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STABLE FREE RADICAL ASSISTED MECHANICAL DEVULCANISATION OF CARBON BLACK FILLED NR VULCANISATES: DEVULCANISATION OF UN-AGED AND AGED SAMPLES

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Devulcanisation of filled rubber vulcanisates through mechanical/ mechano-chemical processes in a two-roll mill is a well-established technique. The general mechanism of mechano-chemical devulcanisation suggests blocking of possible reunion of free radicals produced *via* crosslink scission. Hence the efficiency of shear induced devulcanisation processes can be improved significantly by the effective utilization of a chemical /process that can instantaneously block the reunion of the radicals formed by bond scission. A new concept of blocking the reunion free radicals formed by shear breaking of crosslinks using a stable free radical and thereby increasing the efficiency of devulcanisation is presented. A cyclic nitroxide stable free radical *viz.* 4-hydroxy 2, 2, 6, 6-tetramethylpiperidine 1-oxyl free radical (4-Hydroxy TEMPO abbreviated as 4HT) assisted mechanical devulcanisation of carbon black filled NR vulcanisates (un-aged and aged) in which 4HT was used to block the recombination of the radicals formed by bond scission.

Stable free radical increased the per cent devulcanisation and revulcanisate properties of devulcanised rubber in all cases under consideration. The recombining capacity of different type of cleaved crosslinks (mono-, di- and poly- sulphidic) were found to decisively influence the per cent devulcanisation of samples under shear induced devulcanisation. The influence of factors like cure system, crosslink density, the extent of ageing *etc*. of the original sample on the devulcanisation efficiency and the subsequent revulcanisate properties are discussed in detail.

Key words: Mechanical devulcanisation, Mechano-chemical devulcanisation, Revulcanisate properties, Stable free radical

INTRODUCTION

Devulcanisation is a process of rubber recycling aimed to retrieve polymer chains in used rubber products by selective scission of crosslinks (with minimum main chain scission). The process of devulcanisation envisages maximum retention of vulcanisate properties enabling its maximum reuse in the rubber industry itself. Among the various devulcanisation strategies with inherent merits and demerits, mechano-chemical devulcanisation processes like the De Link process (Sekhar *et al.*, 1998; Sekhar, 2014) and the Lev-Gum process (Goldshtein and

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Kopylov, 2002) carried out at ambient reaction conditions were industrially taken up due to time, cost, and energy savings along with better revulcanisate properties due to minimum main chain scission. On the other hand, studies on mechanical devulcanisation process in which rubber is devulcanised by mechanical shear in the absence of any chemicals are also reported (Madhusoodanan *et al*., 1998).

De Link process (Sekhar, 2014; Newell, 1996) envisages a mechano-chemical devulcanisation process in which mechanical shear exposes fresh rubber surfaces which is being reacted upon by the De Link reactant - a mixture of rubber accelerators and activators – which uncouples the sulphur crosslinks in a vulcanised network. Lev Gum process involves shearing of rubber crumb and a modifying composition in a two-roll mill at ambient conditions (Beirakh *et al*., 2004). The process claims that the superior nature of the recycled rubber obtained by Lev Gum process ensures up to 30 per cent replacement of the total rubber used for each tyre, thereby helps to drastically reduce the cost of the product (Zamir, 2011). Comparable mechanical properties were reported for revulcanised gum samples after chemical and mechano-chemical devulcanisation using benzoyl peroxide as devulcanisation aid in a sigma mixer at 80 °C (Rooj *et al*., 2011). Several reports on the use of disulphides (De *et al*., 1999; Jana and Das 2005a, b, c; Mandal *et al*., 2012; Namsri and Thanawan, 2009) and various other chemicals for mechano-chemical devulcanisation studies were found in literature and are recently reviewed (Joseph *et al*., 2016).

According to the generally accepted mechanism of mechano-chemical devulcanization, crosslink scission would generate free radicals which can potentially recombine if not stabilized. The chemicals used in the mechano-chemical devulcanization processes are claimed to induce targeted crosslink scission and enable subsequent stabilization of free radicals thus generated. A critical review of the literature and work carried out in our laboratory have shown that, the revulcanisate properties of all the mechano-chemical devulcanisation processes mentioned above are comparable with that of the mechanical devulcanisation. If chemicals which are related in no way can bring about same result through similar processes, it might be assumed that it is the process *i.e.* the mechanical shearing and not the chemicals that bring about the result. Therefore it is probable that, among the free radicals formed by the shear breaking of crosslinks, some might have been stabilized by some species in the matrix and a significant number might be recombining leading to a net lower percent of devulcanisation. In this context, it might be hypothesized that during shear induced devulcanisation processes, crosslink breaking and reformation are competitive and any chemical/process which can effectively and instantaneously block the recombination of the radicals formed by bond scission can significantly improve the efficiency of devulcanisation process. Based on this hypothesis cyclic nitroxide stable free radical *viz.* 4-hydroxy 2, 2, 6, 6-tetramethylpiperidine 1-oxyl free radical (4-hydroxy TEMPO abbreviated as 4HT) assisted mechanical devulcanisation of carbon black filled NR vulcanisates in which, 4HT is used an agent to block the recombination of the radicals formed by bond scission at ambient conditions was experimented which substantially improved the efficiency of devulcanisation (George *et al*., 2017; Joseph *et al*., 2017a).

In the present study, 1phr 4-hydroxy TEMPO was used as an aid for mechanical devulcanization of carbon black filled natural rubber (NR) vulcanizates (both aged and un-aged) cured with conventional vulcanisation (CV), semi efficient vulcanisation (Semi EV) and efficient vulcanisation (EV) cure systems. The stable free radical 4-hydroxy TEMPO (4HT) is not expected to influence the crosslink scission which is completely shear mediated. NR vulcanisates of known composition and properties were used to make a reliable estimate of the efficiency of devulcanisation and comparison of revulcaniste properties. Devulcanisation of samples aged in laboratory oven under different conditions was carried out to simulate the devulcanisation of commercially available used rubber products which have undergone different levels of degradation in their service life. The paper also provides the results obtained for a corresponding control experiment in which devulcanisation was carried out mechanically in the absence of the stable free radical for reliable determination of the efficiency of the new devulcanisation process.

MATERIALS AND METHODS

Natural rubber (ISNR 5) obtained from Pilot Crumb Rubber Factory, Rubber Research Institute of India, Kottayam and other commercial rubber chemicals were used to prepare the samples having different cure systems from CV through Semi EV to EV (Table I).

Devulcanisation and revulcanisation

NR vulcanisates of known composition and properties were prepared in the laboratory using CV, semi EV and EV cure systems as given in Table I. Devulcanisation was carried out in a laboratory two-roll mixing mill of 15 x 30 cm size, model 172 (David Bridge & Company, Castleton Rochdale, England) at a friction ratio 1:1.25 (12:15 rpm). Cold water was circulated through the rolls throughout the process to check the possible thermal degradation of the polymer under the influence of temperature generated during the shearing process. The tensile sheets moulded from the original compound were cut into chips of about 1cm^2 size was made into crumb by passing through the two-roll mill and devulcanised by passing the crumb (100 g) through the tight nip (approx. 0.05 mm) of the two-roll mill both in the absence and presence of 4HT (1phr). The designations used for different samples are given in Table 2.

10 g of virgin rubber was blended with 100g of the devulcanised crumb for consistency and processing easiness followed by revulcanisation as per the formulations given in Table I at 150 °C. Tensile sheets prepared from virgin compound

Table 1. **Formulation for original samples and revulcanisation**

Ingredients	Quantity, phr			
	Original compound			Revulcanisation
	CV	semi EV	EV	Quantity
Natural rubber	100	100	100	10
Devulcanised rubber	-	-	-	100
HAF black	40	40	40	-
Aromatic oil	4	4	4	-
N-cyclohexyl-2-benzothiazolesulfenamide	0.6	1.5	2.5	-
N-oxydienthylene-2-benzothiazole sulphonamide	-	-	-	0.8
Insoluble sulphur	2.5	1.5	0.6	1.5

Other ingredients: 2,2,4 trimethyl-1,2 dihydroquinoline (TDQ) - 1.5; Zinc oxide -5; Stearic acid - 2

Table 2. **Designation of samples**

Conditions	CV	Semi EV	EV
Un-aged	CV	SEV	EV
Aged at 70 °C for 7 days	CV70	SEV70	EV70
Aged at 100 °C for 3 days	CV100	SEV100	EV100
Mechanically devulcanised	CV DV	SEV DV	EV DV
4HT assisted devulcanised	CV 4HTDV	SEV 4HTDV	EV 4HTDV
Mechanically devulcanised after ageing at 70 °C for 7 days	CV70 DV	SEV70 DV	EV70 DV
4HT assisted devulcanisation after ageing at 70 °C for 7 days	CV70 4HTDV	SEV70 4HTDV	EV70 4HTDV
Mechanically devulcanised after ageing at 100 °C for 3 days	CV100 DV	SEV100 DV	EV100 DV
4HT assisted devulcanisation after ageing at 100 °C for 3 days	CV100 4HTDV	SEV100 4HTDV	EV100 4HTDV

were aged in the laboratory oven at 70 °C for seven days and at 100 °C for three days and the vulcanisate properties of the aged samples were determined and were used as raw materials for devulcanisation of aged samples. Devulcanisation and revulcanisation of aged samples followed the same protocol as that used for the unaged samples.

Cure characteristics and physical property measurement

Monsanto rheometer was used to monitor the cure characteristics of the samples at 150 °C. Test samples were moulded in an electrically heated hydraulic press to the respective cure times (tc90). Tensile strength and tear strength measurements of the revulcanised samples were performed with a Zwick UTM and the per cent retention of vulcanisate properties after revulcanisation were calculated.

Crosslink density and percent devulcanisation

The crosslink densities (CLD) of the original samples and the residual crosslink densities of the devulcanised samples were determined by swelling method using Flory Rhener equation (Flory and Rehner, 1943; Meyasami, 2012). Correction for filler (Rooj *et al.*, 2011) is also applied while calculating the volume fraction of the swollen samples.

$$Mc = \frac{\rho r \times Vs\left(\varphi^{1/3} - \frac{\varphi}{2}\right)}{\{\ln(1-\varphi) + \varphi + \chi\varphi^{2}\}} \text{ -------(1)}$$

$$\nu = \frac{1}{2Mc} \text{ -----------(2)}$$

$$\varphi = \frac{(Dw - FH)/\rho r}{\left\{(Dw - FH)/\rho r\right\} + \left\{(Sw - Dw)/\rho s\right\}} \text{ ----(3)}$$

φ = volume fraction of rubber in swollen gel

Dw = deswollen weight of sample

ρr = density of rubber

ρs = density of solvent

Sw = swollen weight of sample

F = weight fraction of the insoluble components
H = initial weight of the sample
Mc = Molecular weight between crosslinks
Vs = molar volume of solvent
χ = polymer solvent interaction parameter
ν = crosslink density in mole cm^{-3}

The per cent devulcanisation was calculated following ASTM D 6814-02 as,

Per cent devulcanisation =

$$\left[1-\left(\frac{\text{crosslink density devulcanised sample}}{\text{crosslink density of original sample}}\right)\right] \text{x } 100 \quad ...(4)$$

RESULTS AND DISCUSSION

Devulcanisation of un-aged samples

Number of passes in two-roll mill

All samples prepared in the laboratory (with known formulation and vulcanisate properties) were converted to crumb rubber powder by passing it in a two-roll mill. It was then devulcanised by shearing in the tight nip of the two-roll mill several times. The time required for attaining the required level of devulcanisation varied with the cure system of the sample (Fig. 1). The devulcanisation time reduced with the incorporation of 4HT as a devulcanisation aid in comparison with that of the mechanical devulcanisation of corresponding sample. This indicates the positive influence of 4HT as an effective mechanical devulcanisation aid. The devulcanisation time increased with ageing of samples.

Residual crosslink density and per cent devulcanisation

Crosslink densities of the original and corresponding devulcanised samples are given in Table 3. The residual crosslink densities of the 4HT assisted devulcanised samples were significantly lower than the corresponding mechanically devulcanised sample which are further exhibited in the percent devulcanisation (Fig. 2).

Table 3. **Crosslink densities of original and corresponding devulcanised samples**

Sample	Crosslink density x 10^4, mole/cm^3		
	CV	Semi EV	EV
Original	1.41	1.36	0.76
Mechanical devulcanisation	1.07	0.87	0.21
4HT assisted devulcanisation	0.66	0.6	0.18

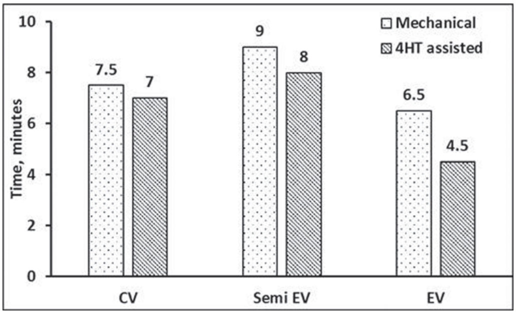

Fig. 1. Time for devulcanisation of un-aged samples after passing through the tight nip of two-roll mill

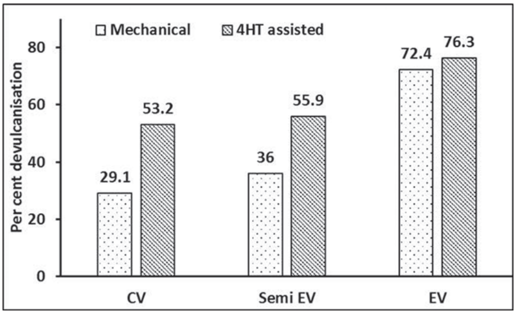

Fig. 2. Per cent devulcanisation of NR samples devulcanised without and with the assistance of 4HT

Variations in the increment of percent devulcanisation between mechanical and 4HT assisted devulcanisation of different samples points to the variation in response of the samples cured with different cure systems towards devulcanisation. Significantly higher percent devulcanisation was attained after 4HT assisted devulcanisation in all cases except for EV cured samples. Comparable percent devulcanisation was attained by CV and semi EV cured samples after 4HT assisted devulcanisation whereas the per cent devulcanisation of mechanically devulcanised CV samples was lower than the corresponding semi EV samples. This indicates that the presence of 4HT even out the response of these samples towards mechanical devulcanisation.

On the other hand, the per cent devulcanisation of both mechanically and stable free radical assisted devulcanised EV samples were comparable. This might be due to (i) the lower crosslink density of the original EV samples enabling better devulcanisation even by mechanical devulcanisation alone and (ii) the crosslink distribution of EV cured samples might be more favorable for effective devulcanisation than the corresponding CV and semi EV cured samples making the assistance of 4HT as a devulcanisation aid less significant. Since, stable free radicals are introduced to prevent the recombination of free radicals generated by crosslink scission, it might be assumed that, the recombining capacity of crosslinks would also be influencing the percent devulcanisation.

Though polysulphidic crosslinks have lower bond dissociation energy and therefore are easier to break under shear, the faster recombining capacity of the broken polysulphide crosslinks might lead to lower effective percent devulcanisation. The recombining capacity might be decreasing in the order poly > di > mono - sulphidic crosslinks. Thus, the vulcanisates containing larger percent of di and mono sulphidic crosslinks with higher bond dissociation energies effectively leads to higher percent of devulcanisation due to the lower recombining efficiency of the resultant free radicals. Addition of the stable free radical effectively blocks the recombining of the polysulphidic free radicals and thus closes the gap in percent devulcanisation between CV and semi-EV samples. The exceptionally higher percent devulcanisation of the EV system on simple mechanical devulcanisation might also be due to the lower crosslink density of the original sample.

Table 4. **Cure characteristics of original and devulcanised NR vulcanisates**

Devulcanisation process	Torque (dNm)			Scorch time	Cure time
	Minimum, M_L	Maximum, M_H	M_H- M_L	min	min
Virgin CV	9.22	77.29	68.07	4.59	12.43
CV DV	48.64	78.01	29.37	1.92	7.54
CV 4HT DV	34.02	78.29	44.27	1.24	6.55
Virgin semi EV	10.57	84.82	74.25	5.76	7.87
Semi EV DV	47.89	83.63	35.74	1.88	5.22
Semi EV 4HT DV	33.94	79.14	45.2	1.36	5.09
Virgin EV	10.79	69.69	58.88	5.76	10.19
EV DV	18.58	78.97	60.39	1.54	4.56
EV 4HT DV	9.46	75.47	66.01	1.45	5.04

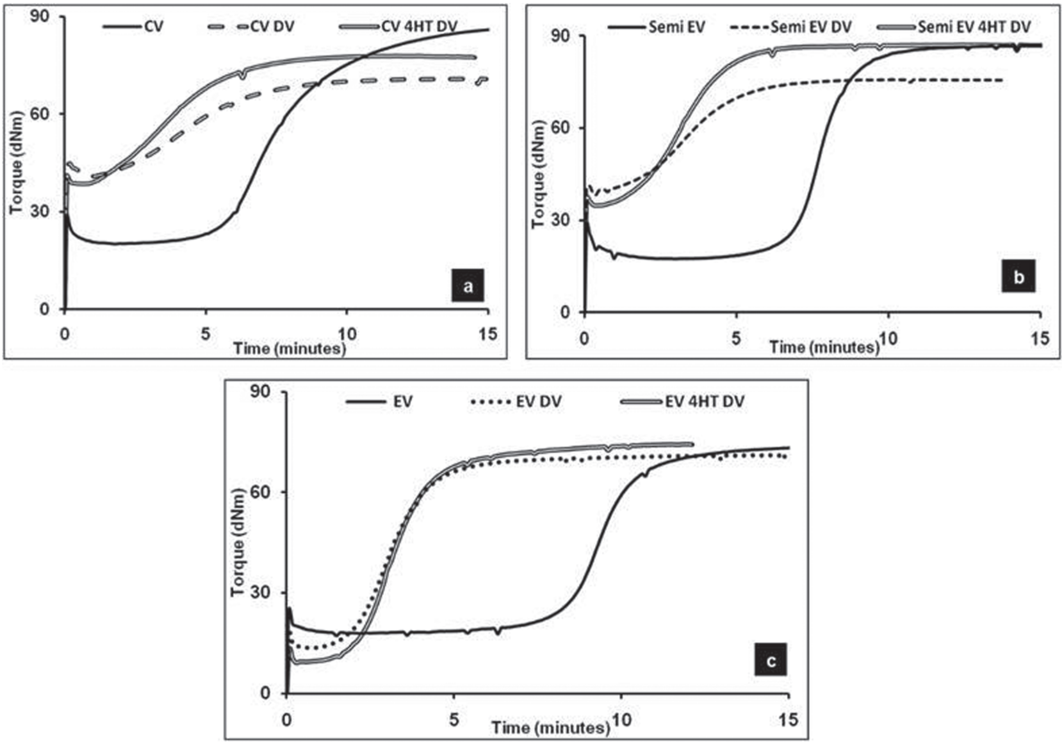

Fig. 3. Cure curves of original and devulcanised a) C V cured; b) semi EV cured and c) EV cured vulcanisates

Cure characteristics

The cure characteristics of the samples (both original and devulcanised) are given in Table 4 and the respective cure curves are outlined in Figure 3. The minimum torque of the devulcanised samples is significantly higher than the corresponding original samples (Isayev *et al*., 1995). On the other hand, the minimum torque of the samples devulcanised with the assistance of 4HT are visibly lower than the corresponding mechanically devulcanised samples. Since minimum torque of the rheometer reading is an indirect indication of the compound viscosity and processability, the lower M_L values associated with the 4HT assisted devulcanised samples might be regarded as a measure of better processability and lower viscosity of the devulcanised sample. As viscous nature of rubber is associated with un-vulcanised raw polymer, it might be assumed that the stable free radical assisted devulcanisation lowers the elastic nature imparted on the rubber by vulcanisation. In other words, the lower minimum torque of the stable free radical assisted devulcanised sample might be regarded as the higher level of devulcanisation associated with it compared to the mechanically devulcanised sample (Tukachinsky, 1996).

Out of the three sets of the samples devulcanised, the minimum torque value of the devulcanised EV cured sample was the lowest both in the case of mechanical devulcanisation and 4HT assisted devulcanisation. The total torque (M_H-M_L) attained by the devulcanised

EV samples during revulcanisation was comparable with that of the original EV sample whereas for CV and semi EV samples, the torque of devulcanised samples during revulcanisation were significantly lower than the corresponding original sample (Isayev *et al*., 1995). The cure time and scorch time of the devulcanised samples are considerably lower than those of the virgin vulcanisates as in any other case of devulcanisation (Tukachinsky,1996; Sun, 2007). The reason for the low scorch of

Table 5. **Mechanical properties of un-aged NR vulcanisates and corresponding revulcanisates**

Sample	Tensile strength, (MPa)	Elongation at break (%)	M100, (MPa)	M200, (MPa)	M300, (MPa)	Tear strength, Nmm^{-1}
CV	27.4±1.20	731±33.50	2.1	4.7	8.3	100±3.6
CV DV	17.3±1.30	563±16	1.7	3.6	6.45	41.4±2.6
CV 4HTDV	19.8±0.44	630±23.60	1.8	3.9	6.7	48.3± 0.8
SEV	28.6±0.18	745±11.20	2.3	5.1	8.8	115 ±3.5
SEV DV	18.3±1.50	634±26.10	1.7	3.4	5.8	39 ±4.6
SEV 4HTDV	22.2±0.98	687±29	1.8	3.6	6.3	49±1.7
EV	24.7±0.70	801±29.40	1.6	3.5	6.2	105.4±4.8
EV DV	22.1±1.10	714±23.50	1.6	3.5	6.1	69±2.4
EV 4HTDV	23.5±0.81	725±19.50	1.7	3.6	6.3	80.1±0.9

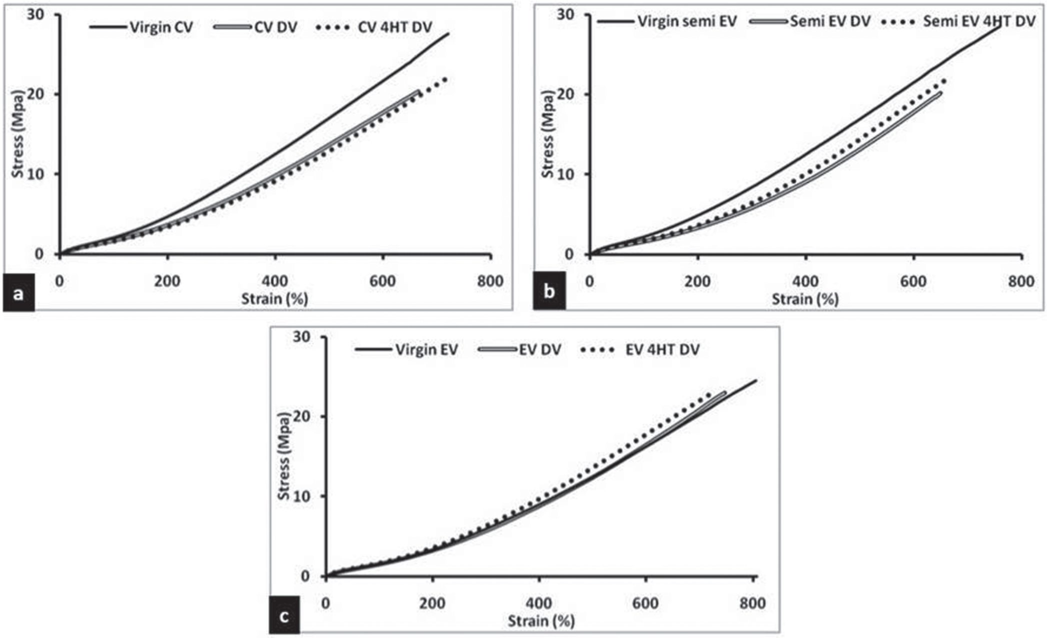

Fig. 4. Stress strain curve of the original and revulcanised a) CV b) semi EV and c) EV cured NR vulcanisates

devulcanised rubber during revulcanisation was recently reported (Joseph *et al.*, 2017b).

Revulcanisate properties

The revulcanisate properties of the devulcanised samples in comparison with the corresponding vulcanisate properties of the original samples are given in Table 5 and the corresponding stress-strain curves are shown in Figure 4. Though all revulcanisate properties of the samples devulcanised using 4HT were higher than the corresponding

Table 6. **Revulcanisation torque of samples devulcanised with and without ageing**

Sample		Torque (dNm)					
		Unaged			Aged at 70°C for 7 days		
		Minimum, (M_L)	Maximum, (M_H)	M_H- M_L	Minimum, (M_L)	Maximum, (M_H)	M_H- M_L
CV	DV	48.6	78	29.4	45.1	67	21.9
	4HT DV	34	78.3	44.3	41.6	76.5	34.8
Semi EV	DV	47.9	83.6	35.7	43.9	78.5	34.6
	4HT DV	33.9	79.1	45.2	38.2	81	42.8
EV	DV	18.6	79	60.4	22	69.4	47.4
	4HT DV	9.5	75.5	66.0	13.6	73.2	59.6

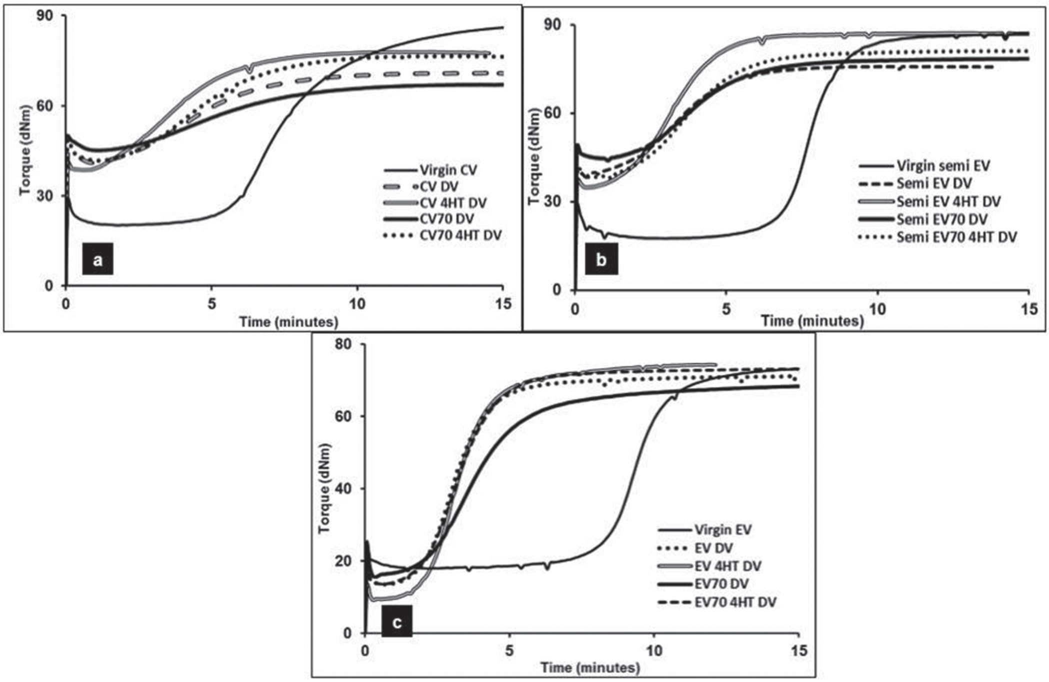

Fig. 5. Revulcanisation cure curves of samples prepared by the devulcanisation of a) CV b) semi EV and c) EV cured NR vulcanisates aged at 70°C in comparison that of the corresponding curves of un-aged samples

Table 7. **Revulcanisate properties of devulcanised samples prepared from samples aged at 70 °C for seven days in comparison with the corresponding original samples**

Sample	Tensile strength, (MPa)	Elongation at break (%)	M100 (MPa)	M200 (MPa)	M300 (MPa)	Tear strength, (Nmm^{-1})
CV	28.2 ±0.64	719 ±26.4	2.3	5.2	9.1	95 ±3.8
CV70	27.9 ±1.10	644 ±27.2	3.0	6.7	11.3	80 ±8.5
CV70 DV	16 ±0.70	595 ±13.8	1.6	3.3	5.8	28.4 ±1.7
CV70 4HTDV	19 ±0.71	627 ±20.4	1.8	3.7	6.4	37.7 ±2.5
SEV	27.2 ±0.88	734 ±90	2.3	5.1	8.8	100 ±6.5
SEV70	26.8 ±1.30	614 ±17.4	3.0	6.7	11.1	69 ±6.8
SEV70 DV	19.4 ±0.50	625 ±11.0	1.8	3.7	6.4	36.1 ±2.2
SEV70 4HTDV	20.1 ±0.61	624 ±17.5	1.9	3.9	6.7	39.4 ±2.4
EV	26.5 ±1.20	735 ±24.4	1.8	4.1	7.3	111 ±9.0
EV70	25.9 ±0.59	678 ±13.1	2.1	4.9	8.6	92 ±13.7
EV70 DV	19.2 ±0.33	776 ±47.1	1.5	3.1	5.4	53.5 ±4.1
EV70 4HTDV	22.2 ±0.26	742 ±6.5	1.6	3.4	5.8	61 ±4.1

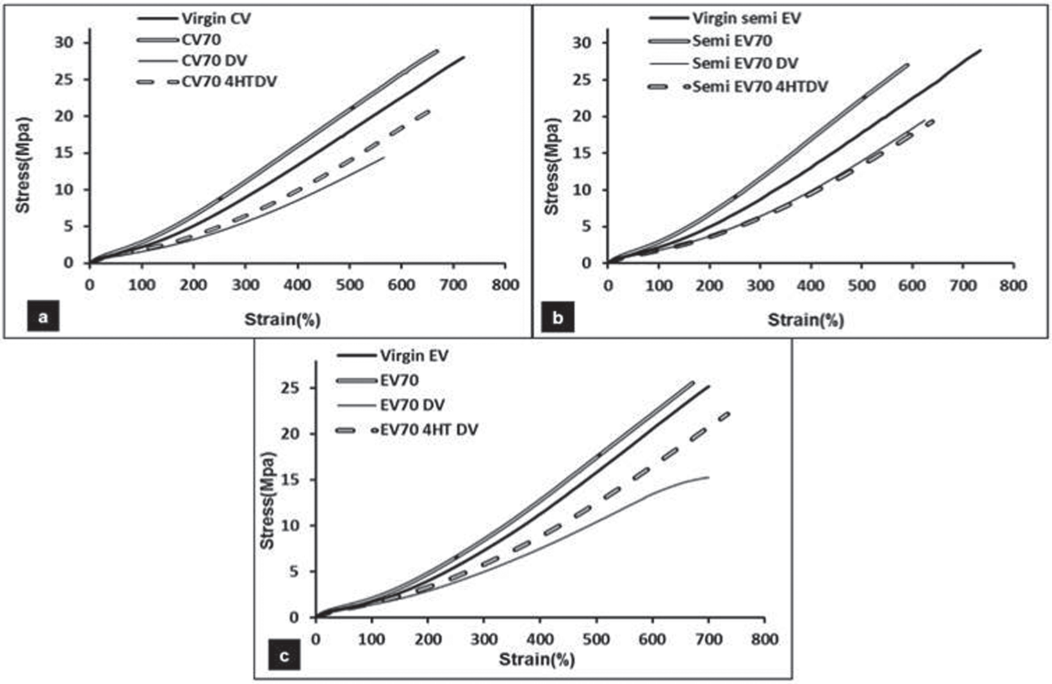

Fig. 6. Stress-strain curves of revulcanisates of a) CV; b) Semi EV and c) EV cured samples prepared from 70°C aged NR vulcanisates in comparison with original sample

mechanically devulcanised samples, the positive influence of 4HT upon mechanical devulcanisation was most significantly evident from the tear strength. On the other hand, the per cent retention of tensile properties was significantly higher than that of the tear strength. In the case of EV samples, the influence of 4HT on revulcanisate tensile properties was marginal whereas the tear strength significantly improved after 4HT assisted devulcanisation. It is worth recalling that, this variation in the response is corresponding to a marginal variation in per cent devulcanisation of the mechanically and 4HT assisted devulcanised EV samples. This further suggests that tear strength of the revulcanised samples are more sensitive towards efficiency of devulcanisation rather

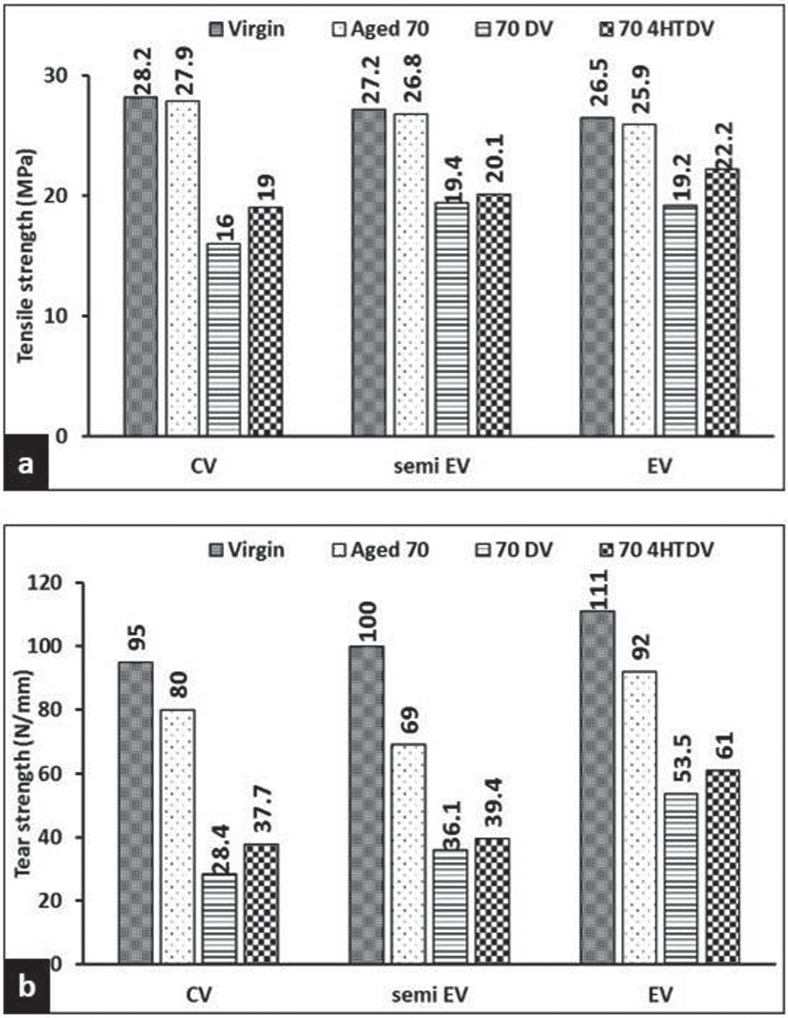

Fig. 7. Comparison of a) tensile strengths and b) tear strength of the revulcanisates with corresponding original vulcanisates

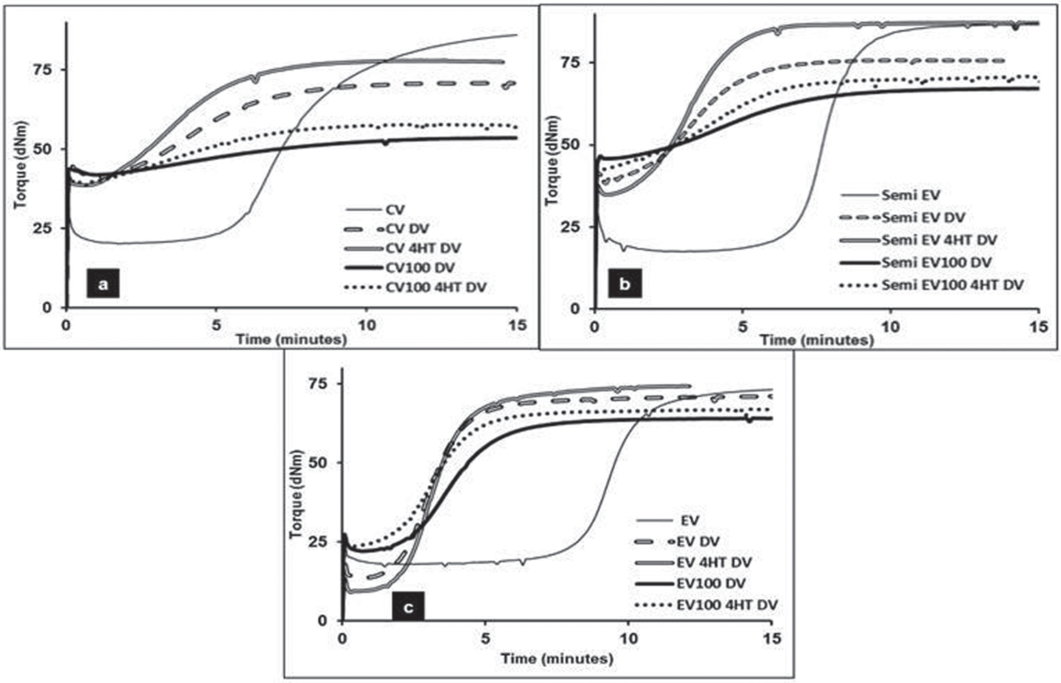

Fig. 8. Cure curves of a) CV cured; b) Semi EV cured and c) EV cured NR vulcanisates devulcanised after ageing at 100°C for 3 days

than tensile properties (Joseph *et al*., 2016). Hence it might be more suitable to assess the efficiency of devulcanisation processes considering the tear strengths of the revulcanisates as one of the main criteria, which is rarely reported.

Devulcanisation of samples aged at 70 °C for seven days

Cure characteristics

Table 6 gives the comparison of cure characteristics of the devulcanised samples prepared after ageing the original sample at

Table 8. **Cure characteristics of NR vulcanisates devulcanised after ageing at 100 °C for three days**

Devulcanised sample	Torque (dNm)			Scorch Time (min)	Cure time (min)
	Minimum (M_L)	Maximum (M_H)	M_H - M_L		
CV100 DV	41.9	53.5	11.6	1.9	10.0
CV 100 4HTDV	40.6	57.8	17.2	2.1	7.8
Semi EV100 DV	43.3	67.2	23.9	1.4	8.0
Semi EV100 4HT DV	42.6	71.1	28.5	1.1	7.1
EV100 DV	22.1	64.4	42.3	1.9	6.2
EV100 4HT DV	25.5	67.0	41.5	1.7	5.2

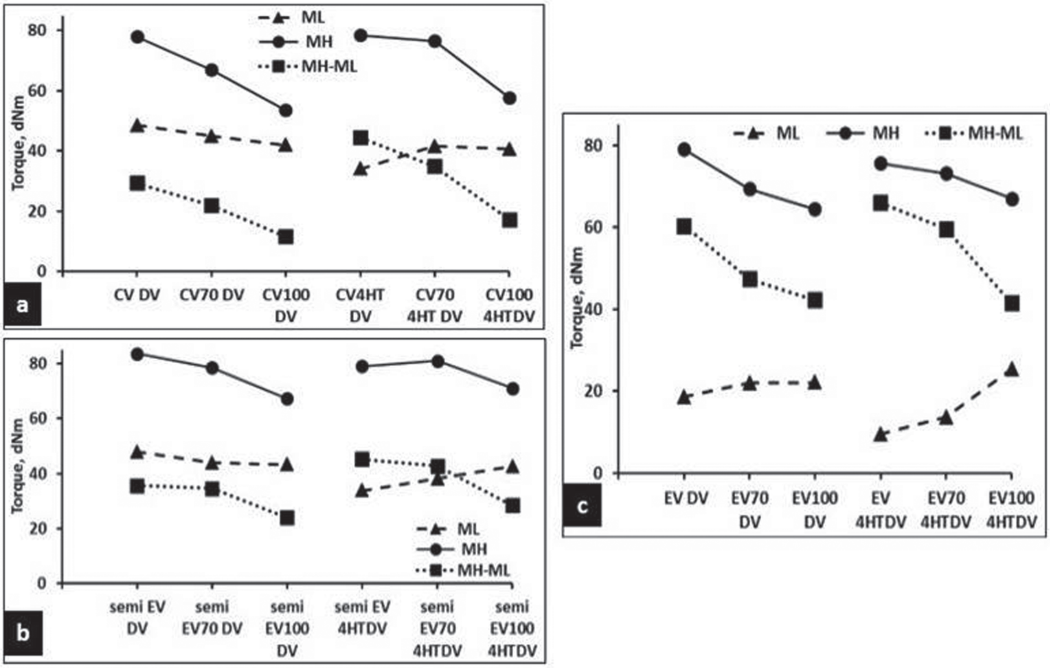

Fig. 9. Comparison of revulcanisation cure characteristics of devulcanised samples prepared from un-aged, aged at 70°C (7 days) and 100°C (3 days) NR vulcanisates

70 °C for seven days with that of the corresponding devulcanised samples prepared from unaged original samples. Both the cure curves (Fig. 5) and cure characteristics indicate that, the minimum torque of the samples devulcanised after ageing at 70 °C were higher than the corresponding values of samples devulcanised without ageing. The extent of lowering of minimum torque in the presence of stable free radical was lower, compared with the corresponding mechanically devulcanised sample. A decrease in the maximum torque was observed for the unaged and aged devulcanised samples with that of the corresponding control.

Revulcanisate properties

The vulcanisate properties of the un-aged, aged and revulcanised NR samples are listed in Table 7 and the stress-strain curves are given in Figure 6. It can be observed that, ageing at 70 °C for seven days in an air oven did not severely deteriorate the tensile strength of the NR vulcanisates whereas the tear strength was significantly reduced. On the other hand, an increase in modulus with corresponding lowering of elongation at break was observed probably due to the residual curing and oxidation effects imparted by ageing conditions (Buttfava *et al.*, 2005). The stress-strain curves indicates that, the increase in modulus is the least in the case of EV cured vulcanisates, followed by CV vulcanisates and the highest for semi EV cured vulcanisates. The modulus values of the revulcanisates from aged samples are comparable with that of the corresponding un-aged vulcanisates.

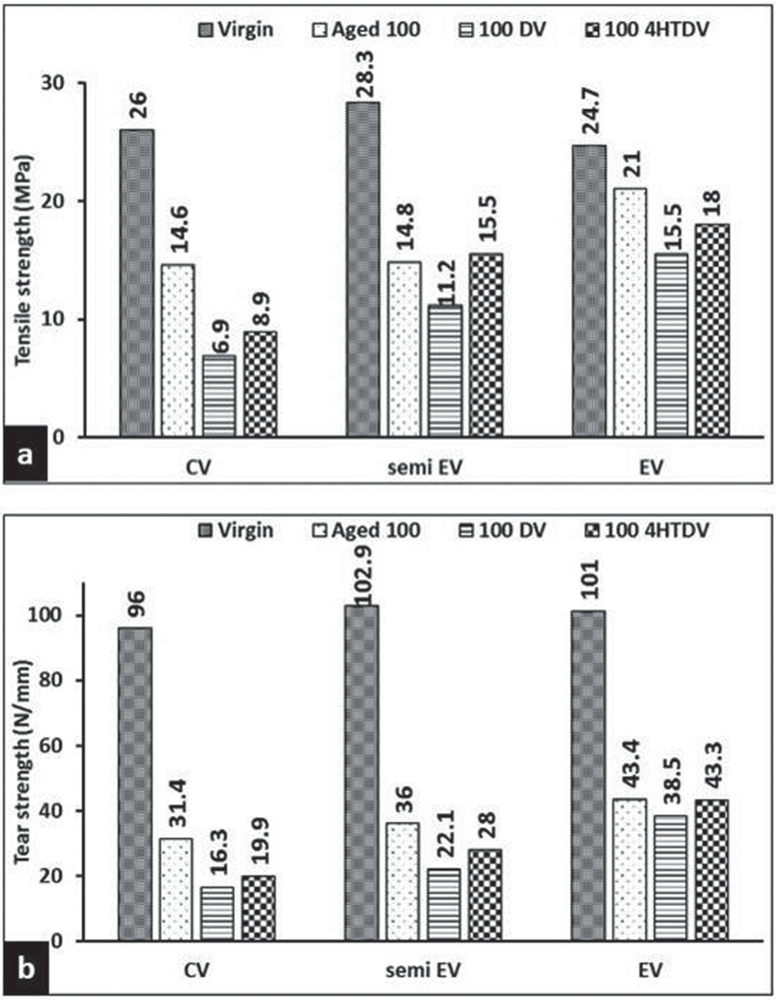

Fig. 10.Comparison of a) tensile strengths and b) tear strength of the revulcanisates with corresponding original vulcanisates

As in the case of devulcanisation of unaged vulcanisates, the revulcanisate properties of the aged samples also have improved notably with the incorporation of 4-hydroxy TEMPO during devulcanisation. Comparison of tensile strength and tear strength of the virgin and aged vulcanisates and the corresponding revulcanisates is illustrated in Figure 7.

Devulcanisation of samples aged at 100°C for three days

Cure characteristics

The cure characteristics during revulcanisation of devulcanised rubber obtained from NR vulcanisates aged at 100 °C for 3 days are listed in Table 8 and the corresponding cure curves are given in Figure 8. The lowering of minimum torque observed with the 4HT

Table 9. **Revulcanisate properties of samples devulcanised after ageing at 100 °C for three days**

Sample	Tensile strength, (MPa)	Elongation at break, %	M100, (MPa)	M200, (MPa)	M300, (MPa)	Tear strength, (Nmm^{-1})
CV	26 ±0.83	689 ±25.9	2.3	5.1	8.8	96 ±5.2
CV100	14.6 ±0.28	340 ±7.5	3.2	7.6	12.6	31.4 ±3.1
CV100 DV	6.9 ±0.53	339 ±18.8	1.6	3.4	5.8	16.3 ±8.3
CV100 4HTDV	8.9 ±0.94	393 ±19.2	1.7	3.6	6.1	19.9 ±2.6
SEV	28.3 ±1.15	697±5	2.4	5.5	9.6	103 ±4.1
SEV100	14.8 ±0.76	293±17.5	3.8	9.1	15	36 ±2.9
SEV100 DV	11.2 ±0.62	407±14	1.9	4.1	7.2	22.1 ± 0.7
SEV100 4HTDV	15.5 ±0.75	531 ±18.1	1.9	4	6.8	28 ±3.7
EV	24.7 ±0.89	690±15.7	1.8	4.2	7.6	101 ±3.7
EV100	21±1.4	512 ±23.3	2.5	6	10.7	43.4 ± 2.3
EV100 DV	15.5 ±1.1	564 ±16.8	1.7	3.6	6.2	38.5 ±3.7
EV100 4HTDV	18 ±0.76	635 ±24.3	1.7	3.5	6	43.3 ±3.4

assisted devulcanised samples is only marginal in comparison with the corresponding mechanically devulcanised samples. Also, the cure torque attained for the revulcanisation of aged samples was significantly low especially in the case of CV and semi EV cured vulcanisates. Comparison of the cure characteristics of samples devulcanised after

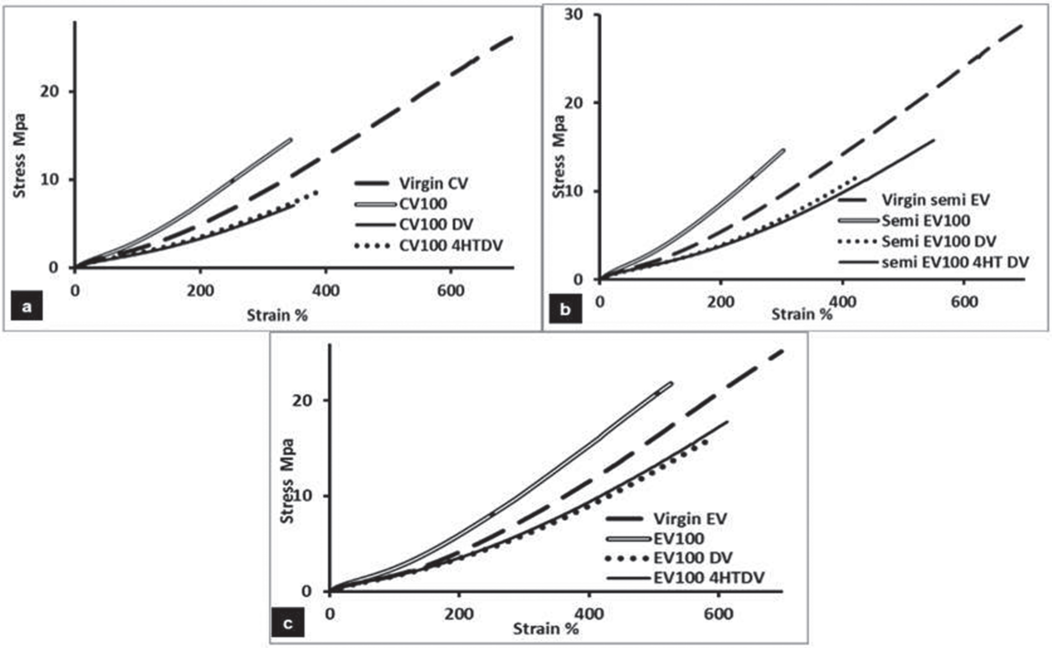

Fig. 11. Stress strain curves of a: CV cured; b: Semi EV cured and c: EV cured NR vulcanisates devulcanised after ageing at 100°C for three days

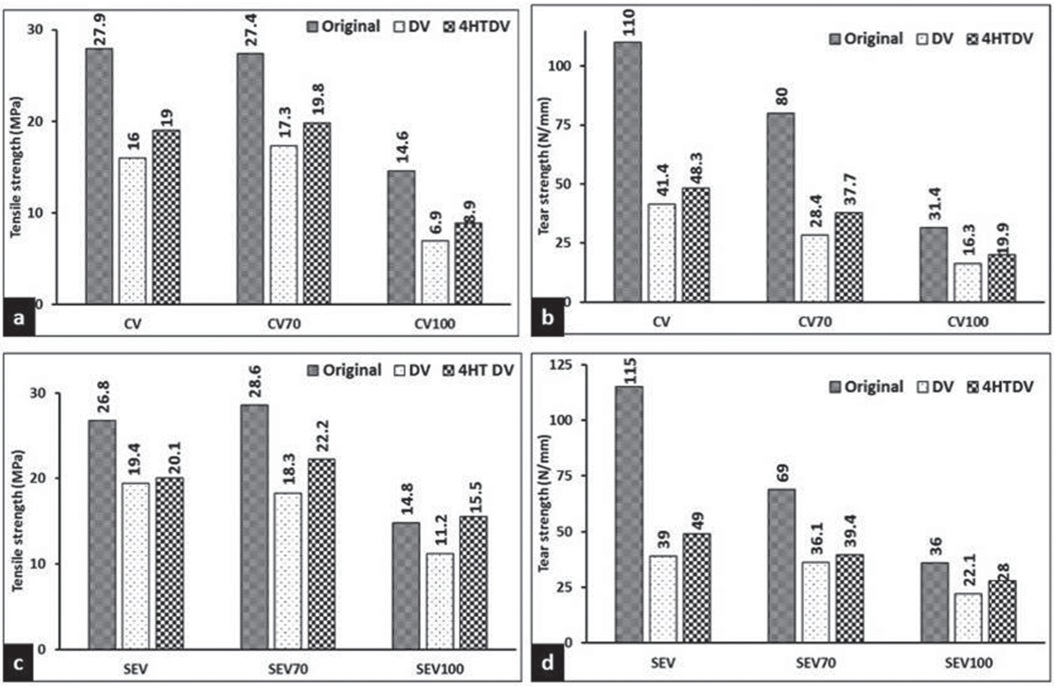

Fig. 12.Tensile strength and tear strengths of original and revulcanised a&b: CV; c& d: semi EV vulcanisates respectively

ageing at 70 °C for seven days and 100 °C for three days with those of the un-aged is given in Figure 9. The minimum cure torque (M_L) of the mechanically devulcanised CV and semi EV samples devulcanised after ageing were lower than that of the corresponding un-aged samples whereas the reverse trend was observed for the 4HT assisted devulcanised samples.

In the case devulcanised CV and semi EV cured samples, the revulcanisation minimum torque (M_L) was significantly higher than the corresponding values of un-aged vulcanisates. This might be due to the high residual crosslink density of the devulcanised samples. As previously mentioned, an increase in the crosslink density of the original vulcanisate by ageing might have led to a corresponding increase in the residual crosslink density of the devulcanised samples. The low initial crosslink density and high reversion resistance attributed to efficient vulcanization, might have limited these effects in EV vulcanisates, leading to a comparatively lower residual crosslink density to the devulcanised EV vulcanisates (as indicated by lowest minimum torque) and highest cure torque on revulcanisation.

Revulcanisate properties

Comparison of tensile strength and tear strength of the virgin, aged and revulcanised samples is given in Figure 10. Severe reduction in vulcanisate properties was observed after ageing at 100 °C for three days. On ageing, EV cured vulcanisates exhibited maximum

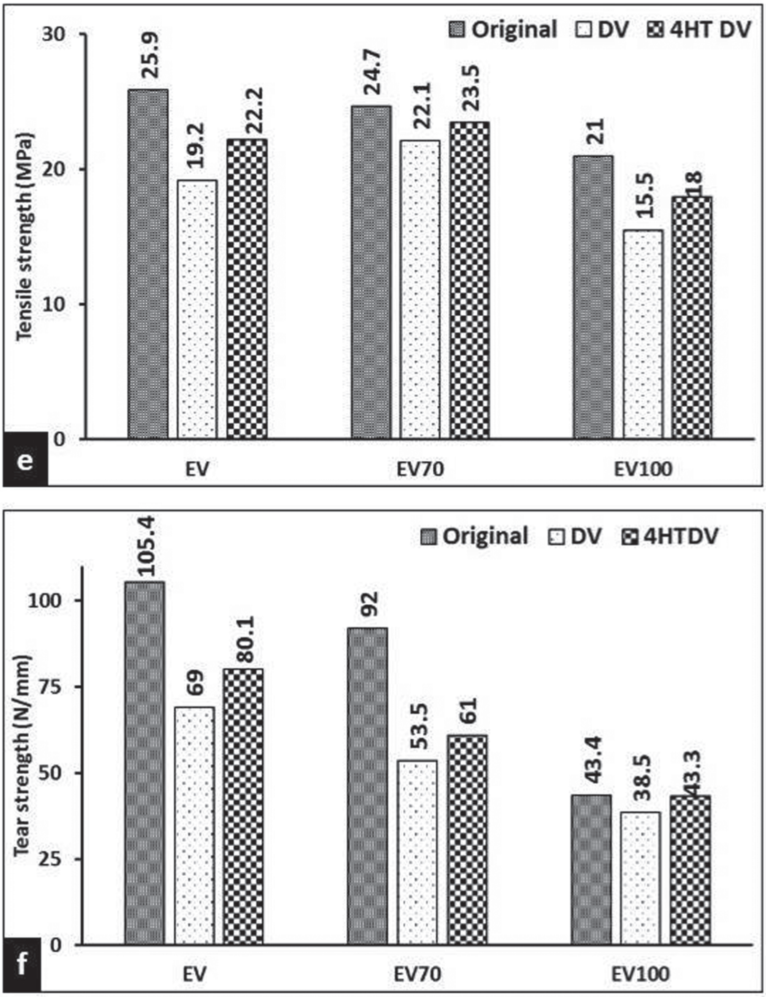

Fig. 13.Tensile strength (**e**) and tear strength **(f)** of original and revulcanised EVvulcanisates

resistance towards deterioration of properties. Table 9 gives the revulcanisate properties of the CV, semi EV and EV cured vulcanisates devulcanised after ageing at 100 °C for three days and Figure 11 illustrates the corresponding stress-strain curves.

Since the initial properties of the aged vulcanisates were low, the revulcanisate properties after devulcanisation were also correspondingly lower. The modulus values of the aged vulcanisates were significantly higher than the original vulcanisates. As, modulus at 100 per cent elongation is a direct indication of the crosslink density of the vulcanisate, the increase in modulus of the vulcanisate on ageing has to be acknowledged on these ground (Bhowmick, and Mangararaj, 1994). Higher initial crosslink density would lead to correspondingly higher levels of residual crosslink density in devulcanised rubber which in turn results in lower revulcanisate properties.

Comparison of revulcanisate properties

A comparison of the revulcanisate properties (tensile and tear strength) of the devulcanised samples (both un-aged and aged) along with the corresponding original properties are given in Figure12 and 13, respectively. From the results of the comparative evaluation of the devulcanised samples before and after ageing, it might be assumed that the decisive factor in the revulcanisate properties of devulcanised rubbers are the state of the material to be devulcanised. Being the percent recovery of vulcanisate properties remaining almost comparable for different samples for a particular devulcanisation process, higher revulcanisate properties can be achieved if the material to be devulcanised is of good quality.

The present study further reveals that, the per cent retention of properties after devulcanisation is highly dependent on the cure system used for initial curing of the vulcanisate. In other words, the level of degradation occurred to rubber to be devulcanised determines the revulcanisate properties of the devulcanised rubber which is in turn is determined by the initial cure system of the vulcanisate. The study also indicates that the stable free radical assisted devulcanisation is a promising method for efficient devulcanisation of rubber vulcanisates.

CONCLUSIONS

4-hydroxy TEMPO assisted mechanical devulcanisation of carbon black filled natural rubber vulcanisates, before and after ageing, is described. Compared to mechanical devulcanisation, stable free radical assisted mechanical devulcanisation significantly improved the percent devulcanisation to 53, 56 and 76 per cent for the CV, semi EV and EV cured samples respectively with corresponding substantial improvement in revulcanisate properties. It is interesting to note that, EV cured NR samples gave significantly higher level of per cent devulcanisation even after mechanical devulcanisation, though the number of polysulphide bonds (easy scission ensured by lower bond dissociation energy) was lowest for EV samples. On the other hand, CV cured samples (highest number of polysulphidic crosslinks) had the highest increment in per cent devulcanisation when 4HT was used as devulcanisation aid which in turn shows the efficacy of 4HT to prevent reunion of broken polysulphidic fragments. This indicates that the variation in recombining capacity of cleaved crosslinks which can decisively influence the per cent devulcanisation of samples and the possible blocking of recombination of crosslink fragments propels the percent devulcanisation of stable free radical assisted devulcanization. The study also indicated that the efficiency of devulcanisation and the subsequent revulcanisate properties depend on factors like cure system used for the preparation and the crosslink density of the original sample and the extend of ageing undergone by the sample.

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REFERENCES

Beirakh, L., Kopylov, M. and Goldstein, V. (2004). Modifier for devulcanization of cured elastomers,mainly vulcanized rubber and method for devulcanization by means of this modifier. *United States Patent* No. US 6831109 B1

Bhowmick, A.K, Mangararaj, D. (1994). Vulcanisation and curing techniques. In: *Rubber Products Manufacturing Technology* (Eds. A. K. Bhowmick, M. M. Hall and H. A. Benarey), Marcel Dekker Inc. New York, 323p.

Buttfava, G., Consalati, M., Mariani, F., Quasso, U. and Ravasio. (2005). Effects induced by gamma irradiation of different polyesters studied by viscometry, thermal analysis and positron annihilation spectroscopy. *Polymer Degradation and Stability,* **89**: 133-139.

De, D., Maiti, S. and Adhikari, B. (1999). Reclaiming of rubber by renewable resource material (RRM). II. Comparative evaluation of reclaiming process of NR by RRM and diallyl sulphide. *Journal of Applied Polymer Science*, **73**: 2951- 2958.

Flory, P. J., Rehner, J. Jr. (1943). Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling. *Journal of Chemical Physics*. **11**: 521-526.

George, B., Joseph, A.M., Madhusoodanan, K.N., Alex, R. and Jacob, J. (2017). Stable free radical assisted devulcanisation of rubber. *Indian patent application No* 201741017633 dated 19/05/2017

Goldshtein, V. and Kopylov, M. (2002). Method and composition for devulcanization of waste rubber.*United States Patent* No.US 6387966 B1.

Isayev, A.I., Chen, J. and Tukachinsky, A. (1995). Novel ultrasonic technology for devulcanization of waste rubber.*Rubber Chemistry and Technology*, **68**: 267-280.

Jana, G.K. and Das, C.K. (2005). Devulcanization of automobile scrap tyres by a mechanochemical process. *Progress in Rubber Plastics and Polymer Recycling Technology,* **21**: 319-331.

Jana, G.K. and Das, C.K. (2005). Devulcanization of natural rubber vulcanizates by mechano-chemical process. P*olymer Plastics Technology and Engineering*, **44**: 1399-1412.

Jana, G.K. and Das, C.K. (2005). Mechanochemical devulcanization of vulcanized gum natural rubber. *Progress in Rubber Plastics and Polymer Recycling Technology*, **21**: 183-199.

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2016). The current status of sulphur vulcanization and devulcanization chemistry: Devulcanization. *Rubber Science*, **29**(1): 62-100.

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2016).Effect of devulcanisation on the crosslink density and crosslink distribution of carbon black filled natural rubber vulcanisates. *Rubber Chemistry and Technology,* **89**(4): 653-670.

Joseph, A.M., Madhusoodanan, K.N., Alex, R. and George, B.(2017a). Stable free radical assisted mechanical devulcanization of carbon black filled natural rubber vulcanizates. *Rubber Chemistry and Technology in press. DOI: Org/ 10.5254/rct.18.81633*

Joseph, A.M., George, B., Madhusoodanan, K.N. and Alex, R. (2017b). Cure characteristics of deculcanised rubber: The issue of low scorch. Rubber Chemistry and Technology, **90**(3): 536-549.

Madhusoodanan, K.N., Mohandas, K.S., Kuriakose, B., Thomas, K.T. and Mathew, N.M. (1998). An efficient mechanical method for reclamation of vulcanized scrap rubber. Paper presented at *International Rubber Conference (IRC),* 7-9 December 1998, Chennai, India.

Mandal, S.K., Alam, N. and Debnath, S.C. (2012). Reclaiming of ground tyre rubber by safe multifunctional rubber additives: I. Tetra benzyl thiuram disulphide, *Rubber Chemistry and Technology*, **67***:* 629-644.

Meyasami, M.A. (2012). Study of scrap rubber devulcanization and incorporation of devulcanized rubber into virgin rubber compounds. Ph.D. Thesis, University of Waterloo.

Namsri, K. and Thanawan, S. (2009). The use of TMTD as devulcanizing agent in waste natural rubber product,Paper Presented at *35th Congress on Science and Technology of Thailand*, 15-19 October, 2009, Chonburi, Thailand.

Newell, R. 91996). The De link process: A unique opportunity to recycle a variety of polymer types. Presented at *The International Rubber Conference*, 17-21 June 1996, Manchester, UK.

Rooj, S., Basak, G.C., Maji, P.K. and Bhowmick., A.K. (2011). New route for devulcanization of natural rubber and the properties of devulcanized rubber. *Journal of Polymer Environment*, **19**: 382-390.

Sekhar, B.C. (2014). A method for producing devulcanized rubber and an apparatus therefor. *International Publication No.WO 2014/042510 A1.*

Sekhar, B.C., Kormer, V.A., Sotnikova, E.N., Mironyuk, V.P., Trunova, L.N. and Nikitina, N.A. (1998). Reclaiming Elastomeric materials. *United States Patent* No. US 5770632.

Sun, X. (2007). The devulcanization of unfilled and carbon black filled Isoprene rubber vulcanizates by high power ultrasound. *Ph.D. Thesis, University of Akron, USA.*

Tukachinsky, A., Schworm, D. and Isayev, A.I. (1996). Devulcanization of tyre rubber by powerful ultrasound. *Rubber Chemistry and Technology*, **69**: 92-103.

Zamir, R. (2011). Recycled rubber redefined. *Polymers and Tyre Asia*, **2**: 66-67.