
NON-REGULATED ACCELERATOR (DCBS / DBBS) INCORPORATED NATURAL RUBBER VULCANIZATES

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Natural rubber vulcanizates incorporating safe sulfenamide single accelerator (N,N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) or N,N-dibenzyl-2-benzothiazolesulfenamide (DBBS)) and binary accelerators (DCBS or DBBS in combination with tetrabenzyl thiuramdisulfide (TBzTD)) were prepared as per efficient vulcanization recipe. The cure characteristics and cure kinetics of the prepared compounds were studied. Mechanical properties, fluid resistance in oil and cytotoxicity of the vulcanizates were also evaluated.

4.1 Introduction

Generally, sulfenamide type of accelerators exhibit long scorch safety. The superior scorch safety of the sulfenamides is due to the longer time required to thermally decompose to mercaptobenzothiazole (MBT) and amine [1]. N, N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS) and N, N-dibenzyl-2-benzothiazole sulfenamide (DBBS) are two accelerators that are coming under this category.

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Druckrey and co-workers [2, 3] have showed that DCBS is a safe non-carcinogenic accelerator based on their animal experiments. DBBS is also believed as a safe accelerator since it is an accelerator based on sterically hindered amines [4, 5]. These accelerators are not included in the list of regulated nitrosamine generating accelerators. Chemical structures of DCBS and DBBS are shown in Figure 4.1.

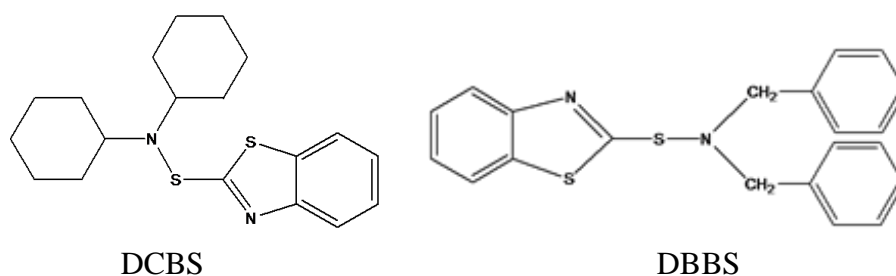


Figure 4.1 Structures of DCBS and DBBS

In compounding of rubbers binary cure systems are generally used for faster cure rate and better reversion resistance [6]. 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 [7].

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 work presented in this chapter.

4.2 Preparation of the mixes containing various dosages of DCBS / DBBS

Table 4.1 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 D₁ and D₆ and the corresponding maximum dosage of the accelerators were used in the

formulations D₂ and D₇. The binary combinations of these accelerators with a fixed dosage of TBzTD (2.2 phr) were used in formulations D₃, D₄, D₅, D₈, D₉ and D₁₀.

Table 4.1 Formulations of the mixes containing various dosages of 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

4.3 Cure characteristics

The cure characteristics of the mixes containing DCBS or DBBS as single accelerator are shown in the Table 4.2. 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 practical applications.

Table 4.2 Optimum cure time and scorch time of 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 were used in single accelerator system, long scorch time was observed. As the dosage of DCBS or DBBS was increased, the optimum cure time increased with a proportional decrement in the cure

rate index. It has been reported that the compounds prepared using DCBS showed high scorch safety and low cure rate index as the dosage increased [8, 9]. DBBS incorporated NR vulcanizates also showed a similar trend.

On the contrary, the binary accelerator systems showed better cure characteristics (Table 4.3). When TBzTD was added as the binary accelerator, scorch time decreased considerably indicating faster cure initiation. The cure rate index (CRI), which is a measure of the rate of the vulcanization process, increased significantly with the addition of TBzTD.

The rheographs of the binary systems containing DCBS or DBBS in combination with TBzTD are shown in Figure 4.2. Addition of the TBzTD reduced the scorch and optimum cure time. However in both the cases, as the dosage of sulfenamide increased the scorch time increased and rate of cure decreased [8, 9]. The vulcanizates containing DBBS showed better scorch safety and cure rate index compared to the vulcanizates containing DCBS.

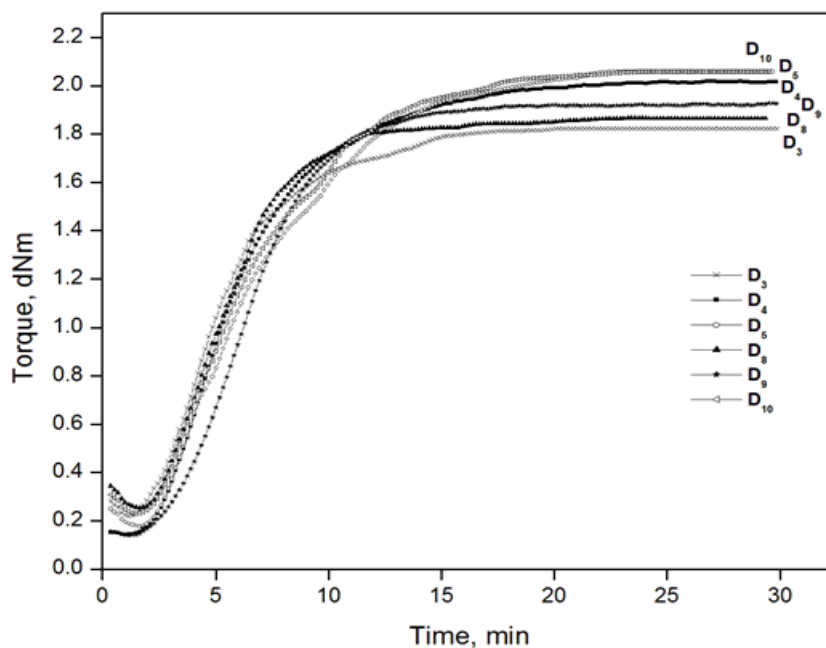


Figure 4.2 Rheographs of the mixes containing binary accelerators (DCBS/DBBS and TBzTD)

Table 4.3 Cure characteristics of the mixes 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
Maximum torque (M _H , dNm)	1.82	2.02	2.06	1.87	1.93	2.06
Minimum torque (M _L , dNm)	0.21	0.14	0.17	0.25	0.15	0.23
M _H – M _L (dNm)	1.61	1.88	1.89	1.62	1.79	1.83

ΔM (i.e. $M_H - M_L$) is considered as the parameter to demonstrate the degree of chemical crosslinking. ΔM is an indication of the chemical interaction between rubber and vulcanizing agent. It shows a marginal increase as the dosage of DCBS and DBBS increases (Table 4.3).

4.3.1 Kinetics of vulcanization

The kinetics of vulcanization was done by the method reported earlier (section 3.B.2.1). For the vulcanization reaction of NR, the rate of crosslink formation is usually monitored by measuring the torque developed during vulcanization. When $\ln(M_H - M_t)$ is plotted against time t , a straight line graph is obtained as shown in the Figure 4.3. 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 proceeded according to first order kinetics.

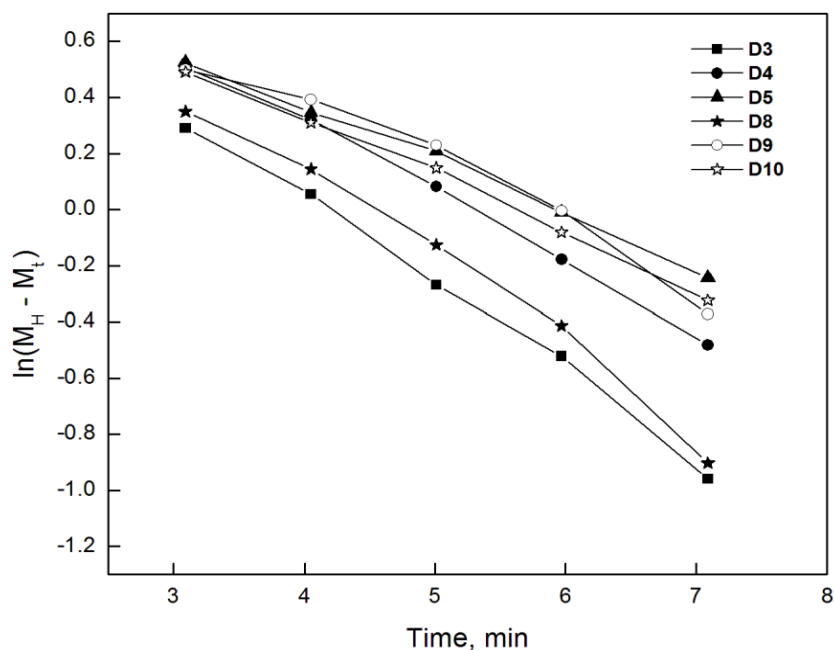


Figure 4.3 Plot of $\ln(M_H - M_t)$ vs. time of NR compounds containing binary accelerators (DCBS/DBBS and TBzTD)

4.4 Mechanical properties of the vulcanizates

4.4.1 Mechanical properties of the NR vulcanizates containing DCBS

The mechanical properties of the vulcanizates containing DCBS are given in Table 4.4. The stress-strain curves of the vulcanizates containing DCBS are given in Figure 4.4. The tensile strength values are higher for the binary accelerator based vulcanizates as compared to the single accelerator based vulcanizates. As the concentration of DCBS increased, the modulus values were found to increase for both the single and binary accelerator systems. As compared to the vulcanizates prepared using single accelerator, the vulcanizate prepared by incorporating the binary accelerators showed higher moduli.

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

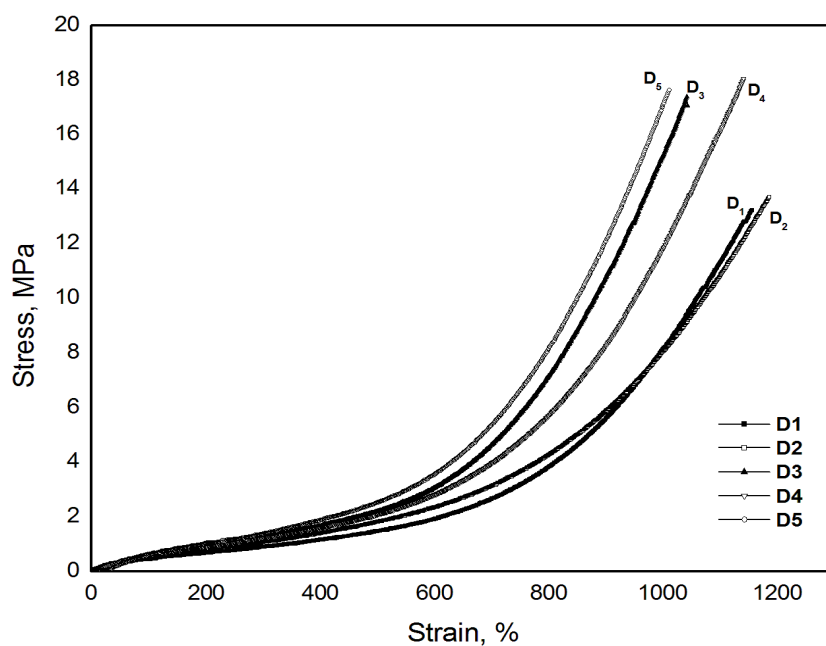


Figure 4.4 Stress-strain curves of NR vulcanizates containing DCBS

The hardness of the single accelerator based vulcanizates increased as the dosage of DCBS increased from 3 phr to 6 phr and the vulcanizates based on the binary accelerators showed more hardness.

Table 4.4 Properties of natural 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

For optimum performance in service, compression set values should be as low as possible [10, 11]. The values of compression set were lower for the vulcanizates containing DCBS and TBzTD compared to the single accelerator based vulcanizates.

Rebound resilience values were 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 [12].

The swelling ratio of the vulcanizates was evaluated in order to find the extent of crosslinking. The calculated values of the crosslink densities are given in Table 4.4. Crosslink density of the vulcanizate increased when the dosage of DCBS was increased from 3 to 6 phr. The crosslink density was further improved by the addition of TBzTD and highest value was obtained at a dosage of 1.5 phr DCBS in the binary system. The tensile

strength and tear strength values were in accordance with the crosslink density values.

Table 4.5 Stress-strain properties of the natural rubber vulcanizates containing DCBS before and after ageing

Sample	Tensile strength (MPa)			Modulus at 300 % elongation (MPa)			Elongation at break (%)		
	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C
D ₁	13.22	13.95	13.24	0.89	0.90	0.85	1156	1180	1208
D ₂	13.40	13.51	13.33	1.06	1.03	1.19	1186	1182	1100
D ₃	17.38	17.45	17.30	1.12	1.10	1.28	1043	1067	990
D ₄	18.05	18.10	18.02	1.16	1.23	1.27	1140	1060	1038
D ₅	17.63	17.66	17.62	1.19	1.37	1.66	1012	970	917

The thermal ageing of the samples was carried out at 70 °C and 100 °C for 24 hours. The stress-strain properties of the vulcanizates are shown in Table 4.5. 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 [13]. Moreover in an efficient vulcanization system, majority of the crosslinks are mono and di sulphidic. These crosslinks are thermally stable [14, 15]. The resistance of the vulcanizates to thermo-oxidative ageing is evident from the Figures 4.5, 4.6 and 4.7.

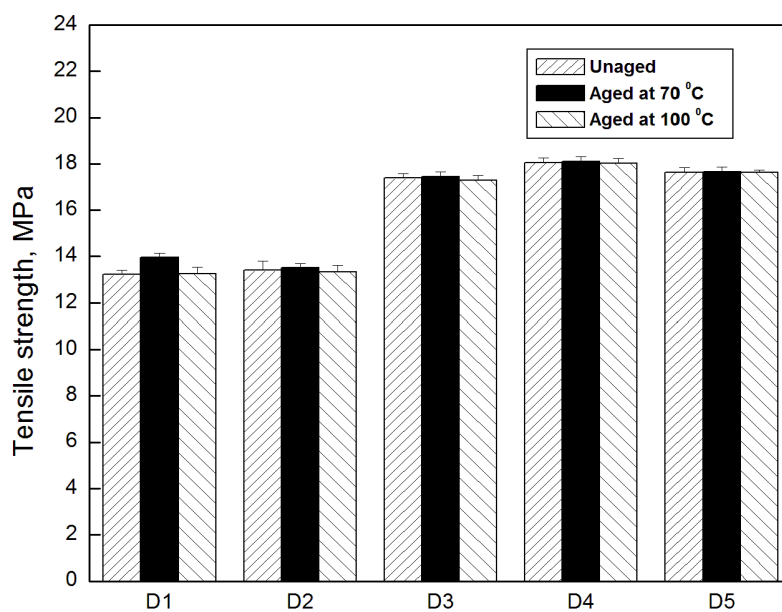


Figure 4.5 Variation in tensile strength of the NR vulcanizates containing DCBS before and after ageing

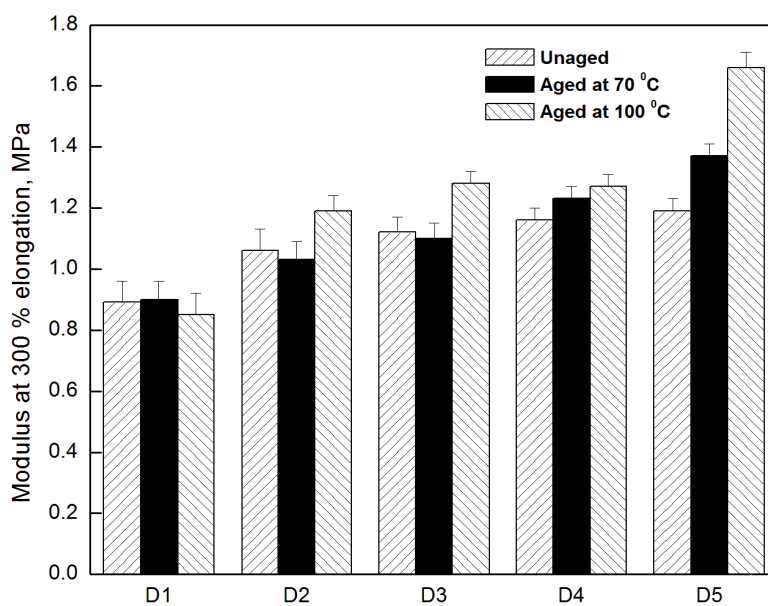


Figure 4.6 Variation in modulus at 300 % elongation of the NR vulcanizates containing DCBS before and after ageing

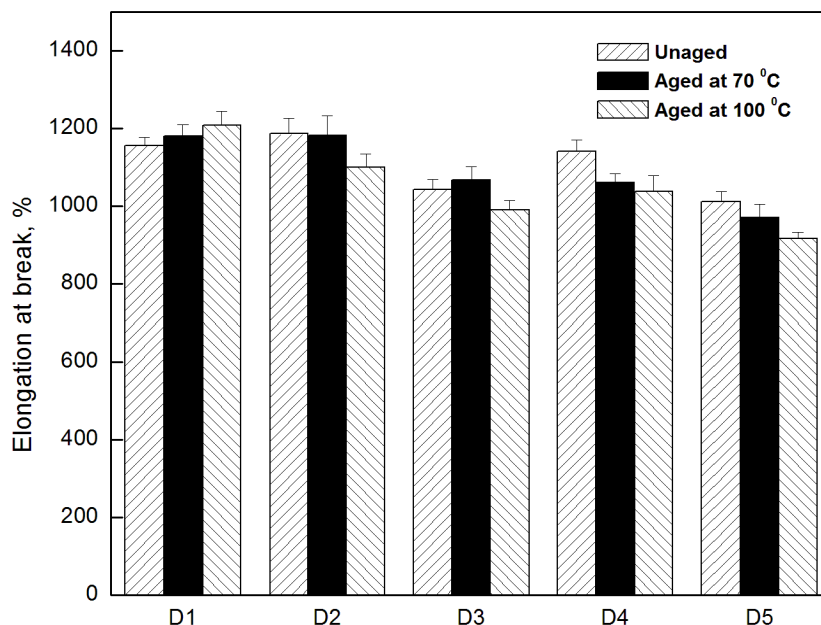


Figure 4.7 Variation in elongation at break of the NR vulcanizates containing DCBS before and after ageing

The vulcanizates 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 maintained their mechanical properties even after thermal ageing.

4.4.2 Mechanical properties of the NR vulcanizates containing DBBS

Stress-strain curves of the vulcanizates containing DBBS are shown in Figure 4.8. The binary accelerator based vulcanizates showed better mechanical properties compared to the single accelerator based vulcanizates (Table 4.6). Highest tensile strength was obtained in the case of the vulcanizate containing 1.5 phr of DBBS and 2.2 phr of TBzTD.

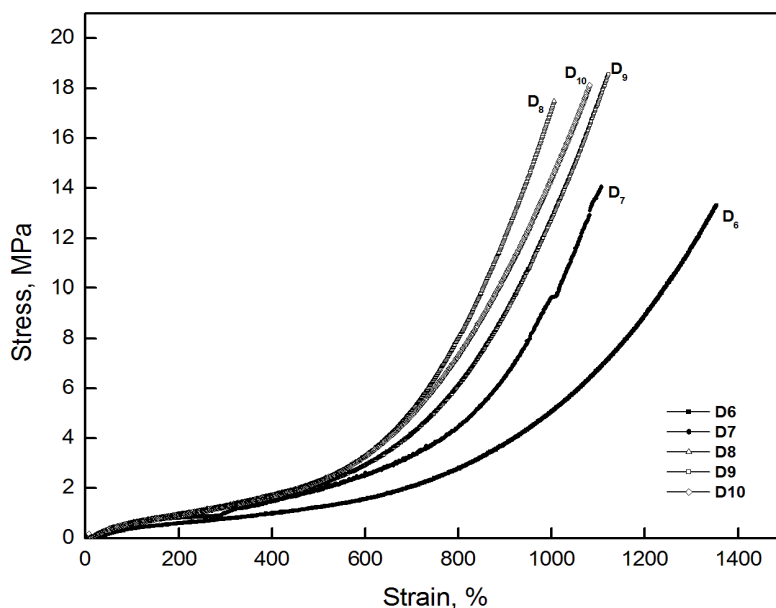


Figure 4.8 Stress-strain curves of NR vulcanizates containing DBBS

Compression set was lowered by the addition of TBzTD and the lowest value was obtained for the vulcanizate containing 1.5 phr of DBBS and 2.2 phr of TBzTD.

Table 4.6 Properties of NR 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 $\times 10^5$ (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

The vulcanizates with the single accelerator, DBBS retained the same rebound resilience even after the introduction of TBzTD indicating that this property is not adversely affected by the addition of TBzTD. The crosslink densities of the vulcanizates determined by the equilibrium swelling measurements in toluene are shown in Table 4.6. The reduction in swelling index with the addition of TBzTD indicates an increase in crosslink density of the vulcanizates. This increase in crosslink density has in turn increased the mechanical properties such as tensile strength, modulus at 300 % elongation and tear strength of the binary accelerators (DBBS and TBzTD) incorporated system. The results showed that these properties are in accordance with the crosslink density values.

Table 4.7 Stress-strain properties of NR vulcanizates containing DBBS before and after ageing

Sample	Tensile strength (MPa)			Modulus at 300 % elongation (MPa)			Elongation at break (%)		
	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C	Un aged	70 °C	100 °C
D ₆	13.32	13.82	13.70	0.78	0.91	0.88	1354	1260	1229
D ₇	14.05	14.08	14.04	0.99	1.01	1.02	1013	1007	971
D ₈	17.48	17.59	17.35	1.21	1.26	1.55	1006	996	919
D ₉	18.55	18.53	18.57	1.24	1.31	1.43	1122	1080	987
D ₁₀	18.13	18.29	18.30	1.26	1.40	1.73	1082	1000	942

Stress-strain properties of the vulcanizates containing DBBS after ageing at 70 °C and 100 °C for 24 hours are shown in Table 4.7. Variation in tensile strength, modulus at 300 % elongation and elongation at break of the vulcanizates before and after ageing are also shown in Figures 4.9, 4.10 and 4.11. Both the single accelerator based vulcanizates and binary accelerator based vulcanizates maintained their mechanical properties even after thermal ageing.

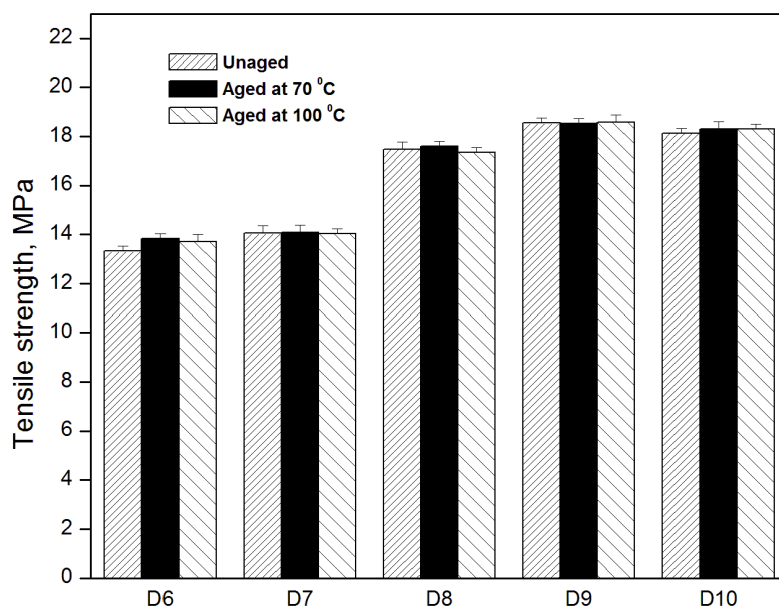


Figure 4.9 Variation in tensile strength of the NR vulcanizates containing DBBS before and after ageing

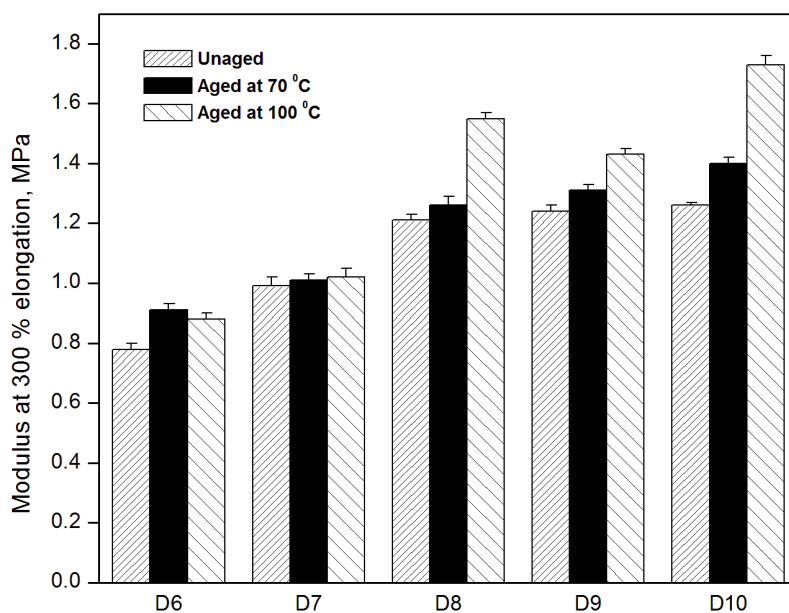


Figure 4.10 Variation in modulus at 300 % elongation of the NR vulcanizates containing DBBS before and after ageing

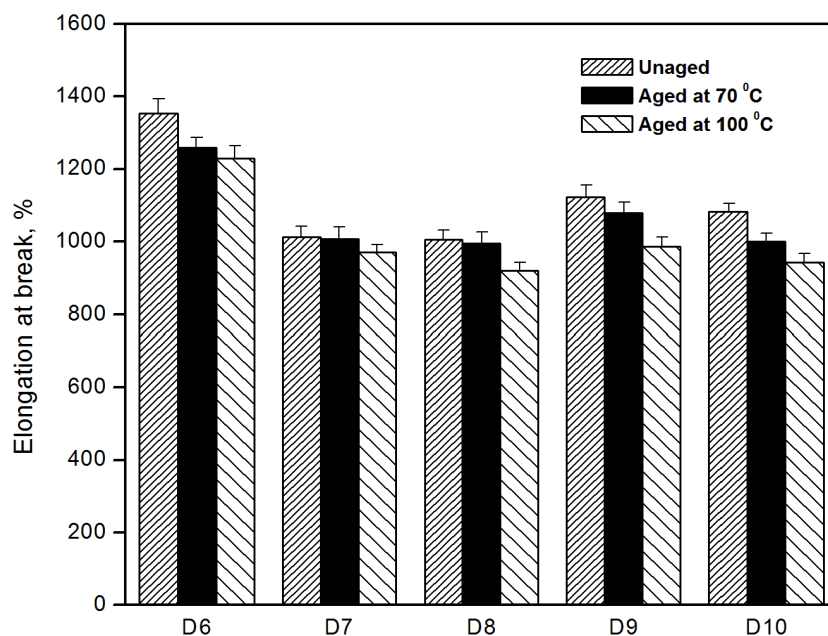


Figure 4.11 Variation in elongation at break of the NR vulcanizates containing DBBS before and after ageing

4.5 Fluid resistance

The fluid resistance of the samples D₄ (1.5 phr DCBS and 2.2 phr of TBzTD) and D₉ (1.5 phr of DBBS and 2.2 phr of TBzTD) were carried out in diesel and lube oil. The percentage change in mass of the gum vulcanizates are shown in the Table 4.8.

Table 4.8 Change in mass (%) of the vulcanizates D₄ and D₉ 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 the vulcanizates after soaking in diesel and lube oil for 72 hours may be attributed to their crosslink densities.

4.6 Cytotoxicity of the vulcanizates containing DCBS / DBBS

Cytotoxicity of the vulcanizates was evaluated by checking the cell viability through MTT assay [16]. Cell morphology of control of MTT assay and confluent cells containing extract of D₄ and D₉ were determined using phase contrast image as shown in Figure 4.12. Control sample of the MTT assay showed large number of fibroblast cells. But in the case of the confluent cells containing the extract of NR vulcanizates containing DCBS or DBBS, a considerable reduction in the number of viable cells was noticed after 24 hours incubation.

A reduction in the number of viable cells in the case of confluent cells containing the extract of vulcanizates was evident from the lower value of optical density as compared to the control cells. The samples containing extract of D₄ (NR vulcanizate containing DCBS) and D₉ (NR vulcanizate containing DBBS) was found to possess 81.18 % and 81.02 % of viable cells. Thus the results of MTT assay showed that the natural rubber vulcanizates containing DCBS and DBBS were safe (non-cytotoxic) [17, 18].

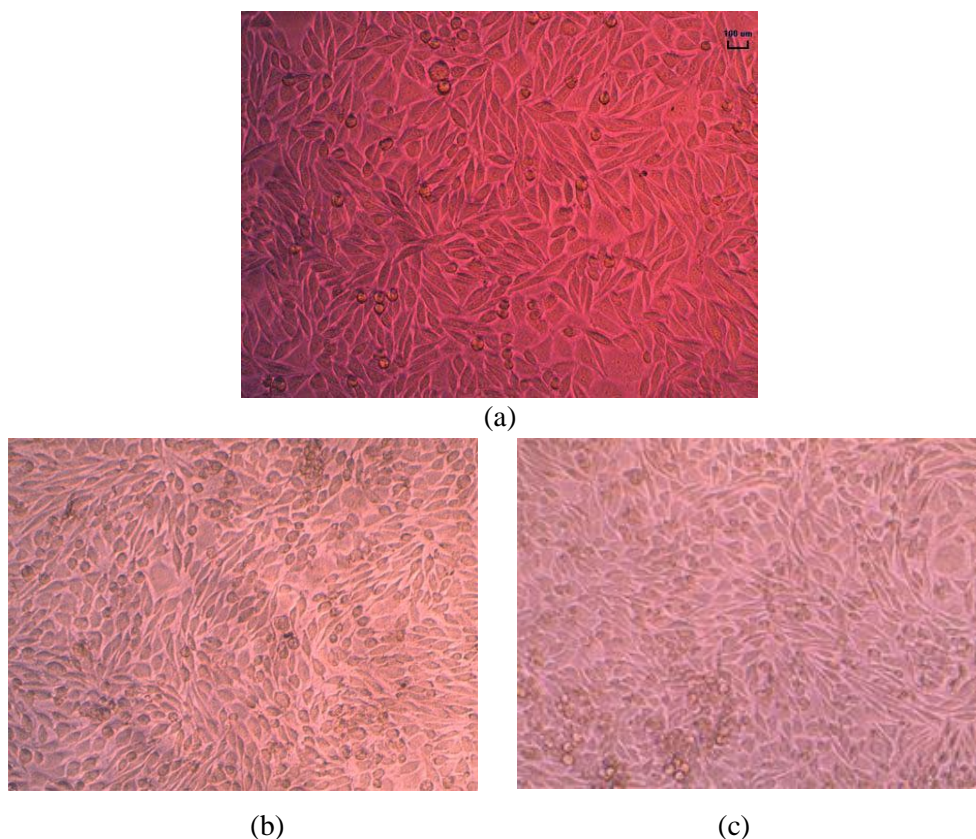


Figure 4.12 Phase contrast image (magnification 20 x) for the determination of cell morphology of: (a) control of MTT assay, (b) extract of NR vulcanizate containing DCBS and (c) extract of NR vulcanizate containing DBBS

4.7 Summary

Natural rubber vulcanizates containing DCBS or DBBS as single accelerator system show very good scorch safety. Addition of 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. Better mechanical properties are obtained for vulcanizates prepared using DCBS or DBBS in binary combination with TBzTD, i.e.

binary accelerator system. Addition of high dosages of DCBS or DBBS improve the mechanical properties of the vulcanizates. The vulcanizates prepared using DCBS or DBBS in binary combination with TBzTD show similar fluid resistance in diesel and lube oil. The MTT assay results verified and confirmed the non-cytotoxic nature of the vulcanizates prepared using DCBS or DBBS.

References

- [1] Hofmann W., Rubber Technology Handbook, Hanser Publishers, New York, (1989), 239.
- [2] Druckrey H., Preussmann R., Ivankovic S. and Schmahl D., Z. Krebsforsch., **69**, (1967), 103.
- [3] Kleiner T, Ruetz L and Bayer A G, DCBS: A preferred accelerator for adhesion compounds and other tyre applications, 148th ACS Rubber Division meeting, Fall 1995, Cleveland, Oh., 17 -20 October, paper 75, page 21.012- R.N.Datta(ed), Rapra Review Reports, vol 12, Rubber Curing systems, (2001).
- [4] Coran A. Y., J. Appl. Polym. Sci., **87**, (2003), 24–30.
- [5] Oury B., Limasset J. C. and Protois J. C., Int Arch Occup Environ Health, **70**, (1997), 261-271.
- [6] Choi S. S, Park B.H., Lee S. G. and Kim B.T., Bull. Kor. Chem. Soc., **23**, (2002), 320.
- [7] Aprem A. S., Sabu T., Kuruvilla Joseph, Nektaria M. B. and Karger K. J., J. Elastom. Plast., **35**, (2003), 29-55.
- [8] Bhowmick A., Malcolm M. H. and Henry A. B. (eds.), Rubber Products Manufacturing Technology, Marcel Dekker Inc., NewYork, (1994), 341.
- [9] Rodgers B. (ed.), Rubber compounding Chemistry and applications, second edition, CRC Press, Boca Raton, (2016), 488.
- [10] Peter A. C. and Norman H., The Rubber Formulary, Noyes Publications, New York, U.S.A., (1999).

- [11] Norman H., Compounding precipitated silica in elastomers, William Andrew Publishing, Norwich, New York, U.S.A., (2007).
- [12] Raju P., Nandan V. and Sunil K.N. K., J Rubb. Res., **10**(1), (2007), 1-16.
- [13] Aprem A. S., Kuruvilla J., Thomas M., Volker A. and Sabu T., Eur. Polym.J., **39**, (2003) 1451–1460.
- [14] Pimolsiriphol V., Saeoui P. and Sirisinha C., Polym-Plas. Technol. Eng., **46**(2), (2007), 113–121.
- [15] Rohana Y. Y. S, Azura A. R. and Ahmad Z., Journal of Physical Science, **22**(2), (2011), 1–14.
- [16] Fotakis G. and Timbrell J.A., Toxicol Lett., **160**, (2006), 171–177.
- [17] Elizabeth K. A., Evaluation of natural rubber latex gloves and vulcanizates with special reference to residual zinc dithiocarbamate accelerator, Ph. D. Thesis, Sree Chitra Tirunal Institute for Medical Sciences and Technology, Thiruvananthapuram, India, (2005).
- [18] Hyun S. B., Ja Y. Y., Dong K. R., Dong-Wook H., Dong H. L., Oh-Hun K. and Jong-Chul P. , Yonsei Med. J., **46**(4), (2005) , 579–583.

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