall that θ is the (assumed) fraction of diffused water reacting chemically with the polymer and that ℓ_c is the molecular weight of the largest separated segments of polymer capable of leaching out of the bulk in a period comparable to the time scale of the experiment. With a monomeric molecular weight of 246 g mole^{-1}, and with θ approaching unity (i.e. *nearly all* the water reacts chemically), we should expect only monomers to leach. Equivalently, if θ is ca. 0.1, chains of up to about 9 monomers may leach. However, θ is unknown from the results presented as we did not undertake a compaign of experiments of absorption followed by drying, because of a lack of available material, as explained previously.

The rate constant for leaching, k, is, in essence, a coefficient of diffusion (or self-diffusion). Therefore, by analogy with equation (3), we hypothesise that it will follow an Arrhenius type relation:

$$k = k_o \exp(-E_k/(RT)) \tag{21}$$

where k_o is a constant and E_k an activation energy for self diffusion. Regression analysis of ln k versus T^{-1}, albeit for only three pairs of values, gives a value of E_k = 74 kJ mole^{-1} (with a correlation coefficient of r = -0.996). The value of E_k is higher than that for water diffusion (E_D = 49 kJ mole^{-1}), which may seem reasonable since the leaching molecules are considerably larger, but this observation must be considered with reserve since other factors may be important (it is not clear what provides the 'driving force' for the leaching process!). The value of k at 70°C may, from the above, be estimated at ca. 10^{-6} s^{-1}. Comparing this with a value of ca. 6×10^{-8} s^{-1} obtained for an epoxy resin in earlier work[5,6], we find a leaching rate constant about 20 times bigger in the present case. This could possibly be a consequence, at least partly, of a less rigid macromolecular network present in an uncrosslinked polymer.

Values of t_s are somewhat artificial, in that t_s is assumed to be an instantaneous cut-off from $t^{1/2}$ diffusion to a plateau and we realise that diffusion rate must diminish asymptotically and not abruptly, in reality. Nevertheless t_s decreases with increasing temperature, as expected. In addition, with the simplified diffusion model represented by equation (9) and equation (10), the product $At_s^{1/2}$ should be approximately constant if we assume $m(\infty)$ to be (virtually) independent of temperature. Using the values of *Table 2*, we find $At_s^{1/2}$ to be ca 4.7×10^{-2}, 4.7×10^{-2} and 5.1×10^{-2} respectively for the temperatures of 60, 75 and 90°C. The agreement is quite acceptable, though too much emphasis should not be put on this because of the simplified diffusion model and lack of irrefutable evidence for the constancy of $m(\infty)$.

Let us consider equation (16) and its asymptotic behaviour as $t \longrightarrow \infty$. We obtain;

$$\frac{\Delta W}{W}(t \longrightarrow \infty) = At_s^{1/2} - Bkt_s \tag{22}$$

Using the values given in *Table 2*, we obtain asymptotic values of $\Delta W/W(t \longrightarrow \infty)$ of ca. -0.134, -0.133 and -0.135 respectively at 60, 75 and 90°C, indicating a final weight reduction *during immersion* of the order of 13%. There is good agreement between all results suggesting final weight loss to be virtually temperature independent, at least in this range. Of course, in reality as time progresses other processes may contribute to the degradation processes, especially with the present polymer which is specifically biodegradable.

Tentative extrapolation to temperatures of 10, 20 and 40°C

As can be seen from *Figure 1*, at the time this paper was written, the results obtained at 10, 20 and 40°C were still far from stabilising at asymptotic values of weight loss. The non-linear regression analysis successfully used for 'complete' sets of data at 60, 75 and 90°C was found not to work adequately on the 'incomplete' results at the lower temperatures and so a different technique was attempted to compare theory and practice. Values of D were calculated previously from the initial gradient (*Table 1*) and by rearranging equation (19), estimates of A were obtained. The assumed saturation time, t_s, could be estimated, within the limits of our assumed, simplified Fickian absorption (cf. equation (9) and equation (10)) from;

$$t_s \approx [m(\infty)/A]^2 \tag{23}$$

In equation (21), we had assumed an Arrhenius type dependence on temperature for k and from the regression analysis applied on results at 60, 75 and 90°C, we can extrapolate to lower temperatures assuming no change in fundamental behaviour (transitions). This assumption would tend to be borne out by the overall features of the experimental data.

Finally, it would seem that as $t \longrightarrow \infty$, $\Delta W/W$ tends towards a constant of ca. -0.134 (taking the average at 60, 75 and 90°C). Assuming this value to be unaffected by temperature, equation (22) may be used to estimate B. The values of the four parameters thus obtained for the three lower temperatures are presented in *Table 3*.

In *Figure 4* we present the results of $\Delta W/W$ versus time of immersion, the latter on a logarithmic scale, together with the predicted behaviour as curves corresponding to equation (15) and (16) and the values of the parameters given in *Table 3*. As can be seen, the agreement is reasonably good, though in all cases experimental values of $\Delta W/W$ tend to be below the predicted curves on the weight loss parts of the graph. Nevertheless, given that parameters were

Table 3 Values of the four parameters A, B, k and t_s at lower temperatures (corresponding to equation (15) and equation (16)) obtained by extrapolation from results at 60, 75 and 90°C, as described in the text

T(°C)	10	20	40
A(s$^{-1/2}$)	9.50×10^{-5}	1.21×10^{-4}	2.80×10^{-4}
B	181	114	78
k(s^{-1})	4.02×10^{-9}	1.18×10^{-8}	8.24×10^{-8}
t_s(s)	25 000	132 000	28 000

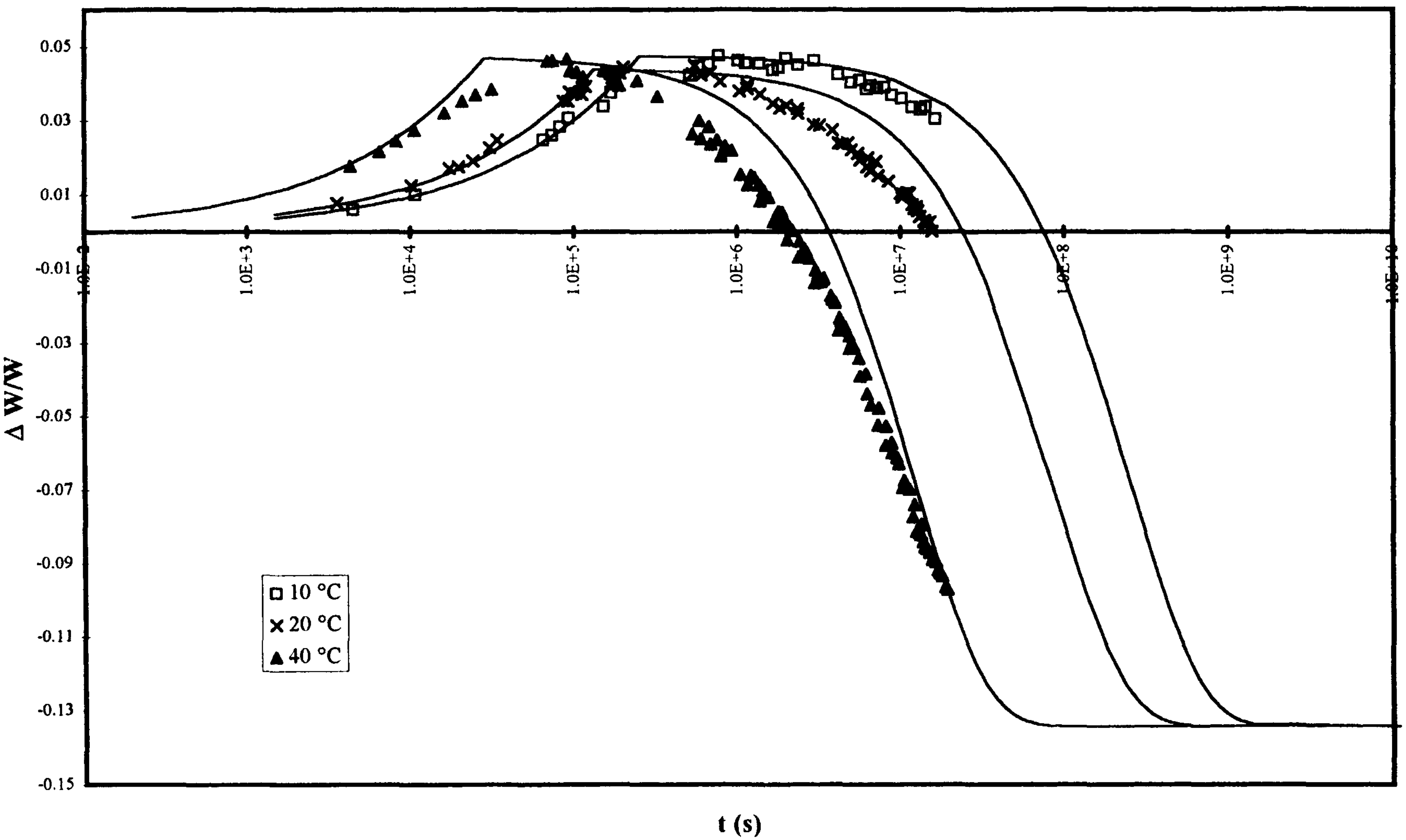

Figure 4 Relative weight change of polymer, $\Delta W/W$, versus t (on a logarithmic scale) at 10, 20 and 40°C and curves obtained by extrapolation from behaviour at higher temperatures

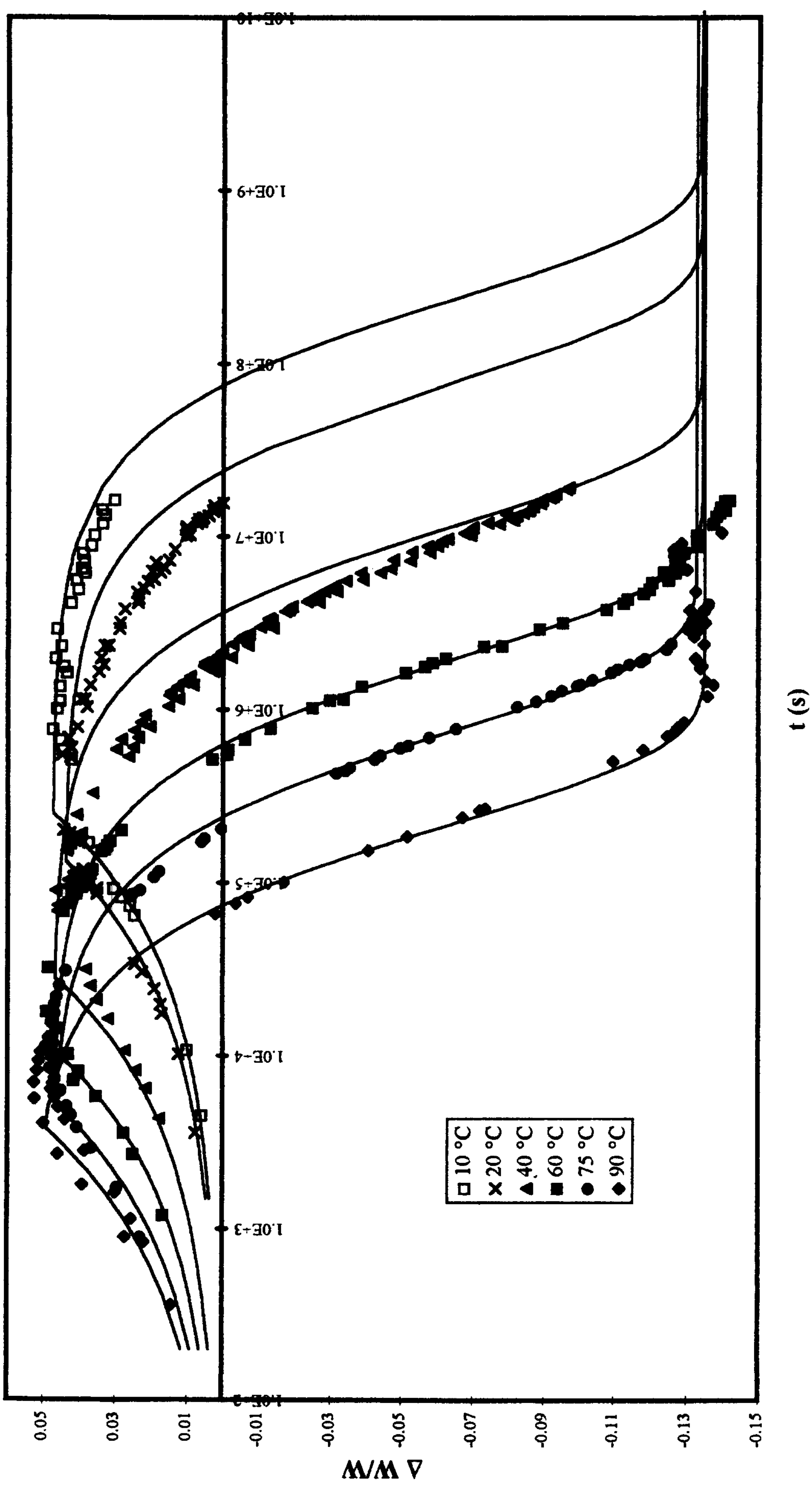

Figure 5 *Figures 3 and 4* combined to give overall impression of weight change behaviour of cellulose diacetate immersed in water at six temperatures

extrapolated, rather than regression analysis performed, and that we are potentially considering something like 5 to 6 decades of time, the agreement is, it is felt, quite acceptable. It is of interest to note that the stable weight should, according to the prediction, be reached after the order of 30 years, 15 years and 3 years respectively at 10, 20 and 40°C—waiting for equilibrium would not really be practical! (In practice, of course, other phenomena could intervene complicating behaviour.)

Finally, in *Figure 5*, the complete set of results for the six temperatures studied is presented on a logarithmic time scale, together with corresponding curves, calculated by non-linear regression analysis for 60, 75 and 90°C and from extrapolated parameters for 10, 20 and 40°C.

DISCUSSION AND CONCLUSION

Overall, we can see that the relatively simple analysis used to explain water uptake followed by leaching of severed low molecular weight species satisfactorily explains weight changes observed with this biodegradable polymer. Nevertheless, certain features remain to be clarified. At present, we do not know what constitutes the 'driving force' for leaching which will, in turn, probably largely control the value of k in the above analysis. In addition, we have used a single value of k though intuitively, one would expect k to be a function of the molecular weight of severed segments. Perhaps the relatively small range of molecular weights involved in leaching renders the simplification of using a single value of k a good approximation. Such factors as concentration gradients, entanglements, molecular orientation and surface structure different from the bulk may also be significant. The model developed assumes that after a time of absorption equal to t_s, depending on the temperature, no further water uptake occurs since saturation is assured. Apart from our simplification of what should properly be considered as asymptotic behaviour, a further potential problem becomes evident. As lower molecular weight species migrate from the bulk, (molecular size) cavities will probably be left. Will these close or could they accept further incoming water? In the latter case diffusion to saturation at t_s will not be realistic and something more akin to Langmuir adsorption[11] would be more appropriate. Nevertheless, despite the simplicity of the treatment and the criticisms that may be levelled at our approach (work in the field clearly remains to be done), we feel that the proposed simple model for absorption of water followed by leaching of low molecular weight species adequately explains the ageing process by hydrolysis in the case of the present uncrosslinked polymer.

ACKNOWLEDGEMENTS

We thank G.Z. Xiao for aid with the non-linear regression analysis.

REFERENCES

1. Sharpe, L. H., *J. Adhes.*, 1972, **4**, 51.
2. Gledhill, R.A. and Kinloch, A.J., *J. Adhes.*, 1974, **6**, 315.
3. Zanni-Deffarges, M. P. and Shanahan, M. E. R., *Inter. J. Adhes. Adhesives*, 1994, **45**, 245.
4. Li, C., Dickie, R. A. and Morman, K. N., *Polym. Eng. Sci.*, 1990, **30**, 249.
5. Shanahan, M. E. R., De'Nève, B. and Auriac, Y., *C.R. Acad. Sci.*, 1993, **317**(II), 763.
6. De'Nève, B. and Shanahan, M. E. R., *J. Adhes.*, 1995, **49**, 165.
7. Bioceta—commercial data sheet.
8. Crank, J., *The Mathematics of Diffusion*, 2nd ed., Oxford University Press, London, 1975.
9. Chen, C. H., and Springer, G. S., *J. Compos. Mater.*, 1976, **10**, 2.
10. Ferry, J. D., *Viscoelastic Properties of Polymers*, 2nd edn., Wiley, New York, 1970, p. 314.
11. Carter, H. G. and Kibler, K. J., *J. Compos. Mater.*, 1978, **12**, 118.