Prediction of State of Cure throughout Rubber Components[†]

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During moulding of many rubber components, temperature gradients persist for a significant fraction of the cure time. Thus the cure conditions are non-isothermal and also non-uniform throughout the component. In consequence, the physical properties of standard testpieces cured isothermally (e.g. 2 mm thick sheet) may be unrepresentative of those of the rubber in the component.

The theoretical framework for calculating isothermal cures representative of a particular temperature history is reviewed. The theory is implemented for specific cases by solving the transient thermal problem using finite element analysis (FEA) together with user defined variables representing the 'equivalent cure time' and the 'representative temperature' of an equivalent isothermal cure. The predictions are compared to experimental results. The overall agreement is good, but the limitations of both the theory and the idealised boundary conditions for the calculations are discussed. Implications for moulding procedures and mould design are also given.

During moulding of many rubber components, especially bulky ones, temperature gradients persist for a significant fraction of the cure time. Thus the cure conditions are non-isothermal and also non-uniform throughout the component. The time in the press and the platten temperature defines the cure condition only for the surface of the moulding and a method is needed for quantifying the amount of cure received at other points in the component. The equivalent cure time at the platten temperature can be calculated for any point at which the temperature history is known, based on the assumption of time-temperature equivalence;[1,2] however, this assumption is not fully justified. In fact, the modulus of sulphur-cured NR vulcanisates increases with decrease in cure temperature. keeping the equivalent cure times (at some reference temperature) constant. It follows that predictions of the physical properties of a vulcanisate, cured in a highly non-isothermal manner, may be problematic. This is unfortunate, since many engineering components must meet tight specifications for properties such as stiffness, and yet the cure conditions are much less likely to be isothermal than for the thin or small specimens which are cured to characterise the material.

A method is outlined in this paper for dealing with this problem by defining, for any cure time-temperature history, not only the equivalent cure time at an arbitrary reference temperature but also an appropriately weighted average temperature that is most representative of the temperature history. This would enable testpieces, for determining the physical properties of the material in a given component, to be prepared using a defined isothermal cure rather than going to the elaboration of using a non-isothermal cure.

An experimental study into the effect of cure regimes on the physical properties of NR vulcanisates, carried out as a degree project by one of the authors (ABI), is reported to illustrate how the method works in practice.

Finite element solutions of transient heat flow during cure of flat sheets of varying thickness and of laminated bearings have been obtained using the commercial package MARC. Coupling the method of defining equivalent cure times and representative cure temperatures with these solutions leads to practical recommendations for sensible cure cycles. The objective is to refine existing rather crude rules of thumb such as the addition of an extra 5 min of cure for each increment of ¼" (6.35 mm) thickness[3].

THEORY

Kinetics of Vulcanisation

The basic assumption[1] is that over some restricted temperature range the rheographs are exactly the same shape but with the time axis progressively compressed as the temperature is raised. The factor, f, by which the time axis is compressed in going from temperature θ_1 to temperature θ_2 $(>\theta_1)$ is given by:

$$f = C^{(\theta_1 - \theta_2)/10} \qquad \dots 1$$

C, the 'temperature coefficient of vulcanisation', has a value of about 1.9 for typical sulphur-based cure systems and cure temperatures. It is necessary to restrict the temperature range because:

(i) *Equation 1* can be derived from the Arrhenius equation by making the approximation that $\theta_2 - \theta_1$ is small compared to the absolute temperature[1].

(ii) For a sufficiently restricted temperature range the shortcomings of the assumption that only the rate is affected by temperature — or equivalently that there is a single activation energy — will not be significant.

For a non-isothermal cure, *Equation 1* may be used to calculate an equivalent cure time t_{eq} at a reference temperature θ_{ref}:

$$t_{eq}(\theta_{ref}) = \int C^{(\theta - \theta_{ref})/10} dt = C^{-\theta_{ref}/10} \int C^{\theta/10} dt \dots 2$$

In this equation θ, or more explicitly $\theta(t)$, represents the temperature history during the cure.

A temperature $\bar{\theta}$ representative of the non-isothermal cure may be calculated as an average, weighted according to the contribution made to t_{eq}:

$$\bar{\theta} = \frac{\int \theta C^{(\theta - \theta_{ref})/10} dt}{t_{eq}(\theta_{ref})}$$

Of course, θ must be independent of the arbitrary value chosen for θ_{ref}, but this is readily shown by cancelling $C^{-\theta_{ref}/10}$ from the top and bottom of the expression:

$$\bar{\theta} = \frac{\int \theta C^{\theta/10} dt}{\int C^{\theta/10} dt} \qquad \dots 3$$

The forms of *Equations 2* and *3* make it clear that temperatures may be measured relative to any reference zero, for example 273 K or the initial temperature of the rubber.

It is suggested that the isothermal cure most representative of actual non-isothermal cure is given by curing at the temperature $\bar{\theta}$ given by *Equation 3* for a time given by *Equation 2*, substituting $\bar{\theta}$ for θ_{ref}

As an example, suppose the temperature profile $\theta(t)$ may be approximated by a ramp up to the maximum value, which is then sustained for a while, followed by a constant rae of cooling (*Figure 1*). Then *Equation 2* becomes, after noting that $C^{\theta(t)/10} = e^{\theta(t)/\Theta}$ where $\Theta = 10/lnC \simeq 16°C$ and carrying out the integration:

$$t_{eq}(\theta_{max}) = \Theta \left(\frac{1}{k_1} + \frac{1}{k_2}\right) + (t_2 - t_1)$$

$$- \Theta \left(\frac{1}{k_1} + \frac{1}{k_2}\right) C^{-\theta_{max}/10} \qquad ... 4$$

The final term is negligible if θ_{max} is large, so that $t_{eq}(\theta_{max})$ is given by the interval between attainment of $\theta_{max} - \Theta$ on the heating and cooling curves. Similarly, calculation of $\bar{\theta}$ for the profile of *Figure 1* leads to:

$$\bar{\theta} = \frac{\theta_{max}(t_2 - t_1) + (\theta_{max} - \Theta)\Theta \left(\frac{1}{k_1} + \frac{1}{k_2}\right)}{t_{eq}(\theta_{max})}$$

$$+ \frac{\theta_{max}\left(\frac{1}{k_1} + \frac{1}{k_2}\right)}{t_{eq}(\theta_{max})} \Theta C^{-\theta_{max}/10} \qquad ... 5$$

Again, the final term is negligible if θ_{max} is large, so that $\bar{\theta} = \theta_{max}$ (for infinite rates k_1 and k_2) while for $t_2 = t_1$ (no duration of the plateau temperature) $\bar{\theta} = \theta_{max} - \Theta$.

Heat Transfer During Cure

Although heat is evolved during vulcanisation,[1,4-7] the quantity is not very large, ΔH being of the order of $10Jg^{-1}$. Taking the thermal capacity of rubber to be $1.6Jg^{-1}K^{-1}$ implies that vulcanisation, as an adiabatic process, will cause a temperature rise of $\Delta H/c \simeq 6°C$. Considering that typical cure schedules involve temperatures of the order of 100°C above ambient, it is clear that the effect of the heat of vulcanisation on the temperature profile will be small compared to that of heat transfer from the press. As a first approximation, the heat of vulcanisation may therefore be neglected in calculations of temperature profile.

The equations governing unidirectional heat flow are then:

within the body $\quad \dfrac{\partial \theta}{\partial t} = \left(\dfrac{K}{\rho c}\right)\dfrac{\partial^2 \theta}{\partial x^2} \qquad ... 6$

boundary condition at the surface:

$$F = H(\theta_s - \theta_o) = -K\frac{\partial \theta}{\partial x} \qquad ... 7$$

The definitions, and where appropriate the values, of the parameters in these equations are given in *Table 1*.

The conductivity, density and thermal capacity of rubber (and hence the thermal diffusivity, $\kappa = K/\rho c$) depend on the formulation details and the temperature[1,4,7]. The thermal

TABLE 1 HEAT FLOW PARAMETERS USED IN *EQUATIONS* 6 AND 7

Parameter	Definition	Units	Approximate values	
t	Time	s		
x	Distance	m		
θ	Temperature	K		
θ_s	Surface temperature	K		
θ_o	Sink temperature	K		
F	Heat flux	$Jm^{-2}s^{-1}$		
K	Thermal condition	$Jm^{-1}s^{-1}K^{-1}$	0 16*	63+
ρ	Density	kgm^{-3}	1000*	7860+
c	Thermal capacity	$JK^{-1}kg^{-1}$	1600*	420+
κ	Thermal diffusivity	m^2s^{-1}	1×10^{-7}	1.9×10^{-5}
H	Film coefficients	$Jm^2s^{-1}K^{-1}$	**	**

*Rubber
+ steel
**A very high value represents the boundary condition $\theta_s = \theta_o$; for natural convection, $H \simeq 6.4Wm^2K^{-1}$
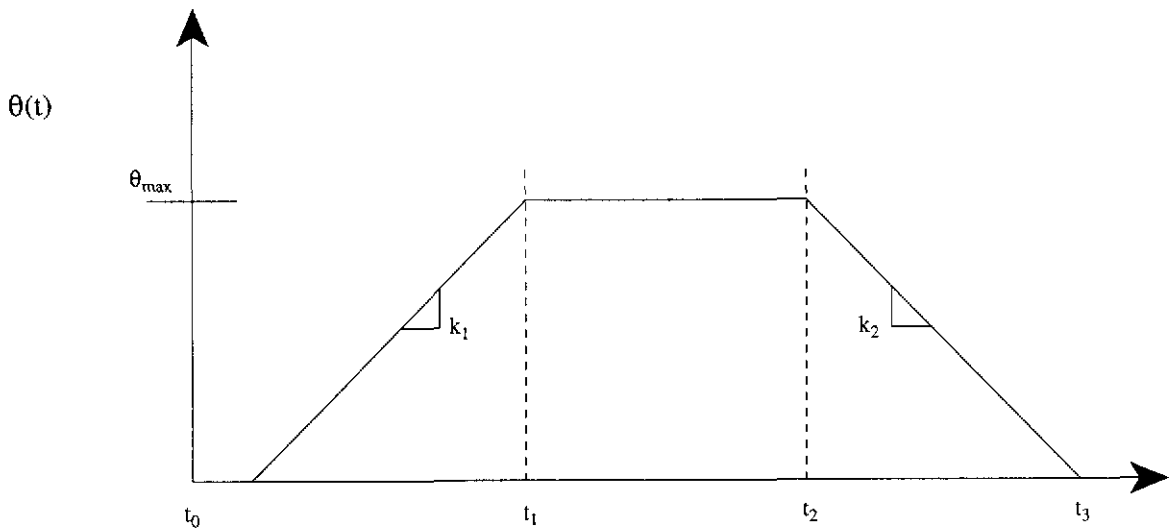

Figure 1. Simple temperature profile based on constant heating and cooling rates.

diffusivity falls by about 10% for a 100°C rise above room temperature[14]. A loading of 40 p.p.h.r. carbon black in NR (equivalent to a volume fraction of about 18%) increases the thermal conductivity by about 50%[1,7], while the density rises by about 10% and the thermal capacity decreases by about 20%[1]. The net effect is that carbon black increases the thermal diffusivity; for metal oxide fillers this effect is even more pronounced[1].

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EXPERIMENTAL STUDIES OF CURE KINETICS AND EFFECT OF CURE HISTORY ON VULCANISATE PROPERTIES

</div>

Materials

Six NR compounds were mixed in a laboratory internal mixer of $5l$ capacity; formulations are given in *Table 2*. Special care was taken to ensure the mixes were homogenous, as checked by taking samples for a curemeter run from two different places for each mix.

For each mix, curemeter graphs were obtained for every 10°C step between 100°C and 170°C; 230×230×2 mm sheets were moulded at each of these temperatures (excluding 100°C, 160°C and 170°C) choosing the cure time as that corresponding to maximum torque for mixes A, B, D and E. For mixes C and F the curemeter graphs did not reach plateau values, so that the maximum torques were obtained by extrapolation using the method outlined by Rigbi[8]. The method also enables estimates to be made of the time to 95% of the torque increase (t_{95}) and these were used as cure times for the peroxide mixes.

Values of the temperature coefficients of vulcanisation C were obtained from the curegraphs. Sheets of rubber (again 230×230×2 mm) were also cured non-isothermally by ramping the temperature up to 150°C and then immediately cooling at the same rate; the rate was chosen in such a way (based on *Equation 4*) that the equivalent cure time at 150°C would be to maximum torque, or to t_{95} for mixes C and F. For these cures, values of $\bar{\theta}$ and $t_{eq}(\bar{\theta})$ (defined in *Equations 2* and *3*) were calculated from the time-temperature history, monitored using a thermocouple. Additional sheets of rubber were cured isothermally for $t_{eq}(\bar{\theta})$ at $\bar{\theta}$ so that their physical properties may be compared with those of the sheets cured non-isothermally.

Test Methods

The main property of interest was the modulus of the vulcanisates, which would depend on the number of crosslinks. Three independent methods of measuring this were used, all at laboratory temperature:

(i) M100, as determined during a tensile test according to *ISO 37*;

(ii) MR100, determined according to *BS 903 Part A41*;

(iii) the swelling ratio in toluene.

For the latter test, the time to equilibrium was first established as being about 3 days for 2 mm NR sheet. Samples approximately 20×10×2 mm were then swollen for at least this length of time, weighing them to the nearest 0.1 mg before and after swelling. Several weights were taken at short intervals after swelling and swabbing the rubber dry, the final result being taken as the value extrapolated to zero time after removing from the solvent. For

<div align="center">5</div>

TABLE 2 FORMULATIONS OF THE COMPOUNDS (PARTS PER HUNDRED OF RUBBER)

Ingredient	Mix					
	A	B	C	D	E	F
SMR CV60	100	100	100	100	100	100
ZnO	5	5	–	5	5	–
Stearic acid	2	2	–	2	2	–
N550	–	–	–	40	40	40
Sulphur	2 5	0 25	–	2 5	0 25	–
Dicumyl peroxide	–	–	2	–	–	2
Santocure MOR	–	2 1	–	–	2 1	–
TMTD	–	1 0	–	–	1 0	–
CBS	0 6	–	–	0 6	–	–

the reason that swelling measurements had been anticipated, the formulations contained no antidegradants, since these could be leached out during swelling and hence confuse the weight measurements

Results

Figure 2 gives an example of a semi-logarithmic plot of t_{s1}, t_{50}, t_{90} and t_{max} *versus* cure temperature All four parameters give reasonable straight line plots with the same gradient in accord with *Equation 1*, from the slope of these lines the value of C can be calculated and is given in *Table 3* along with values for the other compounds

However, the increase in torque $(F_{max} - F_{min})$ decreases with increase in curemeter temperature for mixes A, B, D and E, in conflict with the assumption of exact time-temperature equivalence For the peroxide-cured mixes (C and F) the increase in torque did not show a systematic change with temperature, so within experimental uncertainty it appears that the

basic assumption is fully justified for such mixes

Figures 3 and *4* show the dependence of MR100 and swelling ratio, respectively on cure temperature for mixes A, B, D and E Although the data is a bit scattered discernible trends are recognisable, and the gradients of regression fits are given in *Table 3* Results for the peroxide vulcanisates showed no trend with cure temperature and are omitted from the figures for clarity

Figure 5 compares the properties of the vulcanisates cured non-isothermally and with an equivalent isothermal cure The agreement is good, indicating the method based on *Equation 2* has worked well Furthermore, it appears that the use of a representative cure temperature $\bar{\theta}$ defined by *Equation 3*, for the isothermal cure has also helped to give the good agreement, dividing the discrepancy ΔP between properties of the non-isothermal and equivalent isothermal cures by the slope k of the property *versus* cure temperature, we find that the
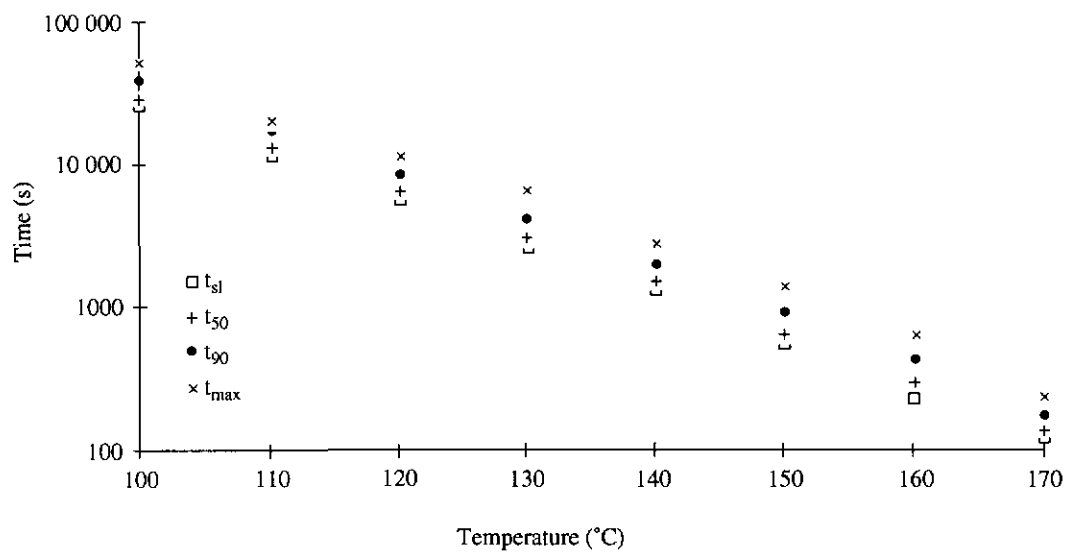
Figure 2: Dependence of curegraph parameters on cure temperature for mix A.
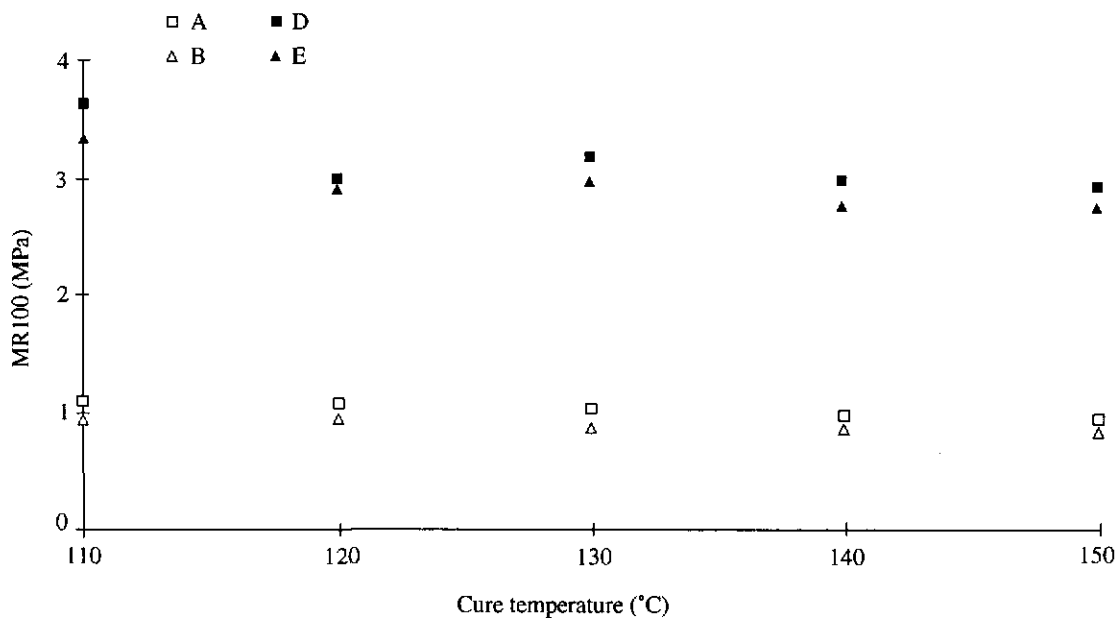

Figure 3: Effect of cure temperature on MR100 for the sulphurcured compounds.
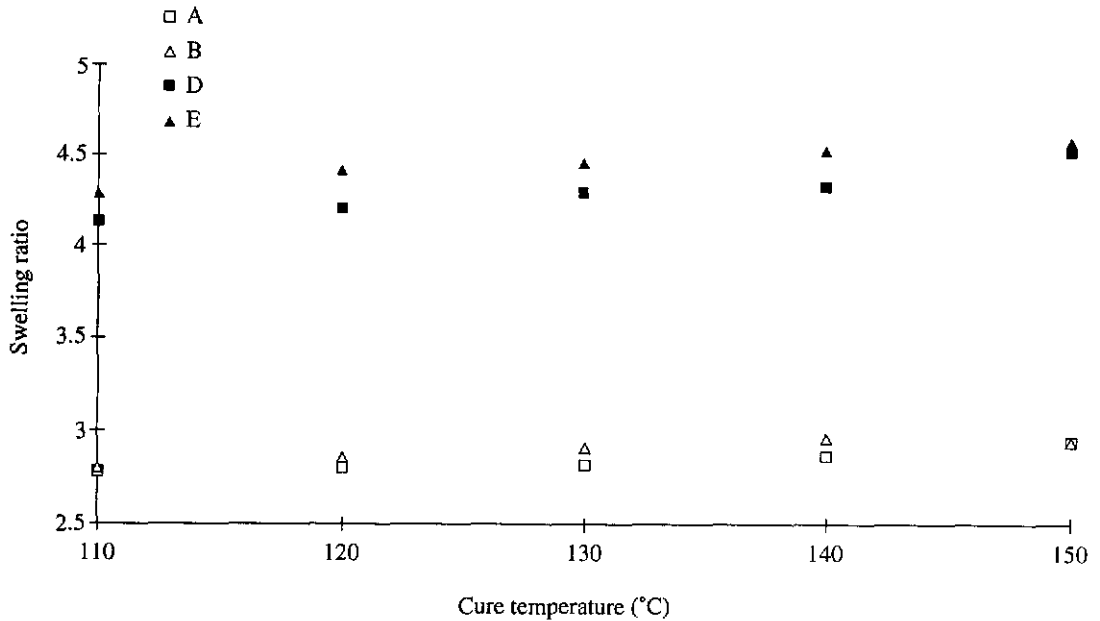
Figure 4: Effect of cure temperature on swelling ratio for the sulphur-cured compounds.

discrepancies are comparable to those arising from quite modest differences in cure temperature (15.6°C at greatest), as shown in *Table 3*.

FEA CURE CALCULATIONS FOR A LAMINATED BEARING

Cylindrical laminated rubber bearings were moulded for a seismic isolation project, and the opportunity was taken to carry out a numerical thermal analysis of the cure process and compare the results with the temperature histories measured using internal thermocouples.

The setting up of an FE mesh was fairly straightforward. The problem is axisymmetric,

and (assuming the top and bottom plattens of the press are at the same temperature) has an additional plane of symmetry which can be utilised to reduce the size of the model. *Figure 6* shows the cross section of the bearing as modelled, including the mould tube. The boundary conditions used were that of no heat flux ($H=O$) leaving the perimeter of the mould tube, and a specified (time dependent) temperature $\theta_s(t)$ at the two ends of the bearing with a very high value for the film coefficient (H). The initial condition was that of a uniform temperature, the material properties used were as given in *Table 1*. It was assumed that these properties were independent of both temperature and state of cure, and that there was no heat of
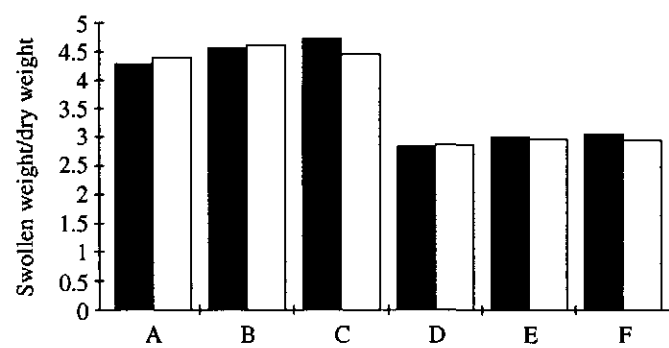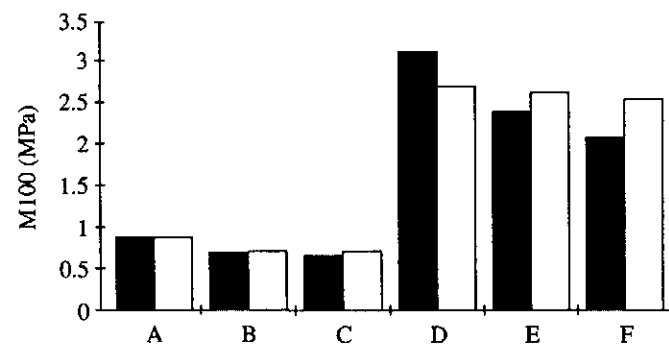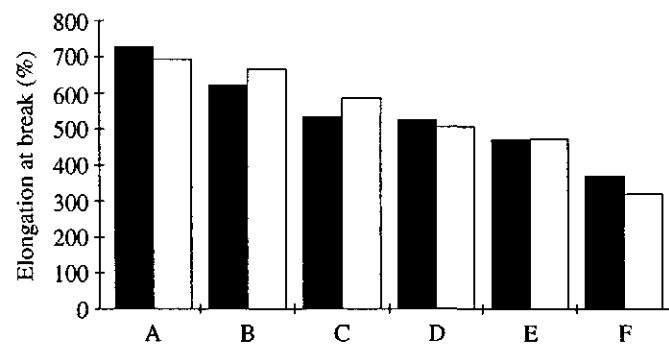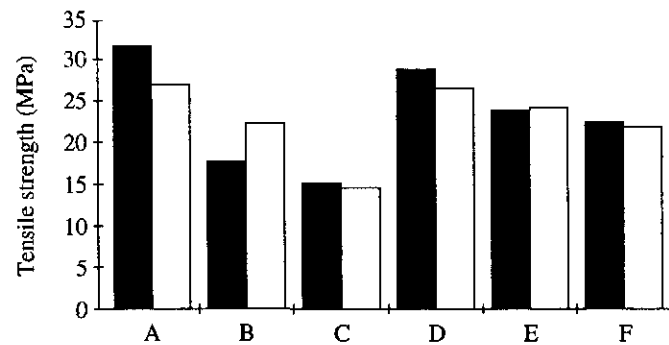
Figure 5. Comparison of properties of vulcanizates cured non-isothermally (■) and with an equivalent isothermal cure (□).

TABLE 3. RESULTS DEDUCED FROM CUREGRAPHS AND TESTS ON VULCANISATES

Properties	A	B	C	D	E	F
Temperature coefficient of vulcanisation C	2.10	1 90	2 50	1 96	1 95	2 61
Target t_{eq} (150°C) for the non-isothermal cures (min)[a]	28	30	62	20	27	56
Ramp rate used for non-isothermal cure[b] (°C min^{-1})	0 96	1.04	0.35	1 49	1.11	0.37
$\bar{\theta}$ (°C)[c]	137	134	141	136	135	142
t_{eq} (θ)[d](min)	77	80	163	55	72	153
Properties for 130°C cure:						
TS (MPa)	30.8	20 1	15 0	28 9	25 4	26 3
EB (%)	715	636	591	532	472	407
M100 (MPa)	0.90	0 78	0.67	3 03	2 81	2 00
MR100 (MPa)	1.02	0.85	0.78	3.17	2.95	2.66
Ratio of swollen weight to dry weight	4.30	4 46	4.68	2.81	2.88	3.08
Change in properties per °C rise in cure temperature (k).						
TS (MPa K^{-1})	0.258	0 117	--	–	–	–
EB (% K^{-1})	0.16	0 77	–	1 94	1.29	–
M100(MPa K^{-1})	–0 003	–0 002	–	–0 011	–0.008	–
MR100 (MPa K^{-1})	–0 005	–0.004	–	–0.015	–0 014	–
Swelling ratio (K^{-1})	0.009	0.007	–	0.004	0.004	–
Change in cure temperature $\Delta P/k$ (°C) that would give same change in properties as between non-isothermal and isothermal cures:						
MR100	–15 6	+2.8	–	–15 5	+9 2	–
Swelling ratio	–15 6	–4 3	–	+10 0	–10.0	–

[a]The t_{eq} (150°C) value give maximum torque (compounds A, B, D and E) or t_{95} (compounds C and F)
[b]Calculated using *Equation 4*, from the target t_{eq} (150°C), ignoring the final term
[c]Calculated from the non-isothermal time-temperature records using *Equation 3*
[d]Calculated from the non-isothermal time-temperature record using *Equations 2 and 3*
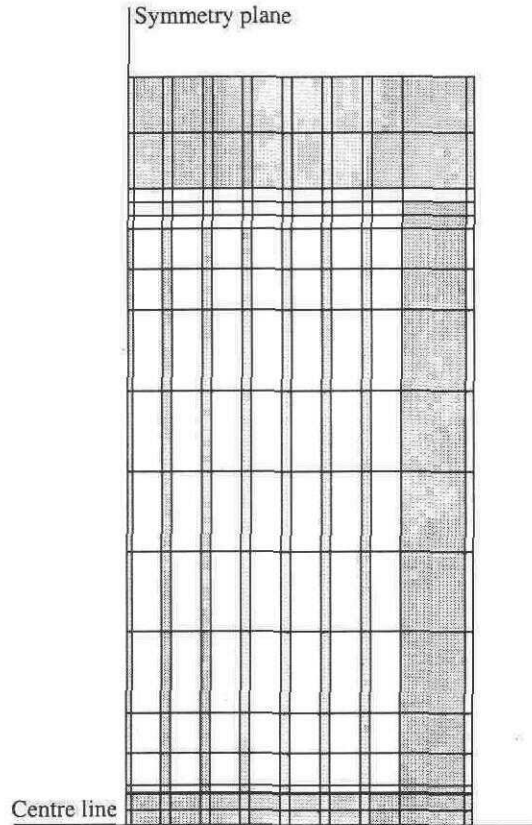
Symmetry plane

Centre line

Figure 6. FE model of cylindrical laminated isolation bearing.
Steel elements – shaded; rubber elements – unshaded

reaction associated with the curing process. Perfect contact between the central pin and the plates was assumed.

A user defined variable was created to represent the equivalent cure time. This was evaluated within a user sub-routine by numerically integrating the appropriate function of temperature (see *Equation 2*). This user defined variable was then available in the post file in the same way as any other variable.

Data taken from thermocouples during curing of one of the prototype bearings was used to obtain two temperature profiles. The first was the average-of all the temperatures on the end flanges of the mould tube which was used as the temperature boundary condition for the FE model (measured surface temperature). The second was the average of the two measurements on the middle steel reinforcing plate, which were taken about one third and two thirds of the way out from the central pin,

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and which were approximately equal (measured internal temperature). This was then compared to the FE prediction of the temperature half way out from the central pin on the middle steel plate (predicted internal temperature). The initial temperature in the FE model was set to the first value of measured internal temperature (21.45°C), and the first few values of measured surface temperature were adjusted so as to start the profile from this same temperature.

In the first run, the predicted internal temperature seemed to lag behind the measured internal temperature. This was assumed to be because an incorrect thermal diffusivity value was used. There is considerable uncertainty in thermal properties of the rubber, so the conductivity was increased to try to get a better fit. The best fit was when the conductivity was increased by 25% compared to the value in *Table 1*. This increased value was only used in the calculations for the laminated bearing. *Figure 7* shows the temperature profiles obtained. The FE prediction of internal temperature is quite good. The fact that the maximum measured temperature is 2.84°C higher than predicted could be due to the effect of the latent heat of vulcanisation, which may also contribute to the need to adjust the thermal diffusivity upwards to achieve the good fit.

The nominal cure temperature was 110°C, so equivalent cure times were evaluated in hours at 110°C. The maximum equivalent cure is determined completely by the temperature boundary condition which is applied directly to the thin end cover layer, and this gives a cure equivalent to 8.85 h at 110°C. The analysis was repeated but with rubber in the central hole, and then with a pin having ten times the conductivity of steel, and finally with all the metalwork having ten times the conductivity of

steel. As expected the maximum equivalent cure time was always 8.85 h. As an indication of the uniformity of cure, the ratio of minimum to maximum equivalent cure time was calculated, and is presented in *Table 4*.

The relatively modest increase in this ratio on insertion of a steel pin suggestss that much of the heat flow during moulding of the actual bearings was occurring normal to the plattens. Therefore, a good understanding of how to cure slabs of rubber could help to give a rough estimate for sensible cure cycles for more complex mouldings.

FEA CURE CALCULATIONS
FOR RUBBER SHEETS

Calculation of Necessary Press Times as a Function of Thickness

The objective of this section is to predict, as a function of its thickness, how long a cure is needed for a rubber sheet, or whether a special strategy is needed such as pre-warming the rubber or lowering the platten temperature. On account of changing the dimensions or running time of the FE problem is relatively time consuming, runs were instead made using a sheet of unit thickness and varying thermal diffusivity and, where necessary, the temperature jump and the film coefficient used during cooling.

Choosing the dimensionless variables:

$T = t/t_p$ where t_p is the press time

$X = x/\ell$ where ℓ is the half thickness of the sheet

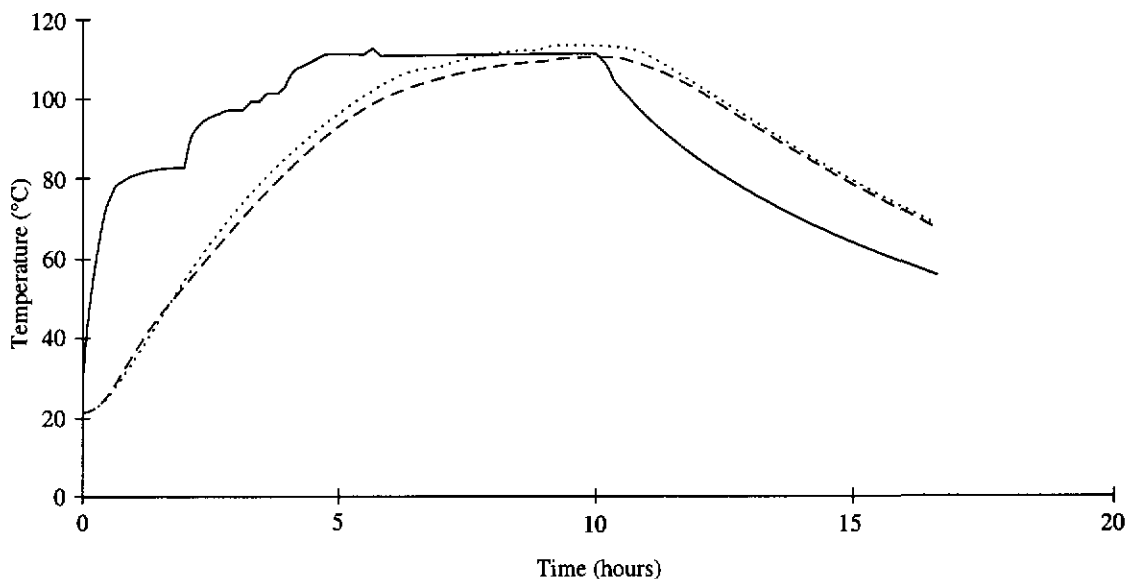solutions are required for *Equations 6* and *7* written in the form:

Figure 7. Comparison of FE predictions and direct measurement of temperature history.
——*flange temperature;* ········ *measured internal tempeature;* – – – *internal temperature predicted by FEA.*
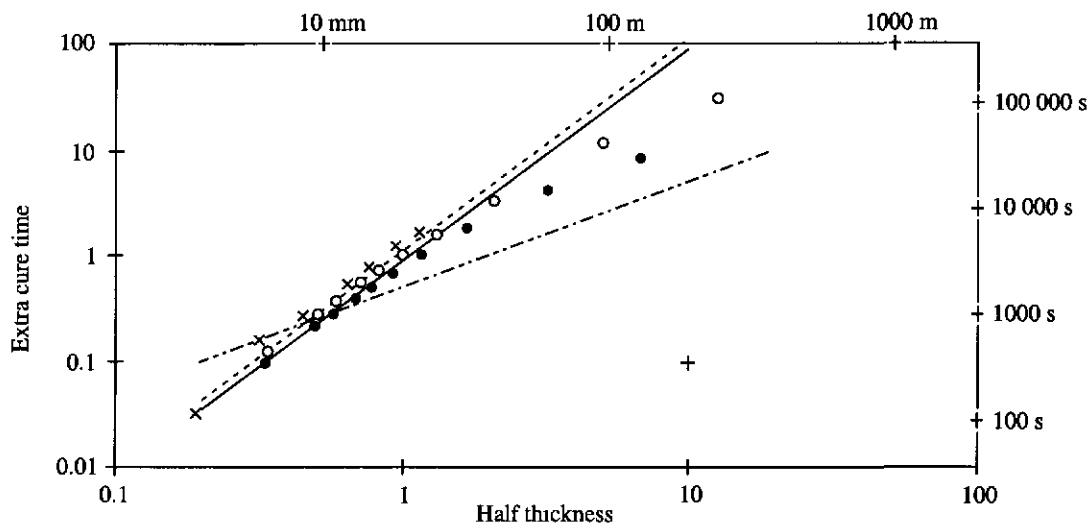
Figure 8. Logarithmic plot of dimensionless extra cure time $(t_p - t_{eq})/t_{eq}$ needed to achieve an equivalent cure time t_{eq} in the centre of a sheet of dimensionless half thickness l/l_o, with near perfect conduction during heating and cooling. ○, ● *results from* Tables 5 $(\Delta\theta = 100°C)$ *and 7* $(\Delta\bar{\theta}= 70°C)$ *respectively using* Equation 10 - - - , __ , *fits to the results at small thicknesses (*Equation 11*), k = 1.1, 0.9 respectively). Dimensioned scales assume $\kappa = 1 \times 10^{-7}$ m^2s^{-1}, $t_{eq} = 3600$ s so that $l_o = 19mm$; × — results derived from Conant et al. nomogram[2]* —··— *Stephen's rule of thumb[3].*

TABLE 4 FEA PREDICTIONS OF EQUIVALENT CURE TIME IN A LAMINATED BEARING
(381 MM DIAMETER, 15 RUBBER LAYERS, EACH 9 MM THICK, 15 STEEL
REINFORCING PLATES, EACH 2 5 MM THICK)

Laminated bearing	Min/max equivalent cure time
Steel pin	0 79
Rubber in central hole	0 73
High conductivity pin	0 89
High conductivity pin and plates	0 94

$$\partial\theta/\partial T = A\partial^2\theta/\partial X^2, A = \frac{t_p}{\ell^2}\kappa \qquad 8$$

$$\partial\theta/\mathrm{a}X1_{x-\pm1} + B(\theta_{x-\pm1} - \theta_E) = 0, B = \ell H/K \qquad 9$$

where θ_E, the temperature exterior to the rubber, is a prescribed function of time The dimensionless group A, the ratio of press time to thermal diffusion time, is called the Fourier number[7] The solutions to a series of problems with different values of A, but in each case with $\theta = 0$ at $T = 0$ for $-1 < X < 1$, $\theta_E = \theta_p$ (the press temperature) for $0 < T < 1$ and $\theta_E = 0$ for $1 < T$ were obtained Each analysis was run until θ fell below $10°$ throughout the sheet, results are given in *Table 5* Each solution provides information on any system with the same value of A and the same initial and boundary conditions for θ and θ_E prescribed in terms of T Large values were used for the heating and cooling film coefficients (B_h and B_c, respectively set to 100) to simulate the case of effectively perfect contact with plattens at the prescribed temperatures

From the definition of dimensionless time, (see text above *Equations 8* and *9* and the parameter A, we have

$$t_p = t_{eq}/T_{eq} \qquad 10a$$

$$\ell^2 = t_p\kappa/A = t_{eq}\kappa/T_{eq}A \qquad 10b$$

Thus, the values of T_{eq} and A given in *Table 5*, together with a value for κ, may be used to calculate pairs (t_p, ℓ^2) meeting a given target for t_{eq} to be achieved in the centre of the pads These may then be plotted on a graph (see *Figure 8*), and by interpolation suitable press times for any value of half-thickness ℓ may be found In *Figure 8* the typical values $\kappa = 1 \times 10^{-7} m^2 s^{-1}$ and $t_{eq} = 3600$ s (at 130°C) have been chosen to define the dimensioned scales on the axes

Alternatively, *Equations 10a* and *10b* may be cast into the non-dimensional form

$$\frac{t_p - t_{eq}}{t_{eq}} = \left(\frac{1}{T_{eq}} - 1\right) \qquad 10c$$

$$(\ell/\ell_o)^2 = 1/T_{eq}A \qquad 10d$$

where $\ell_o = \sqrt{\kappa t_{eq}}$ gives the length scale for heat diffusion after time t_{eq}, according to the Einstein equation $\langle x^2 \rangle = Dt$ Using *Equations 10c* and

TABLE 5 DIMENSIONLESS EQUIVALENT CURE TIMES T_{eq} AND REPRESENTATIVE CURE TEMPERATURES $\bar{\theta}$ AT THE CENTRE OF SLABS CURED AT 100°C ABOVE AMBIENT (AMBIENT TEMPERATURE TAKEN AS 0°, θ_{ref}=100°, CUT-OFF TEMPERATURE = 10°, $B_h = B_c = 100$)

A^a	$T_{eq}{}^b$	$A(1-T_{eq})$	$T_{eqr}{}^c$	T_{eqr}/T_{eq}	$\bar{\theta}$	θ_{max}	$(l/l_o)^d$	$\left(\dfrac{t_p - t_{eq}}{t_{eq}}\right)^e$
0 2	0 0308	0 194	0 0016	0 052	23 6	32 6	12 74	31 5
0 5	0 0779	0 461	0 0218	0 280	52 1	65 1	5 07	11 8
1 0	0 228	0 772	0 136	0 596	77 0	88 3	2 09	3 39
1 5	0 383	0 926	0 292	0 763	86 8	95 8	1 32	1 61
2 0	0 499	1 002	0 422	0 845	91 2	98 2	1 00	1 00
2 5	0 583	1 042	0 519	0 889	93 5	99 1	0 828	0 715
3 0	0 648	1 055	0 593	0 914	95 0	99 7	0 717	0 543
4 0	0 732	1 074	0 689	0 942	96 6	99 9	0 584	0 366
5 0	0 783	1 083	0 750	0 957	97 4	100	0 505	0 277
10 0	0 891	1 094	0 874	0 981	98 8	100	0 335	0 122

[a]Ratio of press time to thermal diffusion time, defined in *Equation 8*

[b]Dimensionless equivalent cure time in the centre of the sheet after the complete cure cycle The equivalent cure time at the surface is equal to the press time, ie unity

[c]Dimensionless equivalent cure time on removal from the press

[d]Given by $\sqrt{1/t_{eq}-A}$ according to *Equation 10d*

[e]Given by $(1/T_{eq}) - 1$ according to *Equation 10c*

10d the results of the FE runs of *Table 5* may be plotted directly onto *Figure 8* without the need for choosing values for κ and t_{eq}, in this case, the dimensionless scales are appropriate

Figure 8 shows that the "5 minutes extra cure per ¼ inch increase in thickness" rule-of-thumb[3] gives about the right magnitude of effect for pads about 10 mm thick, but the linear dependence on l is quite wrong In fact, for large values of A, equivalent to thin sheets (or long press times), the temperature reaches that of the platten (*Table 5*) Thus any further increase in t_p will simply add this amount to $t_{eq}(\theta_p)$

$$t_{eq}(\theta_p) \simeq t_p - k \text{ for constant } l$$
$$\Rightarrow T_{eq}(\theta_p) \simeq 1 - \frac{k}{t_p} \equiv 1 - \frac{k'}{A} \qquad 11$$
$$\Rightarrow A\left(1 - T_{eq}(\theta_p)\right) \simeq k' \text{ for large } A$$

From *Table 5*, it is apparent that $k' = 1\,1$ for $\Delta\theta = 100$°C Making use of the definitions of A and T, *Equation 11* leads to

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$$\frac{t_p - t_{eq}}{t_{eq}} \equiv \frac{1}{T_{eq}} - 1 \simeq k'/AT_{eq} \equiv k'(\ell/\ell_o)^2 \quad \dots 12$$

A line with this equation has been drawn in *Figure 8*. At small values of A, the results fall below this line and nearer to the rule-of-thumb[3]. However, such cure regimes are impractical, the ratio between t_{eq} values at surface and centre being very large; this point is discussed in detail below.

Figure 8 also gives results obtained from the nomogram method of Conant *et al*[2]. These have been calculated on the assumption of $\kappa = 1 \times 10^{-7} m^2 s^{-1}$ and $t_{eq} = 3600$ s. The agreement with *Table 5* is not exact but clearly much better than for the case of the Stephens[3] rule-of-thumb.

Effect of Cooling Rate

In practice rubber components are usually cooled by natural convection after demoulding rather than by leaving them in the press and force-cooling the plattens. This means that the cooling rates are usually lower than as modelled in *Table 5*, and the contribution to T_{eq} after removing from the heat source is greater. A second series of FE runs were made in which a large value for $B_h(100)$ was retained, while the value of B_c during cooling was varied; two values of A were used, 1.0 and 10 corresponding to t_p falling significantly short or being sufficient, respectively, for thermal equilibrium.

Taking ℓ as 4.7 mm, and using the value of κ and of H for natural convection from *Table 1* gives $B_c = 0.18$. Thus, from *Table 6*, $A = 10$, the equivalent cure time in the centre of such a sheet would increase by about 10% if it was allowed to cool by natural convection rather than by perfect conduction.

If we could insulate the sheet after removal from the press, and effectively reduce the film coefficient by a factor of 10 giving $B_c = 0.02$, then the equivalent cure time in the centre of the sheet would be about 90% greater than for natural cooling in air. However, the insulation would have to be maintained for a significant time. For instance, at $T = 4.86$, $T_{eq} = 1.80$, so if the insulation were maintained for about 5 times the time in the press, the equivalent cure time would only be about 80% greater than for natural cooling in air. Note that when the sheet is well insulated, the temperature is more or less uniform during cooling, and therefore the surface gets about the same additional cure as the centre of the sheet. This means that the state of cure will be relatively more uniform than for rapid cooling as seen in *Table 6*.

Thus, for thin sheets, insulating on cooling provides two advantages. Firstly it can reduce the time in the press. In addition it can make the state of cure more uniform. Disadvantages are that the sheet must be insulated for a significant time after removal from the press, and the equivalent cure temperature is reduced.

Cure Strategies for Thick Sheets

For thick sheets, the proportion T_{eqr}/T_{eq} of the cure that takes place in the press becomes small (see *Table 5*), a problem that would be exacerbated by insulation after removal from the press (see *Table 6*). For a sheet 100 mm thick ($\ell = 0.05$ m), with a press time of say 25 000 s (slightly higher than from *Figure 8*) to give $A = 1$, we find that for natural convection $B_c = 2$. *Table 6* shows that T_{eqr}/T_{eq} is significantly lower than for the case of cooling by near-perfect conduction.

If the final T_{eq} is chosen to represent an adequate cure rather than an overcure, then the

TABLE 6 EFFECT OF VARYING THE EFFICIENCY OF HEAT TRANSFER DURING
COOLING ($A = 10$, $B_h = 100$, $\bar{\theta}_p = 100°$)

B_c	T_{eq} (Centre)	T_{eqr}/T_{eq} (Centre)	T_{eq} (Surface)	$\bar{\theta}$ (Centre)
		$A = 1$ ($T_{eqr} = 0\,1360$)		
100	0 2281	0 596	0 944	77 0
20	0 2359	0 577	0 945	76 9
2 0	0 3076	0 442	0 972	76 3
		$A = 10$ ($T_{eqr} = 0\,874$)		
100	0 8906	0 981	0 994	98 8
10	0 8933	0 978	–	98 8
1 0	0 9146	0 956	–	98 4
0 5	0 9353	0 934	–	98 0
0 2	0 9951	0 878	–	96 9
0 1	1 087	0 804	–	95 3
0 05	1 295	0 675	–	92 7
0 02	1 886	0 463	1 961	88 5

state of cure on removal of a very thick sheet from the press would be so small that gases dissolved in the rubber at the moulding pressure could come out of solution, blowing cavities in the rubber Exactly what the minimum practical value for T_{eq}/T_{eqr} and hence A is would depend on the shape of the cure graph, the susceptibility of the rubber to porosity and what degree of overcure would be acceptable. A possible practical lower limit for A is 1 0 corresponding to a maximum value of l

$$l_{max} = \sqrt{t_p \kappa / A_{min}} = \sqrt{t_{eq} \kappa / T_{eq} A_{min}} \qquad 13$$

For example, inserting $t_{eq} = 3600$ s (a typical cure time at 130°C), $A = 1$ 0 and from *Table 5*, T_{eq} ($A = 1$)=0 228 we find $l_{max} = 40$ mm

Thicker sheets would have to be cooled under pressure to avoid the danger of porosity Excessive press time is, however, undesirable on ground of cost For thick sheets a cure strategy is needed which increases the contribution to the cure that occurs while the rubber is in the press The strategy of insulating is obviously inappropriate, and in fact some benefit could be obtained by an increase in press time followed by forced cooling of the demoulded sheet, for example by plunging it in iced water Alternatively the raw rubber could be pre-warmed, for example as individual sheets before plying up

Another possibility is to reduce the cure temperature hence increasing the required equivalent cure time, although this would entail

an increase in the time in a heated press, the eventual state of cure should be more uniform than for a cure at a higher temperature, and the increase in press time may not be as great as if cooling also has to be carried out in the press. This approach may be modelled by repeating the runs of *Table 5* using a lower temperature increase; such results are given in *Table 7* for a 70° increase. Values of ℓ/ℓ_o and $(t_p-t_{eq})/t_{eq}$ are given in *Table 7* and also plotted on *Figure 8*. It is apparent that for the large values of A, corresponding to thinner sheets, the increase in cure time needed is a little lower than for cures at the high temperature, and from *Table 7* it is apparent that k' in *Equation 12* would be 0.9. However, the sensitivity of k' to the cure temperature is relatively modest, and a simple rule-of-thumb for an initial estimate of cure time may be derived from an equation representing the mean of both sets of results in *Figure 8*:

$$\frac{t_p - t_{eq}}{t_{eq}} = (\ell/\ell_o)^2$$

Making use of the definition of ℓ_o (see *Equation 10d*) this becomes:

$$t_p - t_{eq} = \ell^2/\kappa$$

Thus a simple rubber-of-thumb would be to add $10\ell^2$ seconds, where ℓ is the half-thickness in mm, to the cure time, whatever the cure temperature. The cure temperature, however, controls the maximum thickness of slab that can safely be cured in this way.

For small values of A it is apparent from a comparison of *Tables 5* and *7* that we are better off using a smaller temperature jump in that (i) $\theta_p - \theta$ is smaller; (ii) $T_{eq}(\text{surface})/T_{eq}(\text{centre})$ is smaller. Thus, the cure achieved is more

uniform and the representative temperature of the cure is nearer the platten temperature. The disadvantage is that the press-time is increased; the ratio of the equivalent cure time in the press to the total equivalent cure time is increased, but this effect is barely significant.

DISCUSSION

Considerable progress has been made in understanding the factors which affect the ability to cure large rubber components. Prediction of the properties of the vulcanisates firstly requires the ability to predict the temperature history during cure at each point in the component, which can be done using finite element analysis. From the temperature history at a given point, an equivalent cure time and temperature can be calculated. The properties at that point can then be assumed with reasonable accuracy to be the same as for a small sample cured isothermally at that temperature and time.

The approach used in this paper makes use of a minimum number of parameters to characterise the rubber, and in fact K, ρ, c, and C have all been set to reasonably reliable 'default' values *(Table 1)* in an initial approximate analysis. This contrasts with alternative approaches in which the state of cure is defined as the percentage attainment of the maximum curemeter torque rise or of the maximum evolution heat of reaction, calling for a detailed analysis of the cure process for the specific compound of interest[8,9].

The results of finite element analysis have previously been checked against an analytical solution for 1 dimensional diffusion, producing very good agreement. When used to predict the temperature profile in a laminated bearing though, there was a problem in knowing what value to use for the thermal diffusivity of the

TABLE 7 DIMENSIONLESS EQUIVALENT CURE TIMES T_{eq} AND REPRESENTATIVE CURE
TEMPERATURES $\bar{\theta}$ AT THE CENTRE OF SLABS CURED AT 70°C ABOVE
AMBIENT (AMBIENT TEMPERATURE TAKEN AS 0°, θ_{ref}=70°, CUT-OFF
TEMPERATURE = 10°, $B_h = B_c = 100$)

A	T_{eq} [a]	$A(1-T_{eq})$	T_{eqr} [b]	T_{eqr}/T_{eq} [c]	$\bar{\theta}$	θ_{max}	(ℓ/ℓ_o) [d]	$\left(\dfrac{t_p - t_{eq}}{t_{eq}}\right)$ [e]
0.2	0.1061	0.1788	0.0056	0.053	17.6	22.5	6.86	8.42
0.5	0.1934	0 4033	0 0568	0 294	34 0	45 2	3.22	4.17
1.0	0 3550	0.6451	0.2089	0.588	50.8	61.4	1.68	1.82
1 5	0 4935	0 7597	0.3671	0.744	58.1	66.7	1.16	1.03
2 0	0.5910	0.8181	0.4875	0.825	61.7	68.6	0 920	0 692
2 5	0 6652	0 8370	0 5788	0 870	63 9	69 5	0.775	0 503
3 0	0 7144	0.8568	0 6410	0.897	65.0	69.7	0.683	0 400
4.0	0.7815	0.8740	0.7259	0.929	66.5	69.9	0.566	0.280
5.0	0.8228	0.8862	0.7784	0.946	67.3	70 0	0 493	0.215
10 0	0.9109	0.8906	0.8887	0.976	68.8	70.0	0.331	0.098

[a]Ratio of press time to thermal diffusion time, defined in *Equation 8*

[b]Dimensionless equivalent cure time in the centre of the sheet after the complete cure cycle. The equivalent
cure time at the surface is equal to the press time, *ie* unity

[c]Dimensionless equivalent cure time on removal from the press

[d]Given by $\sqrt{1/t_{eq}} - A$ according to *Equation 10d*

[e]Given by $(1/T_{eq}) - 1$ according to *Equation 10c*

rubber. To produce accurate predictions it would be necessary to measure this property for the particular compound being used, ideally as a *function of temperature.*

The heat evolved during vulcanisation also needs to be included to improve the accuracy of the predictions. The literature values are rather variable, reported to range from 1.5 Jg^{-1} to 24 Jg^{-1} for the set of compounds used in a single tyre[9], and a value as high as 75.8 Jg^{-1} has been reported for NR with 2% sulphur. It is not clear which of the several chemical reactions in accelerated sulphur vulcanisation are primarily responsible for evolution of heat[10], but in the absence of accelerator the heat evolved is proportional to the quantity of sulphur[5]. Experimentally, the effect of the evolved heat on temperature histories can be found by comparing internal thermocouple records for mouldings with and without curatives, but otherwise identical. Such experiments confirm that heating is more rapid, and the temperature can overshoot that of the plattens, when curatives are included[11]. However, the effect on final cure is clearly

smaller than if the temperature profiles were raised throughout the cure history by that corresponding to adiabatic vulcanisation (6°C or so), since (i) the heat of vulcanisation is generated only later in the full cure cycle, (ii) the amount of heat flowing in from the plattens will be reduced from that in the absence of heat of vulcanisation.

For uniform slabs the parameter, A, given by the ratio of the time in the press to the time for heat to diffuse to the interior, is of primary importance. If A is less than unity, there are likely to be problems achieving a satisfactory cure. One problem is that both the equivalent cure time and temperature will be significantly lower in the centre of the slab compared to the surface, and another is that the centre may not be sufficiently cured on removal from the press to avoid gas bubbles forming.

The easiest way of avoiding these problems is to increase A, but this can only be done by increasing the time in the press, which, in order not to overcure the surface requires reducing the press temperature. This would result in a change in properties due to the reduced equivalent cure temperature, but the main disadvantage would be inefficient utilisation of the press. This requirement that A is not too small is the basic limitation on the thickness of slabs which may be successfully cured.

Curing sheets of moderate thickness is easy, and there is a simple rule which can be used to calculate the appropriate press time. This is basically to take the desired cure time t_{eq}, and add the thermal diffusion time ℓ^2/κ, where ℓ is the half thickness. This gives better results than the widely used rule-of-thumb whereby an extra 5 min is added for each quarter inch increment of thickness[3]. Application of the rule ensures

that A is greater than one for any thickness of sheet. However, for thick sheets the centre will be somewhat overcured and the ratio of equivalent cure time on the surface to that in the centre will be high. A possible cut-off for application of the rule might be when ℓ^2/κ becomes 50% greater than the target cure time, corresponding to $A = 1.5$. From *Tables 5* and *7*, this would involve less than a factor of three between equivalent cure times on surface and centre. The overcure on the surface may be calculated as $t_p/t_{eq} = (A-1)^{-1} + 1$ (since $A = t_p \kappa/\ell^2$ and, according to the rule, $t_p = t_{eq} + \ell^2/\kappa$) and that in the centre is just $T_{eq}(t_p/t_{eq})$; from *Table 7* the overcure in the centre is just under 50% for $A = 1.5$, while for *Table 5* it is only 15%. Also, for $A = 1.5$, $\bar{\theta}$ is only 12°C lower than the platten temperature.

In the case of thick slabs, other than reducing the platten temperature and increasing the press time, there are a few options which can be considered. Pre-warming the rubber helps, provided the mould can be closed before the rubber starts to scorch. Another strategy might be to do a 'step' cure, where the temperature of the plattens is raised to the final temperature in two or more steps, as in the cure schedule used for the laminated bearing. Another possibility is to leave the slab in the press longer, but then force cool it (for instance in ice water), thereby increasing the proportion of the cure which takes place before the pressure is released. For very thick slabs it may be necessary to cool the mould while it is still in the press.

CONCLUSIONS

The established method of calculating an equivalent cure-time at a reference temperature from a non-isothermal cure (*Equation 2*) has been augmented by defining an equivalent cure

temperature (*Equation 3*). The latter helps to overcome the objection that the established method neglects the dependence of the vulcanisate properties on actual cure temperature. A range of NR vulcanisates cured non-isothermally were found to have little difference in properties to those cured isothermally at the equivalent cure time and temperature.

The equivalent cure time at the maximum temperature θ_{max} of a non-isothermal cure may be estimated from a plot of temperature (*eg.* from an internal thermocouple) by the time between attainment of $\theta_{max} - \Theta$ (where Θ is about 16°C for sulphur vulcanisates) on the heating and cooling curves. The equivalent temperature of cure $\bar{\theta}$ lies between θ_{max} and $\theta_{max} - \Theta$; the equivalent cure time at $\bar{\theta}$ is $C^{(\bar{\theta}_{max} - \theta)/10}$ times that at θ_{max}.

Quite a good prediction of temperature profiles during cure may be made using the finite element package MARC, neglecting effects of heat of vulcanisation and temperature dependence of the thermal properties of the rubber. However, the observed excess of measured internal temperature over that predicted, and the need to use rather a high value of thermal diffusivity to achieve the best fit over the full cure history, suggest that the inclusion of heat of vulcanisation would be a useful refinement, as implemented by Acetta and Vergraud[11].

The extra cure time needed for a thick rubber sheet may be estimated as ℓ^2/κ where ℓ is the half-thickness of the sheet and κ is the thermal diffusivity of rubber (see *Table 1*). Remarkably, this rule works reasonably well regardless of the actual platten temperature chosen. It also ensures that there will be no danger of porosity developing when the press is opened, even though cure in the centre is not complete at that time.

However, if ℓ^2/κ exceeds the target cure time, t_{eq}, at the platten temperature by 50%, selection of a lower platten temperature is suggested. In this way the equivalent cure time will not vary by more than a factor of three through the sheet thickness, and the equivalent cure temperature will be within 12°C of the platten temperature.

Somewhat shorter cure times for thick sheets than specified above (fourth paragraph) are possible and could also be made of techniques such as pre-warming the rubber or cooling under pressure. However, specification of such cures requires more specialised calculations taking into account the actual rubber and platten temperatures and the heat of vulcanisation.

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