ARTICLE

Studies on Dispersion of Insoluble Sulfur in Passenger Car Radial Belt Skim Compound

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ABSTRACT

Good dispersion of compounding ingredients in a rubber formulation is crucial for mechanical performance. After mixing, certain materials like sulfur, recycled materials, and zinc oxide can remain undispersed within the rubber matrix, which can lead to critical flaws and influence performance. Improper dispersion is one of the reasons for poor physico mechanical properties. The influence of temperature, mixing time and storage time of different grades of insoluble sulfur collected from one source are studied along with the standard sample of different sources. To better understand the reason for poor sulfur dispersion and high blooming, all the chemical and physical properties are analysed. The topological structures are evaluated using the thermomechanical techniques. The reason for poor dispersion and premature failure of the rubber specimen has been studied by SEM-EDS. The degradation of insoluble sulfur to soluble sulfur can be negligible during the melt mixing if the mixing is done in a controlled way. The final mixing temperature shall be maintained at 90 °C to 95 °C to restrict the insoluble to soluble sulfur conversion. This paper highlights the methodology of the development of oil-coated sulfur in rubber composites and provides insight into the dispersion of polymeric sulfur in natural rubber-based tyre carcass compounds.

Keywords: Insoluble and soluble sulfur; Rubber compound; Dispersion

1. Introduction

Dispersion of ingredients during rubber compounding is important for ideal mechanical properties, because polymers, fillers, and various rubber additives require a good extent of dispersion to ensure high performance. Poor dispersion, resulting from inadequate mixing or inherently large particle-sized

materials, can lead to a reduction of various mechanical properties such as tensile and tear strength [1-7]. Fine powdery materials such as accelerators, zinc oxide, insoluble sulfur (IS) and fillers like carbon black and precipitated silica are characteristically difficult to disperse in rubber matrix [8-16]. These kinds of ineffectively dispersed filler in rubber matrix can lead to poor mechanical properties. Whereas ineffective curative dispersion can generate non homogenous network and poor cross link density, which exist like critical flaws in the compound that can eventually lead to premature failure [17].

A large quantity of polymeric sulfur is used in the rubber industry. The main difference between soluble sulfur and polymeric sulfur is the nature of the sulfur chains. By nature, rhombic or soluble sulfur dissolves in CS_2 (Carbon di sulfide) and rubber hydrocarbons like cis poly isoprene, EPDM styrene butadiene rubber etc. [18].

Our research investigates the curing properties of the sulfur mixed composites. Mechanical property evaluations are also linked with the dispersion phenomenon. This study is carried out with standard insoluble sulfur (OT 20) with different experimental grades of OT 20. High dosages of insoluble sulfur mixed composites can make small agglomerates in the rubber matrix and create premature failure. The dispersion studies of the Banbury mixed compound and cured pad are carried out with SEM-EDS. Further investigation with an extrudate profile is performed to see the sulfur agglomerates in the rubber composites. In this research, it has been shown that the SEM technique can reveal the presence of small crystals of insoluble sulfur and Hexa (methoxymethyl) melamine (HMMM-65) inside the unvulcanised compound, extrudate profile and cure pad [19]. These crystals are helpful in predicting the early belt separation from steel cords during the service life of tyres.

2. Experimental

2.1 Materials

The Natural rubber (RMA IV) having Mooney Viscosity [ML(1+4)@100°C] 68.0 MU, is obtained from Royale rubbers, Guwahati, India, The tested values of Nitrogen surface area (NSA) and Oil absorption number (OAN) of Carbon Black (N326) are respectively 75.0 m^2/g and 72.0 cc/100 g. Low PCA oil is purchased from Raj Petro Chemicals, Chennai. Experimental grades of insoluble sulfur (80% active content and 20% naphthenic oil binder), are procured from OCCL (**Table 1**).

Table 1. Details of the ingredients with source.

Sl no	Material	Supplier
1	Carbon Black (N326)	Birla Carbon, Renukoot, Uttar Pradesh
2	Zinc Oxide (White seal)	Pondy oxide, Puducherry
3	Peptizer	Acmechem, Bharuch, Gujrat
4	N,N'-ditolylparaphynylene diamine (DTPD)	Acmechem, Bharuch, Gujrat
5	Hexa (methoxymethyl) melamine (HMMM-65) 65% active	Techno Wax Chem, Kolkata
6	Cobalt Stearate	Brochers limited, Franklin, USA
7	Resorcinol	Atul limited, Valsad
8	N,N'-dicyclohexyl-2-benzothiazole Sulfenamide (DCBS)	Acmechem, Panoli, Gujarat
9	Prevulcanised Inhibitor (PVI)	NOCIL, Thane, Maharashtra
10	Insoluble Sulfur (OT20), Reference Insoluble Sulfur (OT20), Exp. 1, Exp. 2 and Exp. 3	Eastman, Malaysia OCCL, Mundra

2.2 Chemical characterization

Ash content

To determine the ash content (ASTM D 4574), about 2 g of preheated sample (125 °C/1 hour) is exposed to 550 °C for 16 hours in a crucible. It is then taken out, covered and allowed to be cooled at room temperature. The covered crucible is again heated for 0.5 hours. The above process is repeated till constant weight. The constant weight of the crucible is taken which leads to the determination of the ash content.

Heat loss

Heat loss of Sulfur (ASTM D 4571) is determined by heating a sample of 2 g in the oven at 125 °C for 1 hour. The loss in weight is noted as heat loss (%).

Oil content

To determine the oil content (ASTM D4573), about 5 g of the sample is heated with saturated n hexane. Then the sample is washed and dried at 70 °C for 1-2 hours. The weight of the sample and wash-out portion is taken which helps to determine the oil content.

Total sulfur

To determine the total sulfur (ASTM D 4573) mathematical calculation is as follows:

Total Sulfur (%) = 100 – Oil content – Ash content

Insoluble sulfur

To determine the oil content (ASTM D4578-06), about 5 g of sample is heated with CS_2 (carbon di sulfide). Then the sample is washed and dried at 70 °C for 1-2 hours. The remaining weight of the sample determines the insoluble sulfur content.

Heat stability

To determine the heat stability (IS 14127), about 1 g of sample is kept in a test tube. In another test tube, 30 mL of paraffinic oil is heated at 105 °C. Then both the samples are mixed and heated for 15 min at 105 °C. After that, the sample is cooled fast to room temperature (RT) and passed through G4 crucible. The sample is washed and dried at 70 °C for 1-2 hours. This test converts insoluble sulfur to soluble sulfur.

Acidity

To determine the acidity (ASTM D 4569) of sulfur, 20 g of sample is mixed with 50 mL of Ethanol solution and titrated with NaOH solution. The titre value indicates the acidity of the sample.

Wet sieve residue

To determine the wet sieve residue (ASTM D 4572), 100 g of sample was passed through a 100 mesh sieve in wet condition. The retained sample in the sieve is dried at 70 °C and the weight of the sam-

ples is taken. The obtained value indicates the wet sieve residue.

2.3 Preparation of rubber compounds

The regular compound is mixed using insoluble sulfur (Source: Eastman) where Experiments 1, 2 and 3 are prepared using three different experimental insoluble sulfur grades from OCCL. The initial mixer temperature is 65 °C and the rotor speed is 60 rpm. The mixing of the polymer is divided into three stages. In the master stage, polymer, oil, carbon black and master chemicals are used. In the repass stage, compounds are poured into the Banbury at a temperature of 65 °C with a rotor speed of 45 rpm. Dump temperature is maintained at 115 °C. In the final stage of mixing, curatives are added into the Banbury at the same temperature of 65°C with a rotor speed of 30 rpm (**Table 2**). In the case of the master, dump temperature is maintained at 125 °C and for the final stage of mixing, the temperature shall be maintained at 90 °C to 95 °C.

Table 2. Formulation of skim compound.

Ingredients	Phr
RMA-IV	100.00
N326	62.00
DBD	0.20
ZnO (Rubber Grade)	7.00
Low PCA Oil	6.00
Co-Stearate	1.30
Resorcinol	1.85
TMQ	1.00
Insoluble Sulphur (OT-20)	5.65
DPPD	2.00
HMMM (65%)	6.65
DCBS	0.75
PVI	0.15
Total	**194.55**

*Phr: Parts per hundred gm of rubber.

In the case (**Figure 1**), we have incorporated one type of polymer at the early stage (0 Sec) of mixing. The rest of the ingredients are unaltered.
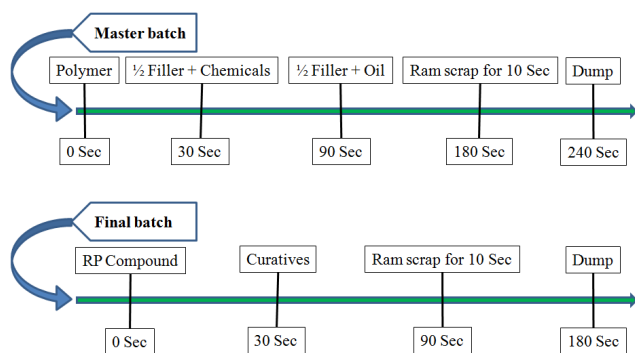
Figure 1. Mixing sequence of the skim compound.

The curing study is performed in Premier MDR2000 (Moving Die Rheometer), Alpha Technologies, Akron, USA under the isothermal condition of 160 °C for 30 min. The curing time has been set with their optimum cure time (tc90) and the tc90 is calculated from the torque time curve. To make the vulcanizate, 60 ± 2 g of compound was taken, and the thickness of the cured pad was made with 2.0 ± 0.2 mm thickness. The sheet has been stored for 24 hours at room temperature for further study.

2.4 Rheological properties

Viscosity: The Mooney viscosity of the rubber compounds is tested by using Mooney viscometer (MV2000, Alpha technologies, Akron, USA, ASTM D1649) and the complex viscosity of tyre tread compound is tested by rubber process analyser (RPA2000, Alpha technologies, Akron, USA) at 100 °C and 2.79% strain with varying frequency sweeps (2 Hz to 32 Hz).

Process safety: Mooney scorch of the rubber compound is well known as process safety, characterized by Mooney viscometer (MV2000, Alpha technologies, Akron, USA, ASTM D1649).

2.5 Physical properties

Cure behaviour: Cure time and cure torques are tested in Premier MDR2000, Alpha technologies, Akron, USA at 160 °C for all compounds.

Tensile tests: The compounds are vulcanised to their optimum cure time (tc90) 1.5 times by using a Hind hydraulic laboratory curing press at 160 °C and 150 kg/cm². Die C dumbbell test specimens are prepared and then tensile properties (i.e., modulus, tensile strength, elongation at break) are tested at Zwick tensile tester model Z010 (Zwick Roell group, Ulm, Germany) at a cross head speed of 500 mm/min according to ASTM D412. The dumbbell hardness test is carried out in Durometer hardness tester according to ASTM D2240.

Material mapping by SEM-EDS: Material mapping is done at RT for test specimens. The equipment used for this study is from Thermofisher Scientific, Dreieich, Germany.

2.6 Processing behaviour

Garvey Die Extrusion test: The compounds are extruded through HAAKE rheomix, Thermofisher, Dreieich Germany. The temperature of extrusion is maintained at 80 ± 2 °C, screw speed at 40 ± 3 rpm and Garvey die orifice at 10 mm. In that way, we can measure the shrinkage of the compound in percentage.

3. Results and discussion

3.1 Chemical characterization

In the case of chemical properties, the oil content of the Exp. samples is higher than the reference sample (**Table 3**). The presence of oil can result in better dispersion of sulfur in the rubber matrix for Exp. compounds. Heat stability is also higher for Exp. samples as compared to references.

3.2 Rheological properties

The cure properties of the compound have shown identical behaviour (**Table 4**). That means the ultimate curing is comparable for all the compounds. Process safety or scorch is similar for all Exp. compounds. Maximum torque indicates the amount of cross-linking which helps to achieve the same extent of reinforcement in the polymer composites.

3.3 Physical properties

The mechanical properties of the rubber composites are depicted below (**Table 5**).

Tensile strength (TS) and elongation at break of

Table 3. Chemical characteristic properties.

Properties	Unit	Ref method No.	Reference	Exp-1	Exp-2	Exp-3
Heat loss	%	ASTM D4571	0.16	0.17	0.05	0.11
Ash	%	ASTM D4574	0.019	0.021	0.018	0.018
Oil content	%	ASTM D4573	18.70	19.72	19.78	19.36
Total sulfur	%	ASTM D4573	81.30	80.28	80.22	80.64
Insoluble sulfur	%	ASTM D4578	95.99	97.16	95.87	97.01
Heat stability	%	IS 14127	89.29	92.57	89.67	92.41
Acidity (as H_2SO_4)	%	ASTM D4569	0.005	0.005	0.004	0.004
Wet sieve residue on 100 mesh	%	ASTM D4572	0.022	0.027	0.018	0.015

Table 4. Rheological data of belt skim compound.

Test Parameter	Unit	Reference	Exp.1	Exp.2	Exp.3
Mooney Viscosity:ML(1+4)@100°C__MU	MU	62	62	60	60
Mooney Scorch test -ML@135°C_Large Rotor_t5	Minutes	7.54	6.96	6.90	6.81
Minimum Torque	lb-in	2.41	2.38	2.26	2.31
Maximum Torque	lb-in	33.42	33.38	33.39	32.66
ts2 (min)	minutes	1.43	1.48	1.39	1.45
t10 (min)	minutes	1.89	1.93	1.88	1.89
t25 (min)	minutes	3.09	3.13	3.15	3.11
t50 (min)	minutes	4.76	4.81	4.89	4.79
t90 (min)	minutes	11.40	11.36	11.52	11.17

Table 5. Physical properties of skim compound.

Test parameter	Standard	Unit	Reference	Exp.1	Exp.2	Exp.3
Modulus at 100%	ASTM D412	MPa	4.9	5.1	4.9	5.1
Modulus at 300%	ASTM D412	MPa	17.7	18.1	17.9	18.0
Tensile strength	ASTM D412	MPa	21.5	21.1	21.1	22.5
Elongation at break	ASTM D412	%	360	352	356	379
Hardness	ASTM D2240	Sh. A	82	79	82	82
Density	ASTM D792	gm/cc	1.181	1.178	1.176	1.176

the Exp. 3 compound shows optimum value compared to the other three compounds. The tensile test is generally conducted to identify the failure population [20]. Tensile strength depends on filler-rubber interaction, filler-filler interaction and sulfur-accelerator ratio in the rubber matrix. An increase in filler-filler interaction reduces the amount of filler-rubber interaction which leads to a lower tensile strength of the rubber composite. Similarly higher sulfur accelerator ratio corresponds to a higher amount of crosslinking that reduces the tensile strength with an increase in stiffness [21]. The dispersion of sulfur in the rubber matrix plays a crucial role in TS. From the above data (**Table 5**) it is observed that all the compounds have good static stiffness up to 300% elongation. However, TS has slightly dropped for Exp. 1 and Exp. 2 compounds may be due to the marginal difference in the dispersion of sulfur in the green compound from Banbury (**Figure 3**). That much of a difference in dispersion does not create any drastic drop in TS. No significant difference was noticed in the case of the density of the green compound. The comparable hardness is evidence of no localised deformation happened in the rubber matrix [22-24]. The SEM-EDS image from the cured pad (**Figure 8**) displays good dispersion and no sulfur agglomeration inside the fractured tested specimen.

3.4 Processability by garvey die extrusion

The dispersion and appearance of the extrudate profiles are depicted below (**Table 6**).

Table 6. Appearance rating of surface smoothness and edge sharpness.

	Surface appearance	Sulfur dispersion	Edge tearing
Reference	A10	A10	A10
Exp. 1	B8	B8	B8
Exp. 2	A9	A9	A9
Exp. 3	A10	A10	A10

A = Excellent to E = Poor (Rate of smooth surface) 10 = Excellent to 1 = Poor (Rate of sharpness and continuity of edge).

The garvey die extrusion image is shown in **Figure 2** in which the role of oil is to flow the compounds in the extruder. And the dispersion is affected by the sulfur agglomeration. That signifies that the less the viscous component more the flow ability, and better processing under stress conditions. So from the above **Table 6**, it has been observed that Exp. 3 and reference compound has shown better surface appearance, sulfur dispersion and edge tearing among all the compounds.

Figure 2. Photographs of garvey die extruded profile (a) Exp. 3, (b) Exp. 2, (c) Exp. 1 and (d) Reference.

3.5 Dispersion study through SEM-EDS

The dispersion of filler in the rubber matrix has been carried out by SEM, which indicates that filler particles are uniformly distributed throughout the matrix. Magnifications of images are fixed at 5000× for all the compounds. Exp. 3 compound has shown

better dispersion among all the compounds. Regular compound along with Exp. 1 and Exp. 2 has shown marginally higher agglomeration whereas Exp. 3 has shown less agglomeration which may give less premature failure in physical properties for Exp. 3 compared with others (**Figure 3**).

Sequence of dispersion Experiment 3 > Reference compound > Experiment 2 ≥ Experiment 1.
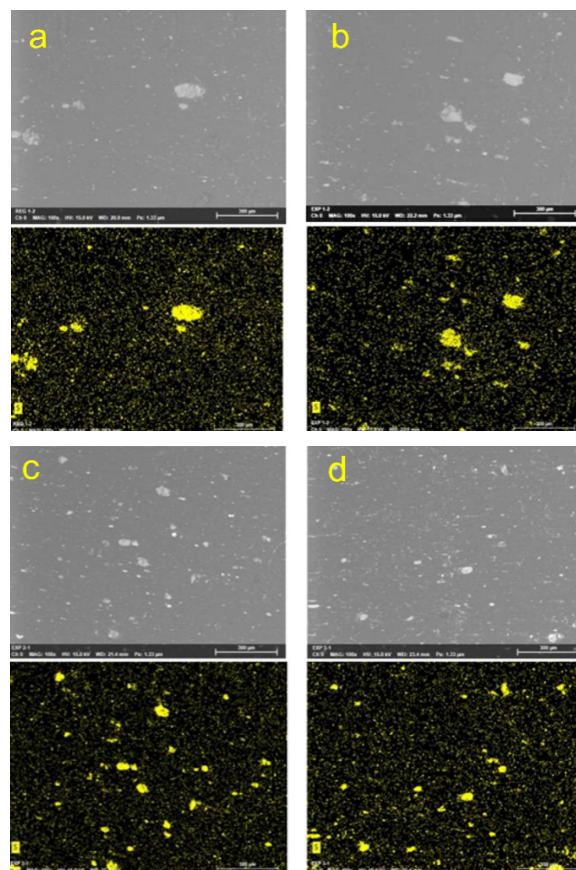

Figure 3. Representative images of dispersion study through SEM at 5000× of the green compound from Banbury (a) Reference, (b) Exp. 1, (c) Exp. 2 and (d) Exp. 3.

It is also observed that the surface roughness is increasing with time (**Figures 4-6**), and this is because of the compound shrinkage. Shrinkage is more for the Exp. 1 and 2 compounds.

From **Figure 7**, it has been observed that no agglomerates of sulfur are in the sections of the extrudate green compound. The same phenomenon is visible for cured slabs also (**Figure 8**). All compounds seem nicely dispersed with minor differences and Exp. 2 compound has shown better dispersion than others.
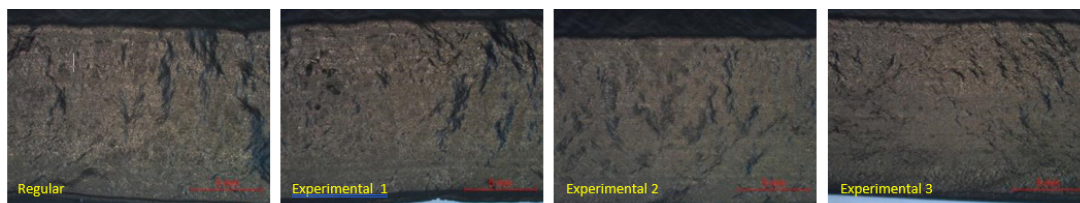
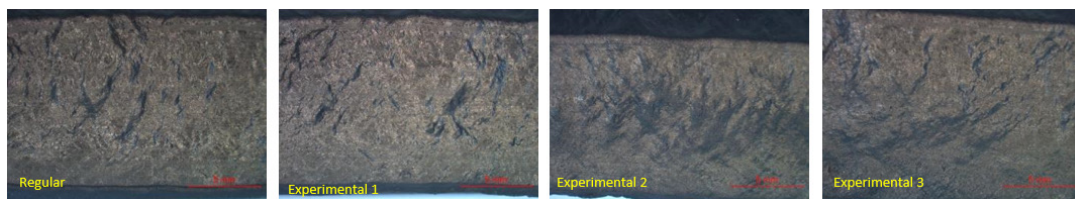**Figure 4.** Representative images of surface appearance immediately after extrusion (green compound) SEM at 5000×.

Figure 5. Representative images of surface appearance after 24 hours of extrusion (green compound) SEM at 5000×.
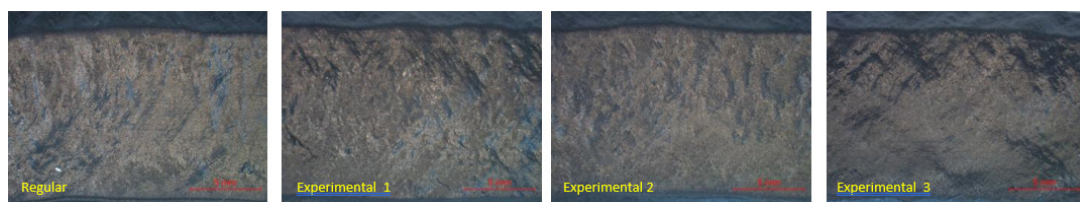

Figure 6. Representative images of surface appearance after 72 hours of extrusion (green compound) SEM at 5000×.
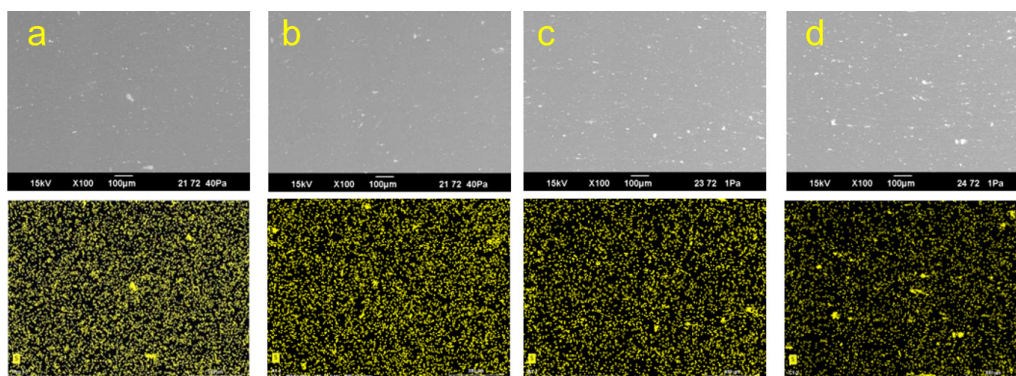

Figure 7. Representative images of dispersion study through SEM at 5000× of the green compound from Extrudate (a) Reference, (b) Exp. 1, (c) Exp. 2 and (d) Exp. 3.
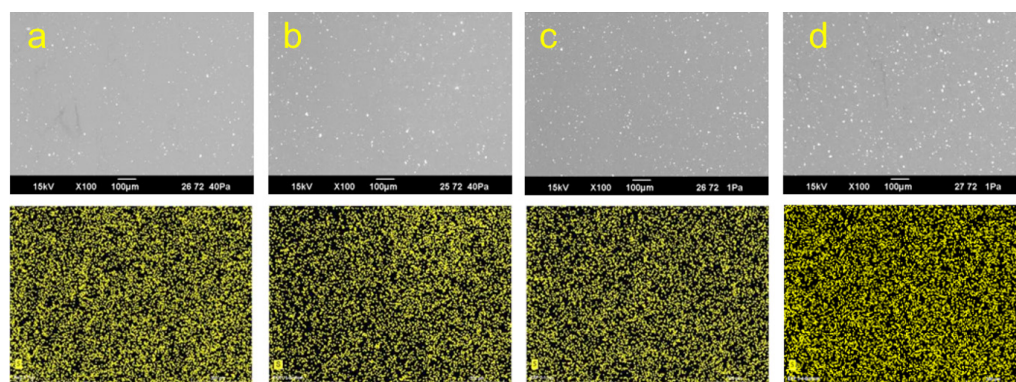

Figure 8. Representative images of dispersion study through SEM at 5000× of cured pad (a) Reference, (b) Exp. 1, (c) Exp. 2 and (d) Exp. 3.

4. Conclusions

The dispersion of filler in the rubber matrix has been carried out by SEM, which indicates that filler particles are uniformly distributed throughout the matrix. From the above study, it has been noticed that the dispersion of the sulfur in the rubber matrix is the crucial factor in getting better physico mechanical properties. The rate of cure is also depending on the sulfur dispersion and homogeneous mixing. Experimental samples have shown better dispersion as compared to the regular sample, which results in less premature failure in physical properties compared with regular. Overall, this study has demonstrated that with proper care with respect to temperature, a natural rubber-based compound containing a high dosage of insoluble sulfur cannot harm the extrudability of the compound at the time of processing.

Author Contributions

Arnab Dutta, B.Tech in Polymer Science and Technology in 2012 from Calcutta University. He has 11 years of experience in the tyre Industry (Birla tyre). Presently working at Hari Shankar Singhania Elastomer & Tyre Research Institute, India. He is looking after raw material development including sustainable materials for tyre application. He is basically the primary responsible person for this entire work.

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Kanhaiya Lal Anjana, MSc in Polymer Science and Rubber Technology from Mohanlal Sukhadiya University, Udaipur. He has been working at Hari Shankar Singhania Elastomer & Tyre Research Institute, India for the last 12 years. He is responsible for analytical characterization.

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Dr. Saikat Das Gupta, Ph.D. in Rubber Technology, working in Research & Development of Tyre & Elastomers for the last 29 years in various positions. He had ~ 50 National and International Papers, 4 patents, 1 book and more than 4 book chapters in his credit. As a part of the management, Dr. Saikat is responsible for financial and moral support.

Dr. Rabindra Mukhopadhyay did his B.Sc. from the University of Calcutta and M.Sc & Ph.D. (Applied Chemistry) Indian Institute of Technology (IIT), Kharagpur, India. Since 1987, he has been heading the R&D centre of JK Tyre and Industries Ltd. He is also the Director and chief Executive of Hari Shankar Singhania Elastomer & Tyre Research Institute (HASETRI), an independent Scientific and Industrial Research Organization (SIRO), promoted by JK Tyre for doing basic and applied research. He has to his credit more than 175 research and technical papers in national and international journals and six patents from his research work. He has more than 40 years of experience in Education, Training and Research in Rubber Science and Tyre Technology. He is a Visiting Faculty at different IITs and national universities in India. He is a Fellow of the Indian National Academy of Engineers, The Institution of Engineers (I), the Indian Rubber Institute, the American Chemical Society, the Indian Society of Analytical Scientists, the Indian Institute of Quality etc. As a chief executive of the organization Dr. Rabindra Mukhopadhyay is responsible for the financial and moral support.

Conflict of Interest

We declare that this manuscript or its content in some other form has not been published elsewhere

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