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European Polymer Journal 37 (2001) 329–334

EUROPEAN
POLYMER
JOURNAL

Chemical kinetics of vulcanisation and compression set

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Received 27 July 1999; received in revised form 21 December 1999; accepted 12 May 2000

Abstract

Different natural rubber-based masterbatches compounded using an efficient sulphur, conventional sulphur, peroxide, and diurethane vulcanisation systems were characterised in terms of cure behaviour, vulcanised to different levels of cure, and then tested for set in compression. Cure system, cure temperature, and duration of cure were amongst others, factors which influenced the rate of cure, the density of crosslinks in the vulcanisate network, as well as the set in compression of the vulcanisates. The reduction in compression set with extent of cure (modifications of the vulcanisate network structure) was exponential and could be characterised in terms of a structural modification constant which defines the rate of network modification with prolonged cure. This constant is similar to the reverse relaxation time in stress relaxation measurements. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber; Set; Compression; Kinetics; Vulcanisation

1. Introduction

The flexibility of rubber molecules permits them to take up irregular and statistically random configurations under thermal motion. The molecules, however, straighten out on the application of a tensile stress and thereby exert a retractive force on the polymer chain ends. Rubber molecules characteristically crosslink in the presence of certain reagents to create a network of covalent, inter-molecular to intra-molecular physical links of various natures and densities. These crosslinks permit the material to resist stresses by regaining their original shapes as long as such crosslinks are not permanently ruptured or rearranged [1].

Stress relaxation in compression is a suitable tool for predicting in-service performance of elastomeric products subjected to constant strain though difficulties associated with extrapolation of results and the relatively long periods for conclusion of tests render the technique unsuitable as a short-term control test [2,3]. Set in compression not only shows this ease of execution but correlates excellently with the state of cure [4–7].

In the light of evidence relating vulcanisate elastic behaviour and state of cure, this study evaluates the influence of extent of cure on the repeatability of set determination and assesses the suitability of common crosslinking systems for the production of natural rubber (NR)-based components subjected to static loads. The study finally ascertains the validity of set measurements by establishing the effect of nature of crosslinks on its interpretation.

2. Experimental

2.1. Compounding of masterbatches

Technically specified NR of grade 5 was used as base elastomer and masterbatches were composed to include four vulcanisation systems presented in Table 1. These are

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PII: S0014-3057(00)00112-9

Table 1
Compositions of masterbatch formulations (pphr)

Ingredients	EV (1)	Conventional (2)	Dicumyl peroxide (3)	Diurethane (4)
NR, 5	100	100	100	100
Carbon black, FEF 550	40	40	40	40
Antioxidant[a]	2.0	2.0	2.0	2.0
Zinc oxide	5.0	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0	1.0
MBTS	1.5	1.0	–	–
TMTD	2.5	0.1	–	–
Sulphur	0.5	2.5	–	–
Dicumyl peroxide	–	–	3.0	–
Novor®950[b]	–	–	–	6.7
ZDMC	–	–	–	2.0

[a] Polymerised 2,2,4-trimethyl-1,2-dihydroquinoline.

[b] Diurethane/dimaleimide curing agent kindly supplied by Dr. Colin Metherel of Rubber Consultants, Tun Abdul Razak Research Centre, Hertsford, England.

1. an efficient sulphur curing system (EV), characterised by a very low sulphur-to-accelerator ratio (0.125 w/w), which form mostly monosulphidic crosslinks at optimum cure [8];
2. a conventional sulphur cure system, which as opposed to EV systems, has a relatively high sulphur to accelerator ratio (2.273 w/w), and would result in predominantly polysulphidic crosslinks at optimum cure [8];
3. a peroxide curing system based on dicumyl peroxide (DCP), known to produce stable carbon–carbon bonds, even on overcure [9];
4. a diurethane system (Novor®) that forms pendent aminophenol groups subsequently used for reaction with a suitable di or polyfunctional reagent to form stable carbon–carbon bonds during crosslinking [10]. The formulation, which is the product of an addition reaction between a nitrosophenol and methylene bis-(4-phenyl isocyanate), dissociates on heating and the nitrosophenol reacts with the rubber molecules to form pendent aminophenol groups.

Base mixtures of NR, carbon black, antioxidant, zinc oxide and stearic acid were prepared in a 2500 ml capacity Banbury internal mixer with a rotor speed of 44 rpm and ram pressure of 0.69 MPa. A batch factor of 15 (81% of full mixer capacity) was used and at a starting temperature of 50°C. Curatives were added on an open two-roll mill in a second stage mixing. The base mixes were then crossblended using a masterbatching technique to ensure uniform dispersion of the ingredients and to minimise between-mix variations. They were then milled to a Wallace rapid plasticity number of 18 at haul-off, equivalent to a limiting viscosity number of 0.248 $dm^3 g^{-1}$ in benzene and to a number-average molecular mass of 1.75×10^5 $g mol^{-1}$ [11]. The uniformity in processability between and within masterbatches was confirmed after an analysis of variance on their mean plasticity numbers ($p = 0.09$).

Cure behaviour: The aptitude to vulcanisation of raw stocks was determined on a Monsanto oscillating disc rheometer (model R 100S) using a 3° rotor oscillation amplitude and frequency of 1.67 Hz, at isothermal temperatures of 140°C, 160°C and 180°C, respectively. The cure rate index (CRI) and other parameters characterising their cure kinetics were estimated from the rheographs of the respective compounds [12].

Vulcanisation procedure: Compounded slabs were compression moulded at 140°C and 160°C. The duration of moulding was estimated using the Gurnie–Lurie approach [13] as the sum of the time to temperature equilibrium in moulds and the time to cure as per the rheographs. Total cure time was varied to produce vulcanisates at 50%, 90%, 100% and 200% of full cure.

Compression set: Set measurements were conducted on type 1 cylindrical test pieces (13.0 ± 0.5 mm diameter and 6.3 ± 0.3 mm thickness), strained to 25% of their original thickness and aged in an oven of controlled ventilation at 70°C for 72 ± 2 h [14].

Statistical analysis: Means and standard deviations were computed for the cure and vulcanisate properties of the different stocks. Treatments of homogeneous means were ranked using the Newman–Keuls test. Correlation of cure characteristics and compression set was performed separately.

3. Results and discussion

3.1. Cure behaviour of masterbatches

Although stocks were similarly compounded, their cure properties were quite different as could be seen in Table 2. Crosslinking was earliest in the peroxide and EV stocks as could be observed from their scorch times (t_{s2}), whereas the diurethane had the least tendency to

Table 2
Cure characteristics of compounds[a]

Cure temperature (°C)	Cure parameter	Cure systems			
		EV	Conventional	Peroxide	Diurethane
140	t_{s2}, min (incipient scorch)	3.0 b	4.0 a	3.0 b	4.0 a
	$t_c(50)$, min (50% full cure)	7.5 c	6.5 c	47.0 a	21.5 b
	$t_c(90)$, min (90% full cure)	11.3 c	8.8 c	149.0 a	90.0 b
	$t_c(100)$, min (full cure)	22.8 c	14.3 c	240.0 c	150.0 b
	$M_{HR} - M_L$, torque units[b]	77.3 a	68.4 b	61.2 b	20.2 c
160	t_{s2}, min (incipient scorch)	1.5 b	1.8 b	1.5 b	3.0 a
	$t_c(50)$, min (50% full cure)	2.7 c	2.5 c	6.8 b	8.4 a
	$t_c(90)$, min (90% full cure)	4.3 c	3.2 c	16.5 b	24.1 a
	$t_c(100)$, min (full cure)	10.0 b	4.5 c	40.0 a	39.1 a
	$M_{HR} - M_L$, torque units[b]	80.0 a	77.6 a	61.9 b	18.6 c
180	t_{s2}, min (incipient scorch)	0.8 b	1.0 b	1.0 b	1.5 a
	$t_c(50)$, min (50% full cure)	1.4 c	1.4 c	2.3 b	4.5 a
	$t_c(90)$, min (90% full cure)	1.9 c	1.7 c	4.3 b	12.5 a
	$t_c(100)$, min (full cure)	5.0 b	2.3 c	7.5 b	15.0 a
	$M_{HR} - M_L$, torque units[b]	74.0 a	70.0 a	59.0 b	15.5 c
140–160°C	Apparent energy of activation E_A (kJ mol^{-1})	67 b	66 b	145 a	76 b
160–180°C		22 b	24 b	44 a	25 b

[a] Mean values with same letter in a row are not significantly different at $p \leqslant 0.05$.
[b] 1 torque unit = 0.05 N m.

pre-vulcanise, especially at the lower cure temperature of 140°C. Temperature meanwhile did not seem to have any bearing on the ranking of the pre-vulcanisation behaviour of the cure systems though their scorch times reduced considerably (50% for the EV, conventional and peroxide systems, and 25% for the diurethane system) with a 20°C increase in cure temperature. There could have been the need to incorporate a pre-vulcanisation inhibitor into the formulations as this would affect neither the crosslink insertion rate nor the optimum crosslink density [11]. However, this was thought unnecessary as formulations were prepared at much lower temperatures (~50°C) than that at which crosslinking is effectively activated.

The highest torque levels were observed with the EV mix followed by the conventional, the peroxide, and then the diurethane systems decreasingly, a ranking which remained the same irrespective of the cure temperature. In terms of the torque level at maximum cure, the conventional and peroxide systems were ranked in the same group of homogeneous means when cured at 140°C and then ranked differently when cured at the higher temperatures of 160°C and 180°C. At the lower temperature of 140°C, peroxide stocks required 150 min to form 90% of the maximum attainable crosslinks, whereas the EV, conventional and diurethane stocks needed just 8%, 6% and 60%, respectively, of this time. These would indicate that a cure temperature of 140°C is low for the effective decomposition or dissociation of dicumyl peroxide before it could participate in the crosslinking of the NR chains. These trends were confirmed on analysis of the time to full cure. At 140°C, the cure time was 240 min for the peroxide and 150 min for the diurethane system, and then changing significantly on increasing the cure temperature (to 160°C) to 40 min for both the systems.

On subjecting all the formulations to prolonged cure, only the conventional mix showed pronounced reversion at 160°C and 180°C, indicative of their instability to thermal and oxidative degradation and hence scission and rearrangement of the predominantly polysulphide bonds (–C–S_x–C–) [8,15].

3.2. Kinetics of crosslinking

Figs. 1 and 2 are Arrhenius plots that show, respectively, a linear dependence of reaction rate constant, K, and CRI on reciprocal temperature, with the sulphur-based compounds recording appreciably higher K and CRI values. The slopes of the curves of the peroxide-based masterbatches were always lower especially in terms of the change in CRI per degree rise in temperature. It could be noted, nonetheless that this value improved from 0.7 to ~2.0 min^{-1} K^{-1} when values obtained at 140°C were ignored.

The cure rate parameters of the different compounded stocks are presented in Table 2. The rate of decrease of the scorch time and the time to maximum cure were consistent with an increase in temperature. The apparent activation energy of crosslinking of the

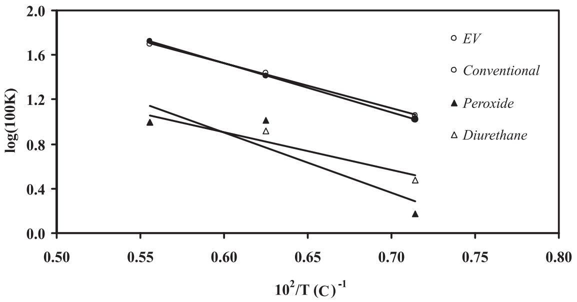

Fig. 1. Arrhenius plot of reaction rate constant, K, as a function of reciprocal temperature.

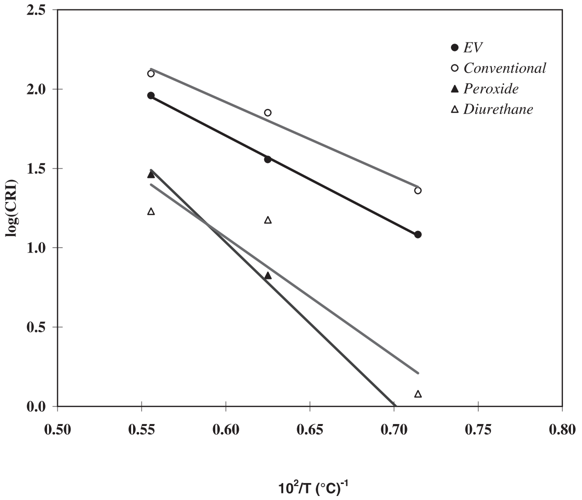

Fig. 2. Arrhenius plot of CRI as a function of reciprocal temperature.

peroxide-based system was extremely higher (~145 kJ mol^{-1}) than those of the other systems when the reaction rates at 140°C and 160°C were considered. These differences reduced considerably (~44 kJ mol^{-1}) when rate constants at 160°C and 180°C were used, irrespective of the cure system.

The Pearson correlation coefficients characterising the relationships between the cure parameters and set in compression, presented in Table 3, show no appreciable effect of time to onset of vulcanisation on compression set. Significant correlations between set and the torque values at prolonged cure confirm the existence of a linear relationship between set and the density of crosslinks in vulcanisates [5].

The duration of cure significantly decreased with set (Figs. 3 and 4) irrespective of the temperature at which stocks were cured. At prolonged cure, accelerated sulphur systems crosslinked much more efficiently with the rearrangement of the polysulphidic bonds to form more stable ones, probably mono and disulphide crosslinks [13].

3.3. Variation of set with extent of cure

Figs. 5 and 6 show the variation in compression set, ζ, with duration of cure of the vulcanisates cured at 140°C and 160°C, and show a decay in set values throughout the curing process. This in turn corresponds to a first order reaction which could be mathematically expressed as

$$\zeta_t = \zeta_0 \exp(-\beta t). \tag{1}$$

However, no restrictive three-dimensional network is expected to be formed before the onset of vulcanisation, and as such, ζ_0 should be zero at $t = 0$. Experimental results obtained show that ζ_0 is a non-zero value; hence, Eq. (1) could be rewritten as

$$\zeta_t = a \exp(-\beta t). \tag{2}$$

The constants a and β as well as the coefficients of determination characterising the compression set reduction process are presented in Table 4. This relation-

Table 3

Pearson correlation coefficients, r, between cure properties of compounded stocks and compression set of their vulcanisates[a]

Parameters	t_{s2} (iv)	$M_{HR} - M_L$ (v)	M_{200} (vi)	K (vii)	CRI (viii)	Set (ix)
(i) Cure system	0.36	-0.91^{**}	-0.89^{**}	-0.64^{*}	-0.53^{*}	0.39
(ii) Cure temperature	0.81^{**}	0.06	-0.10	0.63	0.45	0.13
(iii) State of cure						-0.59^{*}
(iv) t_{s2}		-0.50	-0.39	-0.67^{*}	-0.48	0.31
(v) $M_{HR} - M_L$			0.98^{**}	0.61	0.58	-0.51^{*}
(vi) M_{200}				0.58	0.45	-0.56^{*}
(vii) K					0.91^{**}	0.01
(viii) CRI						0.06

* $p \leqslant 0.05$; ** $p \leqslant 0.01$; DF = 95.

[a] Figures with no asterisk were not significant at $p \leqslant 0.05$.

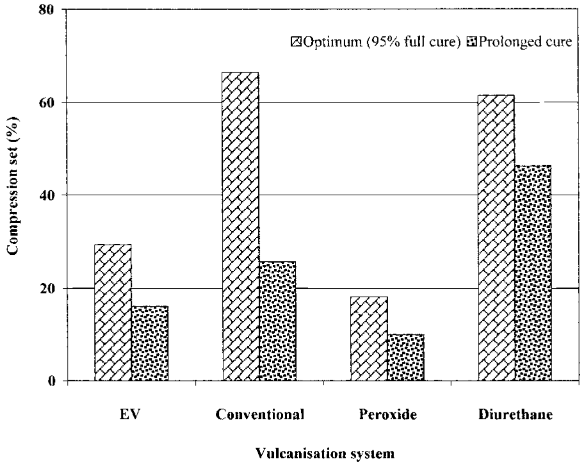

Fig. 3. Effect of cure system and state of cure on set of vulcanisates cured at 140°C.

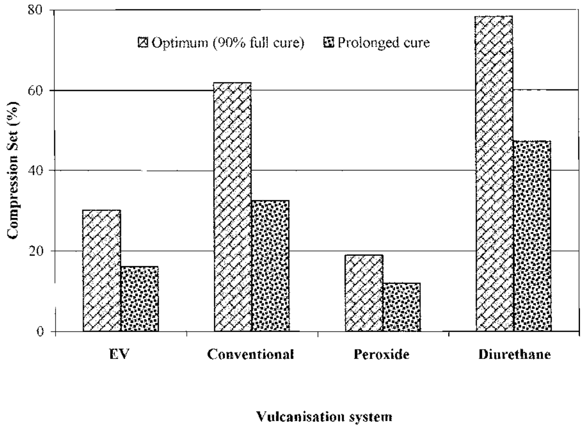

Fig. 4. Effect of cure system and state of cure on set of vulcanisates cured at 160°C.

ship was significant for all the systems involved ($r^2 >$ 0.80 for 140°C $\leqslant$ temperature $\leqslant$ 160°C). Of both the parameters, a and β, characterising the rate of network modification with cure, β was more consistent for each given cure system. The constant a on the other hand varied with cure temperature, being less variable and lower at the higher cure temperature of 160°C.

For vulcanisates cured at 160°C, all the set curves had the same initial slope, which fall in a region corresponding to cure from the onset of crosslinking to the formation of 90% of full cure. For vulcanisates cured at 140°C, however, the initial slopes of the EV and diurethane systems were different from those of the conventional and peroxide-based vulcanisates; hence, their initial rates of reduction in set with cure time were different. Here, curves for the conventional and EV-based mixtures show that though these systems gave different

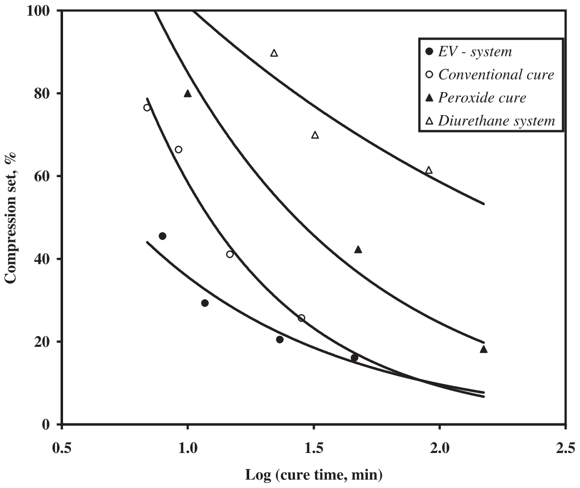

Fig. 5. Variation of compression set with cure time of vulcanisates cured at 140°C.

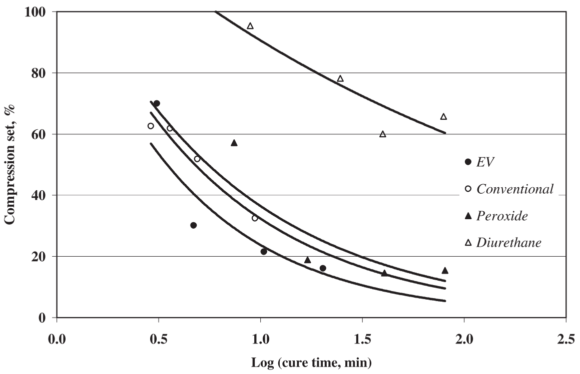

Fig. 6. Variation of compression set with cure time of vulcanisates cured at 160°C.

levels of set in compression when cured for duration less than that required for full cure, the set values of both systems converged to a limiting value of about 10% at prolonged cure. The initial rate of reduction in set was similar for vulcanisates of all the systems cured at 160°C. It could be concluded here that in order to obtain a predictable model that describes the change in vulcanisate network structure with cure, cure temperatures of 160°C and above would be most suitable. Very low cure temperatures to the order of 140°C and below would not only be impracticable for some cure systems involved but would involve extremely high vulcanisation times.

The use of log (time) in Eq. (2) somehow accounts for the temperature effects as confirmed by the fact that its use in the model equation (Eq. 2) considerably improves the coefficients of determination from $0.52 < r^2 < 0.71$ to values of $0.86 < r^2 < 0.99$ for the diurethane and EV stocks, respectively (cured at 160°C).

Table 4
Constants of the exponential function characterising the reduction in compression set (modification in vulcanisate network structure) with extent of cure, derived using Eq. (2)

Cure temperature (°C)	Cure system	β	a	R^2
140	EV	−1.31	132	0.94
	Conventional	−1.84	369	0.99
	Peroxide	−1.24	294	0.97
	Diurethane	−0.55	175	0.90
160	EV	−1.62	120	0.91
	Conventional	−1.35	125	0.96
	Peroxide	−1.23	124	0.80
	Diurethane	−0.45	142	0.83

4. Conclusion

NR-based masterbatches, even when similarly compounded, exhibit different cure behaviour and cure properties depending on the cure system used, the duration and temperature of cure. Whereas temperatures of 140°C and below could be suitable for some cure systems, this is not the case for a peroxide-like dicumyl peroxide, which does not decompose satisfactorily to participate in the vulcanisation process. This is reflected as a more significant increase in the reaction rate following an equivalent increase in temperature. At equivalent levels of cure, the EV and peroxide systems produce vulcanisates with relatively lower compression set when compared to the conventional sulphur and diurethane-based systems.

Compression set diminishes in an exponential manner with the extent of cure of vulcanisates. This relationship could be characterised in terms of a constant, β, that defines the rate of network modification with prolonged cure, which could normally be comparable to the inverse relaxation time in stress relaxation measurements.

Acknowledgements

E.E.E. gratefully acknowledges the financial support of the Common Fund for Commodities (CFC), Amsterdam, through the Professional Association of Natural Rubber in Africa (ANRA) in Abidjan, Côte d'Ivoire.

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