Thermochimica Acta, 39 (1980) 7—20
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THE CURE OF ELASTOMERS BY DICUMYL PEROXIDE AS OBSERVED IN DIFFERENTIAL SCANNING CALORIMETRY *

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(Received 21 September 1979)

ABSTRACT

Differential scanning calorimetry (DSC) has been used to determine the enthalpy changes accompanying the thermal homolysis and subsequent radical reactions occurring in the dicumyl peroxide (DCP) cure of elastomers (NR, EPDM, SBR, BR, NBR and EPM). The thermal degradation of DCP alone, dispersed on kaolin clay and in a hydrocarbon solvent, was also studied.

The degradation of DCP alone results in an exothermic enthalpy change of ~ 215 kJ mole^{-1}. In elastomer systems, the observed enthalpy change can be ordered BR >> SBR > NBR (34% ACN) > NBR (27% ACN) > NR > EPDM ~ EPM.

Low enthalpy values are associated with systems containing predominantly secondary hydrogen atoms (EPDM, EPM). The high enthalpy of cure for BR appears associated with the known ability of the polybutadienyl radicals to propagate a limited chain reaction. The relative extent of cumyloxy radical disproportionation to hydrogen abstraction was determined in each system and this has no apparent effect on the observed enthalpy change.

The method of Borchardt and Daniels was used for data reduction and calculation of apparent activation energies. For DCP degradation alone, the calculated activation energy is in good agreement with literature values. In elastomer systems, the calculated activation energies must be treated with caution because, as pointed out by Borchardt and Daniels, their method does not apply to solid state reactions.

INTRODUCTION

Organic peroxides are an important class of crosslinking agents for both saturated and unsaturated polymers. The mechanism of dicumyl peroxide (DCP) degradation has been extensively studied in both hydrocarbon solvents [1,2] and in polymers [3—11]. In a neutral or alkaline medium, free radicals are formed by thermal homolytic scission of the peroxide bond. The thermal scission reaction is first order and both the rate and activation energy of the process are virtually independent of the nature of the medium. The subsequent hydrogen abstraction reactions of the radicals thus formed depend upon both the availability and ease of abstraction of hydrogen in the hydrocarbon solvent or hydrocarbon polymer. In earlier publications [12, 13], the use of differential scanning calorimetry (DSC) to determine enthalpy changes accompanying the accelerated sulphur vulcanization of

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* Presented at the 9th North American Thermal Analysis Society Meeting, Chicago, IL, 23—26 September, 1979.

elastomers was described. Identical investigations have now been made for the DCP cure of a variety of elastomers. The DCP cure of natural rubber, polybutadiene and styrene butadiene rubbers was previously studied by differential thermal analysis using a high frequency dielectric heating method [14—16], and more recently, limited DSC data have been published [17].

Chemically, the reactions and products formed during peroxide cure are considerably simpler than those encountered with accelerated sulphur vulcanization [18]. The DSC peroxide cure exotherm is analyzed using the Borchardt and Daniels [19] model which has been applied to a number of DSC solid state reactions, e.g. the decomposition of polymerization initiators [20], the cure of epoxy resins [21], and more recently, the oxidation of Guayule and Hevea rubber [22]. Extreme caution must be exercised in attaching significance to kinetic parameters derived using this model for solid state systems in which several reactions are occurring simultaneously, and/or consecutively. The major liquid products formed during DCP cure of elastomers, viz. 2-phenyl-2-propanol and acetophenone, have also been determined using similar methods to those reported in the literature [4].

EXPERIMENTAL

Materials and sample preparation

All materials were standard rubber industry grades and used as supplied. Dicumyl peroxide (Dicup R, 98—100% DCP and Dicup 40 KE, 39.5—41.5% DCP on clay) were supplied by Hercules Inc. Natural rubber was No. 1 ribbed smoked sheet. Polybutadiene (BR Taktene 1220), styrene butadiene rubber (SBR Krylene 1500), and nitrile rubber (NBR Krynac 27 : 50 and 34 : 60) were all supplied by Polysar Inc. The ethylene—propylene—diene elastomer (EPDM) was Nordel 1040 supplied by DuPont Inc. The ethylene—propylene copolymer (EPM) was Vistalon 404 supplied by Exxon Chemical.

All elastomer compounds were milled using standard procedures on a 6-in. × 12-in. mill. Throughout the study 5.0 phr zinc oxide was used in all elastomer samples. After preparation, samples were stored at —40°C prior to use.

DSC analysis

A DuPont 990 thermal analyzer and DSC Cell Base II were used throughout. Samples (10—20 mg) were encapsulated in aluminum holders under nitrogen and the cure exotherms obtained as described in earlier publications [12,13]. Unless otherwise stated, all DSC experiments were conducted at 20°C min^{-1} heating rate. For area measurement the curve was obtained on a time base rather than temperature base. All areas were converted to enthalpy values after calibration of the instrument with indium, tin and zinc metals. Kinetic analysis of the DSC curve is discussed in detail in a later section.

Analysis of liquid products

Samples of the elastomer compound were cured in sealed tubes for the required time at 160°C. After cure, the tube was broken and the entire contents extracted with acetone solvent in a Soxhlet apparatus. After extraction, the solvent was concentrated and then made up to a known value. Gas chromatographic analysis of the acetophenone and 2-phenyl-2-propanol content was made using a Perkin-Elmer 3920 gas chromatograph. The products of interest were well separated on a 12 ft 15% Carbowax 1540 on Chromosorb W (80—100 mesh) column at 160°C with 30 ml min^{-1} helium flow. The conditions were similar to those published in the literature for the analysis of the same products [4,5].

DSC data reduction

The DSC curve records the rate of enthalpy change ($\mathrm{d}H/\mathrm{d}t$) in a system as a function of temperature. The observed $\mathrm{d}H/\mathrm{d}t$ is the mathematical sum of all exothermic and endothermic events occurring at the temperature at which it is determined. Thus, in systems where several reactions are occurring simultaneously or consecutively, correlation of the observed enthalpy with a specific reaction is not possible.

The differential enthalpic curve for stirred liquid phase reactions with rate constant k_T can be written [15]

$$k_T = \frac{(AV/m_0)^{n-1}(\mathrm{d}H/\mathrm{d}t)}{(A-a)^n}$$

where A is the total area under the thermogram, (m_0/V) is the initial concentration of reactant, a is the partial area under the thermogram up to temperature T, $\mathrm{d}H/\mathrm{d}t$ is the rate of enthalpy change at the same temperature, and n is the order of reaction. For a first order reaction, the above equation reduces to

$$k_\mathrm{T} = \frac{\mathrm{d}H/\mathrm{d}t}{A-a}$$

After conversion of exotherm area to enthalpies

$$k_T = \frac{\mathrm{d}H/\mathrm{d}t}{\Delta H - \Delta h(T)}$$

where ΔH is the total enthalpy of all reactions and $\Delta h(T)$ is the partial enthalpy evolved up to temperature T.

Mathematical reduction of the elastomer cure exotherm and the problems encountered with elastomer systems are illustrated in Fig. 1, which illustrates a typical cure exotherm for a natural rubber/3 phr DCP/5 phr ZnO compound. Three characteristic temperatures are used to describe the exotherm: T_0, the temperature of reaction onset; T_p, the temperature of the maximum rate of enthalpy change; and T_c, the temperature of reaction com-

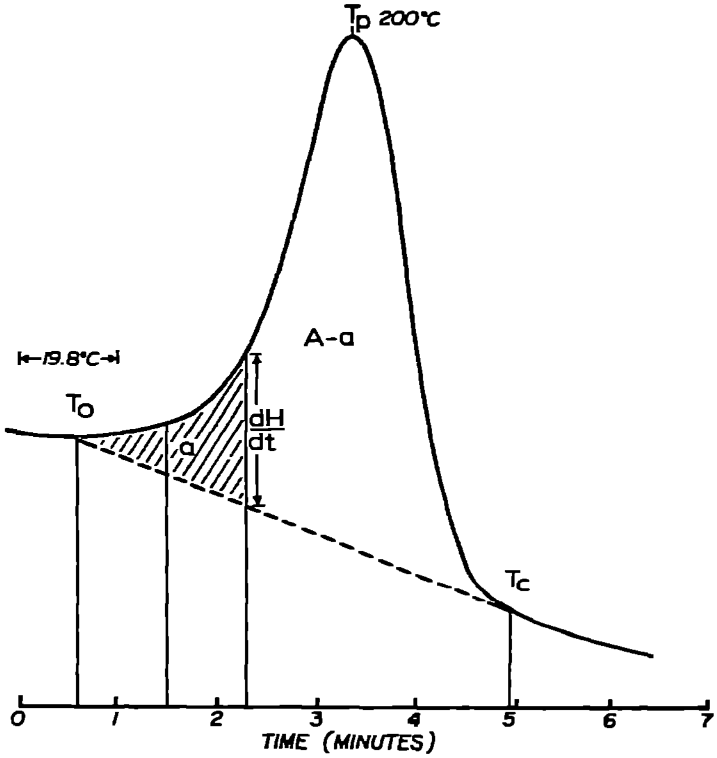


Fig. 1. Typical DSC exotherm for the cure of natural rubber by dicumyl peroxide. Scanned at 20°C min^{-1} (actual calibrated rate shown) on time base. Area calculated for kinetic analysis illustrated. Formulation: NR, 100; DCP, 3.0 and ZnO, 5.0. $\mathrm{d}H/\mathrm{d}t = 0.2$ mcal sec^{-1} in^{-1}.

pletion. These temperatures are dependent upon the heating rate. With elastomer systems, the baseline before T_0 and after T_c rarely returns to the same level; for the present studies, the baseline for area calculations was drawn by connecting T_0 to T_c. The cause of the sloping baseline is the temperature dependence of elastomer heat capacity as previously noted in sulphur vulcanization studies [12]. If the cured sample is cooled and rescanned, then the new curve records only the temperature dependence of the heat capacity and can be virtually superimposed on the baseline drawn from T_0 to T_c. The error in assuming a linear baseline when calculating the exotherm is less than 2%.

Partial areas of the exotherm up to any temperature were calculated using a computer. The input data was the height ($\mathrm{d}H/\mathrm{d}t$) above the electronic zero at equal increments of temperature. The slope of the baseline T_0—T_c was automatically calculated and corrections made to the partial area. In general, data points at 4°C intervals along the temperature axis were sufficient for the required accuracy.

RESULTS

Thermal degradation of dicumyl peroxide

Initial studies by DSC were conducted on the thermal degradation of DCP alone, DCP supported on kaolin clay, and DCP in di-*n*-butyl phthalate.

TABLE 1

Enthalpic analysis of dicumyl peroxide degradation

Heating rate (°C min^{-1})	ΔH (kJ mole^{-1} ± 5 kJ)	E (kJ mole^{-1} ± 8 kJ)	k_d (min^{-1} × 10^2) 140°C
Dicumyl peroxide (DCP)			
20	217	140	0.69
10	212	142	0.70
5	216	138	0.64
40% DCP/clay			
20	277	125	0.85
10	273	121	0.90
5	276	122	0.83
9.1% DCP in di-n-butyl phthalate			
20	276	132	0.41
10	268	142	0.39
5	270	136	0.36
Literature values — DCP in			
dodecane [1]		140	1.7
cumene [2]		144	1.4
paraffin oil [3]		135	1.4
isoprene dimer [4]		134	1.3

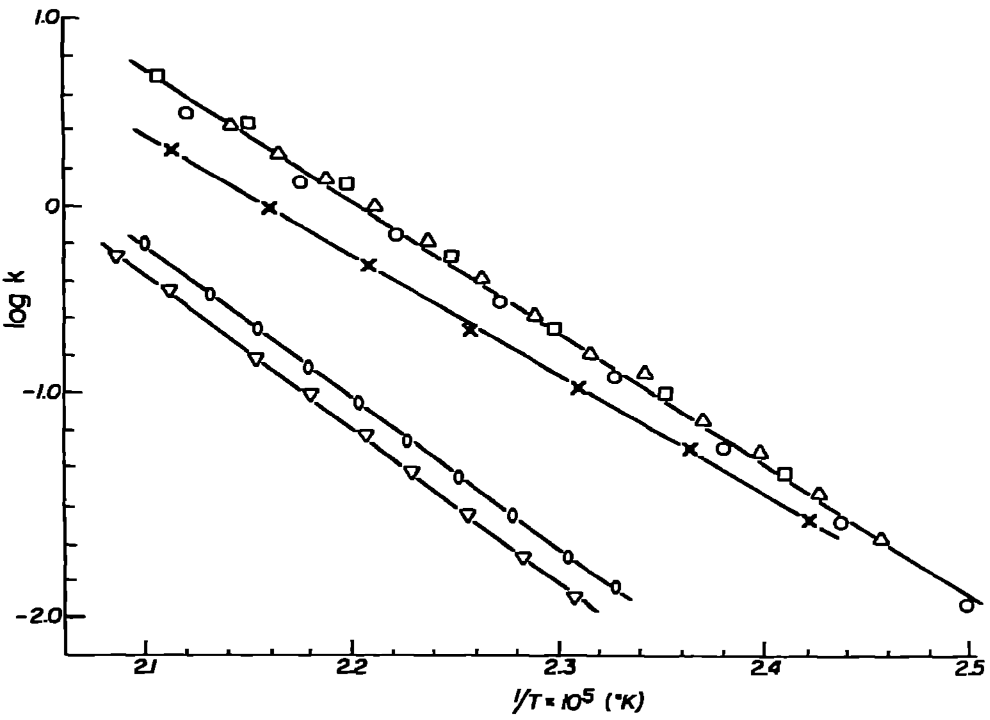


Fig. 2. Arrhenius plots of dicumyl peroxide cure of natural rubber at various scan rates. Rates calculated using the Borchardt and Daniels' method. DCP: □, 20°C min^{-1}, ○, 5°C min^{-1}; △, 2°C min^{-1}. 40% DCP in kaolin clay: ×, 20°C min^{-1}. 9.1% DCP in di-n-butyl phthalate: 0,20°C min^{-1}; ▽, 10°C min^{-1}.

Enthalpic and kinetic data for these systems are summarized in Table 1. Literature values for the activation energy and degradation rate of DCP in various solvents are included for comparison. All literature values were determined under isothermal conditions at 140°C in a variety of solvents.

The effect of heating rate was studied (20—5°C min^{-1} range) and within experimental error, the overall enthalpy of degradation (ΔH) is independent of heating rate. All ΔH values are the average of at least three determinations. Figure 2 illustrates the Arrhenius plots obtained for these materials using the kinetic analysis outlined earlier. Regression analysis of the data displayed in Table 1 resulted in correlation coefficients in excess of 0.999 for the first order assumption.

Peroxide—elastomer systems

DCP cure exotherms were obtained in NR, BR, SBR, EPDM and NBR elastomers for peroxide levels between 0.2 and 5.0 phr. All data were obtained at a heating rate of 20°C min^{-1}. Figures 3 and 4 illustrate the changes obtained in the DSC exotherm with peroxide level in NR and NBR, respectively. For all systems, two maxima were observed in the DSC exotherm when peroxide was at low levels (0.2 phr). As peroxide level increased,

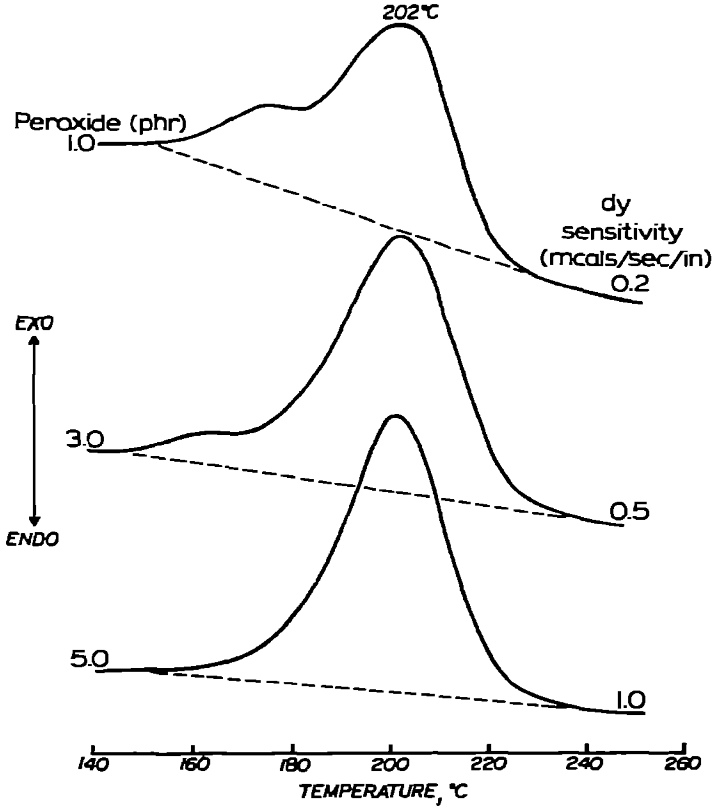


Fig. 3. Effect of dicumyl peroxide level on the enthalpy profile of natural rubber cure. 20°C min^{-1} scan rate. Various calorimeter sensitivities.

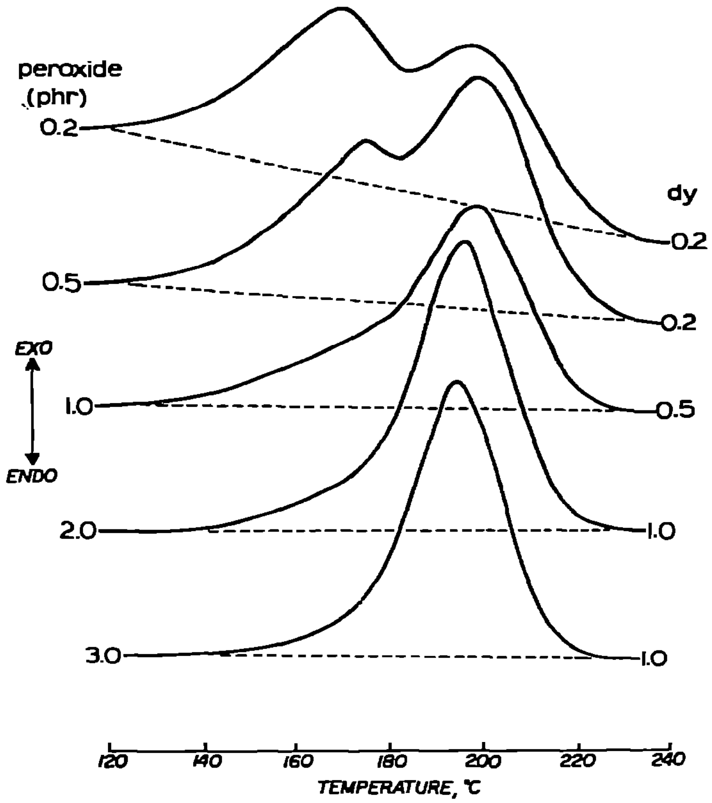


Fig. 4. Effect of dicumyl peroxide level on the enthalpy profile of nitrile rubber cure. 20°C min^{-1} scan rate. Various calorimeter sensitivities.

the first maximum diminished in size but was generally observable as a shoulder leading into the second maximum at all peroxide levels. The origin of the first event is believed to be the reaction of DCP with antioxidants, additives and/or impurities in the commercial elastomer system. All synthetic elastomers have added stabilizers and NR contains up to 6% proteins and resins. At higher levels of DCP, the reaction is small compared to the cure exotherm but is always included in the determined enthalpy of cure.

Table 2 summarizes the enthalpic and kinetic data obtained for these systems at 2.0 phr peroxide and higher. ΔH values are given in both kJ g^{-1} sample and kJ $mole^{-1}$ peroxide consumed assuming complete peroxide utilization. Figure 5 illustrates the dependence of ΔH upon peroxide levels in all elastomers studied. ΔH values were calculated from the total area under the exotherm even when two maxima were apparent. For all elastomers except the NBR materials, ΔH vs. peroxide passes through the origin. NBR scanned in the absence of DCP exhibits an exothermic event starting at ~120°C. Although not very reproducible, the enthalpy of this event was 8 ± 2 J g^{-1} for NBR with 34% ACN, and 5 ± 2 J g^{-1} for the NBR with 27% ACN. No such event was observed in the other butadiene-containing elastomers and this agrees fairly well with the positive intercept on the ΔH axis for NBR materials. For NR, SBR and EPDM, ΔH is constant per mole of peroxide

TABLE 2

DSC enthalpy data — cure of elastomers with DCP (20°C min^{-1} scan rate)

Elastomer	DCP (phr)	ΔH (J g^{-1} sample)	ΔH (kJ mole^{-1} DCP)	E (kJ mole^{-1})	Exotherm temperatures (°C)	
					T_0 *	T_p **
NR	1.0	13.8	405	143	144	200
	2.0	25.8	378	151	144	200
	5.0	69.5	405	150	144	200
EPDM	1.0	12.5	326	141	154	198
	2.0	19.7	297	140	150	200
	5.0	47.3	270	137	140	198
BR	1.0	68.1	1940	138	140	202
	2.0	132.0	1890	163	140	202
	5.0	282.0	1670	200	140	202
SBR	1.0	30.7	890	170	142	200
	2.0	62.2	890	170	142	200
	5.0	153.0	890	210	142	200
NBR (34% ACN)	1.0	40.0	1130	92	112	198
	2.0	61.0	890	128	120	196
	5.0	134.0	810	141	120	194
NBR (27% ACN)	1.0	29.3	840	114	130	197
	2.0	48.0	702	140	130	197
	5.0	105.0	621	141	128	196
EPM	3.0	26.0	253	140	128	198

* Onset temperature.

** Temperature of maximum enthalpy rate change.

consumed up to 5.0 phr. For BR and NBR, however, ΔH per mole of peroxide consumed decreases as peroxide level increases.

Apparent activation energies calculated on the first order assumptions are also shown in Table 2. These results were also obtained by treating the complete exotherm as one peak as observed for DCP thermal degradation. For

TABLE 3

Enthalpic analysis of polybutadiene cure (20°C min^{-1})

DCP level (phr)	ΔH_v (kJ g^{-1} sample)	ΔH (kJ g^{-1} peroxide)	E (kJ mole^{-1})	$k_d \times 10^3$ (min^{-1})	
				202°C	160°C
0.2	16.0	8.4	105	295	18.6
0.5	35.5	7.5	121	396	14.4
1.0	68.1	7.2	138	350	7.5
2.0	132.0	7.0	163	454	5.9
3.0	184.0	6.6	172	464	4.0
5.0	282.0	6.2	200	927	1.4

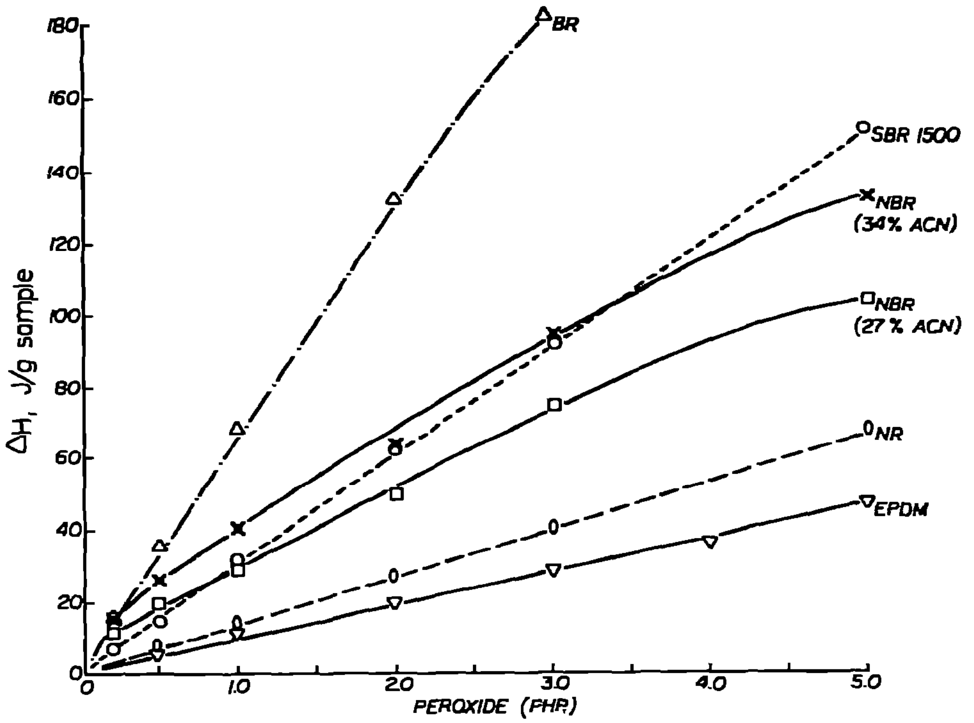


Fig. 5. Enthalpy of cure of various elastomers vs. dicumyl peroxide level. △, BR; ○, SBR; ×, NBR (34% ACN); □, NBR (27% ACN); o, NR; and ▽, EPDM. All compounds contain 5.0 phr ZnO.

TABLE 4

Relative yields of acetophenone and 2-phenyl-2-propanol from dicumyl peroxide cure of elastomers at 180°C

Elastomer	Acetophenone/2-phenyl-2-propanol	% DCP	Lit. values at (°C)
NR	0.34	67.3	0.13 (153) [7]
			0.11 (140) [6]
			0.18 (150) [23]
SBR	0.40	73.7	0.07 (153) [7]
			0.22 (150) [23]
BR	0.54	64.5	0.80 (145) [17]
NBR (27% ACN)	0.65	78.0	
NBR (34% ACN)	0.72	77.0	0.3 (39% ACN at 153) [7]
EPDM	0.78	71.0	
EPM	0.86	81.0	
Polyethylene (HD)			0.63 (150) [23]
Cumene			1.95 (160) [2]
			1.40 (138) [1]
Dodecane			0.68 (138) [1]

NR and EPDM, the apparent activation energies were independent of peroxide level. This is not the case for the BR or NBR materials, as shown by the detailed results for BR in Table 3. The apparent activation energy increases with increasing peroxide content. The rate constants at 202° C (i.e. T_p for BR) show an apparent increase with peroxide level, while those calculated at 160° C decrease with increasing peroxide.

Differences in behaviour of the elastomers are also apparent for the cure onset temperatures (T_0). A very early reaction is observed with NBR materials and this is related to the acrylonitrile content. The T_p values for all elastomers fall within the 196—202° C range at a heating rate of 20° C min^{-1}.

Table 4 records data obtained for the ratio of 2-phenyl-2-propanol to acetophenone for each elastomer system cured isothermally at 180° C. In all cases, the peroxide level was 3.0 phr. Literature values for this ratio are also included in Table 4.

DISCUSSION

The reactions occurring when DCP is thermally decomposed in a hydrocarbon solvent or elastomer can be written [1,10,23]

$$\phi C(CH_3)_2{-}O{-}O{-}C(CH_3)_2\phi \xrightarrow{\Delta} 2\phi C(CH_3)_2O\cdot \tag{1}$$

$$\phi C(CH_3)_2O\cdot + RH \rightarrow \phi C(CH_3)_2OH + R \tag{2}$$

$$\phi C(CH_3)_2O\cdot \rightarrow \phi\overset{CH_3}{\overset{|}{C}}{=}O + CH_3\cdot \tag{3}$$

$$CH_3\cdot + RH \rightarrow CH_4 + R\cdot \tag{4}$$

$$R\cdot + R\cdot \rightarrow R{-}R \tag{5}$$

RH represents either the hydrocarbon solvent or the elastomer containing extractable hydrogen. For elastomer systems, reaction (5) results in crosslink formation. Reaction (2) is hydrogen abstraction by the cumyloxy radical and is in competition with reaction (3), disproportionation of the cumyloxy radical. The ratio of reactions (3) and (2) is determined by measurement of the acetophenone/2-phenyl-2-propanol yield. The difference in activation energy for disproportionation and hydrogen abstraction by cumyloxy radicals in cumene is ~31 kJ $mole^{-1}$ [2] and increasing temperature favours disproportionation. In the overall scheme, the ratio of abstraction to disproportionation does not affect the ultimate chain radical concentration since disproportionation yields a methyl radical capable of hydrogen abstraction from the hydrocarbon solvent or elastomer chain.

The majority of DCP cure studies reported in the literature were made under isothermal conditions at temperatures between 110 and 160°C. In the DSC experiment, the temperatures are considerably higher — all elastomer systems exhibiting a maximum rate of enthalpy change at 198 ± 4°C (T_p, Table 2) at a heating rate of 20° C min^{-1}. The overall enthalpy change determined in DSC corresponds to the sum of the enthalpy changes accompanying all reactions, (1)—(5). Regardless of temperature or solvent, the contribution from reaction (1), homolytic scission of the O—O bond, can be considered constant. The activation energy for homolytic scission of O—O is 140 kJ mole^{-1} [2] which is close to the O—O bond strength in such peroxides. For the remaining reactions, (2)—(5), a significant temperature effect can be anticipated. Radical recombination reaction (5) will primarily be controlled by diffusion, however, the structure of the radical can alter the overall contribution from reaction (5) (see later).

Degradation of DCP

In the absence of RH in the above reaction scheme, only reactions (1), (3) and (5) need be considered in the first approximation. Cumyloxy radicals do not abstract hydrogen from DCP [1,2] and this was confirmed by GC analysis. No 2-phenyl-2-propanol was found, the major product being acetophenone together with a large number of minor unidentified products. The overall enthalpy of DCP degradation was 216 ± 5 kJ mole^{-1} at scan rates between 5 and 20°C min^{-1}. The activation energy calculated by the Borchardt and Daniels method was 140 ± 2 kJ mole^{-1} over the same scan rate range and in excellent agreement with that obtained by other methods.

The enthalpy of degradation of DCP on clay is 276 kJ mole^{-1} and the activation energy is ~124 kJ mole^{-1} as calculated from the DSC data. The lower activation energy suggests that the clay catalyzes DCP decomposition and this has been reported in the literature [24]. Acidic carbon blacks and silicas are also known to catalyze peroxide decomposition, however, an ionic mechanism is involved [3]. GC analysis of DCP—clay degradation products again yielded acetophenone as the major product, but products from ionic degradation could not be excluded without further analysis.

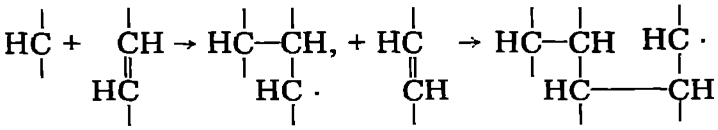
*Di-*n*-butyl phthalate and elastomer systems*

Di-*n*-butyl phthalate was the only hydrocarbon solvent system studied, as low boiling hydrocarbons require the use of high pressure DSC. The overall enthalpy of DCP reactions with this solvent was 270 ± 8 kJ mole^{-1} DCP which is ~54 kJ mole^{-1} DCP higher than that observed for the degradation of DCP alone. Hydrogen abstraction from di-*n*-butyl phthalate will occur predominantly at the secondary hydrogen of the methylene groups because such hydrogens are more readily abstracted and further secondary hydrogens outnumber primary hydrogens by a factor of 2. The observed enthalpy for di-*n*-butyl phthalate/DCP reactions would be expected to be similar to that observed for polymers containing predominantly methylene groups such as polyethylene, EPM and EPDM. The observed enthalpy for the EPDM and EPM (290 kJ mole^{-1} DCP) are in fact the closest to that of di-*n*-butyl phthalate/DCP of all elastomer systems studied.

Examination of the acetophenone/2-phenyl-2-propanol ratios determined at 180°C (Table 4) indicates increased disproportionation at higher temperatures in all elastomer/DCP systems. The percentage of the initial DCP present which can be accounted for by the acetophenone and 2-phenyl-2-propanol products is lower than that observed at lower temperatures. It is possible that secondary reactions occur at higher temperatures; however, it could also be accounted for by DCP reactions with antioxidants or stabilizers present in the commercial elastomers. No correlation is observed between the ratio of disproportionation to hydrogen abstraction and the observed enthalpy of cure for a given system and, therefore, variations in the overall enthalpy cannot be accounted for on the basis of relative contributions from reactions (2) and (3).

NR exhibits the greatest amount of hydrogen abstraction and this reflects the ease of removal of the α-methylenic hydrogen in polyisoprene. The DCP cure efficiency (mole crosslinks formed per mole of DCP consumed) is reported to be close to unity in NR [5,6], and under these conditions, the enthalpy per mole of DCP decomposed would be equivalent to the overall enthalpy per mole of crosslink formation. Efficiencies of peroxide cure of ~10 have been determined for BR [7,9] and 12.5 for SBR [7]. In BR, the polybutadienyl radical formed on hydrogen abstraction is very reactive, having less resonance stabilization than the polyisoprenyl radical. Unsaturation in BR is reduced as cure proceeds and the polybutadienyl radical reacts with unsaturation in such a manner that the chain radical is propagated rather than terminated. A similar mechanism is believed to occur in the SBR—peroxide cure; however, the observed overall enthalpy for SBR is about half of that observed for BR.

The chain reaction may be written [9]



$$\begin{array}{c}|\\\mathrm{HC}\\|\end{array} + \begin{array}{c}|\\\mathrm{CH}\\\|\\\mathrm{HC}\\|\end{array} \rightarrow \begin{array}{c}|\quad|\\\mathrm{HC{-}CH,}\\|\quad|\\\mathrm{HC}\cdot\\|\end{array} + \begin{array}{c}|\\\mathrm{HC}\\\|\\\mathrm{CH}\\|\end{array} \rightarrow \begin{array}{c}|\quad|\qquad|\\\mathrm{HC{-}CH}\quad\mathrm{HC}\cdot\\|\quad|\qquad|\\\mathrm{HC}{-}{-}{-}\mathrm{CH}\\|\qquad\quad|\end{array} \qquad (6)$$

and it has been shown that the reactivity of vinyl side groups is similar to that of the main chain unsaturation.

An estimation of the chain length of the propagating reaction could be made from the enthalpy values for cure if accurate values of the heats of reaction were known. Wald and Winding [15] used this approach in interpretation of enthalpy values obtained for DCP cure of NR, BR and SBR elastomers. If cure proceeded exclusively through hydrogen abstraction, i.e. reactions (1), (2) and (5), a heat of reaction of 316 ± 10% kJ mole^{-1} DCP was calculated from bond energies. On the other hand, if the mechanism involved exclusively disproportionation [i.e. reactions (1), (3), (4) and (5)] a value of 268 ± 10% kJ mole^{-1} DCP was calculated. In all cases, both mechanisms occur but the relative contributions could be calculated from a knowledge of the acetophenone/2-phenyl-2-propanol ratio (Table 4). The estimated heat of reaction of the isopropenyl radical with a vinyl group was 58.5 ± 35% kJ mole^{-1} DCP, and the large uncertainty in this value significantly affects the calculated chain length of the propagating crosslinking reaction. Using these values with the current enthalpy and ketone/alcohol ratio data, we obtain the following estimates for the chain length; NR, 1.7; BR, 27; SBR, 10; NBR (27% ACN), 7; and NBR (34% ACN), 10. Values for EPDM and EPM are close to 1. Using a similar DSC approach to the present work, a chain length of 39 was recently reported [17] for the DCP cure of low molecular weight polybutadiene. Because of the lack of knowledge of the actual heat of reaction for reaction (6), the above values are considered in good agreement with the published values for DCP cure efficiency obtained on actual vulcanizates. NBR appears to be the exception.

NBR crosslinking efficiency is reported to be similar to NR, i.e. close to unity [7], and this is believed to result from interference by the nitrile group. The higher acetophenone/2-phenyl-2-propanol ratio observed for NBR/DCP systems suggests that hydrogen abstraction is more difficult than in the corresponding SBR copolymer. Both SBR, NBR copolymers [25,26] and BR [27] are known to undergo a thermal vulcanization process at temperatures in the range 180—200°C. The DSC curves of SBR and BR do not exhibit any event in this temperature range; however, NBR does show an exothermic event which appears to increase in size with increasing acrylonitrile content. For NBR (34% ACN), the event has an enthalpy of ~8.0 J g^{-1} sample, and for NBR (27% ACN) ~5.0 J g^{-1} sample. The T_p for NBR (34% ACN) is 180°C, while for NBR (27% ACN) it is 202°C. Reducing the observed enthalpy for NBR elastomers to account for the thermal reaction places NBR between NR and SBR in overall cure enthalpy. This reduction does not significantly reduce the estimated chain length of the propagating chain, and we conclude that the derived ΔH of cure must contain contributions from reactions of the acrylonitrile groups which do not lead to crosslinks.

SUMMARY

The objective of the study was to determine whether DSC could be used to monitor the progress of the peroxide cure of unsaturated elastomers. In all cases studied, the observed enthalpy of cure was proportional to the peroxide level added, however, the magnitude of the enthalpy varied with the nature of the elastomer. With the exception of the nitrile elastomer systems, the magnitude of the observed enthalpy appears consistent with our knowledge of the cure mechanism for each elastomer.

The kinetic model used was designed for liquid phase reactions and is not expected to apply to such complex solid state reactions. Nevertheless, the concept of using partial enthalpy evolution to monitor the time—temperature profile of cure provides parameters which are useful in evaluating the commercial cure process.

ACKNOWLEDGEMENTS

The authors thank Dunlop Holdings Ltd. for permission to present this study. Special thanks also go to G.H. Nickel, Z. Szentgyorgyi and E. Tymchyshyn, who contributed in data collection.

REFERENCES

1 M.S. Kharasch, A. Fono and W. Nudenborg, J. Org. Chem., 16 (1951) 105.
2 H.C. Bailey and G.W. Godin, Trans. Faraday Soc., 52 (1956) 68.
3 E.M. Dannenberg, M.E. Jordan and H.M. Cole, J. Polym. Sci., 31 (1958) 127.
4 C.R. Parks and O. Lorenz, J. Polym. Sci., 50 (1961) 287.
5 O. Lorenz and C.R. Parks, J. Polym. Sci., 50 (1961) 299.
6 D.K. Thomas, J. Appl. Polym. Sci., 6 (1962) 613.
7 I.D. Loan, J. Appl. Polym. Sci., 7 (1963) 2259.
8 K. Hummel and G. Kaiser, Kautsch. Gummi, Kunstst., Asbest, 16 (1963) 426.
9 B.M.E. Van der Hoff, I EC Prod. Res. Dev., 2 (1963) 273.
10 K. Hummel and G. Kaiser, Kolloid-Z., 197 (1964) 90.
11 M. Imoto, K. Takemoto and M. Kono, Angew. Makromol. Chem., 1 (1967) 78.
12 D.W. Brazier and G.H. Nickel, Rubber Chem. Technol., 48 (1975) 26.
13 D.W. Brazier, Thermochim. Acta, 18 (1977) 147.
14 S.A. Wald and C.C. Winding, Polym. Eng. Sci., 11 (1971) 57.
15 S.A. Wald and C.C. Winding, Polym. Eng. Sci., 11 (1971) 64.
16 S.A. Wald and C.C. Winding, Polym. Eng. Sci., 11 (1971) 70.
17 I. Gancarz and W. Laskawski, J. Polym. Sci., 17 (1979) 683.
18 A.Y. Coran, in F.R. Eirich (Ed.), Science and Technology of Rubber, Academic Press, New York, 1977, Ch. 7, and refs. therein.
19 H.J. Borchardt and F. Daniels, J. Am. Chem. Soc., 79 (1957) 41.
20 K.E.J. Barrett, J. Appl. Polym. Sci., 11 (1967) 1617.
21 R.B. Prime, Polym. Eng. Sci., 13 (1973) 365.
22 M.A. Ponce-Velez and E. Campos-Lopez, J. Appl. Polym. Sci., 22 (1978) 2485.
23 L.O. Amberg and W.D. Willis, Proc. Int. Rubber Conf., Washington, D.C., 1959.
24 D.H. Solomon, J.D. Swift, G. O'Leary and I.G. Treeby, J. Macromol. Sci., Chem., 5 (1971) 995.
25 H. Luttrop, Kautsch. Gummi, 10 (1957) WT31.
26 W. Scheele and H.D. Skemmer, Kautsch. Gummi, 11 (1958) WT325.
27 J.A. Coffman, Ind. Eng. Chem., 44 (1952) 1421.