

Safe Amine Based Zinc Dithiocarbamates for the Vulcanization of Carbon Black Reinforced Natural Rubber

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ABSTRACT: Binary combination of three safe amine based synthesized zinc dithiocarbamates (ZDC), namely zinc (N-benzyl piperazino) dithiocarbamate (ZBPDC), zinc (N-ethyl piperazino) dithiocarbamate (ZEPDC), and zinc (N-phenyl piperazino) dithiocarbamate (ZPPDC) with mercapto benzothiazole disulfide (MBTS) as an effective accelerator system for the vulcanization of carbon black (N330, N550, and N774) filled natural rubber (NR) composites are studied. A comparison between the safe amine based zinc dithiocarbamates with the unsafe zinc dimethyl dithiocarbamate (ZDMC) in the light of mechanical and aging resistance behavior, introduces the non carcinogenic rubber additives in the filled vulcanization of rubber. Both accelerator and filler have the major importance for improving the mechanical as well as aging resistance behavior of the resultant vulcanizate. Variation in the filler and also filler to oil ratio are done to optimize the mechanical properties. SEM studies of different types of filler with different amounts show that N330 at 30 phr loading composites forms more homogeneity and less aggregated structures. Natural rubber systems with N330 carbon black show the best results with respect to tensile strength, but after the aging N774 carbon black filled system indicates better retention in the tensile strength. ZPPDC-MBTS accelerated vulcanizate shows the better age resistance behavior than ZDMC-MBTS accelerated vulcanizate. From both the points of age resistance and mechanical properties, ZBPDC-MBTS accelerator system is the suitable substitute for ZDMC-MBTS accelerated system in the filled vulcanization of natural rubber composites. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39988.

KEYWORDS: elastomers; crosslinking; mechanical properties; ageing; morphology

Received 21 December 2012; accepted 19 September 2013

DOI: 10.1002/app.39988

INTRODUCTION

Rubber compounds are reinforced with fillers to improve their physical properties. Reinforcement depends on characteristics of filler such as surface area, morphology, and surface activity. Carbon blacks are the most popular reinforcing agents in a rubber compound.^{1–9} Lots of functional groups such as hydroxyl, carboxyl, lactone, pyrone, ketone, quinone, and phenol exist on the carbon black surface in smaller amount.²

In filled rubber compounds, types, and contents of fillers also affect the cure characteristics.^{10–13} The crosslink density is also influenced by the structure and surface chemistry of the reinforcing filler^{10,11}. Cure rate of a filled rubber compound is faster than that of an unfilled one^{11,12}. Carbon black enhances the crosslink density improving the reversion resistance.^{11,14}

Accelerators play a vital role for vulcanization of rubber. The physical and chemical properties of the vulcanizates depend on the type of the accelerators used and also on the condition of vulcanization. Frequently, the use of two or more accelerators simultaneously, instead of a single one, are found to be more

advantageous for technological applications,¹⁵ as these mixed systems generally show higher vulcanization activity (synergism) than the individual accelerators separately.¹⁵ Mixed accelerator systems have, therefore, gathered much attention both from scientific and technical points of view. It is suggested that in a binary accelerator system, the interaction between the accelerators produce reactive compounds, which decompose into free radicals or ions, capable of initiating a reaction between sulfur, rubber and crosslinking process of the latter.^{15–19} Significant contribution with respect to synergistic activity of the binary systems of accelerators during vulcanization of natural rubber (NR) are revealed by Dogadkin et al.,¹⁵ Skinner and Watson,¹⁴ Kempermann and Redetzky,¹⁶ and Krymowsky and Taylor¹⁷. Debnath and Basu also have made some investigations^{18,19} in this regard. Most of the accelerators used in the rubber industry are based on amines that generate N-nitrosamines, which, in most cases, are reported^{20,21} as carcinogens. In this perspective, the whole scenario of the amine based accelerators need to be reviewed thoroughly on the basis of human safety as these nitrosoamines are being transported by rubber products as well

as through air to the surrounding environment of the rubber industry.^{22,23} In this context, observation of Druckrey et al.²⁴ is worth mentioning. They have shown that zinc-dibenzyl dithiocarbamate and N, N-dicyclohexyl-2-benzothiazole sulfenamide form nitrosamines, which are noncarcinogenic in animal experiments. The amines or amine derivatives which do not produce nitrosamines or produce noncarcinogenic nitrosamines are the so-called safe amines. Eisenbrand et al.²⁵ has made a list of these "safe amines." In fact, over a decade, there has been great enthusiasm on searching safe rubber additives. As a result, several safe accelerators based on safe amines are prepared.^{26,27} In a recent article we have shown that safe Bis (N-benzyl piperazino) thiuram disulfide shows synergistic activity and better heat resistant property in presence of Dibenzothiazyl disulfide compared with conventional Tetramethyl thiuram disulfide on gum rubber vulcanization.²⁷ Most of the secondary amines are found to produce nitrosoamines, which are believed to be carcinogens.²⁸ A significant amount of rubber chemicals are obtained from these secondary amines. In fact, a survey shows that these rubber additives and the vulcanizates obtained from these chemicals contain varying proportions of nitrosoamines.²⁹ This investigation aims at finding some rubber accelerators based on safe zinc dithiocarbamates (ZDCs) that can be used to prepare technological vulcanizates, especially in tyre components and long-term servicing materials. It is known that ZDCs do not impart odor or taste to the resulting vulcanizates that exhibit good aging behavior.^{30–32} In our earlier work, we have studied the effect of zinc dithiocarbamate and thiazole-based accelerators on the vulcanization of gum natural rubber.²⁶ It is reported that ZDCs act as booster accelerator in the gum natural rubber vulcanization after combining with dibenzothiazyl disulfide (MBTS).²⁶ We also compared the vulcanizate properties of the synthesized safe ZDCs with the unsafe zinc dimethyl dithiocarbamate (ZDMC). The effect of different types of zinc-dithiocarbamate along with MBTS in the gum vulcanizates established that 3 : 6 milli molar ratio zinc dithiocarbamate-MBTS shows the best synergistic combination with respect to physical properties.²⁶ These binary systems of safe accelerators may have application in the filled vulcanization of diene elastomer and slow-curing butyl rubber. However, systematic investigations in this regard are lacking and the available information is very scanty.

In our earlier work²⁶ our main aim was to investigate the chemical aspects of synergism in the physical properties by using the ZDC and thiazole based binary accelerator systems in the gum vulcanization of natural rubber. It was found that the synergism might be due to the mutual activity of one accelerator by another. Although, the mutual activity of binary accelerator system is same in both gum and filled vulcanization of rubber; however, the extent of synergism may not be same in both the systems. So, we have extended our work in the filled vulcanization of rubber. In this work, carbon black reinforced natural rubber (NR) composite in presence of zinc dithiocarbamates and dibenzothiazyl disulfide at 3 : 6 milli molar ratio are prepared. Generally, 30–40 phr carbon black filler with 10–20 phr (w. r. t. 100g filler) paraffinic oil is used in the filled

vulcanization of rubber. Dispersion of filler is important for enhanced mechanical properties. Oil plays the vital role in filler dispersion as well as plasticity of the rubber compound. Hence, the types and amounts of carbon blacks at various filler to paraffinic oil ratios are investigated. Aging resistance behavior is also important for long-term servicing of materials. Hence, we have further checked the age resistance behavior of these vulcanizates.

EXPERIMENTAL

Materials

Zinc (N-benzyl piperazino) dithiocarbamate (ZBPDC), zinc (N-ethyl piperazino) dithiocarbamate (ZEPDC), and zinc (N-phenyl piperazino) dithiocarbamate (ZPPDC) are prepared in the laboratory.²⁶ 2-Mercapto benzothiazyl disulfide (MBTS) and Zinc dimethyldithiocarbamate (ZDMC) are commercial samples and are used as such or after necessary purification. Natural rubber (RMA-1X), Zinc oxide (Merck), stearic acid (Loba Chemie, India), sulfur (Loba Chemie, India), paraffinic oil (heavy) (Merck) and toluene (Merck) are used as received. Carbon blacks N330 (surface area $83 \pm 6 \text{ m}^2/\text{g}$, average particle size 28–36 nm), N550 (surface area $42 \pm 5 \text{ m}^2/\text{g}$, average particle size 39–55 nm), N774 (surface area $25\text{--}33 \text{ m}^2/\text{g}$, average particle size 60–100 nm) are supplied by Philips Carbon Black (Durgapur, India). We use the aforementioned carbon blacks (not carbon) as filler in our experiment. So, frequently we use the term "filler" in the places of carbon black.

Preparation of Vulcanizates

Rubber is first masticated on a two-roll mixing mill, and then ZnO and Stearic acid is added. Different types of carbon black and paraffinic oil are mixed together with masticated natural rubber in a laboratory two-roll mixing mill for 10 minutes. After complete mixing of carbon black in the natural rubber matrix, sulfur and accelerators are incorporated to the carbon black filled natural rubber and the mixing is done near about for 10 minutes. Total concentration of the accelerator is fixed at 9-milli mole per 100 g of rubber. Mixing composition of different ingredients is presented in Table I.

Curing and Measurement of Mechanical Properties

The cure characteristics of the different stocks are obtained using the Monsanto Rheometer R-100 at 3° arc for 140°C . The data for highest torque (M_H), lowest torque (M_L), maximum rheometric torque (R_∞), scorch time (t_2), optimum cure time (t_{90}), and cure rate index³³ $\{CRI = 100/(t_{90} - t_2)\}$ of the vulcanizates are presented in Table II.

The stocks are cured under pressure at 140°C for optimum cure time (t_{90}) keeping vulcanizates for 24 hour at ambient temperature before measuring the modulus at 100% (M_{100}), 200% (M_{200}), 300% (M_{300}) elongation, tensile strength (T.S.), and elongation at break (E.B. in %) according to ASTM D 412-51 T using dumbbell shaped test pieces in an Amsler (Sweden) tensile tester. Hardness (shore A) of the vulcanizates is measured by a Hirosima Hardness Tester as per ASTM D 1415-56T. The mechanical data concerning modulus, tensile strength, and elongation at break of the vulcanizates are also provided in Table III.

Table I. Mix No. and Composition of the NR Filled Compounds (Ingredients are in phr^a)

Mix no.	NR	ZnO	Stearic acid	Sulfur	ZBPDC (3 milli mole)	ZEPDC (3 milli mole)	ZPPDC (3 milli mole)	ZDMC (3 milli mole)	MBTS (6 milli mole)	N330	N550	N774	Paraffinic oil (heavy)
1	100	5	2	0.5	1.7	-	-	-	1.992	10	-	-	2
2	100	5	2	0.5	1.7	-	-	-	1.992	20	-	-	4
3	100	5	2	0.5	1.7	-	-	-	1.992	30	-	-	6
4	100	5	2	0.5	1.7	-	-	-	1.992	40	-	-	8
5	100	5	2	0.5	1.7	-	-	-	1.992	50	-	-	10
6	100	5	2	0.5	1.7	-	-	-	1.992	30	-	-	4.5
7	100	5	2	0.5	1.7	-	-	-	1.992	30	-	-	3
8	100	5	2	0.5	1.7	-	-	-	1.992	30	-	-	1.5
9	100	5	2	0.5	-	1.328	-	-	1.992	30	-	-	3
10	100	5	2	0.5	-	-	1.616	-	1.992	30	-	-	3
11	100	5	2	0.5	-	-	-	0.916	1.992	30	-	-	3
12	100	5	2	0.5	1.7	-	-	-	1.992	-	20	-	2
13	100	5	2	0.5	1.7	-	-	-	1.992	-	30	-	3
14	100	5	2	0.5	1.7	-	-	-	1.992	-	40	-	4
15	100	5	2	0.5	1.7	-	-	-	1.992	-	-	20	2
16	100	5	2	0.5	1.7	-	-	-	1.992	-	-	30	3
17	100	5	2	0.5	1.7	-	-	-	1.992	-	-	40	4

^aParts per hundred parts of rubber by weight.

Strain sweep analysis is performed using a dynamic mechanical analyzer (Gabo Qualimeter, Germany, model Explexor-2000N). Strain sweep analysis is performed for the cross-linked samples in isochronal frequency of 10 Hz and dynamic strain of 0.2–30% at room temperature.

Measurement of Crosslink Density

The crosslink densities of the carbon black loaded compounds are determined according to the Flory-Rehner equation³⁴ and the crosslink density values are recorded in Table III.

Table II. Curing Properties of Carbon Black Filled Natural Rubber

Mix no.	M_H , dNm	M_L , dNm	R_∞ , dNm	t_2 , min	t_{90} , min	CRI = 100/ ($t_{90} - t_2$), min ⁻¹
1	44.0	2.0	42.0	4.0	14.0	10.0
2	44.0	1.5	42.5	4.0	14.0	10.0
3	45.0	2.0	43.0	4.0	13.0	11.11
4	46.0	2.0	44.0	4.0	12.5	11.76
5	48.0	3.0	45.0	3.5	11.5	12.5
6	49.0	2.0	47.0	3.5	17.0	7.407
7	50.0	3.0	47.0	4.5	18.0	7.407
8	50.5	3.0	47.5	4.0	17.5	7.407
9	50.0	2.0	48.0	4.0	16.0	8.33
10	39.0	2.0	37.0	4.5	20.0	6.452
11	46.0	2.0	44.0	3.5	12.5	11.11
12	45.5	3.0	42.5	5.0	17.0	8.33
13	47.0	3.0	44.0	5.0	16.0	9.091
14	49.0	4.0	45.0	5.5	14.5	11.11
15	44.5	3.0	41.5	5.5	18.0	8.0
16	46.0	3.0	43.0	5.0	18.0	7.692
17	47.0	3.0	44.0	5.0	16.0	9.09

Table III. Mechanical and Aging Properties of Carbon Black Filled NR Vulcanizates

Mix no.	M_{100} (MPa)	M_{200} (MPa)	M_{300} (MPa)	T.S. (MPa)	E.B. (%)	Hardness (Shore A)	Crosslink density $\times 10^4$ (mol.cm ⁻³)	Aging time (day)
1	0.935	1.62	2.91	20.07	650	53	0.82	0
	1.010	1.683	2.993	17.58	600	56	1.281	5
	(108.02) ^a	(103.89)	(102.85)	(87.59)	(92.31)	(105.66)	(156.21)	
2	1.05	2.13	4.09	26.70	650	55	1.04	0
	1.269	2.720	5.077	22.666	580	59	1.294	5
	(120.86)	(127.69)	(124.13)	(84.89)	(89.23)	(107.27)	(124.42)	
3	1.34	3.01	6.35	27.68	660	57	1.23	0
	1.41	3.878	7.932	24.50	540	60	1.554	5
	(105.22)	(128.84)	(124.91)	(88.51)	(81.82)	(105.26)	(126.34)	
4	1.46	3.72	7.60	22.70	600	61	1.38	0
	1.744	4.535	8.722	20.235	470	63	1.738	5
	(124.78)	(121.91)	(114.76)	(89.14)	(78.33)	(103.28)	(125.94)	
5	1.97	5.23	10.46	22.88	550	64	1.76	0
	2.441	5.798	11.59	17.698	390	66.5	2.316	5
	(123.91)	(110.86)	(110.80)	(77.35)	(70.91)	(103.91)	(131.59)	
6	1.43	3.50	7.04	26.97	650	59	1.312	0
	1.581	3.689	7.377	21.078	530	63	1.33	5
	(110.56)	(105.4)	(104.79)	(78.15)	(81.54)	(106.78)	(101.37)	
7	1.44	3.23	6.47	28.40	610	60	1.37	0
	1.68	4.294	7.841	24.456	540	61	1.594	5
	(116.67)	(132.94)	(121.19)	(86.11)	(88.52)	(101.67)	(116.35)	
8	1.58	3.48	7.60	27.54	610	61	1.42	0
	1.609	3.933	8.044	22.70	500	63	1.756	5
	(101.84)	(113.02)	(105.84)	(82.43)	(81.97)	(103.28)	(123.66)	
9	1.38	3.0	6.65	28.02	620	60	1.292	0
	1.803	4.148	7.936	22.90	500	62	1.32	5
	(130.65)	(138.27)	(119.34)	(81.73)	(80.65)	(103.33)	(102.16)	
10	1.174	2.48	5.11	21.69	640	56	0.907	0
	1.435	2.681	5.720	20.915	560	58	0.92	5
	(122.23)	(108.10)	(111.93)	(96.43)	(87.5)	(103.57)	(101.43)	
11	1.54	3.77	7.39	26.63	560	61	1.59	0
	2.002	4.533	9.610	22.935	460	66	1.721	5
	(130.00)	(120.24)	(130.04)	(86.12)	(82.14)	(108.19)	(108.23)	
12	1.25	2.49	4.52	23.69	620	57.5	1.066	0
	1.368	2.344	5.47	19.184	550	62	1.08	5
	(109.44)	(94.14)	(121.02)	(80.98)	(88.71)	(107.83)	(101.31)	
13	1.43	3.03	6.19	24.76	600	59	1.31	0
	1.505	3.574	6.959	21.312	540	64	1.321	5
	(105.24)	(117.95)	(112.42)	(86.07)	(90.00)	(108.47)	(100.83)	
14	1.75	4.23	8.45	24.07	520	62	1.61	0
	1.853	5.374	9.822	24.224	480	66.5	1.750	5
	(105.89)	(127.04)	(116.24)	(100.64)	(92.31)	(107.26)	(108.69)	
15	1.16	2.16	4.49	22.32	600	56.5	0.96	0
	1.307	2.427	4.667	20.096	540	62	1.086	5
	(112.67)	(112.36)	(103.94)	(90.04)	(90.00)	(109.73)	(113.12)	
16	1.25	2.96	5.89	24.02	600	58	1.172	0
	1.469	3.305	6.427	22.669	550	62	1.27	5
	(117.52)	(111.66)	(109.12)	(94.38)	(91.67)	(106.89)	(108.36)	

Table III. Continued

Mix no.	M_{100} (MPa)	M_{200} (MPa)	M_{300} (MPa)	T.S. (MPa)	E.B. (%)	Hardness (Shore A)	Crosslink density $\times 10^4$ (mol.cm ⁻³)	Aging time (day)
17	1.46	3.72	7.77	22.17	530	59.5	1.47	0
	1.775	4.26	8.52	24.31	520	63	1.648	5
	(121.58)	(114.52)	(109.65)	(109.65)	(98.11)	(105.88)	(112.10)	

^a Values in the parentheses indicate the percentage of retention.

$$V_c = 1/M_c = -\{\ln(1 - V_2) + V_2 + \chi V_2^2\} / \{V_s d_r (V_2^{1/3} - V_2/2)\}$$

where V_2 is the volume fraction of the polymer in the swollen specimen, V_s is the molar volume of the solvent, d_r is the density of the polymer, M_c is the molecular weight of the polymer between crosslinks, and χ is the interaction parameter. It is assumed that the interaction between paraffinic oil and toluene does not change the volume fraction of swollen polymer as swollen weight is very much greater relative to the weight of the paraffinic oil used.

The volume fraction of a rubber network in the swollen phase is calculated from equilibrium swelling data as

$$V_2 = (W_2/d_2) / \{(W_1/d_1) + (W_2/d_2)\}$$

where W_1 is the weight fraction of the solvent, d_1 is the density of the solvent, W_2 is the weight fraction of the polymer in the swollen specimen and d_2 is the density of the polymer. For the natural rubber-toluene system, $\chi = 0.3795$, the molar volume of toluene V_s is 106.2 cm³/mol, and the density of toluene is 0.87 g/cm³. Density of the polymer is determined by Archimedes principle.

$$d_2 = w_0 d_0 / (w_0 - w_1)$$

where d_2 is the density of polymer, d_0 is the density of water = 1 g/cc, w_0 is the weight of sample in air, w_1 is the immersed weight of sample.

Scanning Electron Microscopy (SEM)

Field emission scanning electron microscopy (FE-SEM) using the NEON 40 (Carl Zeiss, Germany) electron microscope is used to study the morphological features of the samples. The state of dispersion of the carbon black in the composites is investigated on the tensile fractured surface. The fractured surfaces of the natural rubber composites are coated with a thin layer of platinum (layer thickness 3 nm) using a sputter coater (BALTEC SCD 500 Sputter Coater), which avoids charging effects to proceed the SEM investigations.

Aging

Nellen and Sellers³⁵ developed the correlation between oven and natural aging of selected tire compounds and revealed that for the tread and carcass compounds 4- and 8-day periods in the oven at 70°C corresponds approximately to 1 and 2 years respectively of natural aging. In the aging experiment, vulcanizates obtained at optimum cure are aged at (70 ± 1)°C in an oven provided with forced air circulation for 1–5 days. In each day the specimens thus aged are kept for a further period of 24 h at room temperature before measuring the physical properties.

RESULTS AND DISCUSSION

The effects of carbon black (filler) loading, filler to paraffinic oil ratio, different zinc dithiocarbamates, and also the different types of filler on the curing, mechanical, and aging resistance properties of natural rubber are described below.

Effect of Carbon Black (N330) Loading (10–50 phr) on the ZBPDC-MBTS Accelerated Vulcanizate

First of all, we study the effect of filler (N330) loading on the natural rubber vulcanizates in the presence of ZBPDC : MBTS (3 : 6) curing system along with 20 phr (w.r.t. filler) paraffinic oil by varying the filler from 10 to 50 phr with respect to rubber. Cure data are recorded in Table II and physical properties are recorded in Table III. From Table II, it is clear that maximum rheometric torque (R_{∞}) as well as highest torque (M_H) increases regularly with increasing the filler content (mix 1–5) for the ZBPDC-MBTS accelerated sulfur vulcanizates. As we are concerned about the optimum cure time (t_{90}) and cure rate index (CRI) at different amount of carbon black loading (mix 1–5, Table II), t_{90} value decreases with the increase in loading and CRI increases with the increase in filler content. The scorch time t_2 is more or less same for all the mixes. It is found from Figure 1 (mix 1–5, Table III) that for N330 filler, the modulus at 100% elongation (M_{100}) gradually increases with the increase in the filler content. Similarly, crosslink density of the above system gradually increases with the increase in the filler content. In the same way M_{200} and M_{300} values increases with the increase in the filler content (mix 1–5, Table III). Results reflect the increase in hardness values with the increase in modulus values (mix. 1–5, Table III). As we are concerned about the

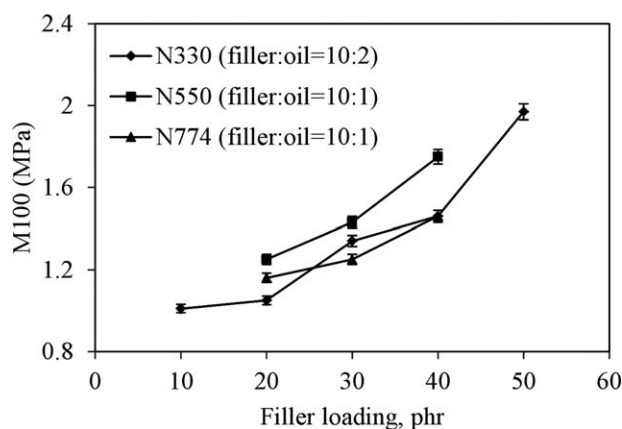


Figure 1. Effect of different types of filler loading on the M_{100} values for ZBPDC-MBTS accelerated vulcanizates.

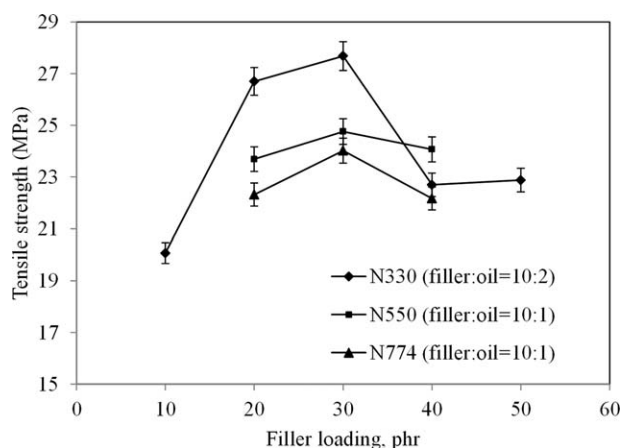


Figure 2. Effect of different types of filler loading on the tensile strength for ZBPDC-MBTS accelerated vulcanizates.

tensile strength of the carbon black (N330) loaded compound, in Figure 2 (mix 1–5, Table III), it shows the regular increase in the tensile strength reaching to an optimum level at 30 phr filler loading. This may be due to carbon black (N330) acts as reinforcing filler due to high surface activity, chemical properties, and nonuniform porous surface that contribute to maximum interphase interaction between polymer chain and fillers.^{36,37}

The dependence of storage elastic modulus (E') on the strain amplitude at very low strain values delivers an understanding about the impact of the filler networking within the rubber matrix.³⁸ Generally, E' remains unaltered with increasing strain for an unfilled rubber system. However, for a filled system, the storage modulus decreases with increasing strain.³⁸ This nonlinear behavior of a filled rubber system is called 'Payne effect'³⁹ and yields information about filler–filler networking in rubber matrix. From the E' vs. strain amplitude curve (Figure 3) it is observed that at low strain amplitude E' increases with increase in the amount of filler indicating strong filler–filler network. However, with increasing the strain amplitude filler–filler networks break down and strong filler–rubber networks forms. It is interesting to note that at 30 phr filler loading E' decreases with

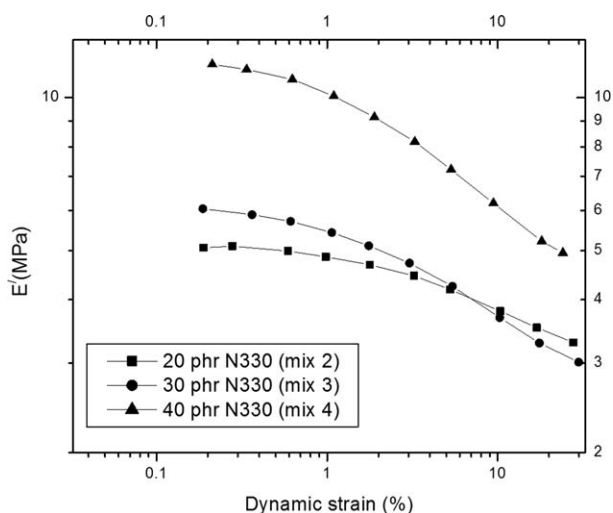


Figure 3. Effect of dynamic strain amplitude on storage modulus.

increasing strain amplitude and reaches the lowest level and it is even below the 20 phr carbon black filled rubber system. This anomalous behavior of the curve may be due to strong filler–rubber interaction at 30 phr filler loading level. As we increase the amount of filler, fraction of filler increases and the fraction of rubber polymer decrease (dilution effect). But the filler–rubber interaction always depends on both the fraction of filler and rubber. Hence, there should be an optimizing point where maximum filler–rubber interaction will arise. Here, we consider the tensile strength as a parameter for optimizing the filler concentration because we assume that at maximum elongation, which corresponds to the tensile strength value, there is a minimum of the filler–filler interactions due to breakdown of filler networks with increasing elongation. Now, filler–rubber interaction increases the tensile strength, whereas filler–filler interaction reduces the tensile strength. As the filler–rubber interaction is maximum at 30 phr filler loading, the tensile strength also shows the highest value at this loading level. After that the tensile strength decreases regularly because of strong filler–filler interaction, and hence, weaker the filler–rubber interaction. This is due to decrease in the fraction of rubber polymer with increase in the filler content (dilution effect) and formation of filler agglomeration.⁴⁰

There are four different types of shape of carbon black aggregates⁴¹: spheroidal, ellipsoidal, linear, and branched; whereas some rough correlations can be expected between such structural aspects and the reinforcing capabilities of the filler, there is no single relationship between a particular type of aggregate shape and the standard classification of carbon black and, furthermore, several shapes may coexist in a given grade. Several aggregates further give weak, giant assemblies called agglomerates.⁴¹ Carbon black structure gives rise to reinforcing effects and therefore the aggregate is the smallest form of a given carbon black grade well dispersed in an elastomer that will still keep all the reinforcing capabilities of the filler.⁴¹

Apart from specific surface area, it sounds logical to expect rubber–filler interactions to depend on the surface activity of the particles. How surface activity is defined is quite unclear as many phenomena might be involved, from Van der Waals proximity forces to specific chemical interactions.⁴² There are no standard methods to measure surface activity.⁴²

Rubber grade carbon blacks contain some quantities of chemically combined hydrogen (0.2–1.0%), oxygen (0.1–4.0%), and even sulfur (up to 1.0%) depending on the quality of the feedstock and the process. A large variety of oxygen containing functional groups, most in minute quantities, has been detected in carbon blacks, for instance carboxyl and hydroxyl groups, phenol, lactones, quinones, ketones, aldehydes, hydroperoxides.^{2,42}

As a result of the interaction of carbon black with sulfur and accelerators active intermediate compounds (possibly also polysulfide compounds) are formed, which are responsible for reinforcement.⁴³ So rubber reinforcement depends on the nature of filler, accelerator, and active filler accelerator intermediates.

Shore A hardness values for different types of carbon black loaded compounds (mix 1–5), generally, increases with increase

in the filler content. So from the above discussion it is clear that the ZBPDC-MBTS (3 : 6) system optimizes at 30 phr of N330 carbon black along with 20 phr (w.r.t. filler) paraffinic oil with respect to tensile strength that measures degree of reinforcement.^{36,37}

Effect of Paraffinic oil (5 to 20 phr w.r.t. Filler) at 30 phr filler Loading on the ZBPDC-MBTS Accelerated Vulcanizate

Our next step of work is to optimize the paraffinic oil level in the new accelerator system. In this study, we varied the oil concentration within 5–20 phr (w.r.t. 30 phr N330 carbon black) in ZBPDC-MBTS (3 : 6) accelerated vulcanizates of natural rubber. The results are recorded in Tables II and III (mixes 3, 6–8). Mix 3, 6–8 (Table II) indicate variation of paraffinic oil at 30 phr carbon black. A certain increase in the filler to paraffinic oil ratio leads to a major change in the R_{∞} values (Table II, mix 3 and 6). After that, there is practically no change in the R_{∞} values (mix 6–8, Table II). When the scorch time (t_2) is concerned, there is a little change in the t_2 values and varies from 3.5 to 4.5 minutes for the change in filler to oil ratio. For optimum cure time (t_{90}), initially the value increases to a certain level and then maintains approximately a constant level with the increase in the filler to oil ratio, but for the cure rate index (CRI) the reverse is true, i.e., first decreases and then reaches a constant level. There is practically no change in t_{90} and CRI values for different amounts of paraffinic oil (mix 6–8, Table II), which indicates that paraffinic oil has little activity in the kinetics of filled rubber vulcanization but it acts as a filler dispersing agent. By changing the filler to paraffinic oil ratio (mix 3, 6–8, Table III) leads to a little higher M_{100} values (Figure 4) and better crosslink density at lower concentration of the paraffinic oil. At lower concentration, paraffinic oil displays higher crosslink density, which affects the modulus at 100% elongation. Modulus at 200% and 300% elongation is also higher for the lower levels of paraffinic oil content but the trend is not regular. There is also an irregularity in the tensile strength value (Figure 5). According to Toki⁴⁴ et al., strain-induced crystallization typically starts from 200% elongation for natural rubber system. So, it is assumed that little irregularities in the tensile properties above 200% elongation may be due to the mass fractions of

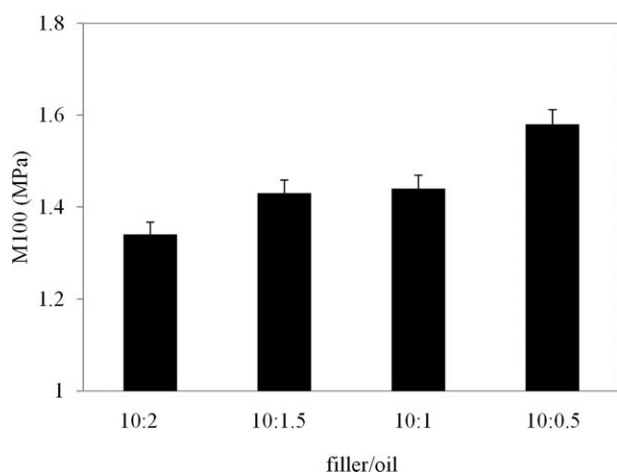


Figure 4. Effect of filler to oil ratio on the M_{100} values for N330 carbon black filled ZBPDC-MBTS accelerated vulcanizates.

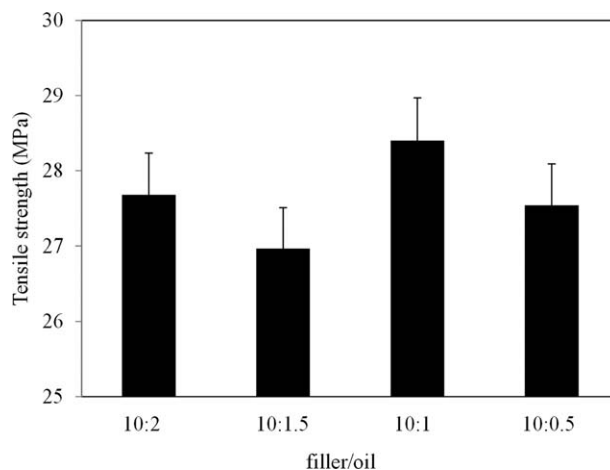


Figure 5. Effect of filler to oil ratio on the tensile strength of N330 carbon black filled ZBPDC-MBTS accelerated vulcanizates.

strain-induced crystals present in the different vulcanizates of the different filler to oil ratio. A little higher tensile strength (Figure 5, mix 3, 6–8) is found at 10 : 1 filler to paraffinic oil ratio for 30 phr filler loading (mix 7). This may be due to maximum filler–polymer interaction as well as reduced plasticity and better crosslink density of the vulcanizates at 10 : 1 filler to paraffinic oil ratio. By increasing a proportion of carbon black to oil ratio (mix 3, 6–8), the crosslinked value increases slightly but the elongation at break value upto 10 : 1 filler to paraffinic oil ratio (Figure 6) is lowered. Actually, higher amount of paraffinic oil leads to decrease in the internal viscosity of the polymer chains. Hence, higher amount of paraffinic oil shows higher elongation at break value. From the above discussion, it can be concluded that filler to paraffinic oil ratio is to be 10 : 1 (i.e., oil is 10 phr w.r.t. filler) for further studies.

Effect of Different Zinc Dithiocarbamates on the 30 phr N330 and 10 phr Paraffinic oil (w.r.t. Filler) Containing Vulcanizate

The results are depicted in Tables II and III. Maximum rheometric torque (R_{∞}) measures the degree of crosslinking.^{45,46}

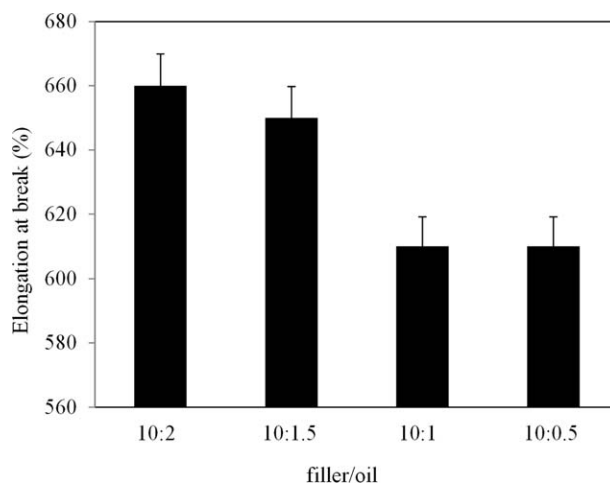


Figure 6. Effect of filler to oil ratio on the elongation at break values of N330 carbon black filled ZBPDC-MBTS accelerated vulcanizates.

Although the R_{∞} value is proportional to the crosslink density according to the literature^{45,46} in case of gum vulcanizates, but in case of filled study this is not true. However, we can get a preliminary idea of crosslinking value from R_{∞} . For the carbon black filled system R_{∞} also depend on the physical interaction via adsorption of rubber in the filler surfaces. But swelling method can determine the exact value of crosslink density as the above factor nullified when swelling occurs. It is very difficult and time consuming to measure the crosslink density from swelling study time to time in the progress of vulcanization and also difficult to measure the optimum curing time. Hence, rheometric measurement of R_{∞} is the best method to determine the progress of crosslinks but it is not suitable for exact crosslink density determination. As higher degree of crosslinking leads to high reinforcing effects, so, it is very reasonable to consider the R_{∞} values in order to explain the efficiency of different accelerating system on the mechanical properties of the filled vulcanizates. Figure 7 indicates the different R_{∞} values for the different accelerating system at 10 : 1 filler to paraffinic oil ratio. It is clear from the figure that the R_{∞} value is highest for ZEPDC-MBTS accelerator system (mix 9) and lowest for ZPPDC-MBTS accelerated system (mix 10). However, ZBPDC-MBTS system (mix 7) shows approximately same value for ZEPDC-MBTS accelerated (mix 9) vulcanizates. For the different accelerator system, ZDMC-MBTS (mix 11) shows the lowest t_{90} values compared with other ZDC-MBTS accelerated stocks. The scorch safety (t_2) of all the stocks varies from 3.5 to 5.5 min. When we concentrate on the t_2 values for different accelerator system, accelerated ZPPDC-MBTS (mix 10) system shows the better scorch safety due to the lower basicity⁴⁷ of the amine moiety. Cure rate index (CRI) for different stocks follow the order:

$$\text{ZDMC-MBTS} > \text{ZEPDC-MBTS} > \text{ZBPDC-MBTS} > \text{ZPPDC-MBTS}$$

Both t_2 and t_{90} depends on the basicity of the amine moiety. As higher the basicity, lower will be the t_2 and t_{90} values,⁴⁷ but the effect is very pronounced for the later. Naturally, the difference

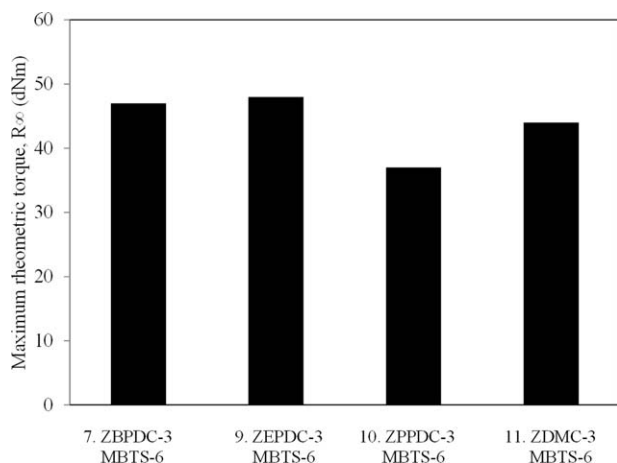


Figure 7. Maximum rheometric torque (R_{∞}) for different accelerator system at 30 phr N330 carbon black and 3 phr paraffinic oil.

between t_{90} and t_2 decreases with increase in the basicity of the amine moiety, and hence, the above order of CRI is obtained.

The above discussion reveals that ZEPDC-MBTS accelerated vulcanizate shows the highest R_{∞} value as well as better curing rate.

For the different accelerator systems (mix 7, 9–11, Table III), ZDMC-MBTS accelerated vulcanizate shows the highest M_{100} and high crosslink density indicating that the cross linking efficiency of ZDMC-MBTS accelerator is better than other accelerator system. At 30 phr N330 carbon black loading level for different accelerator systems (mix 7, 9–11), ZDMC-MBTS accelerated vulcanizate (mix 11) shows the highest value of M_{100} , M_{200} , and M_{300} . This is due to the higher crosslink density of the corresponding ZDMC-MBTS accelerated vulcanizates (mix 11). The modulus values more or less maintain the following trend as

$$\text{ZDMC-MBTS} > \text{ZBPDC-MBTS} \geq \text{ZEPDC-MBTS} > \text{ZPPDC-MBTS}$$

The aforementioned result indicates that the modulus value depends on the crosslink density and also the extent of mono, di, and polysulfidic linkages.⁴⁸

Figure 8 indicates the tensile strength of different accelerator system (mix 7, 9–11, Table III) at 30 phr N330 carbon black loading and follows the order as

$$\text{ZBPDC-MBTS} > \text{ZEPDC-MBTS} > \text{ZDMC-MBTS} > \text{ZPPDC-MBTS}$$

Although the crosslink densities of ZBPDC-MBTS (mix 7) or ZEPDC-MBTS (mix 10) accelerated vulcanizates being comparatively lower than that of ZDMC-MBTS accelerated vulcanizates, (mix 11) the tensile strength is very much greater for the former two systems than the latter. By structural characterization of NR vulcanizates, Debnath and Basu⁴⁸ have shown that disulfidic linkages have the significant role in the enhancement of tensile strength of rubber vulcanizates. Hence, it is believable that the former two accelerated systems produces higher amount of disulfidic linkages, which are responsible for imparting higher tensile strength value than the later two systems.

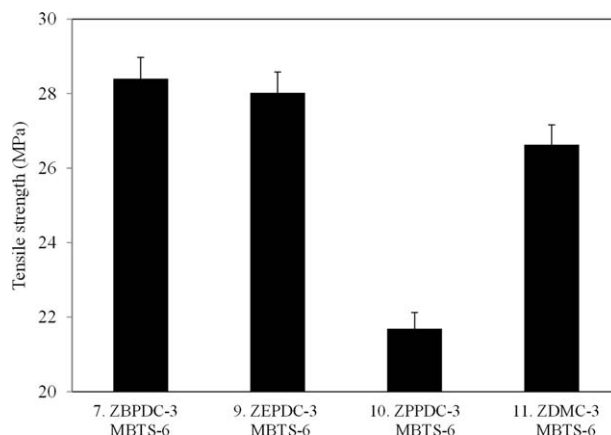


Figure 8. Tensile strength of different accelerator system at 30 phr N330 carbon black and 3 phr paraffinic oil.

This indicates that the maximum tensile strength does not always mean the higher crosslink density but it depends on the nature of crosslinking which is the unique characteristics of the accelerators. It is also to be noted that by proper choosing of accelerator more than 30% increase in the tensile strength is possible in our system (Table II, mix 7 and 10). Hence, choice of accelerator is the key importance in the vulcanization of natural rubber.

Effect of Different Kind of Carbon Black (Filler : Oil = 10 : 1) on the ZBPDC-MBTS Accelerated Vulcanizates

For different type of filler (N330, N550, and N774) we use the ZBPDC-MBTS (3 : 6) accelerated system and vary the amount of filler from 20 to 40 phr. The cure properties are depicted in Table II and physical properties are recorded in Table III. For the different types of carbon black loaded natural rubber vulcanizates show the difference in the R_{∞} values (mix 7, 13, 16, Table II) providing the same concentration of carbon black, paraffinic oil and also with the other ingredients. With increase in the surface area or decrease in the particle size from N774 to N330 carbon black, R_{∞} value increases in the order of $N330 > N550 > N774$. This indicates that N330 shows the highest reinforcing effect in the rubber vulcanization. At 30 phr filler loading (mix 7, 13, 16, Table II) for different types of carbon black filled compounds, the CRI value varies from 7.407 to 9.091. As CRI depends on both t_2 and t_{90} values and varies from filler to filler due to the proportion of different shapes of aggregate present in particular grade of carbon black with different surface activity; hence, it is very reasonable to show different CRI value for different types of carbon black filled systems.

Table III represents the mechanical properties of the rubber vulcanizate. Figure 1 (mix 1–5, 12–14, and 15–17, Table III) depicts that the modulus at 100% elongation (M_{100}) gradually increases with increase in the filler content. Similarly, crosslink density of the above system gradually increases with increase in the filler content. All the modulus values, M_{100} , M_{200} , and M_{300} are comparatively higher for N330 at 30 phr filler loading (mix 7) than the corresponding filler loading of the other filler system (mix 13, 16). This is due to high surface area and low particle size of N330, which imparts high reinforcing effects on the filled vulcanizate.

When we concentrate on the tensile strength of the carbon black loaded compounds in Figure 2 (mix 1–5, 12–14, 15–17, Table III), all types of carbon black shows the regular increase in the tensile strength and reaches to an optimum level at 30 phr filler loading. Above the level of 30 phr of the carbon black, tensile strength regularly decreases resulting in a weak filler–rubber interaction because of the dilution effect and formation of filler agglomeration⁴⁰.

Figure 9 indicates variation of elongation at break for different amounts of filler loading. Increasing the amount of carbon black generally increase the crosslink density (mix 1–5, 12–14, 15–17) and consequently according to Flory-Renher equation, molecular weight between crosslink density, M_c decreases hence higher crosslinking value indicates low elongation at break value.

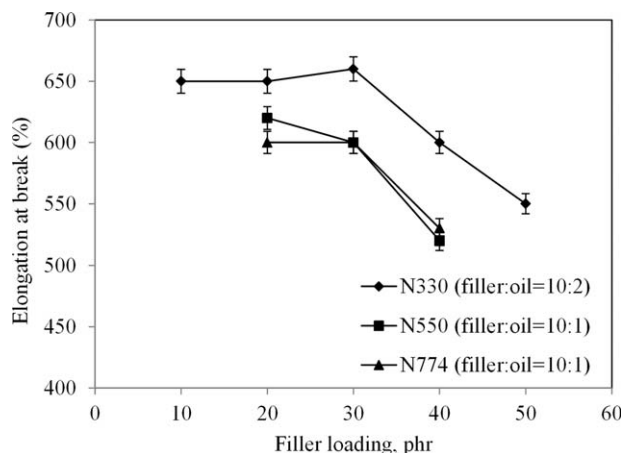


Figure 9. Effect of different types of filler loading on the elongation at break values for ZBPDC-MBTS accelerated vulcanizates.

Shore A hardness values for different types of carbon black loaded compounds (mix 1–5, 12–14, 15–17) generally increase with increase in the filler content. Shore A hardness values for all the other system more or less varies with the crosslink densities (Table III, Mix 1–5, 12–14, 15–17). As the crosslink density increases with increasing the filler content the network becomes rigid. Thus, for the rigidity of the rubber network, hardness value increases with increasing the crosslink density.

The above studies reveal that N330 at 30 phr loading shows the best mechanical properties.

Scanning Electron Microscope (SEM)

Keeping in mind that fillers dispersion may have significant effect on the composites properties, SEM studies are performed to evaluate the extent of dispersion of the carbon black fillers. In the SEM images presented here (Figure 10), white points indicate the aggregated structure of carbon black and black matrix indicates the rubber phase. The SEM images of 30 phr loading for different types of filler are presented in Figure 10(a,c, and d). From the figures it is evident that N330 shows the maximum homogeneity than the other two. Figure 10(b) represents the micrograph of 50 phr loading of N330. It is also evident by comparing Figure 10(a,b) that 30 phr N330 carbon black is better dispersed than 50 phr N330 in the rubber matrix. N330 carbon black filled rubber matrix (mix 3 and 5) show that, at higher concentrations, the filler forms more aggregated structures than that of lower carbon black loaded system [Figure 10(a,b)]. From all the micrographs presented here it is further indicate that N330 carbon black filled vulcanizate shows the better dispersion and more homogeneity at 30 phr loading, which may leads to better mechanical properties.

Aging Resistance Properties

The oxidative aging of the rubber vulcanizates is of the utmost importance for practical purposes. Performance of the vulcanizates of the different carbon black filled stocks during aging is tested and the results are shown in the Table III. Values in the parentheses indicate retention of the physical and mechanical properties after aging. It can be seen from the results that during aging both modulus at 100% elongation and shore-A

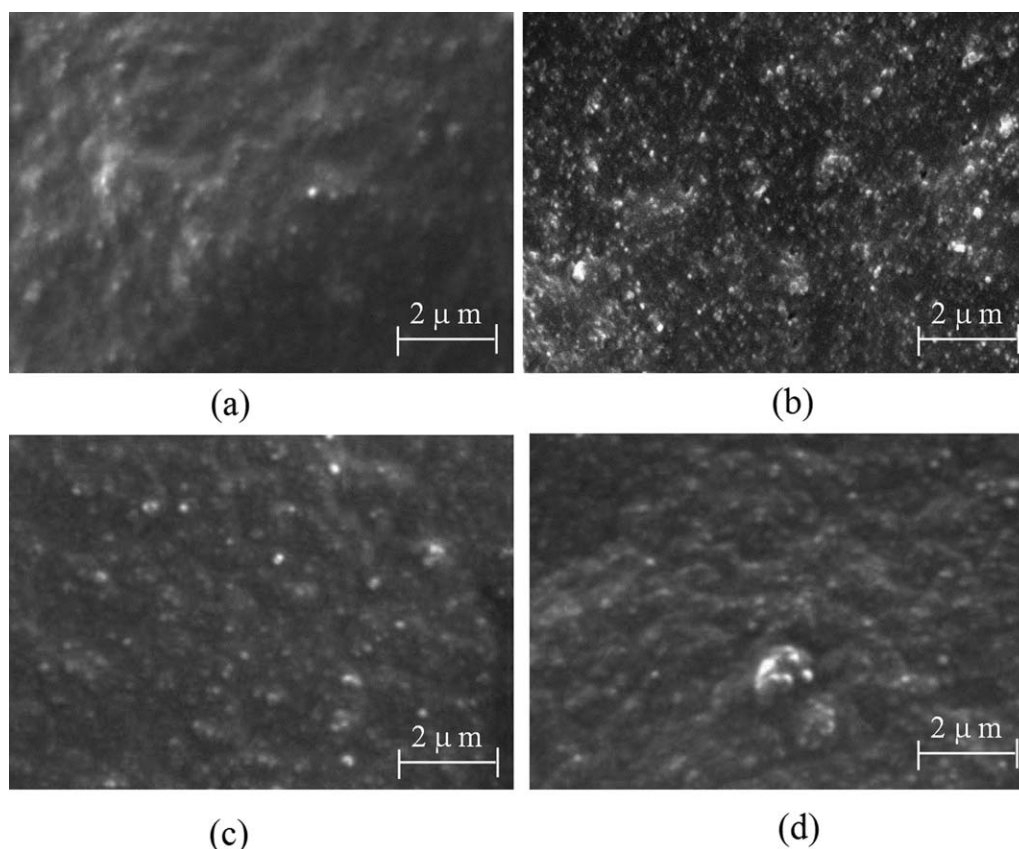


Figure 10. SEM micrographs of vulcanizates, containing different amounts of fillers: (a) 30 phr of N330 carbon black; (b) 50 phr of N330 carbon black; (c) 30 phr of N550 carbon black; (d) 30 phr of N774 carbon black.

hardness values are increased for all the mixes with the order not so much regular. Generally, with increasing the filler content M_{100} increases with higher rate for the N330 (mix 1–5) and N774 (mix 15–17) filled carbon black system. However, the rates of increase in the M_{100} values are more or less same for N550 carbon black system (mix 12–14). By changing proportion of carbon black to oil ratio on N330 carbon black filled system, the rate of change in the M_{100} value varies and 30 phr carbon black with the 3 phr paraffinic oil leads to the maximum value. The order of activity with respect to increase in the M_{100} value for the different type of accelerating systems (mix 7, 9–11) follows:

$$\text{ZEPDC-MBTS} > \text{ZDMC-MBTS} > \text{ZPPDC-MBTS} > \text{ZBPDC-MBTS}$$

M_{100} value is directly proportional to crosslink density of vulcanized rubber.⁴⁹ In general, the reaction of oxygen with elastomers causes both chain scission and crosslinking.⁵⁰ If chain scission dominates during aging, the elastomer softens and eventually may become tacky.⁵⁰ This is the usual behavior of unfilled natural rubber and butyl rubber vulcanizates. Most technical elastomers, that is, filled elastomer eventually harden and embrittle during oxidation, a consequence of the dominant crosslinking reactions.⁵⁰ From the above points, it is clear that the modulus value increases for all the systems because of dominant crosslinking during aging and shows the above order with respect to rate of increase in the modulus values.

This order is not followed for M_{200} and M_{300} values of the above system. Comparing all the data of modulus values, a general order of activity may be drawn as

$$\text{ZEPDC-MBTS} > \text{ZDMC-MBTS} > \text{ZBPDC-MBTS} > \text{ZPPDC-MBTS}$$

The aforementioned order indicates that crosslink density plays in a different way on M_{200} and M_{300} value and the above order is actually found.

This trend is not followed in the case of shore-A hardness values. The highest increase in the shore-A hardness value is found for ZDMC-MBTS accelerated stocks (mix 11). All other accelerator systems show near about same increase in the hardness values after aging. The tensile strength values for all vulcanizates decrease considerably after aging. Retention of tensile strength increases with increasing filler content (mix 1–5) up to 40 phr filler loading, after that, a huge amount of fall occurs in the tensile strength. The different types of filler system (mix 1–5, 12–14, 15–17) N774 show the best value of retention of tensile strength at 40 phr filler loading. Retention of tensile strength is the greatest for ZPPDC-MBTS (mix 10) accelerated stock and least for ZEPDC-MBTS (mix 9) accelerated stock. Retention of elongation at break follows the following order:

$$\text{ZBPDC-MBTS} > \text{ZPPDC-MBTS} > \text{ZDMC-MBTS} > \text{ZEPDC-MBTS}$$

This trend is exactly opposite to the change in M_{100} values after aging. As the M_{100} value increases, crosslinking density increases and the networks become rigid that restricts the elongation of rubber chain.⁵⁰

After aging, the ZDMC-MBTS (mix 11) system gains the highest value of crosslink density, which illustrates the lowest value of elongation at break. This fact is also true for other ZDC-MBTS systems.

Increase of crosslink density,⁵⁰ chain degradation,⁵⁰ and degree of agglomeration⁴⁰ of filler particles all are responsible for decrease in the tensile strength after thermal induced oxidative aging. We found that at a certain increase in the crosslink density, tensile strength increases but filler agglomeration always decreases the reinforcement. Jha⁵¹ has shown in his thesis that the degree of agglomeration affects the final properties of the filled elastomer. They also observed that carbon black fillers with low surface area and shape factor show a low tendency to agglomerate.⁵¹ Like the same way as mentioned earlier, tendency of agglomeration is very much lower for N774 filler because of its low surface area than the other type of filler used. Naturally, N774 carbon black with 40 phr filler loading in the natural rubber vulcanization accelerated by ZBPDC-MBTS system shows the better value in the retention of tensile strength.

By analyzing the rate of M_{100} change vs the square root of aging time, $t^{1/2}$, it is possible to age specimens to an equivalent level of rubbers used in field tyres.⁵² Because oxidative aging is diffusion controlled process, the plot is expected to be a straight line where the slope represents the rate of change in crosslink density.⁵² If we plot M_{100} vs $t^{1/2}$ for different accelerating system then Figure 11 is obtained and its slope provides the rate constant. The rate constant value for ZPPDC-MBTS (mix 10) accelerated vulcanizate is the smallest ($0.3 \text{ kPa s}^{-1/2}$) and that for ZEPDC-MBTS (mix 9) or ZDMC-MBTS (mix 11) accelerated vulcanizate is the highest ($0.7 \text{ kPa s}^{-1/2}$) and ZBPDC-MBTS (mix 7) accelerated system shows the intermediate rate constant value ($0.4 \text{ kPa s}^{-1/2}$). It can be seen that the rate of change in crosslink density of ZDMC-MBTS or ZEPDC-MBTS accelerated

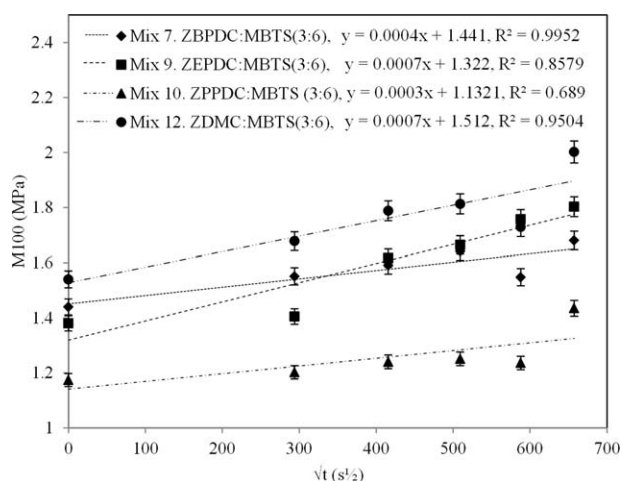


Figure 11. Plot of M_{100} vs $t^{1/2}$ of different accelerator system at 30 phr N330 carbon black and 3 phr paraffinic oil.

vulcanizates are larger than that of ZPPDC-MBTS or ZBPDC-MBTS accelerated vulcanizates, indicating poorer age resistance of former two.

It is also noticed by earlier workers that zinc dithiocarbamates act as accelerators as well as antidegradants.^{30–32} Thus, good age resistance exhibited by all the zinc dithiocarbamate might be due to reproduction of zinc dithiocarbamates in presence of ZnO. To increase the modulus of the vulcanizates of NR during aging, it has to be assumed that prolonged heating at 70°C is apt to cause postvulcanization thereby generating more crosslinks that are also responsible for the increase in hardness values during aging of rubber vulcanizates. With the increase in the number of crosslinks the molecular weight between crosslinks decreases and the network which becomes rigid may restrict the elongation at break and actually this is observed for all the vulcanizates subjected to hot air aging.

CONCLUSIONS

Different types of zinc dithiocarbamate with MBTS as an accelerating agent for different graded carbon blacks filled along with the other ingredients such as ZnO, stearic acid, sulphur, and paraffinic oil for vulcanization of natural rubber are investigated. By increasing the filler concentration both kinetic and mechanical properties are enhanced for ZBPDC-MBTS accelerator system. 30 phr of N330 with 3 phr of paraffinic oil and with the other ingredients for ZBPDC-MBTS accelerated vulcanizate show the highest tensile strength. SEM studies indicate that N330 carbon black follows well dispersion and better homogeneity compared with N550 and N774 carbon black at 30 phr loading level. With increasing the loading of filler content up to 40 phr filler leads to higher retention in the tensile strength after aging. N774 carbon black with 40 phr loading level shows the highest retention in the tensile strength after aging. There is an increase in the modulus and crosslink density values after aging but elongation at break values decrease regularly. ZPPDC-MBTS accelerated vulcanizate shows better age resistance behavior compared with other accelerated systems. From both the points of mechanical properties and age resistance behavior ZBPDC-MBTS accelerator system with 30–40 phr carbon black at 10 : 1 filler to paraffinic oil ratio is the suitable substitute for the corresponding ZDMC-MBTS accelerated system in the filled vulcanization of natural rubber composites.

One of the authors, Md. Najib Alam thankfully acknowledge the financial support by the Council of Scientific and Industrial Research (CSIR), Government of India, for carrying out the present research work. Authors also wish to thank Philips Carbon Black Ltd (Durgapur, India) for supplying the carbon blacks. They are also grateful and highly acknowledge the Department of Elastomer of Leibniz-Institut für Polymerforschung Dresden e.V., 01069-Dresden, Germany for providing the Strain sweep and SEM results of this work.

REFERENCES

1. Cotton, G. R. *Rubb. Chem. Technol.* **1984**, 57, 118.
2. Wolff, S.; Görl, U. *Kautsch. Gummi Kunstst.* **1991**, 44, 941.

3. Gruber, T. C.; Herd, C. R. *Rubb. Chem. Technol.* **1997**, *70*, 727.
4. Ghosh, A. K.; Adhikari, B. *Kautsch. Gummi Kunstst.* **1999**, *52*, 681.
5. Raab, H.; Fröhlich, J.; Göritz, D. *Kautsch. Gummi Kunstst.* **2000**, *53*, 137.
6. Byers, J. T. *Rubber World.* **1998**, *218*, 38.
7. Wolff, S.; Wang, M. J. *Rubb. Chem. Technol.* **1992**, *65*, 329.
8. Boonstra, B. B.; Cochrane, H.; Dannenberg, E. M. *Rubb. Chem. Technol.* **1975**, *48*, 558.
9. Voet, A.; Morawski, J. C.; Donnet, J. B. *Rubb. Chem. Technol.* **1977**, *50*, 342.
10. Cotton, C. R. *Rubb. Chem. Technol.* **1972**, *45*, 129.
11. Chen, C. H.; Koenig, J. L.; Shelton, J. R.; Collins, E. A. *Rubb. Chem. Technol.* **1982**, *55*, 103.
12. Devlin, E. F. *Rubb. Chem. Technol.* **1986**, *59*, 666.
13. Wanpler, W. A.; Gerspacher, M.; Yang, H. H. In Proceedings of the Rubber Division 143rd Meeting; American Chemical Society: Washington, DC, **1993**; Paper No. 26.
14. Skinner, T. D.; Watson, A. A. *Rubb. Chem. Technol.* **1969**, *42*, 404.
15. Dogadkin, B. A.; Feldshtein, M. S.; Belyaeva, E. N. *Rubb. Chem. Technol.* **1960**, *33*, 373.
16. Kempermann, Th.; Redetzky, W. *Mater. Plast. Elastomers.* **1969**, *35*, 73.
17. Krymowski, J. F.; Taylor, R. D. *Rubb. Chem. Technol.* **1977**, *50*, 671.
18. Debnath, S. C.; Basu, D. K. *Kautsch. Gummi Kunstst.* **1992**, *45*, 934.
19. Debnath, S. C.; Basu, D. K. *J. Appl. Polym. Sci.* **1994**, *52*, 597.
20. Fajen, J. M.; Carson, G. A.; Rounbehler, D. P.; Fan, T. Y.; Vita, R.; Goff, U. E.; Wolf, M. H.; Edwards, G. S.; Fine, D. H.; Reinhold, V.; Biemann, K. *Science.* **1979**, *205*, 1262.
21. McGlothlin, J. D.; Wilcox, T. C.; Fajen, J. M.; Edwards, G. S. In Chemical Hazards in the Workplace, Measurement and Control; Choudhary, G., Ed.; American Chemical Society: Washington DC, **1981**; p 283–299.
22. Spiegelhalter, B.; Preussmann, R. In N-Nitroso compounds: Occurrence and Biological effects; Bartsch, H., O' Neill, I. K., Castegnaro, M., Okada M., Eds.; IARC Sci. Publ.No. 41; Lyon: International Agency for Research on Cancer, **1982**; p 231–244.
23. Spiegelhalter, B. *Scand. J. Work Environ. Health.* **1983**, *9*(suppl 2), 15.
24. Druckrey H.; Preussmann R.; Ivankovic S.; Schmahl, D. *Z. Krebsforsch.* **1967**, *69*, 103.
25. Eisenbrand, G.; Preussmann, R.; Spiegelhalter, B. Ger. Pat. 3029, 312.6, **1980**.
26. Alam, M. N.; Mandal, S. K.; Debnath, S. C. *Rubb. Chem. Technol.*, **2012**, *85*, 120.
27. Alam, M. N.; Mandal, S. K.; Debnath, S. C. *J. Appl. Polym. Sci.* **2012**, *126*, 1830.
28. Preussman, R.; Eisenbrand, G. In Chemical Carcinogens; Searle, C. E., Ed.; ACS Monograph 182; American Chemical Society: Washington, DC, **1984**; Vol. 1.
29. Spiegelhalter, B.; Preussman, R. *Carsinogenesis*, **1983**, *4*, 1147.
30. Buckley, D. J. *Rubb. Chem. Technol.* **1959**, *32*, 1475.
31. Dunn, J. R.; Scanlan, J. *Rubb. Chem. Technol.* **1959**, *32*, 739.
32. Fletcher, W. P.; Fogg, S. G. *Rubb. Chem. Technol.* **1958**, *31*, 327.
33. Yehia, A. A.; Stoll, B. *Kautsch. Gummi Kunstst.* **1987**, *40*, 950.
34. Flory, P. J.; Renher, Jr. J. *J. Chem. Phys.* **1943**, *11*, 521.
35. Nellen, A. H.; Sellers, H. M. *Ind. Eng. Chem.* **1929**, *21*, 1019.
36. Katbab, A. A.; Nazockdast, H.; Bazgir, S. *J. Appl. Polym. Sci.* **2000**, *75*, 1127.
37. Premphet, K.; Horonont, P. *J. Appl. Polym. Sci.* **2000**, *76*, 1929.
38. Das, A.; Mahaling, R. N.; Stöckelhuber, K. W.; Heinrich, G. *Comp. Sci. Technol.* **2011**; *71*, 276.
39. Heinrich, G.; Kluppel, M. *Adv. Polym. Sci.* **2002**, *160*, 1.
40. Ahmed, K.; Nizami, S. S.; Raza, N. Z.; Mahmood, K. *Int J Ind Chem* **2012**, *3*, paper no 21.
41. Gruber, T. C.; Herd, C. R. *Rubb. Chem. Technol.* **2000**, *70*, 727.
42. Jean, L. L. *Prog. Polym. Sci.* **2002**, *27*, 627.
43. Blokh, G. A.; Melamed, Ch. L. *Rubb. Chem. Technol.* **1961**, *34*, 588.
44. Toki, S.; Sics I.; Ran S.; Liu, L.; Hsiao, B. S. *Polymer* **2003**, *44*, 6003.
45. Rivlin, R. S.; Thomas, A. G. *J. Polym. Sci.* **1953**, *10*, 291.
46. Arroyo, M.; Lòpez-Manchado, M. A.; Herrero, B. *Polymer* **2003**, *44*, 2447.
47. Morita, E.; D'Amico, J. J.; Young, E. J. *Rubb. Chem. Technol.* **1968**, *41*, 721.
48. Debnath, S. C.; Basu, D. K. *Kautsch. Gummi Kunstst.* **1994**, *47*, 279.
49. Bhawmic, A. K.; Hall, M. M.; Benarey, H. A. In Rubber Products Manufacturing Technology; Marcel Dekker Inc.: USA, **1994**; p 320.
50. Hamed, G. R. In Engineering with Rubber, 2nd ed; Gent, A. N., Eds.; Hanser Gardner Publications, Inc.: Cincinnati, OH, **2001**; Chapter 2, p. 26.
51. Jha, V. Carbon Black Filler Reinforcement of Elastomers, Ph.D. Thesis; University of London: Queen Mary, October **2008**.
52. Kaidou, H.; Ahagon, A. *Rubb. Chem. Technol.* **1990**, *63*, 698.