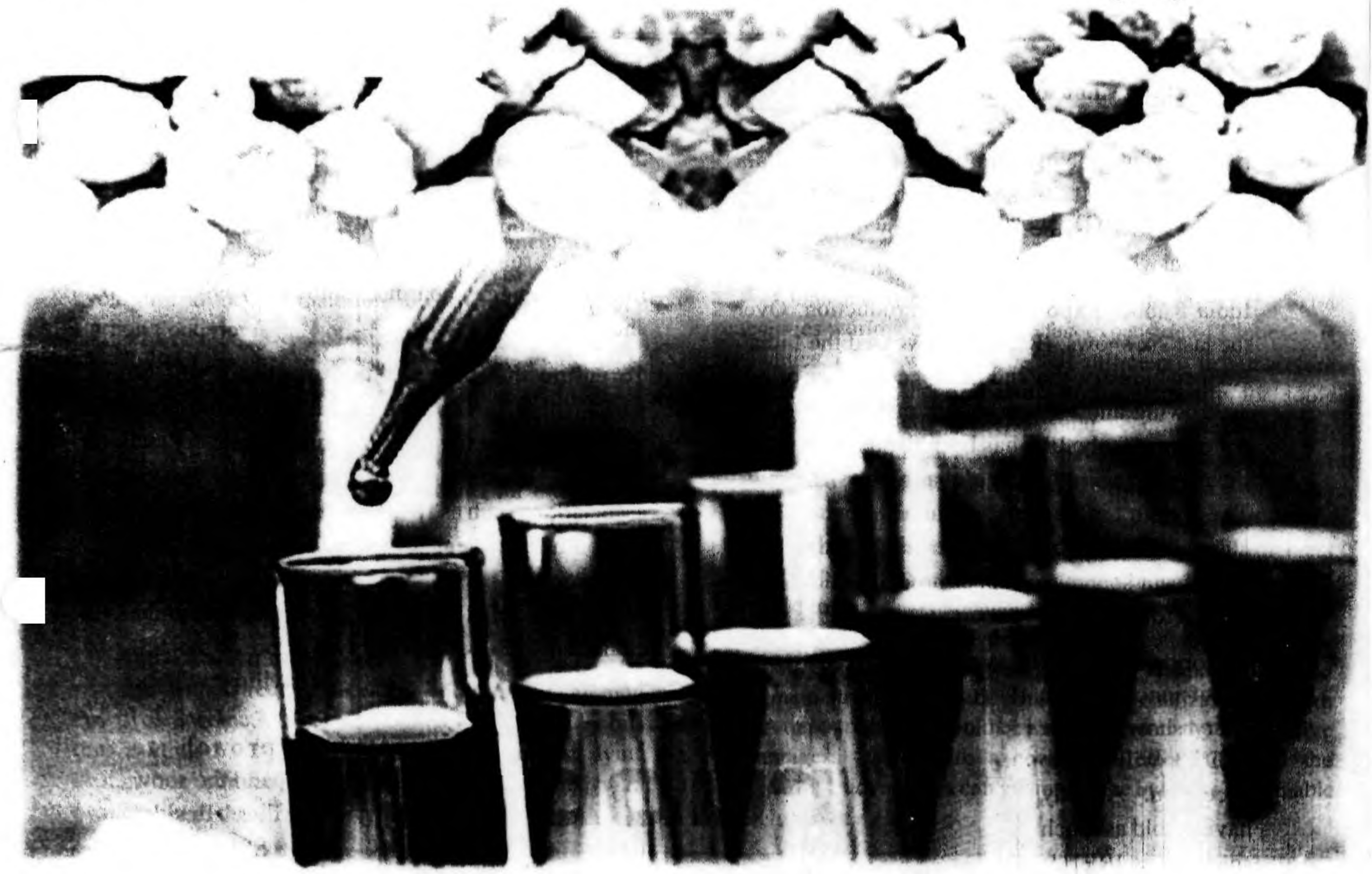
177 George, B



Scorch control in peroxide vulcanisation using a stable free radical

Benny George and Rosamma Ale
Rubber Technology Divisio
Rubber Research Institute of India, Kottyam, Kerala 686 009, Indi

Introduction

Peroxide vulcanisation of rubbers offers various advantages over sulphur vulcanisation like rapid vulcanisation withou reversion at higher temperatures, good compression set, excellent heat ageing properties, possibility to co-vulcanise saturated an unsaturated rubber blends etc. These are attributed to the C-C crosss-links formed during peroxide vulcanisation, which have th same bond strength as the C-C bonds in the polymer back bone. As per the generally accepted mechanism, peroxide vulcanisatio is initiated by the thermal decomposition of organic peroxides to highly reactive free radicals which then abstract hydrogen atom from the elastomer, yielding rubber macroradicals.

These macroradicals combine to form the cross-links. One outstanding problem that restricts the wider industrial use of peroxid vulcanisation is the low scorch safety. If scorch control can be significantly improved, the range of industrial application o peroxide vulcanisation can be broadened. Earlier work to use radical scavengers/co-agent combination to introduce scorc control has not succeeded in bringing about scorch to a level equivalent to sulphur/accelerator combination[1,2,3].

The present paper addresses it and shows that stable nitroxyl free radical, 2,2,6,6-tetramethylpiperidine-1-oxyl(TEMPO), used i bringing about living free radical polymerisation, can control scorch in peroxide vulcanisation in a way similar to the sulphu accelerator system. Use of TEMPO has led to the reduction in cross link density due to the reaction of it with the macro fre radicals generated. A recent US patent described a method to overcome this by modifying the TEMPO[4]*. The present paper show that the reduction in cross-link density can be very well compensated using appropriate coagents.*

Experimental

The EPDM used was keltan 512. Dicumyl peroxide was 40% active and the stable free radical used was TEMPO obtained from Sigma Aldrich, India.

Master batch of EPDM containing 50 phr HAF black, 5 phr paraffinic oil and 1.5 phr TDQ was prepared in an Intermix at 60°C and 70 rpm for 6 minutes. Compounds were prepared by mixing 6 phr DCP(40% active) and TEMPO in the range of 0-1.2 phr in a two-roll mill. Cure characteristics of the compounds were determined at 160,170 and 180°C using ODR R100 Monsanto Rheometer.

Results and discussion

The effect of TEMPO concentration on scorch time

The effect of TEMPO on scorch control of peroxide vulcanisation at 170°C is shown in Figure 1. The figure shows that the scorch time can be effectively controlled by TEMPO. The scorch time increases in TEMPO concentration. The cure characteristics are given in Table 1. It may be noted that the increase in scorch safety is asscociated with a proportionate decrease in MH value indication decrease in cross-link density.

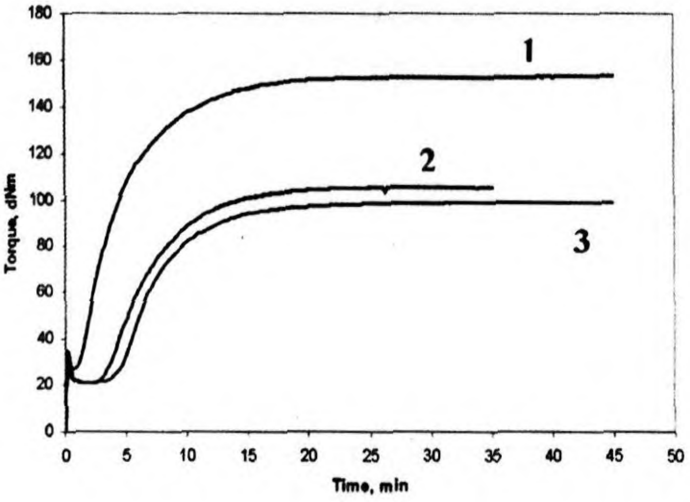


Fig. 1: Effect of TEMPO concentration on scorch time (Designations are same as in the table)

Table 1. Effect of concentration of TEMPO on cure characteristics at 170°C

No	DCP, phr	TEMPO, phr	ML, dN.m	MH, dN.m	MH-ML, dN.m	Ts_1, min	Ts_2, min	Tc_{90}, min	CRI
1	2.4	0	33.67	153.31	119.65	1.42	1.46	11.4	9.97
2	2.4	0.625	20.51	106.1	85.60	2.71	2.96	12.89	-
3	2.4	1.2	20.58	99.51	78.92	3.22	3.68	13.37	9.85

Effect of temperature on scorch time

Figure 2 shows the effect of temperature on scorch time in EPDM compounds containing TEMPO. As expected the scorch time was reduced as the cure temperature is increased at constant DCP/TEMPO ratio. Table 2 gives the cure characteristics of EPDM compound containing TEMPO at various temperatures. It may be noted that the MH-ML values remained almost same at various cure temperatures.

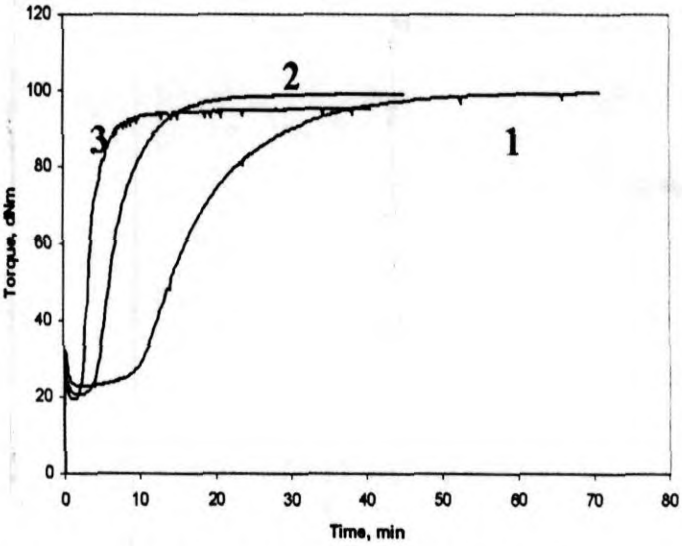


Fig. 2: Effect of cure temperature on scorch time

Table 2. Effect of temperature on scorch time (DCP 2.4 phr, TEMPO 1.2 phr)

No	Temperature, °C	ML, dN.m	MH, dN.m	MH-ML, dN.m	Ts_1, min	Ts_2, min	Tc_{90}, min	CRI
1	160	22.80	99.62	76.82	6.3	7.89	32.44	3.83
2	170	20.58	99.51	78.93	3.22	3.68	13.37	9.85
3	180	19.40	95.44	76.04	1.86	2.03	6.38	22.13

Effect of coagents

Figure 3 shows the effect of various coagents on the scorch time, cure time and state of cure of EPDM compounds containing TEMPO. N, N'-m-Phenylene dimaleimide (Sartomer SR 25) and Zinc dimethacrylate (Sartomer SR 634) were used as coagents. As can be observed from Table 3, the maleimide coagent can very well compensate the reduction in cross-link density caused by the reactions involving TEMPO without significantly affecting the scorch time.

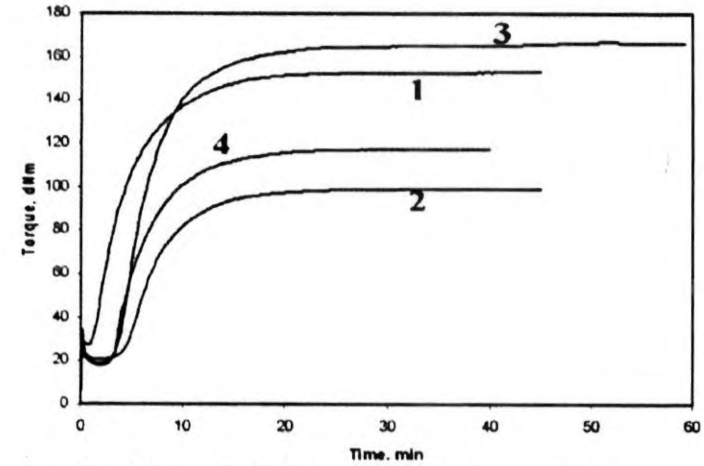


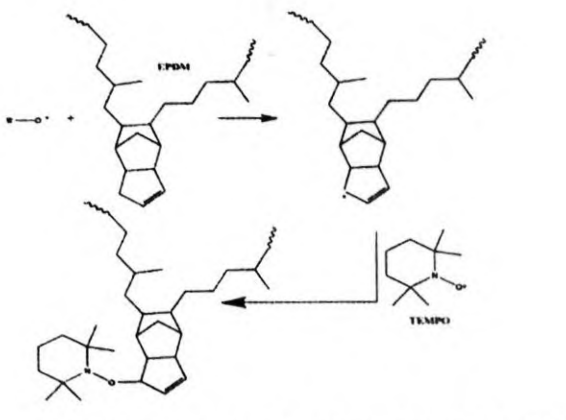
Fig. 3: Effect of TEMPO/coagent combination on scorch time

Table 3. Effect of coagents on cure characteristics (DCP 2.4 phr, TEMPO 1.2 phr, Temperature 170⁰C)

No	SR25, phr	SR 634, phr	ML	MH	MH-ML	Ts_1, Min	Ts_2, Min	Tc_{90}, Min	CRI
1	-	-	33.67	153.31	119.65	1.42	1.46	11.4	9.97
2	-	-	20.58	99.51	78.92	3.22	3.68	13.37	9.85
3	4	-	18.76	166.73	147.97	2.58	2.86	12.67	9.91
4	-	10	18.02	117.32	99.30	2.76	2.97	12.16	10.64

Mechanism of scorch control

TEMPO is a stable nitroxyl free radical. The stability of it arises from the strong stabilisation energy (32 kcal/mol) of the unpaired electron shared between the two hetero atoms[5]. The nitroxyl free radical is stable towards other nitroxyl and oxygen free radilcals like the cumyloxy radical formed by the thermal dissociation of DCP. But it readily reacts with carbon centred free radicals generated by the abstraction/addition reactions of cumyloxy radicals during vulcanisation.This prevents the formation of cross-links during the initial stages of vulcanisation until TEMPO radicals are consumed (Scheme 1).



Scheme 1: Mechanism of scorch control by TEMPO

Scorch control in polydiene rubbers

Table shows the capability of the stable free radical in controlling scorch in peroxide vulcanisation of natural rubber. As expected the addition of TEMPO reduced the MH value. The loss of cross-link density could be regained by the addition of suitable coagent.

Table 4. Effect of TEMPO in scorch control in natural rubber (Cure temperature 170⁰C)

	CRI	MH	ML	MH-ML	TC_{100}	TC_{90}	Ts_1	Ts_2
DCP (2 phr)	5.12	91.68	14.05	77.63	55.38	21.24	1.72	1.87
DCP/ TEMPO (2/1 phr)	2.49	59.48	8.06	51.42	84.93	42.69	2.48	2.79
DCP/ TEMPO/ SR25 (2/1/4 phr)	7.02	75.53	7.20	68.30	80.33	16.8	2.58	2.95

Conclusion

The capability of nitroxide free radical to selectively react with carbon centred free radical generated is utilised to induce scorch control in peroxide vulcanisation of EPDM. Scorch time could be controlled in a way similar to sulphur/accelerator combination. The scorch time depends on the concentration of the stable free radical at a fixed peroxide level. The loss of cross-link density due the reaction of the TEMPO free radical with the rubber free radical generated could be compensated with N, N'-m-Phenylene dimaleimide coagent.

References

1. D.J Elliot in "Developments in Rubber technology-1: Improving Product Performance", A. Wheelan and K.S. Lee Ed., Applied Science Publishers Ltd., London, 1979.
2. F. Debaud, L. Keromnes, A. Defrancisci, J.M. Brennan and L.H. Palys, Rubber World, 236 (3), 32 (2007).
3. M.M.A Grima, A.G. Talma, R.N. Datta and J.W.M. Noordermeer, Rubber Chemistry and Technology, 79, 694 (2006).
4. M. Esseghir, B.I. Chaudhary, J.M. Cogen, J. Klier, J. Jow, R.F.Eaton and S.M. Guerra, US 2009/0069469.
5. L.B. Volodarsky, V.A. Reznikov and V.I. Ovcharenko,"Synthetic Chemistry of Stable Nitroxides", CRC press, Florida, 1994.