*Rubber Science*, **32**(1): 68-82, 2019 *RESEARCH ARTICLE*

# STABLE FREE RADICAL ASSISTED MECHANICAL DEVULCANISATION: DEVULCANISATION OF NR/BR BLENDS

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Received: 12 March 2019 Accepted: 22 April 2019

Joseph, A.M., Madhusoodanan, K.N., Alex, R. and George, B. (2019). Stable free radical assisted mechanical devulcanisation: Devulcanisation of NR/BR blends. *Rubber Science*, **32**(1): 68-82.

This paper investigates the effect of polybutadiene rubber content on the efficiency of stable free radical (4-hydroxy tempo, 4HT) assisted mechanical devulcanisation of NR/BR blends. Further, the effectiveness of this novel process in the real world is tested by the devulcanisation of commercial NR/BR blends like buffing dust obtained from pre-cured tyre tread and ground tyre rubber (GTR). Based on the minimum torque ($M_L$) values recorded for devulcanised samples, which is indirectly related to the viscosity of the sample, it was observed that comparable level of devulcanisation can be achieved for NR/BR blends upon mechanical devulcanisation (control process) irrespective of the BR content in the blend. In 4HT assisted mechanically devulcanised samples, a higher per cent devulcanisation was indicated by further reduction in $M_L$ values. The revulcanisate tensile properties of the 4HT assisted devulcanised blends were significantly higher than the corresponding mechanically devulcanised samples whereas the positive influence of 4HT upon the tear strength of revulcanised samples significantly reduced with increase in BR content of the blend. The 4HT assisted devulcanisation of buffing dust and used rubber samples like GTR proposed the feasibility of stable free radical as an effective devulcanisation aid. The revulcanisate properties of the buffing dust and GTR devulcanised with the assistance of 4HT were higher than that obtained for the corresponding mechanically devulcanised sample. The revulcanisate properties of GTR were lower than that of buffing dust indicating the role BR content and the quality of sample (effect of ageing) used for devulcanisation upon the revulcanisate properties.

**Keywords**: Mechanical devulcanisation, Mechano-chemical devulcanisation, Revulcanisate properties, Stable free radical

## INTRODUCTION

Recycling is the process of converting waste or end of life products to re-usable materials. It is an alternative to "conventional" waste disposal that can prevent the waste of potentially useful materials and can reduce the consumption of fresh raw materials, air pollution (from incineration), and water pollution (from landfilling). Recycling of used rubber products, mostly tyres, is a global concern due to their highly stable crosslinked structure created through the process of vulcanisation. In the literal sense, recycling of a material would produce a fresh supply of the same material which is often difficult or too expensive to achieve. Hence, recycling of tyres suggest their reuse via converting it to different materials/products for many applications (Joseph *et al*., 2016; a

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Chem-Risk, 2009; Abraham *et al*., 2011; Ayyer *et al*., 2012; Reschner, 2008; Myhre, 2005; Schnecko, 1994; Raghavan, 2005; Hammer and Gray, 2004; Bandyopadhyay *et al*., 2008). With an objective to ensure environmentally sound management of wastes as close as possible to its source of generation, Basel Convention, an international treaty that was designed to reduce the movements of hazardous waste between nations, recommended strategies for recycling of used tyres like re-use by re-treading and various methods for energy and material recovery (UNEP/CHW.9/18, 2008).

Devulcanisation of used rubber products is a material recovery strategy which involves selective scission of crosslinks with negligible main chain scission to ensure maximum retention of original properties. It was introduced with an intention to increase the volume of recycled rubber used in the rubber industry. But, early methods of devulcanisation, known as reclamation process, resulted in inferior quality reclaimed rubber, due to high levels of main chain scission along with crosslink scission, through unhealthy techniques limiting its large scale consumption (Blow, 1998; Myhre, 2005; Watabe, 1980; Anderson, 1985). On the other hand, compounding advantages still favours the use of reclaimed rubber (Blow, 1998) and several studies have been carried out on the various aspects of reclamation processes and reuse of the resulting reclaimed rubber (Joseph *et al*., 2016a; Edirisinghe *et al*., 2011; Rattanasom *et al*., 2005). Contemporary devulcanization strategies aim to achieve higher degree of crosslink scission coupled with minimum polymer chain degradation through high temperature and pressure, mechanical, mechano-chemical, microwave or ultrasonic energies, using solid phase modifiers and shear or biotechnological innovations (Joseph *et al*., 2016c; Gupta and Maridass, 2003; Khait, 2005; Benko; 2004; Zhang, 2009; Lima and Carlos, 1997; Matsushita, 2003; Morin, 2002; Novotony, 1978; Hunt and Hall, 1994; Bani *et al*., 2011; Isayev and Chen, 1994; Roberson and Boron, 1998; Dinzburg and Berdichevsky, 2002; Roy *et al*., 2005; Yusof and Ahmad, 2010; Straube *et al*., 1994; Chrostofi *et al*., 2010; Kim and Park, 1999; De *et al*., 1999; Jana *et al*., 2007; Sekhar *et al*., 1998; Rooj *et al*., 2011; Goldshtein and Kopylov, 2002; Mandal *et al*., 2012).

Blending of elastomers usually aims at improvement in the performance characteristics of rubber products. Blends of NR and BR contribute to cost reduction and improved performance for tyres (Mangaraj, 2002). The fact that, 70 per cent of the world's polybutadiene production is consumed by tyre industry primarily in the sidewall, tread, wire coat, ply coat and inner liner in various proportions (https://en.wikipedia.org/wiki/Polybutadiene; www.eng.buffalo.edu/Courses/ce435/Polymer_in_auto/auto.ppt). Flanderijn tested several conditions for the devulcanisation of BR with the use of DPDS in order to elaborate the best conditions for an efficient process (Flanderijn, 2012). It was observed that addition of DPDS leads to effective devulcanisation of BR and prolonged devulcanisation time reduces the degree of devulcanisation due to recombination of the broken crosslinks. Hong and Isayev studied the ultrasonic devulcanisation of sulphur cured natural rubber (NR)/styrene butadiene rubber (SBR) blends with the goal of understanding the devulcanisation of rubber vulcanisates in which two networks of different natures were present (Hong and Isayev, 2002). Microwave devulcanisation of ground tyre rubber (GTR) which contained blends of natural rubber (NR) and styrene-butadiene rubber (SBR) as polymeric material was carried out to understand the physical and chemical changes that occur in the ground tyre rubber after different microwave exposure periods (Garcia *et al*., 2015). It was observed that, substantial amounts of the NR chain scission occurred during the treatment and efficient compatibilization of the elastomeric phases has taken place.

Investigations on various aspects of devulcanisation of ground tyre rubber (GTR) using different devulcanisation techniques have been previously carried out (Buford and Pittolo, 1982; Dierkes, 2005; Anne and Evans, 2006; Acetta and Vergnaud, 1981). Comparative study on the effect of twin screw extruder (TSE) and internal mixer (IM) for ground tyre rubber devulcanization was carried out by Ujianto *et al*. (2017). The study showed that in TSE, temperature alone significantly influence devulcanization whereas temperature, rotor rotation, rotor rotation-processing time interaction, temperature-rotor rotation-processing time interaction, *etc*. significantly influence devulcanisation in IM. Continuous ultrasonic devulcanization of ground tire rubber of different sizes were conducted using an ultrasonic co-rotating twin-screw extruder which proved that the optimization of ultrasonic treatment for individual samples is extremely important for producing the devulcanized rubber that neither undertreated nor overtreated (Liang, 2013). Devulcanisation of GTR under the application of high-energy ball milling was also reported (Formela *et al*., 2013; Cavalieri *et al*., 2003; Padella *et al*., 2001). Mechano-chemical devulcanisation of old tyre powder at high temperatures using a Banbury mixer and a Brabender (Furukawa *et al*.,1981), devulcanisation of GTR from passenger car tyres swelled in oil containing devulcanisation aids using an internal mixer (Reschner, 2008), mechano-chemical devulcanisation of GTR using a laboratory tworoll mill (Saiwari *et al*., 2011; Premachandra *et al*., 2011) devulcanisation of rubber crumb from used tyres employing super critical carbon-dioxide in a twin screw extruder (Tzoganakis and Zhang, 2004), incorporation of devulcanised rubber waste from end-of–life tyres produced by continuous shear reaction technology (Lamminmaki *et al*., 2006) *etc.* are also reported.

Stable free radical assisted mechanical devulcanisation is a novel strategy developed recently in our laboratory. This method addresses the issue of recombining of the radicals formed from crosslink scission and the consequent reformation of the once cleaved crosslinks during mechanical devulcanisation using a stable free radical (George *et al*., 2017; Joseph *et al*., 2018). Addition of a small quantity of a stable free radical during mechanical shearing significantly reduce the residual crosslink density of the devulcanised rubber, with corresponding substantial improvement in revulcanisate properties.

Majority of the studies on devulcanisation of NR/BR blends are carried out using commercial sources of used rubber like GTR whose initial properties and level of ageing were unknown making it impossible to access the efficiency of devulcanisation. Moreover, those samples would be a heterogeneous mixture of blends of polybutadiene with different rubbers, predominantly NR, in different ratios contributed from different parts of tyres limiting the capability of such studies to observe the trends involved in devulcanisation. The present paper intends to investigate the effect of polybutadiene rubber content on the efficiency of stable free radical assisted mechanical devulcanisation of NR/BR blends prepared in the laboratory by varying the BR content in the blend from zero to 50 per cent. Further, the effectiveness of this novel process is tested through devulcanisation of commercially available used rubber products like pre-cured tyre tread buffing dust and GTR.

## MATERIALS AND METHODS

Natural rubber (ISNR 5) obtained from Pilot Crumb Rubber Factory, Rubber Research Institute of India, Kottayam, butadience rubber (BR) (Cisamer PBR 1220, cis content 96%) and commercial rubber chemicals were used to prepare carbon black filled rubber vulcanisates of known composition and properties. Laboratory grade toluene and acetone were used for characterization of devulcanised rubber. Stable free radical 4-hydroxy-2, 2, 6, 6-tetramethylpiperidine-N-oxyl (4-Hydroxy TEMPO, abbreviated as 4HT) purchased from Merck India was used as devulcanisation aid. Commercial pre-cured tyre tread buffing (buffing dust) and ground tyre rubber (GTR) having 40 mesh size were used for devulcanisation.

### Devulcanisation

Carbon black filled NR vulcanisates and NR/BR blends of different ratios were prepared using the formulation given in Table I. The masterbatch was prepared using an internal mixer (40 °C, 70rpm) of one litre capacity. The curatives were added into the master batch on a laboratory two roll mixing mill and tensile sheets (150mm x150mm x2 mm) were moulded in a hydraulic press for their respective cure times ($t_{c90}$) at 150 °C.

Devulcanisation was carried out in a laboratory tworoll mixing mill (15cm x 30cm) at a friction ratio 1:1.25 (12:15 rpm). Cold water was circulated through the rolls during devulcanisation to prevent excessive heat build-up during the shearing process to ensure minimal thermal degradation of the polymer. The tensile sheets moulded from the original compounds were cut into chips of about $1cm^2$ size and made into crumb by passing through the two roll mill which was then mechanically devulcanised with 4-hydroxy TEMPO (4phr). The control process without using stable free radical was also carried out in each case. For 4HT assisted devulcanisation, the buffing dust/GTR was mixed with the required amount of 4HT in a high speed mixer prior to devulcanisation. The composition of the buffing dust and GTR was determined by Thermogravimetric Analysis (Shimadzu, TGA-50) under nitrogen and oxygen (above 550 $^{0}$C) atmosphere at a heating rate of 10 $^{0}$C, is given in Table 2.

Table 1. **Formulation for preparation of original NR/BR blends and their revulcanisates**

| Ingredients | Original sample | Revulcanisates |
|---|---|---|
| | phr | |
| Rubber hydrocarbon | 100[@] | 100 |
| HAF | 50 | - |
| Naphthenic oil | 6 | - |
| Zinc oxide | 5 | 3 |
| Stearic acid | 2 | 2 |
| Antioxidants* | 2.5 | - |
| CBS | 1.2 | 2 |
| Insoluble sulphur | 1.3 | 0.5 |

[@] NR/BR ratio was varied as 100/0, 80/20, 70/30, 60/40 and 50/50, CBS-N-Cyclohexylbenzothiazole 2-sulphenamide, *1phr TDQ (2,2,4-trimethyl-1,2,-dihydroquinoline and 1.5phr 6ppd (1,3-dimethyl butyl-N′-phenyl-p- phenylenediamine)

### Characterisation of devulcanised rubber

The crosslink densities (CLD) of the original samples and the residual crosslink densities of the devulcanised samples were determined by swelling method applying Flory Rhener equation (Flory and Rehner, 1943; Meyasami, 2012; Rooj *et al*., 2011).

Table 2. **Composition of buffing dust and GTR from thermogravimetric analysis**

| Components | | Buffing dust | | GTR | |
|---|---|---|---|---|---|
| | | Percentage | phr | Percentage | phr |
| Polymer | NR | 40 | 70 | 26 | 50 |
| | BR | 17.2 | 30 | 26 | 50 |
| Carbon black | | 31.4 | 55 | 33.8 | 65 |
| Acetone extractable | | 6.9 | 12 | 5.2 | 10 |
| Ash | | 5 | 8 | 9 | 17 |

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

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

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

φ = Volume fracton 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 interation parameter

ν = Crosslink density in mole $cm^{-3}$

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

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

The buffing dust and GTR, being powdered rubber, restricted the determination of initial crosslink density of these samples through swelling method.

## Revulcanisation

All devulcanised samples were blended with 10 per cent virgin NR for consistency and easy handling and was then revulcanised using the previously optimized revulcanisation formulation given in Table 1. Rubber Process Analyzer, RPA 2000 was used to monitor the cure characteristics at 150 °C (at a frequency of 1.67Hz at an angle 0.5°) and the samples were moulded in an electrically heated hydraulic press for their respective cure times ($t_{c90}$). Tensile and tear strength measurements of the revulcanised samples were performed on a Zwick UTM at a test speed of 460 mm/min.

Table 3. **Revulcanisation formulation used for devulcanised buffing dust and GTR**

| Ingredients | Quantity(phr) |
|---|---|
| Devulcanised rubber | 100* |
| Natural rubber | 10 |
| Zinc Oxide | 3 |
| Stearic acid | 2 |
| TDQ | 1.5 |
| CBS | 1.5 |
| Insoluble sulphur | 0.8 |

*Rubber hydrocarbon (RH) =50, CBS (N-Cyclohexylbenzothiazole 2-sulphenamide), TDQ (2,2,4-trimethyl-1,2,-dihydroquinoline)

The buffing dust and GTR were devulcanised with and without the assistance of 4-hydroxy TEMPO (2phr) and revulcanised as referred in Table 3.

## RESULTS AND DISCUSSION

### Effect of BR content on the devulcanisation of NR/BR blends

The role of BR content on the efficiency of devulcanisation of NR/BR blends was investigated through devulcanisation of semi EV cured vulcanisates containing varying amounts of NR and BR. The BR content in the blends was varied from zero to 50 parts. The samples were devulcanised with the assistance of 4HT and the effect of BR content in the blend on number of passes for devulcanisation, residual crosslink density, cure characteristics on revulcanisation and the revulcanisate properties were compared.

#### *Number of passes for devulcanisation*

From the earlier observations on devulcanisation of NR vulcanisates (Prasannan, 2015; Joseph *et al*., 2017b), it is evident that the number of passes required for the devulcanisation depend upon factors like crosslink density of the sample and cure system employed. The required number of passes through the tight nip to achieve the optimum level of devulcanisation is considerably lowered by the incorporation of stable free radical as a devulcanisation aid (George *et al*., 2017; Joseph *et al*., 2016a & 2018). The effect of NR:BR blend ratio on required number of passes through the tight nip of the tworoll mill for devulcanisation of 200g of virgin vulcanisate with and without the assistance of 4-hydroxy TEMPO (4phr) is represented in Figure 1.

For NR and NR /BR blend vulcanisates with BR content up to 30 parts, the required number of passes for optimum devulcanisation was significantly lowered in 4HT assisted devulcanisation. In addition, all samples up to 30 parts BR formed a sheet around the mill-roll during both mechanical and 4HT assisted devulcanisation. For

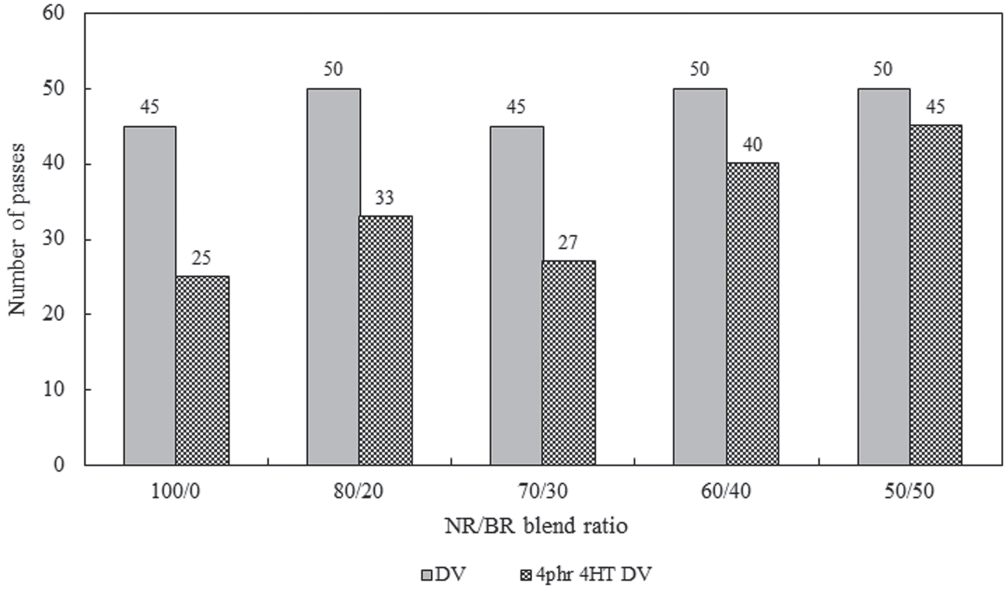

Fig. 1. Number of passes required for devulcanisation of NR/BR blends

mechanical devulcanisation of blends of higher BR content (40 and 50 parts), the numbers of passes was limited to 50 numbers as the devulcanised rubber did not show any tendency to form a sheet but tend to undergo degradation. On the other hand, 4HT assisted devulcanisation of samples having higher BR content formed sheets and the state of devulcanisation resembled almost that of the devulcanised NR sample at 40-45 passes through the tight nip.

### *Residual crosslink density and per cent devulcanisation*

Residual crosslink densities of the devulcanised samples were compared with the crosslink density of the corresponding virgin vulcanisates and per cent devulcanisation was determined. The residual crosslink densities of mechanically devulcanised NR/BR blends up to 70/30 ratio could only be determined as the devulcanised samples having 40 and 50 parts BR did not form sheet around the mill-roll. The crosslink densities of the virgin vulcanisates and the residual crosslink densities of the corresponding devulcanised samples are given in Table 4.

The residual crosslink densities of the stable free radical assisted devulcanised samples are significantly lower than that of the mechanically devulcanised samples. The abnormally lower initial crosslink density of the 70/30 blend may be due to experimental error during compounding. The per cent devulcanisation of NR vulcanisates was the lowest whereas the blend samples have comparable values.

### *Cure characteristics*

The cure characteristics of the virgin vulcanisates and that of the corresponding devulcanised samples during revulcanisation are given in Table 5.

The cure characteristics of the original vulcanisates were similar with marginal increase in scorch and cure time at higher BR content. The devulcanised samples had shorter scorch times, higher minimum torque, and lower maximum torques in comparison with the corresponding virgin vulcanisates (Joseph *et al*., 2017a; 2017b; 2016a; 2016b & 2018). The minimum torque of the 4HT assisted devulcanised samples were lower than that of the mechanically devulcanised samples resulting in an increase in the total torque of these samples which is in correlation with previous observations (Joseph *et al*., 2016a; 2016b & 2018). The comparable minimum torques of the virgin samples indicates that the BR content in the vulcanisate did not influence the minimum torque. In addition, since the minimum torque indirectly relate to the

Table 4. **Crosslink densities of the original and devulcanised NR/BR blends with corresponding per cent devulcanisation**

| NR/BR blend ratio | Crosslink density x10$^4$, mole/cm$^3$ | | | Per cent devulcanisation, % | |
|---|---|---|---|---|---|
| | Virgin | DV | 4HT DV | DV | 4HT DV |
| 100/0 | 0.97 | 0.77 | 0.45 | 20.2 | 53.5 |
| 80/20 | 1.1 | 0.69 | 0.43 | 37.8 | 61.6 |
| 70/30 | 0.84 | 0.58 | 0.44 | 30.9 | 60 |
| 60/40 | 1.2 | - | 0.46 | - | 62 |
| 50/50 | 1.2 | - | 0.49 | - | 59.4 |

Table 5. **Cure characteristics of original and corresponding devulcanised NR/BR blends**

| Vulcanisate/ NR/BR Blend Ratio | Semi EV cured | | | | |
|---|---|---|---|---|---|
| | Torque (dNm) | | | | |
| | Minimum, $M_L$ | Maximum, $M_H$ | $M_H$ - $M_L$ | Scorch time, min. | Cure time, min. |
| Original 100/0 | 1.5 | 18.9 | 17.4 | 2.1 | 5.3 |
| 100/0 DV | 4.5 | 14.8 | 10.3 | 0.8 | 5.1 |
| 100/0 4HTDV | 2.2 | 14.1 | 11.9 | 1.1 | 4.3 |
| Original 80/20 | 1.4 | 14.5 | 13.1 | 2.8 | 5.8 |
| 80/20 DV | 5 | 15.1 | 10.1 | 1.4 | 5.9 |
| 80/20 4HTDV | 2.5 | 12.7 | 10.2 | 1.4 | 4.8 |
| Original 70/30 | 1.6 | 11.7 | 10.1 | 3.5 | 6.8 |
| 70/30 DV | 5.2 | 15.3 | 10.1 | 1.4 | 6.1 |
| 70/30 4HTDV | 2.9 | 13.9 | 11 | 1.5 | 5.8 |
| Original 60/40 | 1.9 | 15 | 13.1 | 3.3 | 6.5 |
| 60/40 DV | 5.5 | 15.5 | 10 | 1.6 | 6.2 |
| 60/40 4HTDV | 3.2 | 14.7 | 11.5 | 1.4 | 5.4 |
| Original 50/50 | 2.1 | 16 | 13.9 | 3.4 | 6.6 |
| 50/50 DV | 5.9 | 16.7 | 10.8 | 1.7 | 6.6 |
| 50/50 4HTDV | 3.6 | 15.5 | 11.9 | 1.4 | 5.5 |

viscosity of the sample, the comparable values for minimum torque of mechanically devulcanised samples point to the similar viscosity of the devulcanised samples corresponding to their similar level of devulcanisation. On the other hand, the lower minimum torque of the 4HT assisted devulcanised samples might be indicating the higher percent devulcanisation of these samples (Isayev and Ghose, 2005; Joseph *et al*., 2016a & 2018). The increase in minimum torque of the devulcanised blends in comparison with devulcanised NR sample indicates the presence of BR tend to decrease the devulcanisation efficiency.

### *Revulcanisate properties*

The revulcanisate properties of the devulcanised samples in comparison with the corresponding properties of the virgin vulcanisates are illustrated in Figure 2 and are listed in Table 6. Generally, the mechanical performance of NR vulcanisate is much superior to BR vulcanisates and hence intermediate values were expected for the blends based on the blend ratio. The tensile strength of the original vulcanisates decreased with increase in BR content in the blend (Chiu and Tsai, 2006) while tear strength increased with BR content up to 70/30 NR/BR blends. The reduction in tear strength with BR content was more prominent with 60/40 and 50/50 blends.

Revulcanisate properties of the mechanically devulcanised samples were significantly inferior to the corresponding virgin vulcanisates which is consistent with the significantly higher residual crosslinks in

Table 6. **Mechanical properties of original blends and their corresponding revulcanisates**

| Vulcanisate/ Blend ratio | Tensile strength, MPa | Elongation at break, % | M100, MPa | M200, MPa | M300, MPa | Tear strength, N/mm |
|---|---|---|---|---|---|---|
| Original 100/0 | 25.4 ±0.57 | 547 ±28.8 | 2.9 | 6.2 | 11.1 | 108.5 ±6.5 |
| 100/0 DV | 11 ±0.52 | 310 ±20.4 | 2.5 | 5.4 | 9.7 | 47.7 ±1.6 |
| 100/0 4HTDV | 19.4 ±1.1 | 454 ±16.7 | 3 | 5.4 | 9.7 | 67.2 ±1.2 |
| Original 80/20 | 23.5 ±0.22 | 556 ±45.4 | 3.0 | 6.4 | 10.8 | 117.8 ±2.6 |
| 80/20 DV | 12.7 ±1.3 | 311 ±23.3 | 3.5 | 6.8 | 11.9 | 41.2 ±1.8 |
| 80/20 4HTDV | 20.2 ±1.3 | 486 ±17.3 | 2.7 | 5 | 9 | 51.9 ±1.4 |
| Original 70/30 | 21.7±0.37 | 547 ±15.8 | 3 | 6.2 | 10.7 | 124.6 ±5.4 |
| 70/30 DV | 15.7 ±1.6 | 305 ±34.8 | 3.0 | 5.7 | 12.2 | 38 ±1.01 |
| 70/30 4HTDV | 22.5 ±0.61 | 455 ±15.1 | 2.9 | 5.4 | 9.8 | 54.7 ±2.8 |
| Original 60/40 | 21.6 ±0.57 | 524 ±14.02 | 2.9 | 6.2 | 10.6 | 77.2 ±6.8 |
| 60/40 DV | 9.8 ±0.35 | 260 ±29.7 | 2.8 | 5.6 | - | 35.7 ±3.9 |
| 60/40 4HTDV | 13.4 ±0.76 | 361 ±9.02 | 2.9 | 5.4 | 9.9 | 39.3±1.6 |
| Original 50/50 | 21.3 ±1.1 | 546 ±28.2 | 2.8 | 6 | 10.2 | 62.7 ±2.6 |
| 50/50 DV | 10.4 ±0.39 | 276 ±6.01 | 2.6 | 6 | - | 31 ±2.6 |
| 50/50 4HTDV | 13.6 ±0.73 | 341 ±7.8 | 3.1 | 5.9 | 11 | 34.2 ±3.9 |

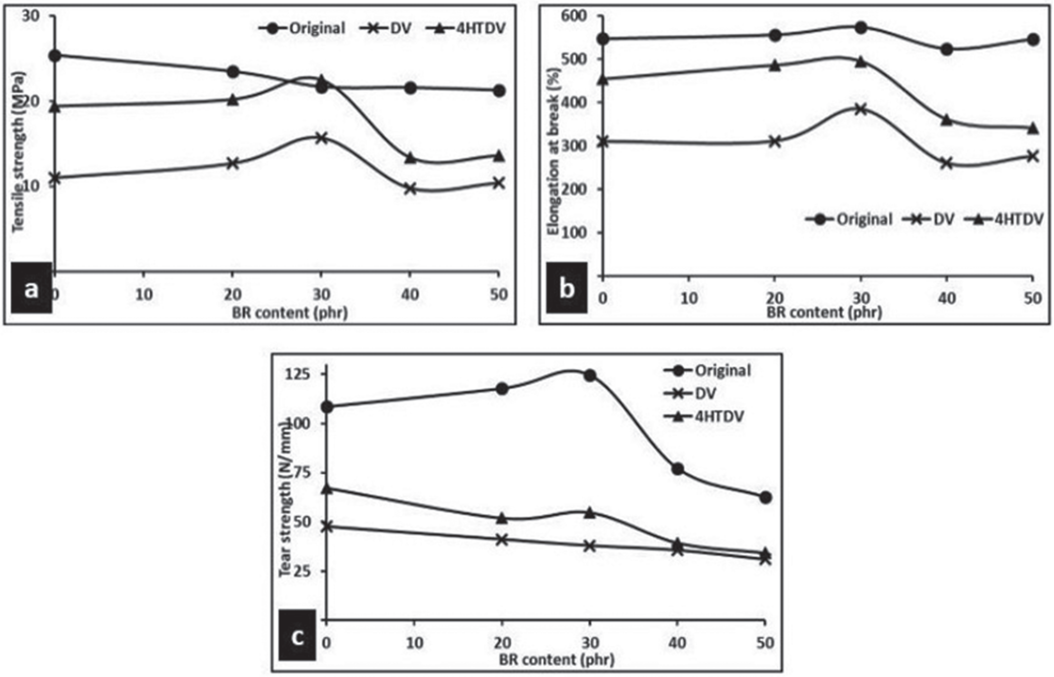

Fig. 2. Revulcanisate **a:** tensile strength **b:** elongation at break and **c:** tear strength of devulcanised samples in comparison with the corresponding properties of original samples

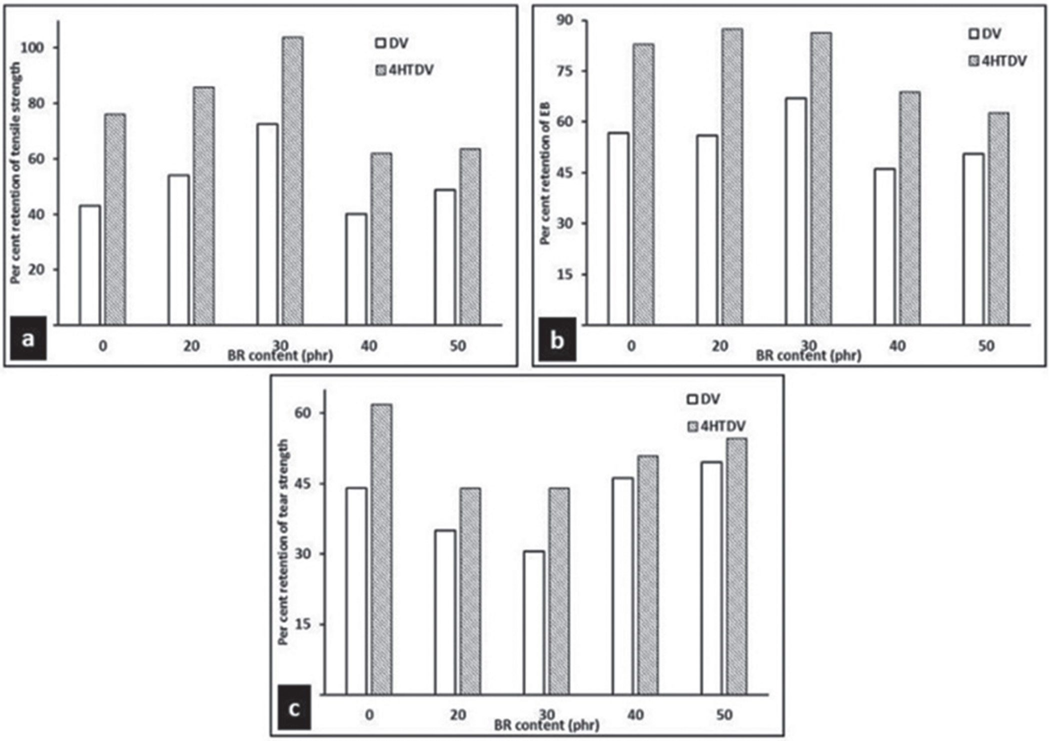

Fig. 3. Per cent retention of vulcanisate properties after revulcanisation of NR/BR blends
a: tensile strength b: elongation at break c: tear strength

these samples. At higher BR concentrations in the original blend (40 and 50 parts), a significant drop in revulcanisate properties of the corresponding devulcanised samples are noticed. On the other hand, the revulcanisate properties of the 4HT assisted devulcanised samples are significantly higher owing to the lower residual crosslinks in these samples. The tensile strength of the 4HT assisted devulcanised samples improved significantly compared with the corresponding mechanically devulcanised samples. But, it can be observed that, since the absolute value of tensile strength dropped with the increase in BR content in the blend and the hike in tensile strength brought in by the action of 4HT became less relevant. The positive influence of 4HT upon the tear strength of revulcanised samples significantly reduced with the presence of BR content and became marginal for blends with higher BR content.

Since the vulcanisate properties of the virgin vulcanisates are different, the analysis of the revulcanisate properties along with corresponding per cent retention values might be more informative. The retention of tensile strength, elongation at break and tear strength of the revulcanised samples are illustrated in Figure 3. Significant improvement in the retention of tensile strength and elongation at break were obtained when 4HT was used as a devulcanisation aid. However for tear strength, the positive influence of 4HT was marginal which is in contrary to the previous observations regarding the devulcanisation of NR vulcanisates (Joseph *et al.*, 2016a & 2018).

## Devulcanisation of pre-cured tyre tread buffing and GTR

### *Number of passes for devulcanisation*

Devulcanisation of buffing dust was carried out both in the presence and absence of 4HT (4phr). As obvious from Figure 4, the required number of passes through the tight nip of the tworoll mill significantly reduced when 4HT was used as a devulcanisation aid. This observation might be indirectly indicating the potential application of stable free radical assisted devulcanisation for commercial sources of waste rubbers also.

### *Residual crosslink density of devulcanised samples*

The residual crosslink density of buffing dust devulcanised without and with the assistance of 4HT are given in Table 7 (The residual crosslink density of mechanically devulcanised GTR could not be determined and hence no comparison could be made). It can be observed that, residual crosslink density of the 4HT assisted devulcanised buffing dust is 53.7 per cent lower than that of the corresponding mechanically devulcanised sample. This is a direct indication of the higher devulcanisation efficiency associated with 4HT assisted devulcanisation of buffing dust.

Table 7. **Residual crosslink densities of mechanically and 4HT assisted devulcanised buffing dust**

| Devulcanisation | Crosslink density x $10^4$, mole/cm$^3$ | Reduction, % |
|---|---|---|
| Mechanical | 0.54 | 53.7 |
| 4HT assisted | 0.25 | |

### *Revulcanisation*

Cure characteristics and revulcanisate properties of mechanically and 4HT assisted devulcanised buffing dust and GTR are given in Table 8. The results shows that the minimum torque of 4HT assisted devulcanised samples were lower than that of the corresponding mechanically devulcanised samples and the maximum torques were comparable. Hence, the change in torque of the 4HT assisted

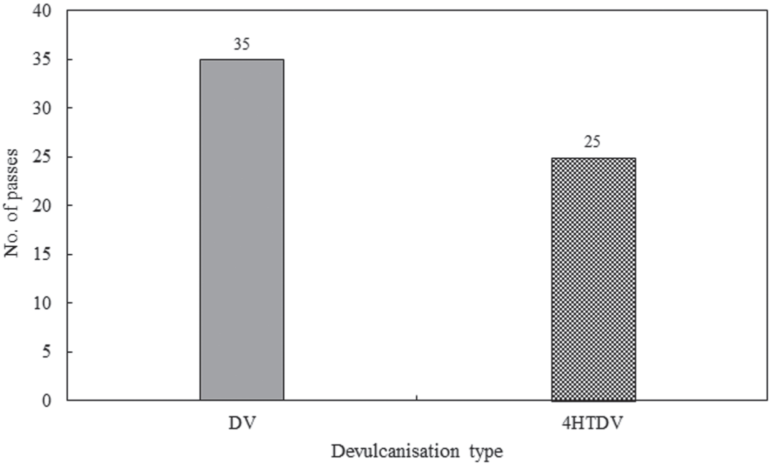

Fig. 4. Required number of passes for devulcanisation of buffing dust without and with the assistance of 4HT

Table 8. **Cure characteristics and revulcanisate properties of mechanically and 4HT assisted devulcanised buffing dust and GTR**

| Sample | | $M_L$ | $M_H$- $M_L$ | $ts_2$, min | Tensile strength, MPa | EB, % | M100, MPa | M300, MPa | Tear strength, N/mm |
|---|---|---|---|---|---|---|---|---|---|
| | | dNm | | | | | | | |
| Buffing dust | DV | 5.1 | 7.5 | 2.9 | 13.8 | 318 | 4.7 | 8.9 | 25.2 |
| | 4HTDV | 3.5 | 9.6 | 2.9 | 16.6 | 451 | 4.8 | 8.8 | 35.4 |
| GTR | DV | 6 | 5.7 | 2.5 | 7.74 | 244 | 2.9 | - | 20.6 |
| | 4HTDV | 4.3 | 8.1 | 2 | 10.8 | 300 | 3.1 | 11 | 30 |

devulcanised samples were higher than the corresponding mechanically devulcanised samples. Besides, the revulcanisate properties of the 4HT assisted devulcanised buffing dust is significantly higher than those obtained for the corresponding mechanically devulcanised sample.

## CONCLUSION

Stable free radical assisted mechanical devulcanisation of NR/BR blends was studied with respect to the influence of BR content in an NR/ BR blend. The per cent retention of vulcanisate properties indicates that, the efficiency of devulcanisation dropped with increase in the BR content in the NR/BR blend. In all cases, 4-Hydroxy TEMPO acts as a good devulcanisation aid that can ensure (i) higher level of devulcanisation, (ii) lower devulcanisation time and (iii) higher revulcanisate properties.

The 4HT assisted devulcanisation of commercially available used rubber samples like buffing dust and GTR proposed the feasibility of stable free radical as an effective devulcanisation aid with commercial potential. The revulcanisate properties of the buffing dust and GTR devulcanised with the assistance of 4HT were higher than that obtained for the corresponding mechanically devulcanised sample. The revulcanisate properties of GTR were lower than that of fresh buffing dust obtained from pre-cured tyre tread indicating the role of quality of sample (effect of ageing) in addition to the higher percent of BR in GTR.

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