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# MECHANICAL DEVULCANIZATION OF CARBON BLACK FILLED NATURAL RUBBER VULCANIZATES: EFFECT OF CROSSLINK DENSITY

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The present study aims to find the correlation between the crosslink density of the freshly prepared sample to be devulcanised and the efficiency of mechanical devulcanization in a two roll mill. Efficiently vulcanized (EV) carbon black filled natural rubber vulcanizates with varying crosslink densities were mechanically devulcanised on a two-roll mixing mill and the efficiency of devulcanization was determined from the residual crosslink densities of the devulcanized samples and the corresponding revulcanizate properties. With increasing crosslink density of the starting material, the tear and tensile strengths of the sample first increased, reached a maximum and then decreased. The percent devulcanization associated with these samples on mechanical devulcanization ranged between 70-80 per cent irrespective of their difference in original crosslink density. Hence, the absolute value of the residual crosslink density is high when the original crosslink density is high leading to poor revulcanizate properties irrespective of the higher per cent devulcanization attained. Thus, the original crosslink density of the sample to be devulcanized appears to be one of the most important factors that defines the revulcanizate properties of the devulcanized samples.

**Key words**: Crosslink density, Devulcanization, Natural rubber, Vulcanization

## INTRODUCTION

Devulcanization of used rubber products is an extremely significant problem for the rubber industry from the viewpoint of economic and environmental concerns. Vulcanized rubbers have three dimensional crosslinked structures that do not decompose easily. Recycling methods envisage the conversion of used rubber products into any reusable form whereas devulcanization is a recycling strategy which aims at selective scission of crosslinks in the vulcanized network to retrieve the polymer for reuse in the rubber industry itself. The currently employed devulcanization methods (Warner, 1994; Joseph, *et al.*, 2016) involve the application of high temperature and or pressure (Gupta and Maridass, 2003; Khait, 1997; Benko *et al.*, 2004; Zhang *et al.*, 2009; Luis *et al.*, 1997; Matsushita *et al.*, 2003; Morin *et al.*, 2002), microwave (Novotny *et al.*,1978; Hunt and Hall, 1994; Bani *et al.*, 2011), ultrasonic energies (Isayev and Chen, 1994; Roberson and Boron, 1998; Dinzburg and Alexander, 2002), biotechnological reactions

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(Roy *et al.*, 2006; Yusof and Ahmad, 2010; Straube *et al.*,1994; Christofi *et al.*, 2010; Kim and Park, 1999) or the action of solid phase modifiers along with mechanical shear (mechano-chemical) at ambient temperatures (De *et al.*, 1999; Jana *et al.*, 2007; Sekhar *et al.*,1998; Rooj *et al.*, 2011; Goldshtein and Kopylov, 2002; 2003; Mandal *et al.*, 2014; George *et al.*, 2017). Thermal and microwave assisted devulcanization result in severe polymer degradation, whereas complication of the method makes ultrasonic devulcanization less favorable. Large space and time requirements challenge the biotechnological devulcanization processes. Hence, mechanical or mechano-chemical devulcanization processes are considered to be more feasible due to time, cost, and energy savings. The possibility of minimum main chain scission ensured by ambient reaction conditions is an added advantage.

The present study aims to find the correlation between the crosslink density of samples frishly vulcanized and the efficiency of mechanical devulcanization of the same on a two roll mill. Efficiently vulcanized (EV) carbon black filled NR vulcanizates prepared in the laboratory with varying crosslink densities were mechanically devulcanized in a two roll mill and the efficiency of devulcanization was determined from the residual crosslink densities of the devulcanized samples and the corresponding revulcanizate properties. Carbon black filled EV vulcanizates prepared using the same accelerator sulphur ratio but with varying crosslink densities were used for devulcanization to ensure better control of the processes and proper assessment of the efficiency of devulcanization.

## 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 nine sets of samples with varying crosslink densities. Laboratory grade tolune was used for crosslink density determination of original and devulcanized samples.

### Preparation of original samples

Carbon black filled natural rubber vulcanizates were prepared as per formulations given in Table 1. A constant accelerator/sulphur ratio of 4:2 was maintained while varying the amount of curatives to obtain vulcanizates of nine different crosslink densities designated as sample I to sample IX based on the increasing curative loading.

### Devulcanization

Mechanical devulcanization was carried out in a laboratory two roll mixing mill of 15 cm x 30 cm size at a friction ratio 1:1.2. Tensile sheets moulded from the original compound were cut into chips of approximately 1 cm$^2$ size was made into crumb by passing through the two roll mill and devulcanized by passing through the tight nip (approx. 0.05 mm). The possible temperature rise during devulcanization was checked by continuous cooling of the rolls by circulating cold water through the rolls which minimized the chances of thermal degradation of the polymer main chain. The devulcanized samples were designated as DV I to DV IX, corresponding to the original samples *viz.* sample I to sample IX, respectively.

### Cure characteristics and physical property measurement

Rubber Process Analyzer (RPA 2000) was used to monitor the cure characteristics at 150$^{O}$C. Test samples were then moulded by compression molding method in an electrically heated hydraulic press for their respective cure times (tc$_{90}$). Tensile strength

Table 1. **Formulation for original compounds**

| Ingredients | Quantity (phr) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | I | II | III | IV | V | VI | VII | VIII | IX |
| Natural Rubber | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| CBS | 1.25 | 2.08 | 2.5 | 2.9 | 3.3 | 3.75 | 4.17 | 5 | 7.5 |
| Insoluble sulphur | 0.3 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1 | 1.2 | 1.8 |

Common ingredients: HSL – 1.5; ZnO – 5; Srearic acid – 2; HAF black – 40; Naphthenic oil – 4

and tear strength measurements of the samples were performed with a Zwick UTM at a test speed of 460 mm min$^{-1}$ following the respective ASTM standards.

### Mooney viscosity

Processability of rubber is typically characterized by its viscosity accessed by Mooney viscosity determination. The Mooney viscosities of the original and the devulcanized samples at 100$^0$C were determined using Mooney Viscometer (EKT 200 TM) and the variation in processability of different devulcanized samples after mechanical devulcanization were compared.

### Crosslink density

The crosslink densities (CLD) of the original samples and the residual crosslink densities of the devulcanized samples were determined by swelling method applying Flory Rhener equation using toluene as the solvent (Flory and Rehner, 1943; Meyasami, 2012).

### Percent devulcanization

The per cent devulcanization of the devulcanized samples was calculated following ASTM D 6814-02.

### Revulcanization

100 g of the devulcanized crumb was blended with 10 g of virgin rubber and revulcanized using the formulation given in the Table 2. Curatives for revulcanization were added considering the rubber content of the devulcanised rubber to be 50 per cent. The cure characteristics were determined using rubber process analyser, the samples were moulded for their respective cure times and the vulcanizate properties were determined following the ASTM standards.

Table 2. **Revulcanization formulation for devulcanized samples**

| Ingredients | Quantity (phr) |
|---|---|
| Devulcanized rubber | 100 |
| Natural rubber | 10 |
| N-Oxydiethylene-2-benzothiazole sulfenamide (MOR) | 0.8 |
| Insoluble sulphur | 1.5 |

Other ingredients: Anti oxidant, HSL – 1.5; ZnO – 5; Srearic acid – 2

## RESULTS AND DISCUSSION

### Crosslink density of original and devulcanized samples

Table 3 shows the crosslink density of the original samples and the residual crosslink density of the corresponding devulcanised samples. The crosslink density of the original samples steadily increased with increasing amounts of curatives owing to the formation of more number of crosslinks. Sample I had the least crosslink density while sample IX had the highest and the others had intermediate crosslink

Table 3. **Crosslink density of original and devulcanized samples**

| Curative dose for original sample | | Sample | Crosslink density x $10^4$ (mole/cm$^3$) |
|---|---|---|---|
| CBS | Sulphur | | |
| 1.25 | 0.3 | I | 0.43 |
| | | DV I | 0.097 |
| 2.08 | 0.5 | II | 0.81 |
| | | DV II | 0.21 |
| 2.5 | 0.6 | III | 0.91 |
| | | DV III | 0.18 |
| 2.9 | 0.7 | IV | 1.00 |
| | | DV IV | 0.23 |
| 3.3 | 0.8 | V | 1.20 |
| | | DV V | 0.25 |
| 3.75 | 0.9 | VI | 1.30 |
| | | DV VI | 0.27 |
| 4.17 | 1 | VII | 1.50 |
| | | DV VII | 0.39 |
| 5 | 1.2 | VIII | 1.80 |
| | | DV VIII | 0.48 |
| 7.5 | 1.8 | IX | 2.70 |
| | | DV IX | 0.73 |

densities corresponding to the amount of curatives used.

As the initial crosslink density of the sample increased from 0.43 x $10^{-4}$ mole/cm$^3$ for sample I to 2.7 x $10^{-4}$ mole/cm$^3$ for sample IX, the residual crosslink density of the devulcanized samples also rose from 0.097 x $10^{-4}$ to 0.73 x $10^{-4}$ mole/cm$^3$. The table thus indicates that the absolute value of residual crosslink density in the devulcanized sample depends on the original crosslink density of the sample to be devulcanized to a great extent. Hence, if the crosslink density of the sample to be devulcanized is higher, the residual crosslink density of the corresponding devulcanized sample will also be higher and the percent devulcanization associated with them will then become insignificant as the higher residual crosslink density of the revulcanized sample will influence the revulcanizate properties adversely.

The percent devulcanization associated with different samples ranged between 73 to 80 per cent (Figure 1). The residual crosslink density of the samples followed the same trend as that of the original crosslink density of the corresponding samples and hence the percent devulcanization remained comparable. The concept of shear induced devulcanization is based on the clear differences in the bond energy and the elastic constants between the carbon-carbon and the sulfur-sulphur bonds which accounts for the preferential selective scission of the sulphidic crosslinks over the main chain carbon-carbon bonds. Since the accelerator sulphur ratio is kept constant, the percent distribution of crosslinks in all the vulcanizate networks is expected to be the same irrespective of variations in the crosslink density. The constant shear force applied by the mill ensures that the amount of shear experienced by the bonds to be the same in all vulcanizates which might have led to comparable per cent devulcanization in all samples. Consequently, samples with higher initial crosslink densities might have ended up with higher residual crosslink densities when devulcanized. The adverse effect of

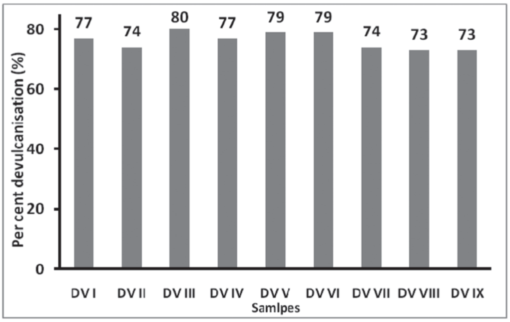

Fig. 1. Per cent devulcanization of different samples

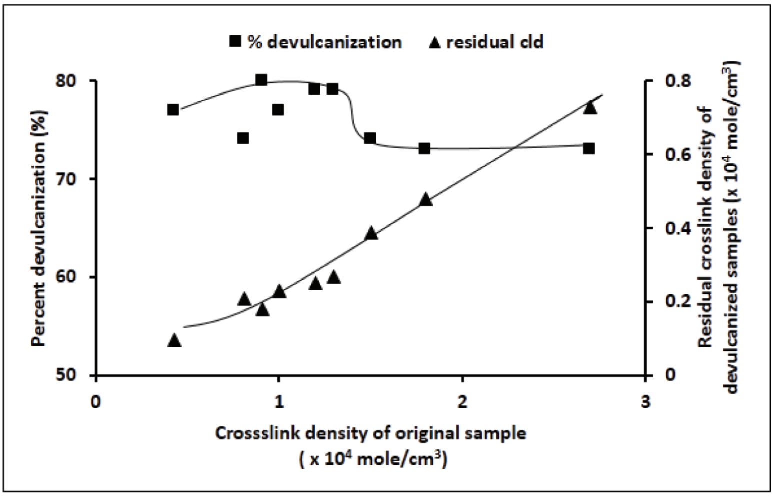

Fig. 2. Crosslink density of original sample Vs per cent devulcanization and residual crosslink density

higher crosslink densities of the original samples on the devulcanization process observed as higher residual crosslink density of the corresponding devulcanized samples and the comparable percent devulcanisation of all the samples is further outlined in Fig. 2.

## Mooney viscosity

The Mooney viscosities of the devulcanized samples in comparison with the original compound are given in Table 4. The Mooney viscosities of the devulcanized samples steadily increased from samples DV I to DV IX corresponding to the residual crosslink density and the crosslink densities of the respective original samples. The Mooney viscosities of the devulcanized samples DV I to DV IV were well below the viscosity of the control compound. This might be due to the combined effect of low residual crosslink density along with the viscosity reduction brought in by the main chain degradation occurred during mechanical devulcanization carried out under the shearing in tight nip of the two roll mill. As Mooney viscosity is an indication of the processability of the samples, the samples I to IV appear to have comparable process ability with the original sample which indicates that these samples can be used as partial or complete substitutes for the original compound according to the vulcanizate property requirements.

## Cure characteristics

The cure characteristics of the original and the corresponding devulcanised samples are given in Table. 5 and the corresponding cure curves are given in Fig. 3. The maximum torque ($M_H$) increases from sample I to IX

Table 4. **Mooney viscosities of devulcanized samples**

| Mooney viscosity | Original | DV I | DV II | DV III | DV IV | DV V | DV VI | DV VII | DV VIII | DV IX |
|---|---|---|---|---|---|---|---|---|---|---|
| [ML(1+4)] | 43 | 11 | 23 | 31 | 31 | 42 | 51 | 80 | 95 | >100 |

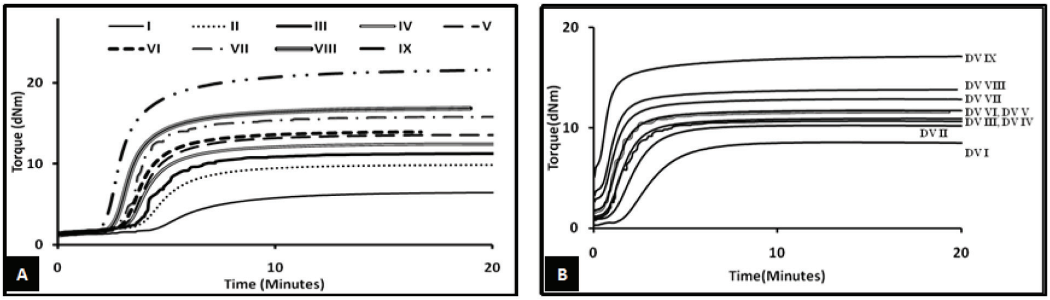

Fig. 3. Cure curves of (A) original and (B) devulcanized samples

with the increase in the amount of accelerator and sulphur even though the accelerator sulphur ratio is kept constant. Correspondingly, the $M_H$-$M_L$ values also increased. As the amount of accelerator and sulphur increased, the cure time and scorch time reduced as the sample attains the optimum crosslink density at a faster rate.

The revulcanization cure characteristics of the devulcanized samples show similar cure kinetics with short induction times and fast vulcanization compared with the original sample. The scorch time of all the devulcanized samples reduced considerably compared with the original samples. The order of reduction of scorch time was similar to that observed with the scorch time reduction occurred with the original samples with increasing curative loading. The scorch time decreased from sample DV I to sample DV IX just as in the case of sample I to sample IX. The low scorch safety associated with revulcanisation of devulcanised samples is an unsolved issue in devulcanized rubber and was recently revisited. Although several reasons like crosslink precursors (Myhre, 2012) or residual accelerator derivatives present in the devulcanized samples (Isayev *et al.*, 1995), unreacted curatives (Myhre, 2012; Gibala and Hamed, 1994) or structural modifications like cyclic sulphide structures (Levin *et al.*,1997) were being proposed as the cause, the recent study pointed that the MBT released from the crosslink formation from crosslink precursors present in the devulcanised samples are responsible for reduced scorch safety during revulcanisation of devulcanized samples (Joseph *et al.*, 2017).

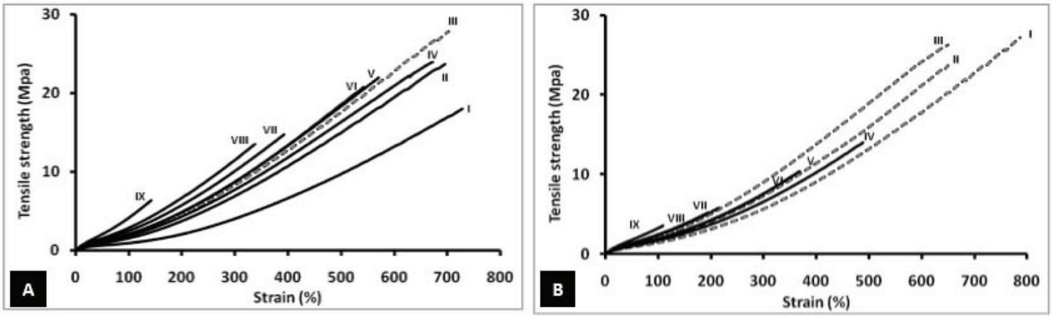

Fig. 4. Stress strain curves of the (A) original and (B) revulcanized samples

## Mechanical properties

The tensile and tear properties of the original and the corresponding revulcanized samples are given in Table 6 and the corresponding stress-strain curves are in Figure 4.

It can be observed that all the properties of original vulcanizates systematically changes with increase in the amount of sulphur and CBS (Rao, 2012). Both the tensile strength and the tear strength of the original samples initially increased with increasing curative loading, reached a maximum and then decreased on further increase in crosslink density. Effect of crosslink density can be different on tear strength, tensile strength, modulus, hysteresis and so on.

Gee and Flory (1947) and have explored the dependence of tensile strength of natural rubber vulcanizates on degree of crosslinking and they demonstrated that there was a maximum for tensile strength as crosslink density increases. As crosslink density increases, material becomes more elastic and hence hysteresis continuously goes down while modulus and hardness increase monotonically. Tensile and tear strength first passes through a maximum as crosslink density increases and then decrease steadily to a low degree when crosslink density becomes high. A relationship between strength of vulcanizates and crosslink density was developed (Flory, 1949). When an un-crosslinked elastomer is deformed, polymer chains may slide past one another

Table 5. **Cure characteristics of original and revulcanized samples**

| | Torque (dNm) | | | Scorch time, | Cure time, |
|---|---|---|---|---|---|
| Sample | Minimum $M_L$ | Maximum $M_H$ | $M_H$-$M_L$ | $ts_2$ min | $tc_{90}$ min |
| I | 1.1 | 6.5 | 5.4 | 5.4 | 11 |
| DV I | 0.27 | 8.6 | 8.3 | 2.2 | 5.7 |
| II | 1.6 | 9.9 | 8.3 | 4.2 | 8.3 |
| DV II | 0.8 | 10.2 | 9.4 | 1.5 | 4.3 |
| III | 1.4 | 11.3 | 9.9 | 4.2 | 7.7 |
| DV III | 1.0 | 10.7 | 9.7 | 1.2 | 3.8 |
| IV | 1.4 | 12.5 | 11.1 | 3.5 | 6.9 |
| DV IV | 1.2 | 11 | 9.8 | 1.1 | 3.5 |
| V | 1.5 | 13.6 | 12.1 | 3.4 | 6.9 |
| DV V | 1.6 | 11.6 | 10 | 1 | 3.4 |
| VI | 1.2 | 13.9 | 12.7 | 3.2 | 6.5 |
| DV VI | 1.8 | 11.7 | 9.9 | 0.9 | 3.1 |
| VII | 1.5 | 15.9 | 14.4 | 3 | 6.7 |
| DV VII | 2.9 | 12.9 | 10 | 0.8 | 3 |
| VIII | 1.2 | 16.9 | 15.7 | 2.7 | 6.2 |
| DV VIII | 3.8 | 13.8 | 10 | 0.7 | 2.9 |
| IX | 1.3 | 22 | 20.7 | 2.2 | 7.2 |
| DV IX | 6.3 | 17.1 | 10.8 | 0.5 | 3.8 |

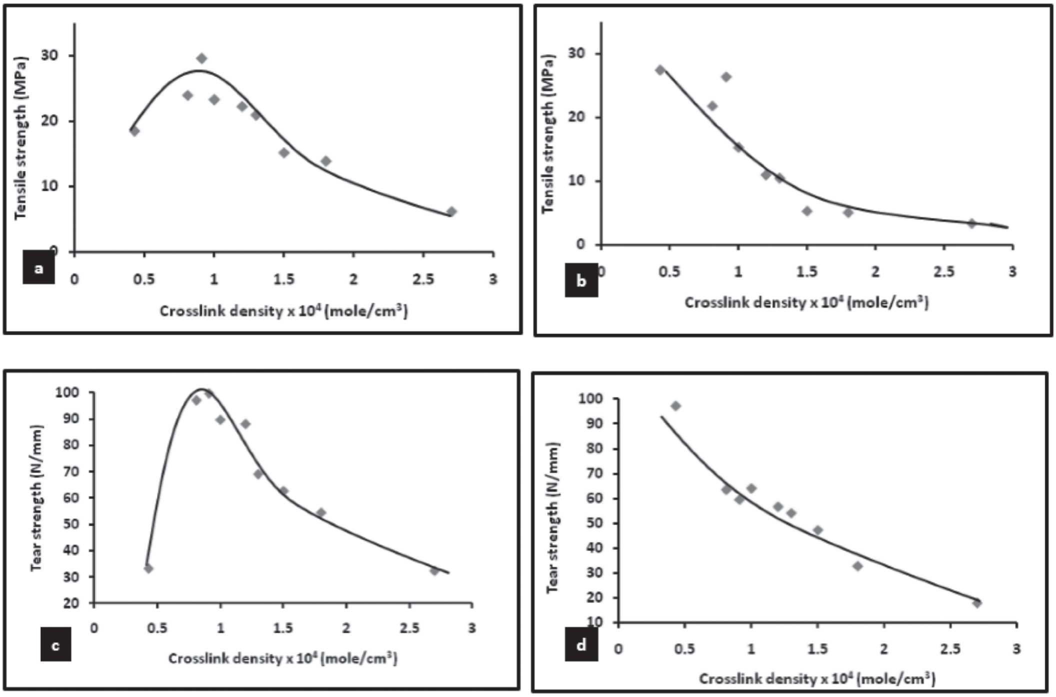

Fig. 5. Variation of tensile strength (a & b) and tear strength (c & d) of the original and revulcanised samples with respect to crosslink density of original sample

and disentangle. When a few crosslinks are added, molecules become more branched which can help prevent disentangle. When crosslinking is further increased above gel point, strength becomes even higher because fracture cannot happen without breaking chemical bonds. However, if the crosslink density is too high, rubber network will gradually lose the ability to dissipate input energy through molecular motion and become brittle and the strength goes down.

The stress-strain curves of the revulcanized samples resemble that of the original samples but for the difference that the strain crystallization in the revulcanized samples occurs at lower strain than the corresponding original samples. Figure 5 suggests that the tensile strength and tear strength of the original samples were optimum about a crosslink density of $1\text{x}10^{-4}$ moles/cm$^3$. The corresponding revulcanisate tensile strength and tear strength of the devulcanised samples having original crosslink density not more than $1\text{x}10^{-4}$moles/cm$^3$ were high where after it lowered significantly with further increase in crosslink density of the original sample.

The tensile and tear properties of the devulcanized samples might also be influenced by their revulcanized crosslink densities. Revulcanizate properties of the devulcanized samples given in Table 6 indicates that very good revulcanizate properties are obtained for devulcanised samples prepared from original vulcanisates of lower crosslink densities. This might be in accordance with the lower residual crosslink densities and high percent devulcanization associated with these samples. As the

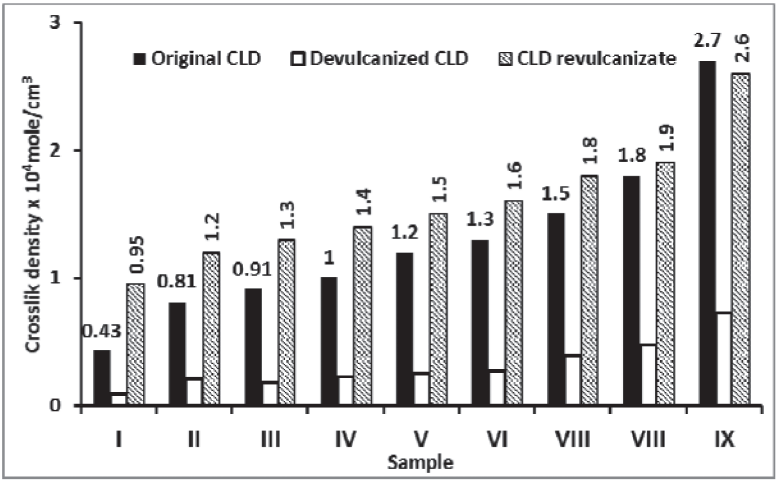

Fig. 6. Comparison of crosslink density of original samples and revulcanized samples

crosslink density of the original samples gradually increased, the revulcanisate properties dropped considerably owing to the higher residual crosslink densities of the samples after devulcanization.

The crosslink density of the revulcanized samples also reveald that irrespective of the common revulcanization cure system used, the crosslink density attained by different devlcanised samples are different (Fig. 6). The crosslink density of the revulcanized sample with high initial crosslink densities or high residual crosslink densities of the devulcanized samples are high and vice versa. The crosslink densities of the revulcanized samples are higher compared with the crosslink density of the corresponding original samples. The crosslink density of the revulcanized samples ranges from 0.95 x $10^{-4}$mole/cm$^3$ to 2.6 x $10^{-4}$mole/cm$^3$ where as that of the original samples varied from 0.43 x $10^{-4}$ to 2.7 x $10^{-4}$ mole/cm$^3$.

It is observed that in the present system, the tensile strength of the revulcanizates are higher or comparable with that of the corresponding original sample when the original cross link density of the samples are at or below the optimum value of 0.9x$10^4$moles/cm$^3$(samples I to III). The tensile strength then drops steeply for other samples having high original crosslink densities. But in the case of the tear strength, only the revulcanizate of one sample with original crosslink density much below the optimum value (sample I) could give very high tear strength on revulcanization. At and around the optimum crosslink densities of the original sample, the tear strength of the revulcanizates decreased slowly and systematically.

Figure 7 shows the variation of tensile strength and tear strength of original samples and their respective revulcanized samples. The trends observed might be an indication that it is not the higher devulcanization percent alone but also the residual crosslink density attained by the devulcanized samples that decides the efficiency of devulcanization. Another observation is that the tear properties of the revulcanized samples are more sensitive to the efficiency of devulcanization rather than the tensile properties.

Table 6. **Mechanical properties of original and corresponding revulcanized samples**

| Sample | Tensile strength (MPa) | Elongation at break (%) | M100 (MPa) | M200 (MPa) | M300 (MPa) | Tear strength (Nmm$^{-1}$) |
|---|---|---|---|---|---|---|
| I | 18.6 | 767.1 | 1.1 | 2.4 | 4.4 | 33.3 |
| DV I | 27.4 | 819.4 | 1.5 | 3.2 | 5.7 | 97.0 |
| II | 24.0 | 711.4 | 1.5 | 3.6 | 6.7 | 97.1 |
| DV II | 21.8 | 592.1 | 1.9 | 4.3 | 7.7 | 63.4 |
| III | 29.7 | 710.5 | 2.0 | 4.8 | 8.5 | 99.7 |
| DV III | 26.4 | 638.3 | 2.0 | 4.4 | 7.8 | 59.5 |
| IV | 23.4 | 610.3 | 2.0 | 4.5 | 8.1 | 89.7 |
| DV IV | 15.3 | 461.7 | 1.8 | 3.9 | 6.9 | 64.0 |
| V | 22.3 | 555.7 | 2.1 | 5.0 | 8.9 | 88.1 |
| DV V | 11.0 | 333.9 | 1.9 | 4.2 | 7.6 | 56.6 |
| VI | 21.0 | 541.5 | 2.2 | 5.0 | 8.9 | 69.1 |
| DV VI | 10.5 | 373.5 | 2.0 | 4.4 | 7.7 | 54.1 |
| VII | 15.2 | 375.1 | 2.6 | 5.8 | 10.1 | 62.7 |
| DV VII | 5.4 | 220.8 | 2.2 | 4.9 | - | 47.3 |
| VIII | 14.0 | 321.8 | 2.9 | 6.8 | 11.6 | 54.5 |
| DV VIII | 5.1 | 192.5 | 2.5 | 5.4 | - | 32.8 |
| IX | 6.2 | 137.8 | 4.2 | - | - | 32.4 |
| DV IX | 3.4 | 102.5 | 3.3 | - | - | 18.0 |

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## CONCLUSIONS

The role of crosslink density of the original sample on the mechanical devulcanization of efficiently vulcanized carbon black filled NR vulcanizates was studied. With increasing crosslink density of the original sample, the tear and tensile strengths of the sample increased, reached a maximum and then decreased. The percent devulcanization

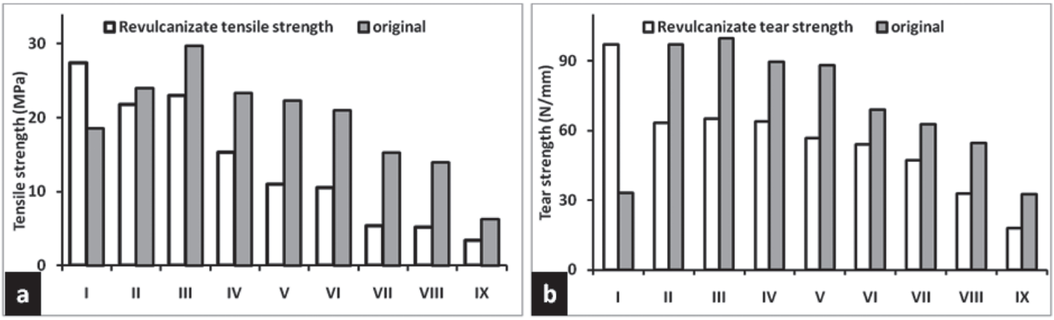

Fig. 7. Variation of a) tensile strength and b) tear strength of the original and revulcanized samples

associated with these samples on mechanical devulcanization ranged between 70 to 80 per cent irrespective of their difference in original crosslink density. This might be due to the common accelerator to Sulphur ratio existing among the samples. As a result, the absolute value of the residual crosslink density is high when the original crosslink density is high leading to poor revulcanizate properties irrespective of the higher per cent devulcanization attained. Thus, the original crosslink density of the sample to be devulcanized appears to be an important factor that defines the revulcanizate properties of the devulcanized samples.

## REFERENCES

Bani, A., Polacco, G. and Gallone, G. (2011). Microwave induced devulcanization forpoly (ethylene-propylene-diene) recycling. *Journal of Applied Polymer Science*, **120:** 2904-2911.

Benko, D., Beers, R., Lee, S. and Clark, K. (2004). Devulcanization of cured rubbers. *US patent* 20040132841 A1, July 8, 2004.

Christofi, N., Geoffrey, J. and Edward, D. Rubber treatment method. (2010). *US patent* 7737191 B2, June 15, 2010**.**

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 diallylsulphide. *Journalof Applied Polymer Science* **73:** 251-2958.

Dinzburg, B. and Alexander, B. (2002).Method and apparatus for devulcanization of crosslinked elastomers.*US Patent*6416705 B1, July 9,2002.

Flory, P. J. and Rehner, J. Jr. (1943). Statistical mechanics of cross-linked polymer networks II. Swelling. *Journal of Chemical Physics*. **11:**521-526.

Flory, P. J., Rabjohn, N. and Shaffer, M. C. (1949).Dependence of tensile strength of vulcanized rubber on degree of cross-linking. *Journal of Polymer Science*, **4:** 435-455.

Gee, G. (1947). Tensile strength of pure gum natural rubber compounds. *Journal of Polymer Science,***2:** 451- 462.

George, B., Joseph, A.M., Madhusoodanan, K.N., Alex, R. and Jacob, J. (2017).Stable free radical assisted devulcanization: *Indian Patent Application No. 201741017633, May 19, 2017.*

Gibala, D. and Hamed G, R. (1994).Cure and Mechanical behavior of rubber compounds containing ground vulcanizates. Part I—Cure Behavior. *Rubber Chemistry and Technology*, **67**: 636-648.

Goldshtein, V. and Kopylov, M. (2003) Method and composition for devulcanization of waste rubber. *US patent* 6541526 B1 1 April 2003**.**

Goldshtein, V. and Kopylov, M. (2002).Method and composition for devulcanization of waste rubber.*US patent* 6387966 B1, May 14 2002.

Gupta, B. R. and Maridass, B. (2003).Recycling of waste tire rubber powder. Devulcanization in a counter rotating twin screw extruder. *Kautschuk Gummi Kunststoffe*, **56**: 232-236.

Hunt, J. R. and Hall, D. Process for reclaiming elastomeric waste. *US Patent* 5362759 A**,** November 8,1994.

Isayev, A. I. and Chen, J. (1994).Continuous ultrasonic devulcanization of vulcanized elastomers.US patent 5284625 A, February 8 1994.

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

Jana, G. K., Mahaling, R. K., Rath, T., Kozlowska, A., Kozlowski, M. and Das, C. K. (2007). Characterization of styrene butadiene rubber and microwave devulcanized ground tire rubber composites. *Polimery*.**52**: 131-136.

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

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

Khait, K. (1997). Solid-state shear extrusion pulverization process.*Rubber World*, May 1997, 38-39.

Kim, J. K. and Park. J. W. (1999). The biological and chemical desulfurization of crumb rubber for the rubber compounding. *Journal of Applied Polymer Science,* **72:** 1543-1549.

Levin, V.Yu., Kim, S. H. and Isayev, A.I. (1997). Vulcanization of ultrasonically devulcanized SBR elastomers. *Rubber Chemistry and Technology*, **70**:120-128.

Luis, C., Oliveira, Da. and Lima, C. (1997). Process for reclaiming cured or semi-cured rubber. *US Patent* 5677354 A, October 14, 1997.

Mandal, S. K., MdAlam, N., Roy, K. and Debnath S. C. (2014).Reclaiming of ground rubber tire by safe multifunctional rubber additives: II. Virgin natural rubber/reclaimed ground rubber tire vulcanizates. *Rubber Chemistry and Technology,* **87**: 152-167.

Matsushita, M., Mouri, M., Okamoto, H., Fukumori, H., Sato, N., Fukuta, M., Honda, H., Nakashima, K., Watanabe, T., Otsuka, S., Okazaki. and OWaki, M. (2003). Method for reclaiming crosslinked rubber.*US Patent* 6632918 B1, October 14, 2003.

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

Morin, J. E., Williams, D. E. and Farris, R. J. (2002). Anovel method to recycle scarp tyres: High pressure high temperature sintering. *Rubber Chemistry and Technology*, **75**: 955-969.

Myhre, M., Saiwari, S., Dierkes, W. and Noordermeer, J. W. M. (2012).Rubber recycling: chemistry, processing, and applications. *Rubber Chemistry and Technology*,**85:** 408-449.

Novotny, D. S., Marsh, R. L., Masters, F. C. and Tally, D. N. Microwave devulcanization of rubbers. *US Patent* 4104205 A, August 1, 1978.

Rao, T. (2012). *Effect of crosslink density and N660 carbon black on tearing behaviors of natural rubber vulcanizates*. Thesis Presented to The Graduate Faulty of The University of Akron In Partial Fulfillment of the Requirements for the Degree Master of Science Tingling December, 2012.

Roberson, P. R. and Boron, T. M. (1998).Method and apparatus for continuous devulcanization of rubber.*US patent* 5799880 A, September 1,1998.

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 and Environment,***19:** 382-390.

Roy, R.V., Das, M., Banerjee, R. and Bhowmick. A. K. (2006). Comparative studies on crosslinked and uncrosslinked natural rubber biodegradation by Pseudomonas sp. *Bioresourcces Technology*, **97**: 2485-2488.

Sekhar, B. C., Kormer, V. A., Sotnikova, E. N., Mironyuk, V. P., Trunova, L. N. and Nikitina, N. A. (1998). Reclaiming Elastomeric materials. *US patent* 5770632 A, June 23,1998.

Straube, G., Straube, E., Neumann, W., Ruckauf, H., Forkmann, R. and Loffler, M. (1994). Method for reprocessing scrap rubber. *US patent* 5275948 A, January 4,1994.

Warner, W.C. (1994). Methods of devulcanization. *Rubber Chemistry and Technology*, **67**: 559- 566.

Yusof, F. and Ahmad, A. A.(2010). Enzymatic devulcanization of waste rubber products in preparation for recycling, Paper presented at National Biotechnology Seminar, May*24–26 May, PWTC, Kuala Lumpur, Malaysia.* 2010.

Zhang, Y.,Shen, J., Chen, T.,Xu, Z., Chen, X. and Zhang, M. (2009). Process for devulcanization of rubber. *US patent* 20090082475 A1, 2009.