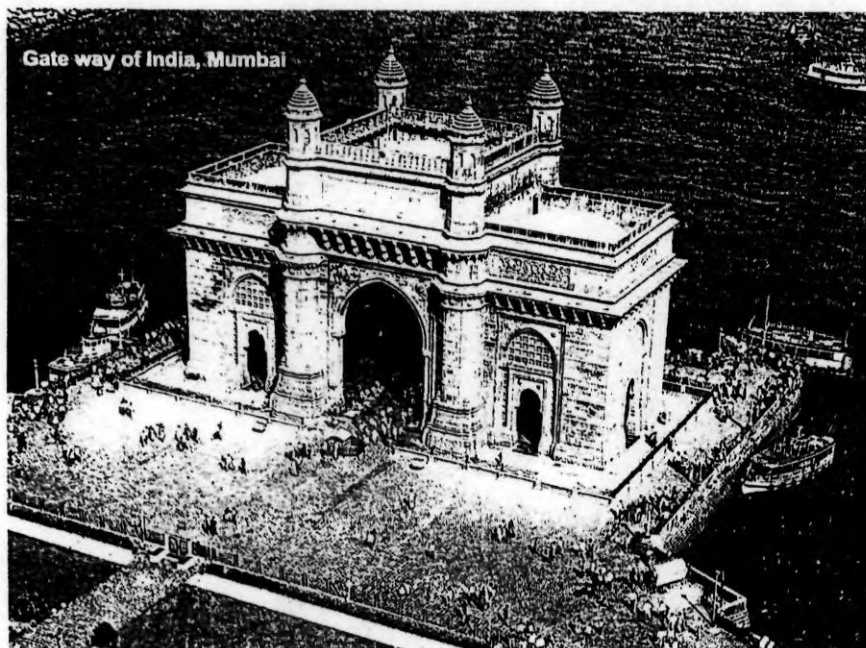


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Delayed action peroxide vulcanisation of EPDM

(EA-046)

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Introduction

Peroxide vulcanisation of rubbers offers various advantages over sulphur vulcanisation like rapid vulcanisation without reversion at higher temperatures, good compression set, excellent heat ageing properties, possibility to co-vulcanise saturated and unsaturated rubber blends etc. These are attributed to the C-C cross-links formed during peroxide vulcanisation, which have the same bond strength as the C-C bonds in the polymer back bone. As per the generally accepted mechanism, peroxide vulcanisation is initiated by the thermal decomposition of organic peroxides to highly reactive free radicals which then abstract hydrogen atoms from the elastomer, yielding rubber macroradicals. These macroradicals combine to form the cross-links. One outstanding problem that restricts the wider industrial use of peroxide vulcanisation is the low scorch safety. If scorch control can be significantly improved, the range of industrial application of peroxide vulcanisation can be broadened. Earlier work to use radical scavengers/co-agent combination to introduce scorch 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 in bringing about living free radical polymerisation, can control scorch in peroxide vulcanisation in a way similar to the sulphur/ accelerator system. Use of TEMPO has led to the reduction in cross link density due to the reaction of it with the macro free radicals generated. A recent US patent described a method to overcome this by modifying the TEMPO⁴. The present paper shows 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 60⁰C 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 180⁰C 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 with increase in TEMPO concentration. The cure characteristics are given in Table 1. It may be noted that the increase in scorch safety is associated with a proportionate decrease in MH value indicating decrease in cross-link density.

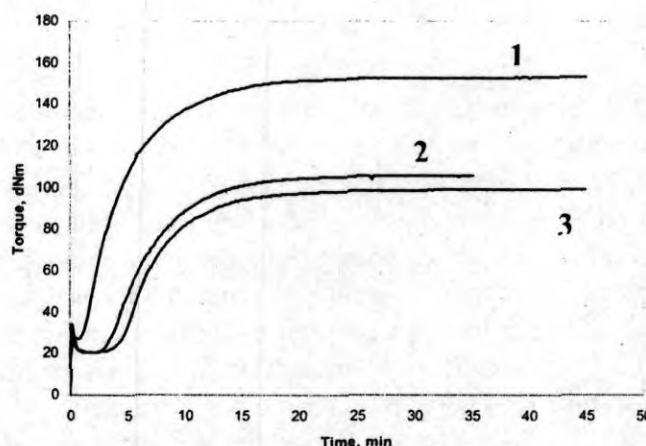


Fig.1 : Effect of TEMPO concentration on scorch time
(Designations are same as in the table)

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.

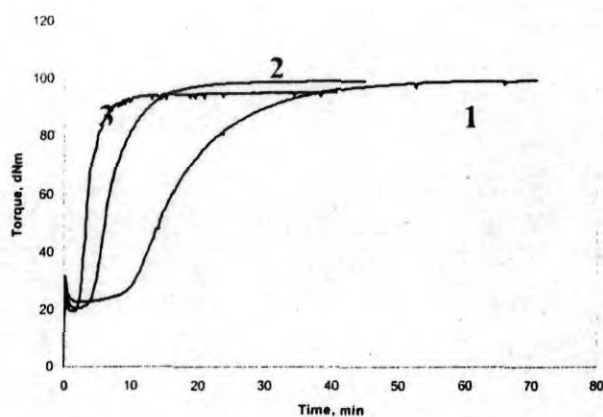


Fig. 2 : Effect of cure temperature on scorch time

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.

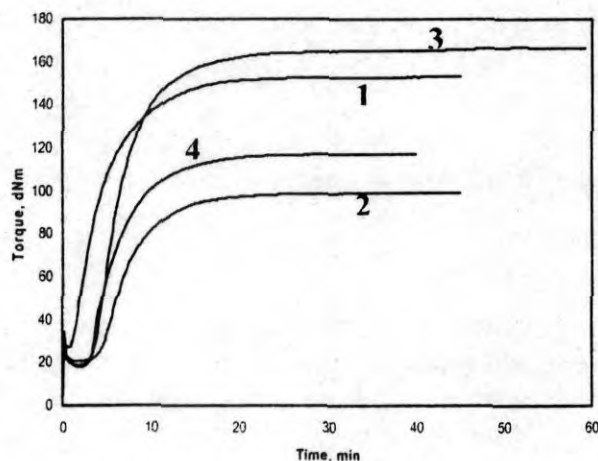


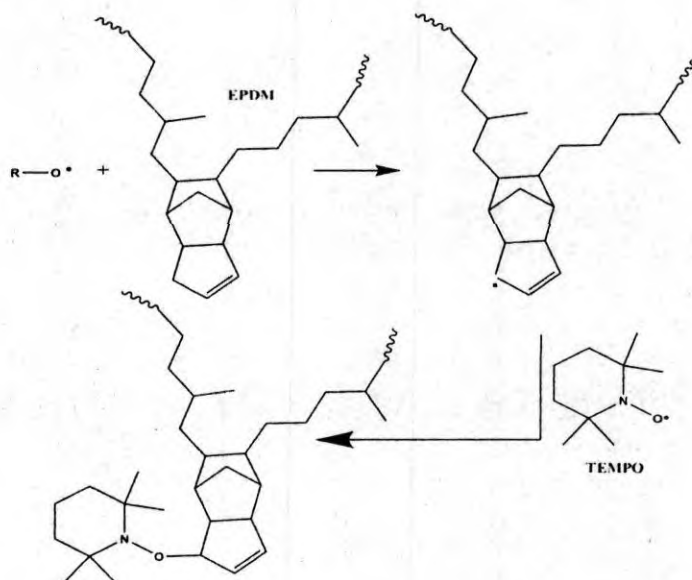
Fig.3 : Effect of TEMPO/coagent combination on scorch time

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	T _{S1} , Min.	T _{S2} , Min.	T _{C90} , 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 atoms⁵. The nitroxyl free radical is stable towards other nitroxyl and oxygen free radicals 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

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.

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