



Energy Efficient Functionalization of Low Tg Polymers and their Properties

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ABSTRACT

Rubbers as low Tg polymers are industrially relevant due to their unique chemical and physical structures enabling modification including network formation for end use. The ability to form cross-links is achieved through the addition of appropriate chemical additives. In situ functionalization is a convenient route. Natural rubber (NR) with its isoprene as the repeating unit and enormous physical entanglement is considered a right template in understanding the functionalization. As most of these reactions are thermal energy induced, a simple laboratory technique of generating molecular friction through dielectric collision was attempted. Microwave energy generator like domestic microwave oven fulfills the requirement. NR suffers from poor solvent, weather, and thermal resistance. Synthetic rubbers that address these requirements were also investigated for functionalization. NR as the template was used for functionalizing in its latex stage. Chlorination and generation of in situ alumina were experimented. In addition to the chemical modification, thermal-induced physical changes were also observed. Modified NR as base polymer was studied for adhesive film formation in respect of loss of tackiness and generation of adhesive interface with the substrates. Finely divided alumina so formed in the latex stage is expected to offer interesting set of properties of NR including tire components.

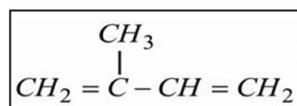
Key words: Rubber, Functionalization, Microwave energy assisted, Natural rubber.

1. INTRODUCTION

1.1. Natural Rubber (NR) Latex

It is obtained from the plantation and the field latex is a weakly stable aqueous suspension of dry rubber (solid content) ranging between 35% and 40%. The biological dispersing agents maintain a low viscosity even at a high solid content. However, the suspension is biologically weak and it requires preservation. It is achieved with the addition of ammonia or formaldehyde. The field latex in the given form is commercially uneconomic as it contains more water. Concentration process through high speed centrifuging is an industrial operation. Table 1 describes the composition of field latex and the concentrated latex. The dry rubber content is enhanced to 60% and it is stabilized. This latex of 60% concentration is known as cenex.

With the addition of ammonia and lauric acid, it is preserved and can be stored for future use. NR is a polymer of isoprene. To understand the structure of rubber, we shall concentrate on the structure of Isoprene. Isoprene is a conjugated diene containing double bonds at alternate position.



The structure of isoprene: Monomer of NR.

By observing the structure of NR, we can infer that there is no polar group in this structure. As a result of this, the intermolecular forces of attraction are weak Van der Waal forces of attraction. These forces of attraction are further weakened because of the cis-configuration of all the double bonds that do not permit the close interaction of polymer chains. Thus, NR (Cis-polyisoprene) does not have a straight chain but has a coiled structure. As a result of this, it gets the elastic property. The rubber hydrocarbon with allylic hydrogen atoms in every repeating unit is chemically and can be effectively used for chemical modification. There are a number of such modified NR forms and epoxidized NR and pre-vulcanized latex are technologically important. Facile functionalization is theoretically possible with the right reagents [1-3]. However, the challenge is maintaining the colloidal stability of the latex. The isoprene unit in the rubber

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Table 1: NR latex.

Field latex	Percentage	Concentrated latex (centrifuged latex)	Percentage
Rubber hydrocarbon (RHC)	36.0	RHC	60.0
Protein carbohydrates	1.4	Total solid	61.5
	1.6	Nonrubber solid	1.5
Lipids	1.0	Mechanical stability, sec	475
Inorganic solids	0.5	Alkalinity, %	1.6
Water	58.5	VFA No.	<0.15

VFA: Volatile fatty acid, NR: Natural rubber

hydrocarbon is chemically more active as it is on the constant random motion. The reagent used for functionalization has to target the active site of the rubber hydrocarbon. The interaction between the reagent and the rubber hydrocarbon can be accelerated in many ways [4,5]. The dipole and induced dipole interaction enabled in a dielectric heating in a microwave chamber was considered as an effective technique. A voltage of several kV was impressed between the electrodes, and a magnetic field is applied parallel to the axis such that electric and magnetic fields are perpendicular to each other [6]. Electrons ejected by the cathode accelerate in the radial direction at first, but because of the magnetic field, they start to follow cycloid paths. If the magnetic field is strong enough, the electrons cannot reach the anode but form a rotating space charge. The resonant cavities of the anode interact with the electrons by either accelerating or decelerating them. The reaction can occur rapidly, less energy consuming, and above all, the activation through heating occurs internally at the molecular/rubber segment level within the reaction system [7]. As a dispersion in water, the presence of water in latex can handle any excess heat dissipation.

The salient features of this initiative are:

1. The reaction medium (NR latex) sourced from biological substance and environmentally sustainable sources.
2. With the right choice of stabilizing/preserving techniques the reaction/functionalization occurs in liquid state and as a result with better temperature control.
3. Necessary reaction activity through internal heating as an inherent mechanism (molecular friction enabled through dipole-dipole interaction).
4. As the reaction occurs in liquid state and possibly activating every chemically active site in the rubber hydrocarbon, modification such as *in situ* reinforcer can be generated. This possibility is considered a breakthrough for products that require particulate filler reinforcement.

The carbon black of furnace grade is predominantly used for reinforcement. Particulate filler reinforcement

enhances abrasion resistance and tear strength. The furnace process of carbon black presents strong aggregation. The aggregates are the result of partial combustion or dehydrogenation of syrupy carbochemicals which are called as carbon black feedstock (CBFS). The mode of fusion of these droplets (structure) and the surface area are considered primary variables. Nonblack fillers obtained through precipitation process may result in finely dispersed fillers with little or no energy being expended. Particle size relates to hysteresis and failure properties. Aggregate shape (structure) affects rheology (flow characteristics, thixotropy, shear-dependent behavior, etc.) and rubber modulus at low strains.

Considering the potential advantages of liquid state functionalization, NR latex as reaction template is attempted and the findings are discussed in this paper.

2. EXPERIMENTAL

2.1. Material Used

Concentrated latex from ARASU RUBBER Corporation, Nagercoil, Sodium hypochlorite, coconut oil, palm oil, common salt (NaCl), sodium hydroxide (NaOH), glacial acetic acid, ammonia, aluminum chloride, zinc oxide, CI resin (coumarone indene resin), rubber seed oil, triallyl isocyanurate, carbon black, general purpose furnace grade, zinc diethyldithiocarbamate, tetramethylthiuram disulfide, and n-cyclohexyl-2-benzothiazole sulfenamide were used.

2.2. Preparation of Chlorinated Latex

In a beaker containing 50 ml coconut oil + 50 ml palm olein oil, 4 g of NaOH was added and it is identified as lauryl acid soap solution. This solution was then kept in the microwave reactor chamber for 2-3 min. After the reaction, 5 ml of sodium chloride (electrolyte to maintain the latex stability) + 350 ml distilled water + 250 ml of NR latex were added. This mixture is identified as mother stock solution. The mother stock solution and the chlorinating agent (NaOCl) are described in Table 2.

After the reaction time was over, it was coagulated with glacial acetic acid and made as a sheet. This coagulated sheet was then dried for 24 h at 70°C

in hot air oven. This sheet was then examined in Fourier transform infrared (FTIR) for the presence of chlorinated group. The modified NR was then compounded with accelerators, activators, processing aids, and cross-linking agent according to the compounding recipe described in Table 3.

2.3. Preparation of Samples

1. Dumbbell specimen (tensile specimen), tear specimen were prepared from compression molded test sheets and were tested as per ASTM D 412 and ASTM D 624.
2. The modified NR ("chlorinated") was studied for its adhesion in toluene as the solvent. Here, the substrates used were pre-cross-linked strips. The adhered portion in the lap jointed specimens was cured and consolidated in hot air oven for 4 h at 70°C. Similar specimens were prepared using poly chloroprene rubber (CR)-based adhesive for comparison. The samples including peel adhesion were tested on UTM.

2.4. In Situ Alumina Preparation

50 ml of liquor ammonia containing 600 ml of NR latex was taken in a beaker and 5 ml, 10 ml, and 15 ml of aluminum chloride was added. After thoroughly mixing the content of compositions given in Table 4, the container was exposed to microwave radiation for

Table 2: NR latex system for microwave energy assisted chlorination.

Mother stock solution (ml)	NaOCl (ml)	Reaction time (min)
160	10	1
160	20	2

NR: Natural rubber

Table 3: Rubber formulation for evaluation of "chlorinated" NR.

Ingredients	Phr
Modified NR	100
ZnO (activator)	3.0
Stearic acid (activator)	1.0
Carbon black (GPF)	50
Tackifier (C. I. resin)	2.0
RSO	20.0
ZDC	2.0
TMTD (tetramethylthiuram disulfide, accelerator)	2.0
CBS (sulfenamide, accelerator)	2.0
Sulfur (cross linking agent)	0.5
TAIC (cross-linking promoter)	1.0

CBS: N-cyclohexyl-2-benzothiazole sulfenamide, RSO: Rubber seed oil, ZDC: Zinc diethyldithiocarbamate, accelerator, NR: Natural rubber

1, 2, and 3 min. On the expiry of reaction time, the contents were further stirred and kept for maturation. The latex was coagulated with glacial acetic acid (~1% concentration), and the coagulum was made into a thin sheet and dried in hot air oven for 24 h at 70°C.

The *in situ* alumina containing NR was characterized in scanning electron microscopy (SEM) for the presence of particulate fillers both in terms of size and dispersion. The modified NR was compounded with accelerator, activators, processing aid, curing agent to characterize the mechanical properties (Table 5).

The test slabs were compression molded at 160°C for 20 min and the test specimens were prepared from the cured slabs.

3. RESULTS AND DISCUSSION

3.1. Microwave-assisted Latex Stage Functionalization of NR

The mechanical properties of chlorinated NR are given in Tables 6 and 7.

Tensile strength is a measure of load-bearing ability of a cross-linked soft vulcanizate. This ability is affected by the structural uniformity of the network, the presence of particulate (reinforcing or diluents) fillers, chain segment softeners. Further, within the cross-linked network, the quality (covalent, ionic, segmental knots, etc.) and the density of the cross-

Table 4: Preparation of reaction system of *in situ* alumina in NR latex.

Latex NR (ml)	Liquor ammonia (ml)	Aluminum chloride (g)
600	50	18
600	50	36
600	50	54

NR: Natural rubber

Table 5: Formulation for evaluation *in situ* alumina in NR matrix.

Ingredients	Phr
Modified NR	100
ZnO	3.0
Stearic acid	1.5
TMQ (quinoline based antioxidant)	1.0
6 PPD (p-phenylenediamine, antiozonant)	1.0
Carbon black (HAF)	45
Aromatic rubber process oil	5.0
CBS	1.5
Sulfur	1.5

NR: Natural rubber, CBS: N-cyclohexyl-2-benzothiazole sulfenamide

Table 6: Tensile strength of “chlorinated” NR.

Specimen no.	Max. load (kgf)	Max. displacement (mm)	Tensile strength (MPa)
1	13.43	61.38	11.67
2	14.0	60.38	11.8
3	12.7	50.38	11.22
4	13.26	60.87	11.02
5	14.25	61.28	11.91
6	12.96	51.28	11.30
7	14.56	62.48	12.4
8	15.01	63.14	12.50
9	14.94	62.60	12.6

links affect the tensile properties (load at break and strain/elongation at break). That way, the consistency in the tensile strength can capture the presence of possible contamination including the occurrence of incomplete cross-linking.

The failure properties in tensile and tear mode in Tables 6 and 7 imply that the test specimens have not been much affected by the process adopted for chlorination.

3.2. Peel Strength

The peel strength was tested as per ASTM D903. The comparison was made between chlorinated NR and CR. The values are given in Table 8. Two key observations from these values is: i. The chlorinated NR as adhesive gives the consistent bond strength of 11-12 kgf and the regular CR (polychloroprene W-grade) as adhesive offers similarly consistent bond strength but 4-5 kgf higher than the modified NR. The marginally lesser bond of modified NR implies that not every isoprene unit was modified/chlorinated. Besides, the microwave energy in the presence of chlorinating agent might have caused additional modification including cyclization. IR study may help in structural elucidation and it is discussed in the next section.

Hence, from Table 8, we confirm that the chlorinated NR has improved its peel strength value close to CR.

3.3. Functional Group Characterization of Chlorinated NR

The formation of chlorinated repeating units and their density are depicted in Figures 1-4.

The coagulated sheet of chlorinated NR was studied for vibrational spectra in FTIR. In addition to some new peaks, the C-Cl stretch vibration was observed. The prominent peaks are given in Table 9.

The tensile and tear properties and the peel adhesion of modified NR are in conformity with structural modification. The structural changes are primarily

Table 7: Tear strength of chlorinated NR.

Specimen no.	Load (N)	Thickness (mm)	Tear strength (kN/M)
1	34.79	1.98	17.57
2	35.47	1.94	18.28
3	33.32	1.97	16.91
4	36.84	2.0	18.42
5	33.90	1.96	17.3
6	34.98	1.99	17.54
7	35.18	1.97	17.85
8	35.28	1.95	18.09
9	37.04	1.98	18.70

NR: Natural rubber

Table 8: Lap joint peel strength values.

Chlorinated NR (Kgf)	CR (Kgf)
11	16
11.5	15
11.9	15.5
11.3	15.7
11	16.2
12	15.4
11.8	16

NR: Natural rubber, CR: Chloroprene rubber

the formation of allylic chlorination or replacement of an allylic hydrogen atom by chlorine. The distinct vibrational peaks given in Table 9 concur with the proposed modification.

3.4. In Situ Alumina Generation Phase in NR Matrix

Here, aluminum chloride was incorporated with ammonia and then it was dispersed in latex. The reaction mixture was exposed to microwave radiation. It was coagulated and made into a thin sheet. This modified NR was studied for SEM. The results are given in Figures 5-7.

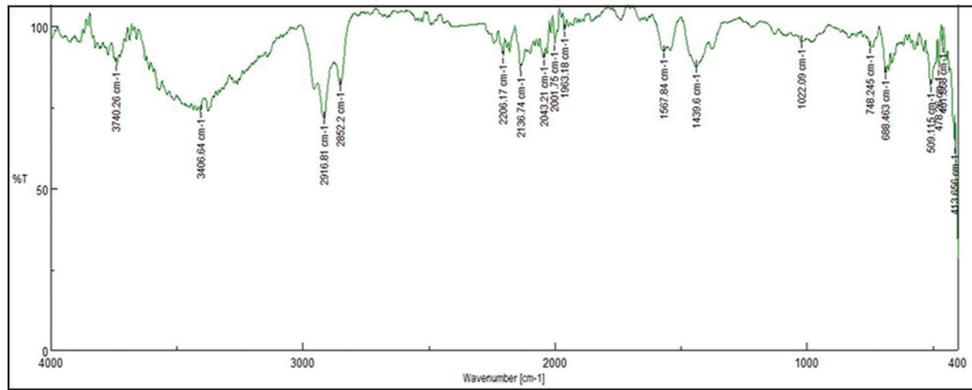


Figure 1: Vibrational spectra of natural rubber latex coagulated sheet (plain, control).

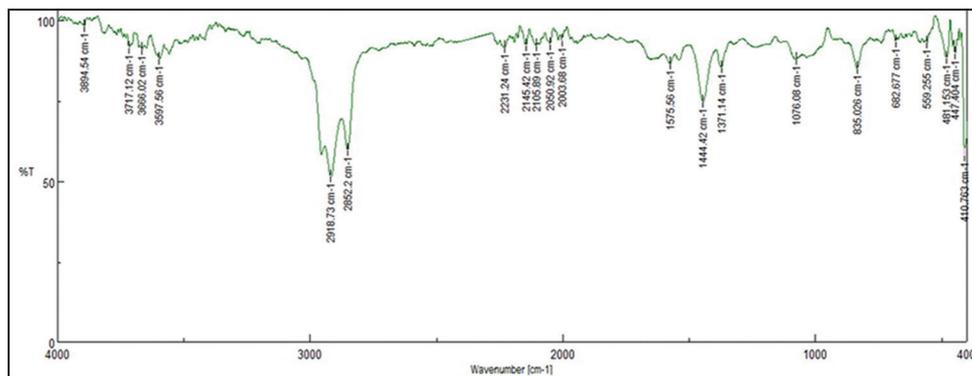


Figure 2: IR spectra of chloroprene rubber (for comparison).

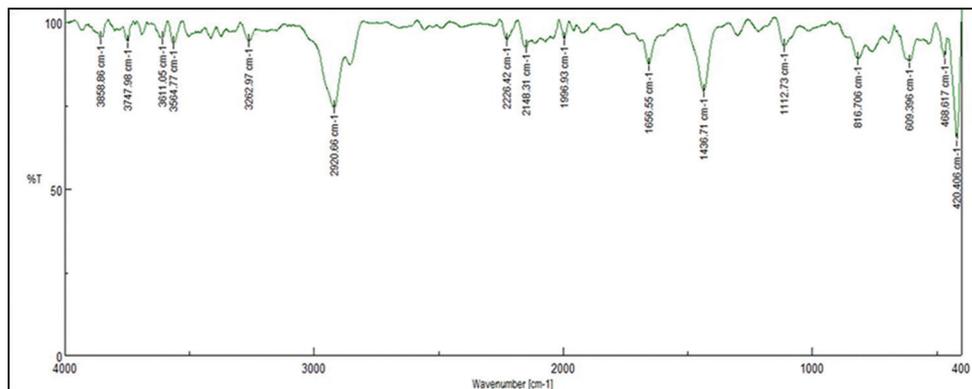


Figure 3: Natural rubber latex treated with chlorinating agent (NaOCl, 10 g).

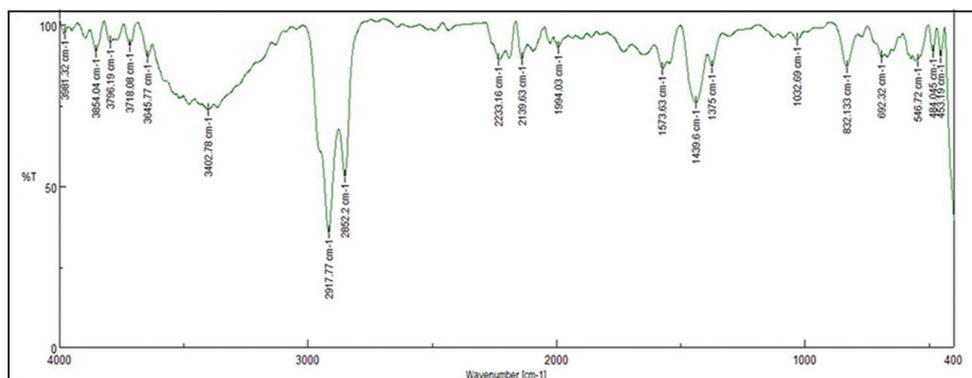


Figure 4: Natural rubber latex treated with chlorinating agent (NaOCl, 20 g).

Table 9: Summary of vibrational spectra studies of chemically modified NR.

Wave no. cm^{-1}	Bond	Functional group	NR	NaOCl 10 (g)	NaOCl 20 (g)	CR
600-500	C-Cl	Halo compound	✗	✓	✓	✓
850-550	C-Cl	Halo compound	✗	✓	✓	✓
2840-3000	C-H	Alkane (stretching)	✓	✓	✓	✓
1375-1450	C-H	Alkane (medium)	✓	✓	✓	✓

NR: Natural rubber, CR: Chloroprene rubber

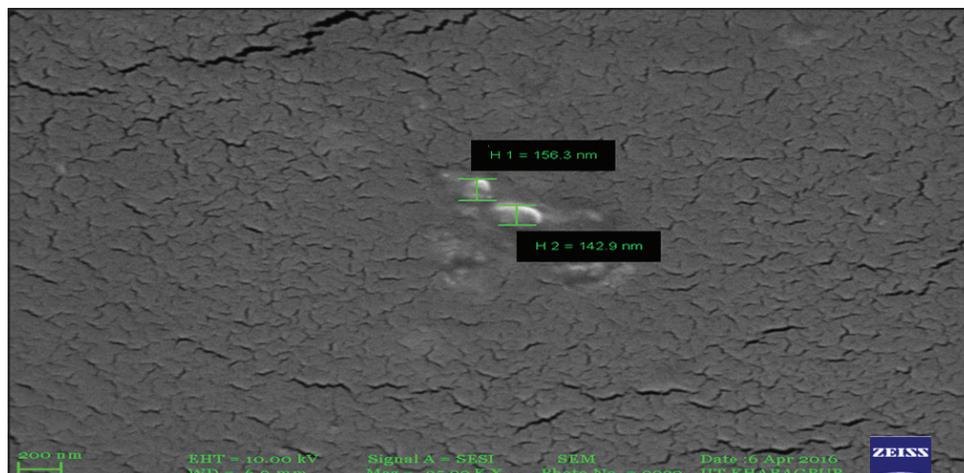


Figure 5: Scanning electron microscopy image for 5 Phr aluminum chloride.

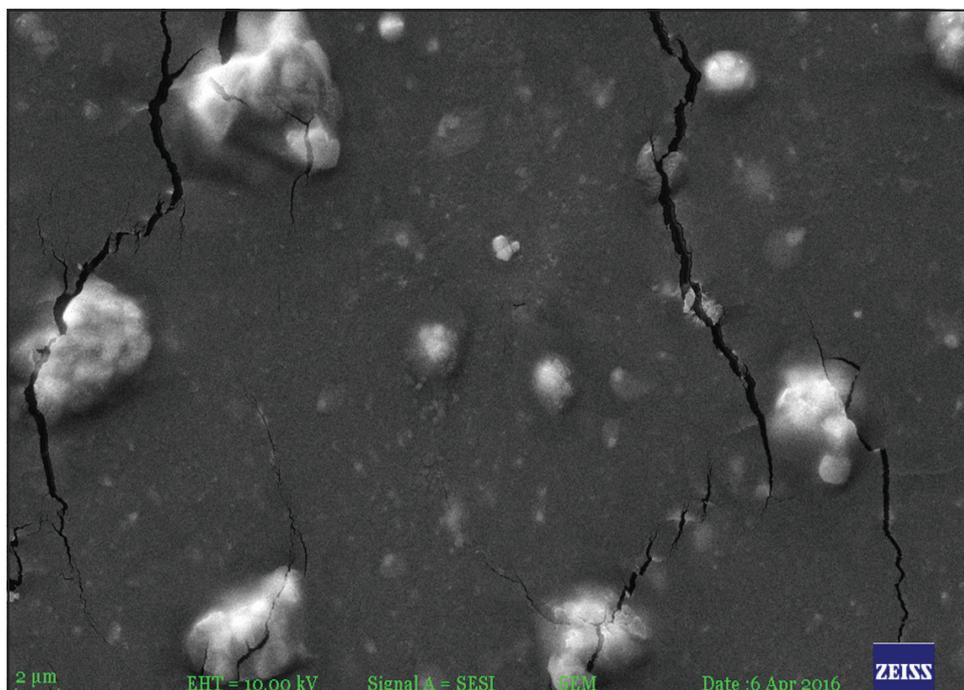


Figure 6: Scanning electron microscopy fractograph of aluminum oxide (*in situ*) in Natural rubber latex (10 g of aluminum chloride).

The fractographs (Figures 5-7) present interesting features. The fractured surfaces show fissures along the line of forces. The fissures in some cases appear as wide cracks. The tip of the cracks that encounter whitish globular particles (alumina formed *in situ*

in the present investigation) gets diverted. This is precisely what is expected of reinforcing particulate fillers, delaying the point of complete rupture. Second, 5 g of AlCl_3 has either released little or no alumina. The fissures are running laterally, across

the width (Figure 5). The 20 phr addition (Figure 7) presents a more uniform distribution of hydrolyzed product (alumina). At the same time, the presence of agglomeration (heavier alumina particles) is conspicuous in 10 and 20 phr addition. However, in 10 g addition (Figure 6), the particle size is closer to $2\ \mu$ as compared to slightly bigger particles in 20 phr addition (Figure 7) where the size is closer to $10\ \mu$. In Figure 5, it is understandable that the resolution of $200\ \mu$ would not have captured particles of finer size (5 g, AlCl_3).

3.5. *In situ* Alumina in NR Latex: Mechanical Properties

The modified NR was compounded according to the formulation given in Table 5 and cured at specific temperature and time. The values of mechanical properties are given in Tables 10 and 11. Several

observations may be drawn from the experimental data. A higher dosage of *in situ* filler has not weakened the matrix through a dilution effect. On the contrary, it has added to load at failure in tension and tear. An increase in tensile strength of 4 MPa is a definite possibility as the dosage was increased. The rubberiness (elongation at break) has not been impaired with the formation of the particulate filler. The elongation values display a greater consistency, and there was no scatter in the strain at the point of break. Tear strength, which measures the strength of the vulcanizate in shear as well, records at least 5 units more with the increase in the formation of alumina. These observations are of technological implications in respect of NR-alumina system. NR is known for its high gum strength, tack and fatigue life. Filler addition is required for enhancing its solid characters such as abrasion resistance and tear strength. The presence of alumina alters the thermal

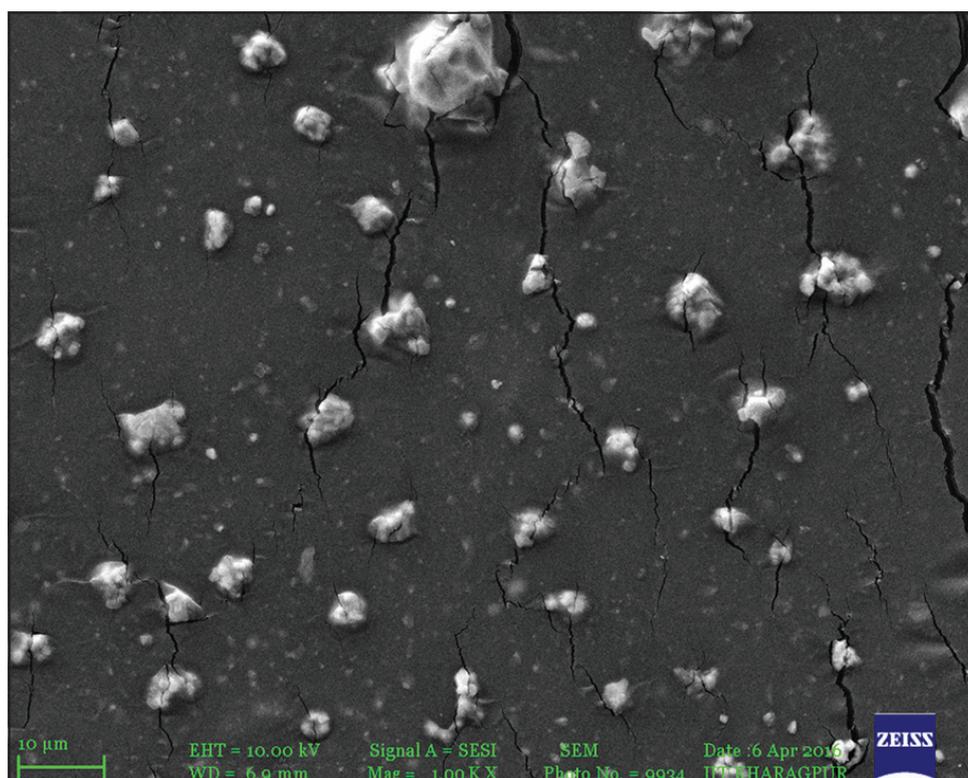


Figure 7: Scanning electron microscopy fractograph of aluminum oxide (20 phr, *in situ*) dispersed in Natural rubber matrix.

Table 10: Tensile strength of *in situ* alumina (10 g).

Specimen	Max-load	Tensile strength (MPa)	Elongation at break	Tear strength (N/mm)
1	15.25	13.62	333	19.92
2	16.85	14.52	325	20.84
3	15.23	14.74	314	20.87
4	16.60	14.88	304	20.05
5	15.80	14.94	300	
Average	15.94	14.54	315	20.42

Table 11: Tensile strength of in situ alumina (20 g).

Specimen	Max-load (kgf)	Tensile strength (MPa)	Elongation at break	Tear strength (N/mm)
1	20.25	17.82	429	28.82
2	19.85	17.92	413	25.54
3	19.23	17.96	405	24.67
4	20.60	17.98	396	24.69
5	20.80	17.64	445	
Average	20.14	17.86	417	25.93

conductivity of rubber system. Rubber hydrocarbon is susceptible to weathering including crack formation and growth. This phenomenon is promoted by heat content which is related to hysteresis. At the same time, rubberiness inferred in terms of strain at break (elongation at break) is largely required for traction or in simple terms friction. Friction is impaired as the cross-linked soft vulcanizate is degrading or aging, which is generally called as weathering. This weathering can be regulated with suitable additives. However, thermal-related degradation is effectively addressed by filler networking. The filler like alumina is one such solution. Dispersion of finely divided alumina is a shear-intensive process, and the rubber would be subjected to considerable loss of chain regularity which is detrimental to failure properties. Filler addition with fine dispersion and at the same time, preserving the complete structural regularity of NR as it is obtained from the field will ideally suit the requirement. The first step in the direction to achieve the desired result has been confirmed with the consistency in the tensile and tear strength data.

4. SUMMARY CONCLUSION

- Centrifuged latex stabilized with electrolytes can be functionalized
- Chlorine liberating reagents releasing nascent chlorine in microwave-assisted reaction and chlorinate NR
- The extent of chlorination is statistically uniform and leaves behind structural modification besides replacing allylic hydrogen
- Chlorinated NR compares with CR in adhesion properties measured in terms of peel strength of vulcanized substrates
- The addition of rubber seed oil promotes fast drying and promotes chemical cross-linking
- Aluminum chloride hydrolyzes into aluminum hydroxide in latex medium

- The *in situ* generation of aluminum hydroxide is confirmed by fractograph
- The *in situ* alumina as a constituent of NR vulcanizates exhibit consistent mechanical properties. Higher dosages promote uniform dispersion, delay the point of rupture in tensile and tear mode.

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***Bibliographical Sketch**



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