Non-regulated Accelerator (DCBS/DBBS) Incorporated Natural Rubber Formulations - Cure Characteristics and Mechanical Properties

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***Abstract*- The vulcanizates prepared using non-regulated nitrosamine generating accelerators are reported as non-carcinogenic. Efficient vulcanization system containing non-regulated single accelerator (either N, N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) or N,N-dibenzyl-2-benzothiazolesulfenamide (DBBS)) was used for the preparation of safe natural rubber vulcanizates. Safe vulcanizates were also prepared using the sulfenamide accelerator (DCBS or DBBS) in binary combination with safe tetrabenzyl thiuramdisulfide (TBzTD). Comparative study based on cure characteristics and mechanical property evaluation proved that binary accelerator based vulcanizates are the best choice. Fluid resistance in oil and cytotoxicity of the binary accelerator based vulcanizates were assessed.**

***Keywords*-Non-regulated accelerator, Efficient vulcanization, Cure characteristics, Binary accelerator, Cytotoxicity**

I. INTRODUCTION

Most of the conventional accelerators used in rubber formulations are regulated nitrosamine generating chemicals and are carcinogenic [1-3]. Nitrosamines are formed by the reaction between secondary amines and nitrosating agents [4] as shown in the equation:

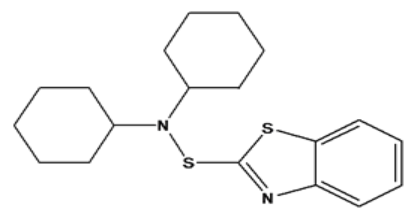
$$R_2NH + N_2O_3 \rightarrow R_2N.NO + HNO_2$$

The secondary amines are formed by the decomposition of many rubber accelerators, and thus can be present in vulcanized rubber articles [5].

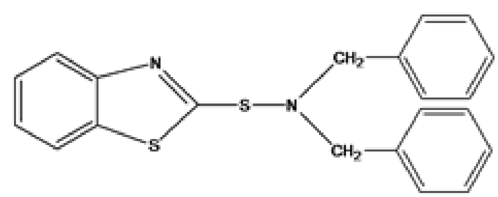
The International Agency for Research on Cancer (IARC) classifies nitrosamines as Group 2A (probably carcinogenic to humans) and Group 2B (possibly carcinogenic to humans) [6].

Certain secondary amines, because of their specific structure will produce safe or non-regulated nitrosamines.

DCBS is reported as non-carcinogenic accelerator [7, 8]. DBBS is also believed as a safe accelerator as it is an accelerator based on sterically hindered amines [9, 10]. Chemical structures of DCBS and DBBS are shown below:



Chemical structure of DCBS



Chemical structure of DBBS

Single accelerator systems are the most widely studied because of the widespread use and simplicity of their cure mechanism. Binary accelerator formulations involve the use of two different accelerators in the system, often leading to improved properties. Binary accelerator based cure system is generally used in rubber formulations for improving the cure rate and for getting better reversion resistance [11, 12].

The natural rubber formulations based on safe single accelerator (either DCBS or DBBS) and their combination with the non-regulated TBzTD have been used for the studies presented in this paper.

II. EXPERIMENTAL

A. Materials

Natural rubber (ISNR-5) used in this study was obtained from the Rubber Research Institute of India (Kottayam, Kerala, India). The antioxidant used N-(1,3-Dimethyl butyl)-N'-phenyl-p-phenylene diamine i.e. 6PPD, the accelerators DCBS, DBBS, and TBzTD were supplied by Merchem Ltd, Kochi, Kerala. Zinc oxide, stearic acid and sulphur were supplied from Associated Rubber Chemicals, Kochi.

B. Compounding and Testing

Table 1 shows the composition of the various mixes prepared. Minimum dosage of the single accelerator required in the EV system in the case of DCBS and DBBS were used in the formulations D_1 and D_6 and the corresponding maximum dosage of the accelerators were used in the formulations D_2 and D_7. The binary combinations of these accelerators with a fixed dosage of TBzTD (2.2 phr) were used in formulations D_3, D_4, D_5, D_8, D_9 and D_{10}.

TABLE I

FORMULATIONS OF THE MIXES CONTAINING DCBS / DBBS

Ingredients	**D_1**	**D_2**	**D_3**	**D_4**	**D_5**	**D_6**	**D_7**	**D_8**	**D_9**	**D_{10}**
NR (g)	100	100	100	100	100	100	100	100	100	100
ZnO (phr)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid (phr)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
6PPD (phr)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
DCBS (phr)	3.0	6.0	1.0	1.5	2.0	-	-	-	-	-
DBBS (phr)	-	-	-	-	-	3.0	6.0	1.0	1.5	2.0
TBzTD (phr)	-	-	2.2	2.2	2.2	-	-	2.2	2.2	2.2
Sulphur (phr)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

The compounding of NR was done on a two roll open mill as per ASTM D 3184. The rheographs of the mixes and their cure characteristics were obtained using Rubber Processing Analyser as per ASTM D 5289. The test specimens were prepared by molding in an electrically heated hydraulic press at 150 °C. Tensile strength and tear strength were measured according to ASTM D 412 and ASTM D 624 respectively using a Shimadzu Universal Testing Machine, model-AG-1 series at a cross head speed of 500 mm/min. The ageing of the samples were done in a hot air oven at 70 °C and 100 °C for 24 hours according to ASTM D 572. The hardness (Shore A) of the samples was determined using Mitutoyo hardmatic hardness tester according to ASTM D 2240. Compression set at constant strain was measured according to ASTM D 395. Rebound resilience was determined by vertical rebound method according to ASTM D 2632. The crosslink densities of the vulcanizates were determined using equilibrium swelling data [13 -17]. The fluid resistance of the samples were carried out in diesel and lube oil according to the ASTM D 471. Cytotoxicity of the material was measured from the percentage viability of the cells by using the method of MTT (3-(4,5 dimethylthiazol-2-yl)-2,5-diphenyltetrazoliumbromide) assay and the test procedure is based on ISO 10993-5 [18, 19]. The MTT enters the cells and passes into the mitochondria where it is reduced to an insoluble, coloured (dark purple) formazan product. The cells are then solubilised with an organic solvent (dimethyl sulfoxide DMSO (Himedia)) and the released, solubilised formazan product was measured at 540 nm. Since reduction of MTT can only occur in metabolically active cells the level of activity is a measure of the viability of the cells. Optical density was read at 540 nm using DMSO as blank in a microplate reader (ELISASCAN, ERBA). Control samples are the cells (L929 cells) to which polymer solution is not added.

$$\%\ \text{viability} = \frac{\text{Optical density of test specimen}}{\text{Optical density of control sample}} \times 100$$

III. RESULTS AND DISCUSSION

A. Cure characteristics

The cure characteristics of the mixes containing DCBS or DBBS as single accelerator are shown in the Table 2. From the cure characteristics, it is observed that the optimum cure time required for the single accelerator systems are very high and they are not suitable for applications. However the binary accelerator systems show better cure characteristics.

TABLE II

OPTIMUM CURE TIME AND SCORCH TIME OF THE MIXES CONTAINING SINGLE ACCELERATOR AT 150 °C

Properties	**D_1**	**D_2**	**D_6**	**D_7**
Scorch time t_{10} (min)	9.93	11.57	12.95	21.07
Optimum cure time t_{90} (min)	52.37	85.74	40.82	57.53
Cure Rate Index (CRI, min^{-1})	2.36	1.35	3.59	2.74

When DCBS and DBBS are used in single accelerator system, long scorch time was observed. As the dosage of DCBS or DBBS increased the optimum cure time increased and therefore cure rate index decreased. It has been reported that the compounds prepared using DCBS show high scorch safety and low cure rate index [20, 21]. The results of the present investigations show that DBBS too show similar trend.

When TBzTD is added as the binary accelerator (Table 3), scorch time decreased considerably indicating faster cure initiation. The cure rate index (CRI), which is a measure of the rate of vulcanization process, increases significantly with the addition of TBzTD.

The rheographs of DCBS and DBBS in binary combination with TBzTD are shown in Fig. 1. Addition of the TBzTD reduced the scorch delay and optimum cure time. However as the dosage of sulfenamide increased the scorch time increased and rate of cure decreased [20, 21].

TABLE III

CURE CHARACTERISTICS OF THE MIXES CONTAINING BINARY ACCELERATOR AT 150 °C

Properties	**D_3**	**D_4**	**D_5**	**D_8**	**D_9**	**D_{10}**
Scorch time t_{10} (min)	2.77	2.98	3.07	2.90	3.36	3.74
Optimum cure time t_{90} (min)	10.97	12.32	13.47	9.65	10.83	12.99
Cure Rate Index (CRI, min^{-1})	12.19	10.71	9.62	14.80	13.39	10.81

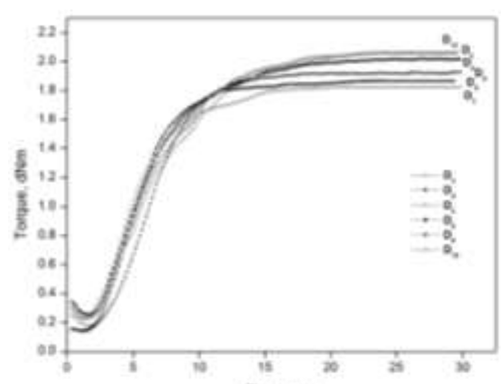


Fig. 1 Cure curves of the compounds containing binary accelerators

The kinetics of vulcanization was studied from rheographs by the method given below [22-25]. The general equation for the kinetics of a first order chemical reaction is:

$$\ln (a - x) = -kt + \ln a \qquad (1)$$

where, a is the initial reactant concentration, x is reacted quantity of reactant at time t, and k is first order rate constant.

For the vulcanization of rubber, the rate of crosslink formation is monitored by measuring the torque developed during vulcanization. The torque obtained is proportional to the modulus of rubber. Since modulus and torque are analogous, the following substitutions can be made.

$$a - x = M_H - M_t \qquad (2)$$

$$a = M_H - M_L \qquad (3)$$

M_H and M_L are the maximum and minimum torques, and M_t, the torque at time t. So the equation becomes:

$$\ln (M_H - M_t) = -kt + \ln (M_H - M_L) \qquad (4)$$

When $\ln (M_H - M_t)$ is plotted against time t, a straight line graph is obtained as shown in the Fig. 2.

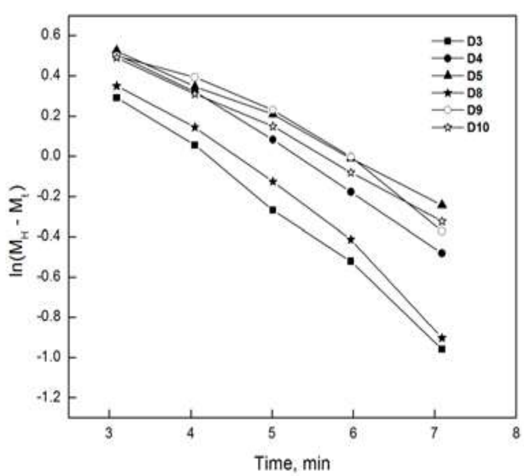


Fig. 2 Plot of $\ln(M_H - M_t)$ vs. time of NR compounds containing binary accelerators

Even though linearity is claimed for the plots theoretically, minor deviations from linearity are experimentally observed for certain points. The observed linearity in the plots confirm that the cure reaction of the samples follow first order kinetics. Regardless of concentration of DCBS and DBBS, all vulcanization reactions proceed according to first order kinetics.

B. Mechanical properties of NR vulcanizates prepared using DCBS/DBBS

The stress-strain curves of the vulcanizates prepared using DCBS or DBBS are given in Fig. 3 and Fig. 4.

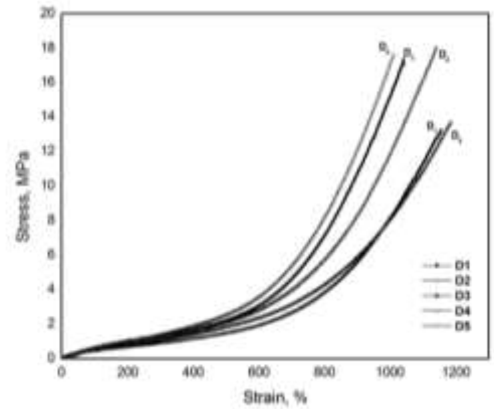


Fig. 3 Stress-strain curves of the NR vulcanizates containing DCBS

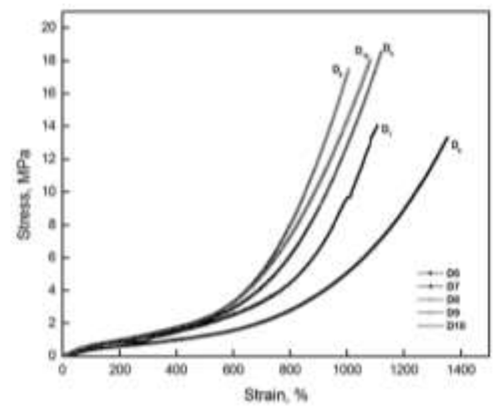


Fig. 4 Stress-strain curves of the NR vulcanizates containing DBBS

The mechanical properties of the vulcanizates containing DCBS and DBBS are given in Table 4 and Table 5. The tensile strength values are higher for the TBzTD containing binary accelerator based vulcanizates as compared to the single accelerator based vulcanizates. It was reported that binary accelerator systems enhance the efficiency of sulphur intake during crosslinking, which in turn improves the mechanical, chemical and service properties of finished rubber goods [12]. It is found that as the concentration of DCBS or DBBS increases, the modulus values also increase for both the single and binary accelerator systems. As compared to the vulcanizates prepared using single accelerator, the vulcanizates prepared by incorporating the binary accelerators show high moduli.

Tensile strength and the tear strength of the vulcanizates increased when the concentration of DCBS or DBBS increased and is observed for both single and binary accelerator systems. Of all the combinations, comparatively high tensile strength is observed for the vulcanizate containing 1.5 phr of DCBS/DBBS and 2.2 phr of TBzTD. This could be correlated with the observed crosslink density of the vulcanizates.

The hardness of the single accelerator based vulcanizates increased when the concentration of DCBS/DBBS changes from 3 phr to 6 phr and the vulcanizates based on the binary accelerators show more hardness.

The values of compression set are lower for the vulcanizates containing DCBS/DBBS and TBzTD as compared to the single accelerator based vulcanizates. For optimum performance in service, compression set values should be as low as possible. Low set values mean that the material has recovered nearly to its original height, and there is very little residual deformation [26, 27]. Rebound resilience values are comparable for both single and binary accelerator based vulcanizates. Under impulsive loading conditions the deformation of a viscoelastic matrix is more elastic and hence the systems show better resilience [28].

TABLE IV

PROPERTIES OF THE RUBBER VULCANIZATES CONTAINING DCBS

Properties	D_1	D_2	D_3	D_4	D_5
Tensile strength (MPa)	13.22	13.40	17.38	18.05	17.63
Modulus at 300 % elongation (MPa)	0.89	1.06	1.12	1.16	1.19
Elongation at break (%)	1156	1186	1043	1140	1012
Tear strength (N/mm)	20.37	22.96	26.34	26.86	26.63
Hardness (Shore A)	25	27	31	31	32
Compression set (%)	17.65	17.52	15.41	15.23	15.74
Rebound resilience (%)	66	65	65	66	66
Crosslink density x10^5 (mol/g rubber hydrocarbon)	2.80	3.20	3.39	3.84	3.67
Swelling index	4.89	4.64	4.35	4.07	4.08

TABLE V

PROPERTIES OF THE RUBBER VULCANIZATES CONTAINING DBBS

Properties	D_6	D_7	D_8	D_9	D_{10}
Tensile strength (MPa)	13.32	14.05	17.48	18.55	18.13
Modulus at 300 % elongation (MPa)	0.78	0.99	1.21	1.24	1.26
Elongation at break (%)	1354	1013	1006	1122	1082
Tear strength (N/mm)	20.05	20.81	28.15	28.22	28.18
Hardness (Shore A)	24	26	32	33	33
Compression set (%)	18.58	17.47	15.68	15.26	15.37
Rebound resilience (%)	65	66	65	66	66
Crosslink density x10^5 (mol/g rubber hydrocarbon)	2.55	2.67	3.63	4.01	3.97
Swelling index	4.98	4.94	4.24	3.92	4.04

Crosslink density of the vulcanizate increases when the dosage of DCBS or DBBS changed from 3 to 6 phr. The crosslink density improved by the addition of TBzTD and shows highest value at a dosage of 1.5 phr DCBS/DBBS in the binary system. The tensile strength and tear strength values are in accordance with the crosslink density.

The thermal ageing of the samples was carried out at 70 °C and 100 °C for 24 hours. The tensile strength values registered a slight increase after thermal ageing at 70 °C for all the samples. The slight increase in tensile strength may be due to the formation of additional crosslinking. This is possible since the samples were cured for optimum cure time, which results in formation of only 90 % of the total crosslinks [29]. Moreover as the efficient crosslinking system is selected, majority of the crosslinks are mono and disulphidic. These crosslinks are thermally stable [30, 31]. The resistance of the vulcanizates to thermo-oxidative ageing are shown in Fig. 5 and Fig. 6.

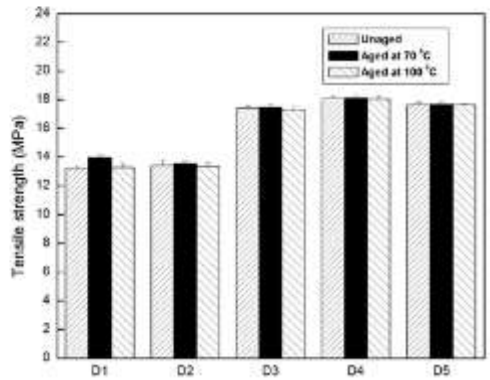


Fig. 5 Variation in tensile strength before and after ageing of the NR vulcanizates containing DCBS

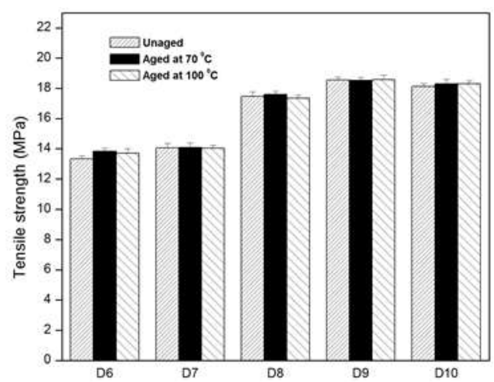


Fig. 6 Variation in tensile strength before and after ageing of the NR vulcanizates containing DBBS

The vulcanizates prepared using DCBS aged at 100 °C do not show considerable variation in tensile strength from that of the unaged vulcanizates. Both the single accelerator based vulcanizates and binary accelerator based vulcanizates prepared using DCBS/DBBS maintain their mechanical properties even after thermal ageing.

C. Fluid resistance

The fluid resistance of the samples D_4 (1.5 phr DCBS and 2.2 phr TBzTD) and D_9 (1.5 phr of DBBS and 2.2 phr TBzTD) were carried out in diesel and lube oil. The percentage change in mass of the vulcanizates is shown in the Table 6.

TABLE VI

CHANGE IN MASS (%) OF THE VULCANIZATES D_4 AND D_9 IN DIESEL AND LUBE OIL

Sample	Change in mass (%)	
	Diesel	Lube oil
D_4	257	114
D_9	254	113

Comparable fluid resistance shown by both the vulcanizates after soaking in diesel and lube oil for 72 hours may be attributed to the similarity in their crosslink densities. It is also observed that the change in mass (%) of the vulcanizates is much lower for lube oil than that for the diesel oil. It may be due to the high viscosity of lube oil.

D. Cytotoxicity

Cytotoxicity of the vulcanizates was evaluated by checking the cell viability through MTT assay [18, 19]. Cell morphology of control of MTT assay and confluent cells containing extract of D_4 (NR vulcanizate containing DCBS) and D_9 (NR vulcanizate containing DBBS) determined using phase contrast image are shown in Fig. 7.

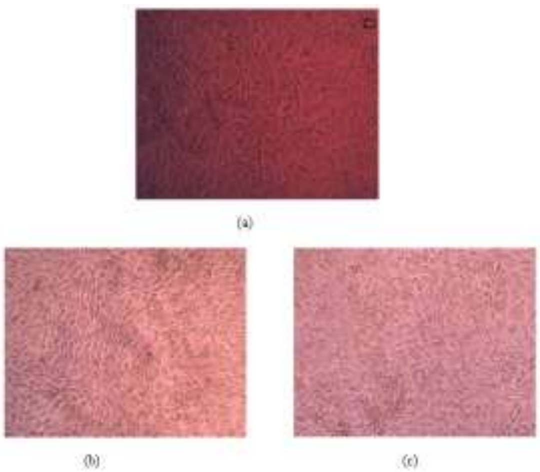


Fig.7 Phase contrast image (magnification 20 x) for the determination of cell morphology of: (a) Control of MTT assay, (b) extract of NR vulcanizate containing DCBS and (c) extract of NR vulcanizate containing DBBS

Control sample of the MTT assay shows large number of fibroblast cells. In the case of the confluent cells containing the extract of NR vulcanizates containing DCBS and DBBS after 24 hours incubation, reduction in number of viable cells were noticed.

A reduction in the number of viable cells in the case of the vulcanizates was also evident from the lower value of optical density as compared to the control cells. The samples containing extract of D_4 (NR vulcanizate conataining DCBS) and D_9 (NR vulcanizate containing DBBS) was found to possess 81.18 % and 81.02 % of viable cells. If the confluency of healthy cells is greater than 80 %, it is taken as non-cytotoxic [32, 33]. Thus the MTT assay showed that the natural rubber vulcanizates containing DCBS and DBBS are safe (non-cytotoxic).

IV. CONCLUSIONS

Natural rubber vulcanizates containing DCBS or DBBS as single accelerator system show very good scorch safety. Addition of the TBzTD to the system reduces the scorch time and optimum cure time. As the dosage of DCBS or DBBS increases the optimum cure time increases and cure rate index decreases. Kinetic studies show that the cure reaction follows first order kinetics. Addition of higher dosages of DCBS or DBBS improves the mechanical properties of the vulcanizates. The fluid resistance of the samples containing DCBS or DBBS are same after soaking in diesel and lube oil. The MTT assay results verified the non-cytotoxic nature of the vulcanizates prepared using DCBS or DBBS.

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