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STABLE FREE RADICAL ASSISTED MECHANICAL DEVULCANIZATION OF CARBON BLACK FILLED NATURAL RUBBER VULCANIZATES: ROLE OF CARBON BLACK FILLER

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The present paper describes the role of type and amount of carbon black filler present in the NR vulcanizates on the devulcanization efficiency and revulcanizate properties. NR vulcaniszates filled with four different types of carbon black, N220 (20-25nm), N330 (26-30nm), N550 (40-48nm) and N660 (49-60nm) with varying particle size were used for the study. The original NR vulcanizates were mechanically devulcanisized in a two roll mill, both in the presence and absence of a stable free radical, 4-Hydroxy TEMPO (4HT). In all the cases, the per cent devulcanization was significantly higher in stable free radical assisted devulcanization. The type of filler present in the vulcanizate does not seem to have a decisive role on the revulcaniszate properties especially when stable free radical was used as a devulcanization aid. In 4HT assisted devulcanization of carbon black filled natural rubber, irrespective of the particle size of the carbon black filler used for the reinforcement of NR, the revulcanizate properties of the devulcanized rubber obtained were comparable with the original vulcanizate properties of the N660 filled NR vulcanizate. Studies on the effect of N330 content of the original sample upon devulcanization efficiency also revealed that the revulcanizate properties of the stable free radical assisted devulcanized samples were significantly better than that of the corresponding mechanically devulcanised samples.

Key words:, Vulcanization, Devulcanization, Stable free radical, Crosslink density

INTRODUCTION

Recycling of used rubber products has become an important matter of concern due to environmental, monetary and health issues. Devulcanization of used/end-of-life rubber products is a recycling strategy which aims at selective scission of crosslinks with minimal main chain scission, thereby ensuring better reuse of devulcanized rubber as a raw material in the rubber industry itself.

The various devulcanization methods are recently reviewed by Joseph (Joseph *et al*, 2016a). Mechanical/mechano-chemical devulcanization processes which attempt to achieve devulcanization by the action of mechanical shear at ambient conditions, with or without the assistance of a chemical

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modifier, is the most successful devulcanization practice due to cost and time effectiveness and the possibility of high quality of devulcanized rubber the process could deliver. (Chapman, 2007; Goldshtein and Kopylov, 2003; Sekhar *et al*., 1998). The mechano-chemical devulcanization processes envisaged stabilization of crosslink fragments generated through bond scission under the influence of shear by the chemicals employed. In addition, these processes suggest the possibility of targeted crosslink scission by the devulcanization agents employed. Stable free radical assisted mechanical devulcanization of rubber vulcanizates is a recent innovation in the field of mechano-chemical devulcanization in which the entire crosslink scission is expected to be shear mediated while the stable free radical would instantaneously stabilize the free radicals generated from crosslink scission (George *et al*., 2017; Joseph *et al*., 2018).

Though carbon black as reinforcement plays a vital role in the processing characteristics of rubber compounds and its vulcanizate properties, its role in devulcanization and the re-vulcanizate properties have received only limited attention. The effects of carbon black on the ultrasonic devulcanization of NR vulcanizates were studied by Hong and Isayev (Hong and Isayev, 2001) which indicated a minimum of residual crosslink density at intermediate amplitude, which is independent of CB content. The devulcanized CB-filled NR upon revulcanization retained its strain-induced cystallizability with the tensile strength and elongation at break at about 50 and 70 per cent level of the original vulcanizates. The effects of ultrasound on devulcanization of unfilled and carbon black filled isoprene rubber (IR) were studied by Sun (Sun, 2007) which showed that devulcanization of filled IR resulted in more main chain scission than in unfilled IR due to the immobility of bound rubber at the filler surface which leads to lower properties in revulcanized rubbers than in virgin rubber. The present paper describes the results of the investigations on the effect of type and amount of carbon black present in the original vulcanizate on the devulcanization efficiency and revulcanizate properties of the mechanical/stable free radical assisted devulcanized samples.

MATERIALS AND METHODS

NR (ISNR 5) obtained from Pilot Crumb Rubber Factory, Rubber Research Institute of India, Kottayam, and commercial rubber chemicals were used to prepare carbon black–filled NR vulcanizates of known composition and properties. Laboratory grade toluene and acetone were used for characterization of devulcanized rubber. Stable free radical 4-Hydroxy TEMPO (4HT), [4-Hydroxy - 2, 2, 6, 6-tetramethylpiperidine 1-oxyl] was purchased from Merck.

Preparation of original samples

Carbon black filled NR vulcanizates were prepared with 40phr N220 (Intermediate Super Abrasion Furnace black, ISAF), N330 (High Abrasion Furnace black, HAF), N550 (Fast Extrusion Furnace black, FEF) and N660 (General Purpose Furnace black, GPF) fillers to study the role of filler type. Carbon black filled NR vulcanizates with varying N330 concentration from 20 - 60phr were used to study the effect of carbon black concentration on the devulcanization efficiency and revulcanizate properties. The respective formulations are given in Table 1.

Devulcanization

Devulcanization was carried out in a laboratory two-roll mixing mill (15 cm x

Table 1. **Formulation used for the preparation of original vulcaniszates and revulcanizates of devulcanized samples**

Ingredients	Original compound (phr)		Revulcanization (phr)
	Filler type	Filler amount	
Natural Rubber	100	100	10
Devulcanized rubber	-	-	100 *
Carbon black	40 [@]	20 [@@]	-
Naphthenic oil	4	2 [#]	-
ZnO	5	5	3
Stearic acid	2	2	2
TDQ	1.5	1.5	1.5
CBS	0.6	0.6	1.5
Insoluble sulphur	2.5	2.5	0.8

*Rubber hydrocarbon (RH) =50, [@] Fillers used: N220, N330, N550 and N660 blacks, [@@] N330 amount was varied as 20 – 60phr, [#] Oil = 10phf

30 cm) at a friction ratio 1:1.25 (12:15 rpm) at a nip gap of approximately 0.05 mm. Cold water was circulated through the rolls during devulcanization to prevent an increase in temperature during the shearing process and to ensure minimal thermal degradation of polymer. The 2mm thick tensile sheets molded from the original compounds were cut into chips of about 1 cm^2 and made into crumb by passing them through the two-roll mill that was then devulcanized mechanically and with the assistance of stable free radical at a concentration of 4phr. In 4HT-assisted devulcanization, the crumb rubber was mixed with the required amounts of 4HT in a high-speed mixer before devulcanization.

Characterisation of devulcanized rubber

Processability analysis was carried out by strain sweep (Dick, 2003) of the devulcanized rubber samples using an RPA 2000 rubber process analyzer (Alpha Technologies, Akron, OH, USA). Variable strains were applied, via the oscillating lower die of the RPA 2000 instrument. Torque, modulus, and viscosity were measured at a pre-programmed frequency of 6 cycles/min and a temperature of 60°C. The rotation angle was increased as 0.05°, 0.11°, 0.26°, 0.61°, 1.4°, 3.22°, 7.4°, 17.02°, and 39.128°. The processability of the devulcanized samples was compared from the strain versus tan delta plots.

Crosslink density, percent devulcanization and Horikx Analysis

The crosslink density (CLD) of the original samples and the residual CLDs of the devulcanized samples were determined by swelling method applying the Flory-Rhener equation with correction for filler based on which the percent devulcanization was estimated. The experimental details of these are presented elsewhere (Meyasami, 2012; Joseph *et al*., 2016b; 2018). Horikx analysis provides the extent of main chain scission vs. the crosslink scission. For crosslink scission, almost no sol is produced until most of the crosslinks have been removed, whereas for main chain scission much more sol is produced for the same decrease in CLD (Shi *et al.*, 2013).The experimental details of the analysis are also given elsewhere (Joseph *et al.*, 2016b; 2018).

Revulcanization

Ten grams of virgin rubber was blended per 100 g of the crumb for consistency and easy handling after devulcanization and was then revulcanized using the previously optimized revulcanization formulation given in Table I considering the rubber hydrocarbon content of the devulcanized sample to be 50 per cent. The RPA 2000 was used to monitor the cure characteristics at 150°C (at a frequency of 1.67 Hz at an angle 0.58), and the samples were molded in an electrically heated hydraulic press for their respective cure times (t_c90) at 150^0C. Tensile strength and tear strength measurements of the revulcanized samples were performed with a Zwick universal testing machine (Zwick USA, Kennesaw, GA, USA) at a test speed of 460 mm/min.

RESULTS AND DISCUSSION

Effect of type of carbon black used in original vulcanizate

The influence of type of carbon black present in the sample to be devulcanized was studied by monitoring the devulcanization efficiency and corresponding revulcanizate properties of NR vulcanizates filled with N220 (ISAF), N330 (HAF), N550 (FEF) and N660 (GPF) blacks, respectively. Besides, the effect of stable free radical on the devulcanization of these samples was analyzed.

Number of passes through the tight nip

The number of passes required for devulcanization of NR vulcanizates filled with different carbon black fillers are given in Table 2. The required number of passes through the tight nip for devulcanization lowered significantly by the use of 4HT as devulcanization aid. Mechanical devulcanization of NR vulcanizates filled with very small and large sized carbon black fillers is more difficult than those vulcanizates containing intermediate sized carbon black fillers. On the other hand, the incorporation of 4HT as a devulcanization aid lifted the restriction imparted by the filler size upon mechanical devulcanization and led to comparable number of passes for all samples irrespective of the type of carbon black filler present in the vulcanizate.

Table 2. **Required number of passes for devulcanization of NR vulcanizates filled with different carbon blacks**

Carbon black	Number of passes through 0.05mm nip gap	
	Mechanical	4HT assisted
N220	60	39
N330	50	40
N550	50	42
N660	60	36

Residual crosslink density and per cent devulcanization

The crosslink densities of the original vulcanizates and the corresponding

Table 3. **Crosslink densities of original and devulcanized samples containing different types carbon black fillers and the corresponding per cent devulcanization***

Carbon black	Crosslink density x10^4, mole/ cm^3		
	Virgin	Mechanical	4HT assisted
N220	1.26	0.98 (22)	0.77 (39)
N330	1.40	1.11 (21)	0.80 (43)
N550	1.48	1.13 (24)	0.85 (43)
N660	1.33	1.00 (25)	0.80 (40)

* (Values in parentheses indicates per cent devulcanization)

Table 4. **Cure characteristics of original NR compound containing different carbon black fillers and corresponding devulcanized rubber samples**

Compound	Torque (dNm)			Scorch time, min	Cure time, min
	Minimum, M_L	Maximum, M_H	M_H- M_L		
Virgin N220	1.7	15.5	13.8	4.1	11.4
N220 DV	6.4	15	8.6	1.2	5
N220 4HT DV	2.7	13.3	10.6	1	4.7
Virgin N330	1.4	15.1	13.7	3.9	10.9
N330 DV	5.9	13.3	7.4	1.3	4.9
N330 4HT DV	2.7	12.7	10	1	4.4
Virgin N550	1	14.7	13.7	3.7	10
N550 DV	6.2	13.5	7.3	1.4	4.8
N550 4HT DV	2.5	12.7	10.2	1	4.4
Virgin N660	1	13.9	12.9	4.2	10.5
N660 DV	5.7	13.1	7.4	1.4	4.8
N660 4HT DV	2.6	12.3	9.7	1	4.3

devulcanized samples given in Table 3 show that the residual crosslink densities 4HT assisted devulcanized samples are significantly lower than the corresponding values of mechanically devulcanized samples. Correspondingly, the per cent devulcanization of 4HT assisted devulcanized samples are significantly higher than that of the corresponding mechanically devulcanized samples .The particle size of the carbon black has not significantly influenced the per cent devulcanization within either mechanical or 4HT assisted devulcanized samples.

Cure characteristics

The cure characteristics of the original and devulcanized NR vulcanizates containing different type carbon black fillers are listed in Table 4. The cure characteristics of the virgin samples were comparable irrespective of the type of filler present in them. In the case of devulcanized samples, higher minimum torque, lower maximum torque, lower total torque, low scorch time and cure time were observed in comparison with the corresponding virgin vulcanizates (Joseph *et al*., 2017a; Tukachinsky,1996). The scorch time and cure time of the vulcanizates devulcanized mechanically or with the aid of 4HT were comparable, but a lower minimum torque and a corresponding higher total torque were associated with the 4HT assisted devulcanized samples (Joseph *et al*., 2017b).

Table 5. **Crosslink densities of revulcanized samples in comparison with corresponding original vulcanizates containing different types of carbon black**

Filler present in vulcanisate	Crosslink density x10^4, mole/ cm^3		
	Virgin	Revulcanised after	
		DV	4HT DV
N220	1.26	1.74	1.71
N330	1.4	1.84	1.77
N550	1.48	1.57	1.8
N660	1.33	1.63	1.82

Revulcanizate properties: Comparison with vulcanizate properties of the original sample

The revulcanizate crosslink densities of the devulcanized samples in comparison with the corresponding virgin vulcanizates are given in Table 5. The crosslink densities of the revulcanized samples were higher than the corresponding virgin vulcanizates. The revulcanizate properties of the devulcanized samples in comparison with the original vulcanizate properties are given in Table 6. The shore A hardness of the virgin vulcanizates were almost comparable. In the case of revulcanized samples, the hardness of all the mechanically devulcanized samples were comparable but lower than the corresponding virgin vulcanizate especially in the case of vulcanizates filled with lower particle sized carbon blacks. Generally, the hardness of 4HT assisted devulcanized samples were higher than the corresponding mechanically devulcanized samples. The tensile and tear strengths of the original vulcanizates decreased as the size of the filler increased from N220 to N660. The trend is more obvious with tear strength. The low tensile and tear strengths of the N550 and N660 filled vulcanizates might be due to the low reinforcing effect of these fillers owing to their larger size compared with N220 and N330 blacks.

Significantly higher revulcanizate propereties were obtained when 4HT was used as a devulcanization aid. Irrespective of the particle size of the filler used for the preparation of original sample, tensile strength of the revulcanizates of the devulcanized samples was mostly comparable within a system. The elongation at break of the revulcanized samples prepared from mechanically devulcanized vulcanizates decreased with increasing particle size of the filler present in them *i.e.* from N220 to N660. On the other hand, irrespective of the particle size of the carbon black, the 4HT assisted devulcanized

Table 6. **Original vulcanizate properties and revulcanizate properties of devulcanized samples filled with different types of carbon black**

Vulcanisate	Hardness (shore A)	Tensile Strength (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
Virgin N220	67	26.5	629	2.0	4.6	8.4	111.9
N220 DV	63	12.8	382	1.8	4	8.1	39.4
N220 4HT DV	65	20.1	478	2.0	4.2	8	63.2
Virgin N330	68	25.3	584	2.1	5.2	9.5	116.4
N330 DV	63	13.4	361	1.9	4.5	9.2	36.8
N330 4HT DV	66	18.7	506	1.8	4	7.5	59.6
Virgin N550	66	22	533	2.2	5.6	10	67.9
N550 DV	64	11.8	333	2	4.9	9.7	32.4
N550 4HT DV	66	17.5	441	2	4.5	8.9	50.7
Virgin N660	65	23	556	2.0	5.1	9.3	62.5
N660 DV	64	7.6	246	2.1	5.0	-	35.8
N660 4HT DV	64	18.0	473	1.9	4.4	8.1	61.0

Table 7. **Effect of different types of carbon black on per cent retention of revulcanizate properties**

Vulcanisate	Per cent retention (%)					
	Tensile Strength	Elongation at break	M100	M200	M300	Tear strength
N220 DV	48.5	60.6	90	88.5	95.5	35.2
N220 4HT DV	75.8	76	101.9	100.6	103.5	56.5
N330 DV	53.2	61.8	87.5	85.6	96.4	31.6
N330 4HT DV	73.9	86.7	84.1	77.2	78.5	51.2
N550 DV	53.7	62.4	91.6	86.4	96.5	47.7
N550 4HT DV	79.6	82.6	89.9	82.6	88.3	74.7
N660 DV	33.1	44.2	104.5	99.2	-	57.3
N660 4HT DV	78.6	85.1	95.1	86	86.7	97.6

samples had comparable elongation at break values after revulcanization. However, the respective modulus values were comparable for all the revulcanizates. As observed with previous studies on the effect of stable free radical on the devulcanization of NR vulcanizates, the tear strengths of the revulcanizates were considerably improved when devulcanization was carried out with the aid of stable free radical (Joseph *et al.*, 2018).

The impact different types of carbon black ,used for the reinforcement of original sample, on percent retention of properties by the corresponding revulcanized samples are listed in Table 7. While drawing inferences from the per cent retention values, the results might mislead if not evaluated along with the absolute values in this case. It can be observed that, the percent retention of tear strength increased significantly corresponding to the increase in the particle size of filler present. The higher per cent retention of tear strength associated with the revulcanizates of carbon blacks of higher particle size were due to the significantly lower tear strength of the corresponding virgin samples.

Revulcanizate properties: Comparison with the vulcanizate properties of original NR/N660 sample

Comparison of vulcanizate properties of virgin NR/N660 samples with the revulcanizate properties of devulcanized samples is represented in Figure 1. Irrespective of the type of filler system used for the preparation of original vulcanizate, the 4HT assisted devulcanized rubber can provide revulcanizate properties almost comparable with the original N660 vulcanizate. This observation might be indicating that, the un-devulcanized parts present in the devulcanized rubber matrix might be acting as filler with a particle size comparable with the particle size of N660 black during revulcanization, thereby leading to a reinforcement level associated with N660 black in a rubber vulcanizate. Thus, the revulcanizate properties of the devulcanized samples could not rise above the vulcanizate properties attainable by N660 filled NR vulcanizate.

In the case of mechanically devulcanized samples, these vulcanized moieties present in the devulcanized rubber might be still of

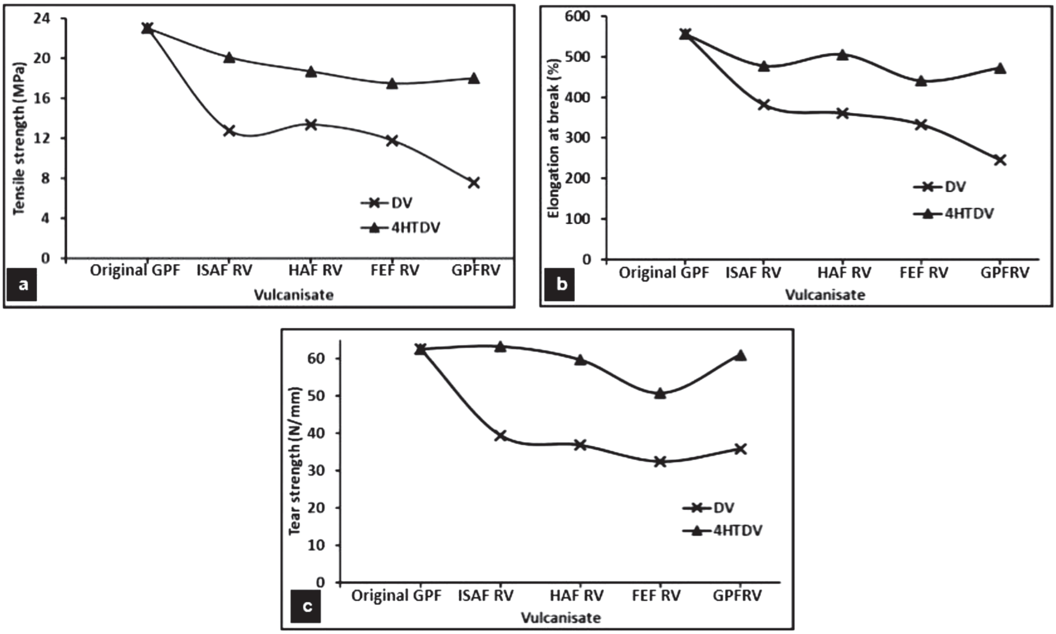

Fig. 1. Comparison of revulcanizate a: tensile strength; b: elongation at break and c: tear strength of the samples containing different carbon blacks with original properties of NR/N660 vulcanizate

higher particle size or the number of such moieties would be so large that, they could not be properly dispersed in the matrix to exert any reinforcing effect. They might be acting as points of weakness and result in lower revulcanizate properties. The higher per cent devulcanization associated with 4HT assisted devulcanization might also be ensuring the vulcanized moieties to disperse within the devulcanized rubber just like filler and influence the revulcanizate properties of the devulcanized rubber based on the particle size of these structures. In the case of devulcanized samples prepared by the devulcanization of original NR vulcanizate filled with N660 black, the revulcanizate properties shows a tendency to improve over that of corresponding sample with N330. This might be due to the uniformity in the size of fillers – both N660 and

Table 8. **Revulcanizate properties of 4HT assisted devulcanized samples filled with different carbon blacks and corresponding properties of original N660 filled vulcanizate**

Vulcanisate	Hardness (shore A)	Tensile Strength (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
Virgin N660	65	23	556	2.0	5.1	9.3	62.5
N220 4HT DV	65	20.1	478	2.0	4.2	8	63.2
N330 4HT DV	66	18.7	506	1.8	4	7.5	59.6
N550 4HT DV	66	17.5	441	2	4.5	8.9	50.7
N660 4HT DV	64	18.0	473	1.9	4.4	8.1	61.0

vulcanised moieties- present in the vulcanizate rendering more effective reinforcement to attain higher revulcanizate properties. The revulcanizate properties of the samples devulcanized with the assistance of 4HT along with the corresponding vulcanizate properties of the original N660 filled NR vulcanizate is given in Table 8.

Effect of amount of carbon black present in original vulcanizate

The role of carbon black content present in the samples to be devulcanized on the devulcanization efficiency and the resultant revulcanizate properties were studied using N330 filled NR vulcanizates. The N330 content in the vulcanizates was varied from 20phr to 60phr. The original vulcanizates were devulcanized, characterized by determining the percent devulcanization, sol fraction and processability associated with the devulcanized samples and was correlated with the revulcanizate properties.

Required number of passes through tight nip for devulcanization

The amount of filler present in the sample to be devulcanized is also found to influence the number of passes/ time required for the devulcanization of the sample. In mechanical devulcanization, the number of passes for 20phr and 30phr N330 filled vulcanizates were limited to 30 as it became increasingly difficult to devulcanize the sample further owing to excessive roll sticking. The number of passes reduced from 50 to 45 and further 40 as the carbon black content increased from 40, 50 and 60 respectively. But, in the case of 4HT assisted devulcanization, the vulcanizate had a better response towards devulcanization and roll sticking was minimized. The 4HT assisted devulcanization of 20phr N330 vulcanizates were limited to 25 passes to avoid excessive sticking on to the roll. This problem was further reduced with higher loadings of N330. The required number of passes through the tight nip for devulcanization lowered significantly (30-35 passes) when the stable free radical 4HT was used.

Processability analysis

The processability of devulcanized samples was ascertained based on the tan delta values of the devulcanized samples in the uncured state at 60C. The plot of log tan delta values against log strain of the devulcanized samples along with the corresponding original compounds are plotted in Figure 2(a-c). Since tan delta value represents the ratio of viscous quantity of the rubber to the elastic quantity, a higher tan delta value denotes a higher viscous behavior and lower elastic behavior of the corresponding sample. Upon devulcanization, the crosslinks which imparts the elastic nature to the vulcanizates are cleaved thereby bringing back the viscous nature of the raw rubber as the prominent nature. As the efficiency of devulcanization increases, the viscous content is expected to increase with a corresponding increase in the tan delta values.

Figure 2a demonstrates the lowering of uncured tan delta response with increasing concentrations of carbon black due to the increase in the density of carbon black aggregate-aggregate network leading to a higher uncured elastic modulus response (Chuayjuljit *et al*., 2002) thus lowering the tan delta value with increase in filler content. The tan delta variations of devulcanized samples are under the influence of two opposing tendencies. Although devulcanization ideally

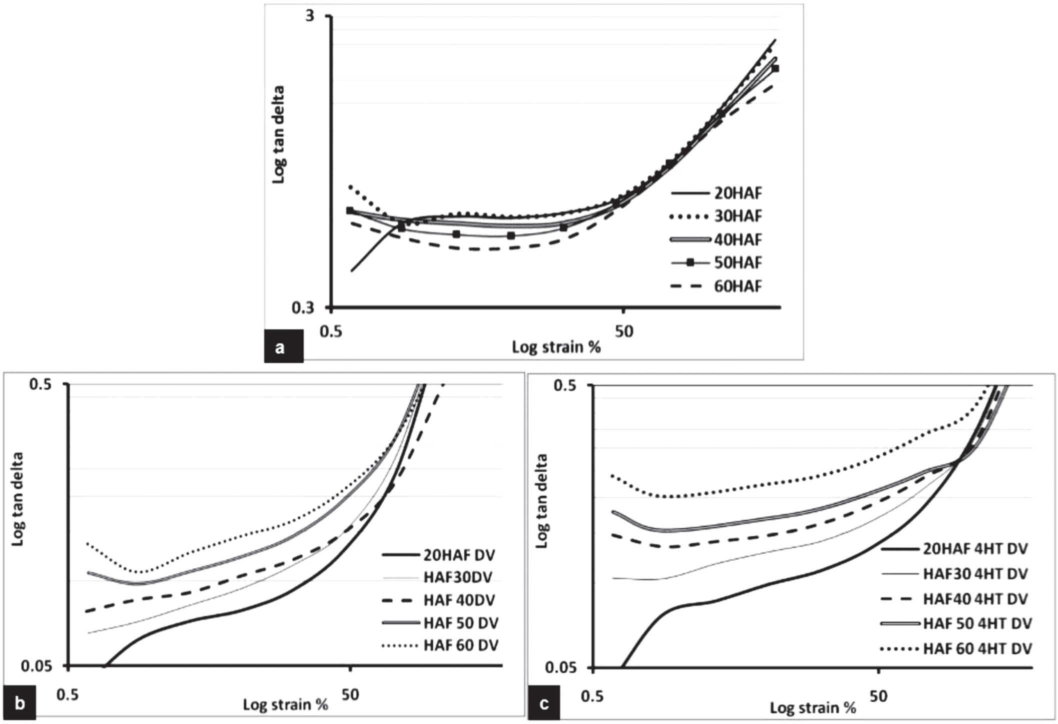

Fig. 2. Effect of N330 concentration on the processability of **a:** virgin **b:** mechanically devulcanized samples and **c:** 4HT assisted devulcanized samples based on tan delta values

envisages crosslink scission to ensure retrieval of un-crosslinked elastomer, it practically could render a sample with significant number of crosslinks (vulcanized moieties which might act as filler) still present. Hence devulcanized rubber with varying per cent devulcanization shows corresponding variations in the tan delta response based on the variation in its elastic and viscous components but still remain as cured elastomer even in the uncured state. Thus, the uncured tan delta response of the devulcanized samples followed the trend corresponding to the cured rubber with varying filler content and not that of the uncured elastomer more probably when the per cent devulcanization is low. The increased filler loadings reduce the amount of rubber available for crosslinking and increase the interface area between rubber and filler which results in an increase in tan delta value with filler loading (Fig. 2b and 2c) (Dick and Pawloski, 1993; 1995).

On the other hand, the tan delta values of the 4HT assisted devulcanized samples were significantly higher than that of the corresponding mechanically devulcanized samples indicating higher viscous part of the former due to its higher percent devulcanization (Joseph, 2017b).

Residual crosslink density and per cent devulcanization

The crosslink densities of the original vulcanizates and the residual crosslink densities and per cent devulcanization of the corresponding 4HT assisted devulcanized samples are given in Table 9. The crosslink density of the original vulcanizate increased with increase in filler content in the vulcanizate. This is due to the strong interaction between rubber molecules and the surface of the carbon black particles as carbon black has little influence on chemical crosslink density introduced by vulcanization (Fei *et al.*, 2012). A corresponding increasing trend is observed with the residual crosslink density of the devulanized samples also. At lower filler content and lower crosslink density of the original vulcanizate, the per cent devulcanization was higher and vice versa. The observation is similar to the inferences drawn from the processability analysis.

Table 9. **Crosslink densities of original sample and 4HT assisted devulcanized samples with varying N330 loading and their corresponding per cent devulcanization**

Vulcanizate/ N330 loading		Crosslink density x10^4, mole/cm^3	Per cent devulcanization (%)
20phr	Virgin	1.24	-
	4HT DV	0.54	56
30phr	Virgin	1.3	-
	4HT DV	0.61	53
40phr	Virgin	1.34	-
	4HT DV	0.67	50
50phr	Virgin	1.41	-
	4HT DV	0.75	47
60phr	Virgin	1.52	-
	4HT DV	0.82	46

Horikx analysis

The Horikx plot of the samples with varying N330 content after 4HT assisted devulcanization is given in Figure 3. The figure indicates that, the sol fraction of the devulcanized rubber increases marginally with increase in the filler loading of the original vulcanizate. Also, the data moves closer to the directed scission curve. This indicates that, the increase in the sol fraction of the devulcanized samples with increase in the filler content of the original vulcanizate might be attributed to the increase in the main chain scission associated with these samples during devulcanization.

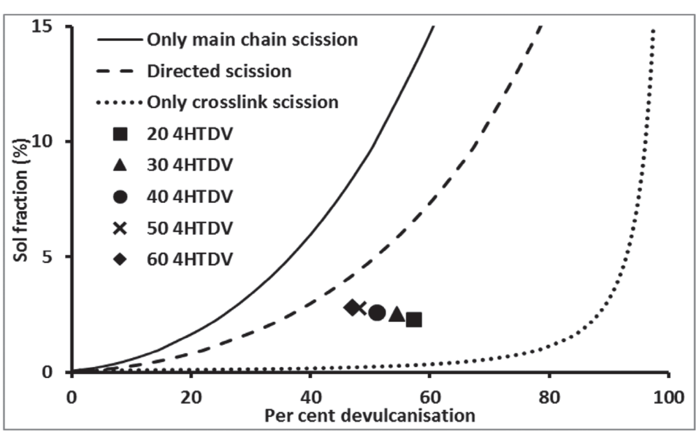

Fig. 3. Horikx plot of 4HT assisted devulcanized NR vulcaniszates with varying N330 loading

Cure characteristics

The cure curves of the original and the corresponding devulcanized samples during revulcanization are out lined in Figure 4 (a-c). Both the minimum torque and maximum torque of the virgin NR vulcanizates and that of the devulcanized samples during revulcanization increased with the increase in N330 content in the sample. For devulcanized samples, the hike in minimum torque with increasing filler concentration is more prominent than the increase in maximum torque. The increase in minimum torque with N330 loading in virgin compound might be because the N330 particles would lead to greater adhesion between the filler and the rubber. Though higher than the minimum torque of virgin vulcanizate, the minimum torque of 4HT assisted devulcanized samples were lower than the corresponding mechanically devulcanized samples resulting in a higher total torque than the corresponding mechanically devulcanized samples. The scorch time of the virgin and devulcanized vulcanizates decreased marginally as the N330 loading increased while the scorch time and cure times of the devulcanized samples were significantly lower than the corresponding virgin vulcanizates.

Revulcanizate properties

The revulcanizate properties of the devulcanized samples are listed in Table 10. The general observations that can be made from the revulcanizate properties are

(I) The tensile strength and elongation at break of the virgin vulcanizates

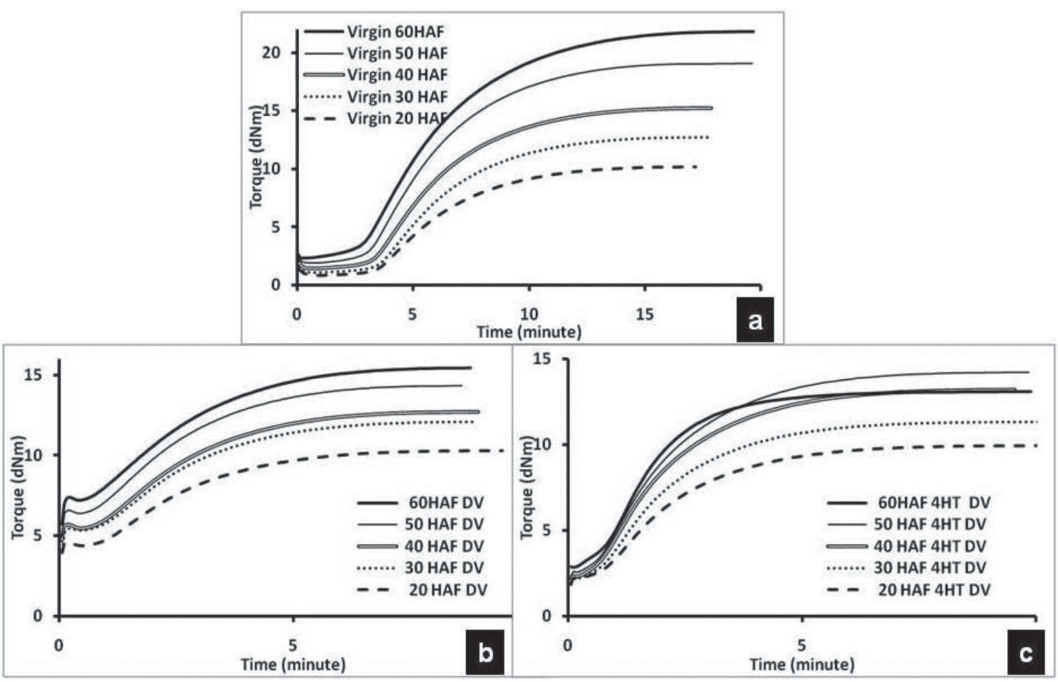

Fig. 4. Cure curves of **a:** virgin vulcanizates and revulcanization cure curves of corresponding **b:** mechanically and **c:** 4HT assisted devulcanized samples containing different amounts of N330 filler

Table 10. **Vulcanizate properties of original and revulcanized NR samples filled with different amounts of N330 black**

N330 (phr)	Vulcanizate	Tensile Strength (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength (N/mm)
20	Virgin	27.6	692	1.2	2.6	5	58.9
	DV	13.3	398	1.7	3.5	6.9	27.7
	4HT DV	20.9	505	1.6	3.4	6.6	46.5
30	Virgin	25.3	620	1.7	3.9	7.3	82.4
	DV	13.5	364	2.0	4.4	8.9	30.6
	4HT DV	20.8	482	2.1	4.7	8.7	57
40	Virgin	25.6	592	2.3	5.4	7.4	103
	DV	12.9	326	2.3	5.5	11.1	33.5
	4HT DV	22.2	457	2.5	5.5	10.1	57.9
50	Virgin	24.4	562	2.7	6.6	11.5	107.6
	DV	15.5	336	2.7	6.5	12.7	33.2
	4HT DV	20	415	2.6	6	11.4	59.5
60	Virgin	24.4	493	4.3	9.7	15.4	123.8
	DV	11.7	256	3.1	7.8	-	33
	4HT DV	22.9	414	3.1	7.6	14.4	62.5

decreased and the modulus values and tear strength increased with increasing N330 loading

(II) Thetensile strength and tear strength of the revulcanizates after mechanical devulcanization were comparable while the elongation at break decreased and modulus increased with increasing N330 loading

(III) The revulcanizate properties of the 4HT assisted devulcanized samples were significantly higher than that of the mechanically devulcanized samples

As the chemical structure of the different vulcanizates considered in this study are different owing to the variation in carbon black content in the vulcanizate, the resultant physical properties will also vary. Hence, it appears that, the state of devulcanization and the revulcanizate properties of various vulcanizates studied could not be cross compared. As observed from previous studies, higher retention of the revulcanizate tensile properties can be achieved by moderate levels of devulcanization and the tear properties are the most sensitive markers for efficiency of devulcanization (Joseph *et al*., 2016b; Joseph *et al*., 2017b; Joseph *et al*., 2018). But in this case, it has to be assumed that, the effect of per cent devulcanization upon tear properties were masked by the increase in the amount of filler present in the vulcanizate which was found to improve the tear properties specifically.

CONCLUSION

The role of carbon black filler type and amount of filler present in the virgin NR vulcanizates on the devulcanization efficiency and revulcanizate properties were investigated. The studies pointed that, irrespective of the comparable per cent devulcanization after mechanical devulcanization of NR samples containing different carbon blacks, the revulcanizate tensile properties tend to decrease with increasing particle size of the filler while the 4HT assisted devulcanized samples had comparable revulcanizate tensile strength. Besides, though the revulcanizate tear strength of the samples was comparable, the per cent retention of tear strength after revulcanization increased with increase in the size of filler present in the vulcanizate both in the case of mechanical and 4HT assisted devulcanization. It was observed that the type of filler present in the vulcanizate does not have a decisive role on the revulcanizate properties especially when stable free radical was used as a devulcanization aid. Irrespective of the type of filler system used for the preparation of original vulcanizate, the 4HT assisted devulcanization can provide revulcanizate properties almost comparable with that of the original N660 vulcanizate. This indicates that the residual crosslinked parts present in the devulcanized rubber matrix might be acting as filler during revulcanization with a particle size comparable with the particle size of N660 black, thereby attaining the reinforcement level comparable with N660 black filled virgin natural rubber vulcanizate. The revulcanizate properties of devulcanized NR vulcanizates with N330 content 20 to 60phr suggested that, all revulcanizate properties were better with 4HT assisted devulcanized samples.

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