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MECHANICAL PROPERTIES OF RUBBER OBTAINED BY SURFACTANT SENSITIZED COAGULATION OF FRESH NATURAL RUBBER LATEX

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Fresh natural rubber (NR) latex coagulates immediately by sensitization with suitable surfactants. When surfactants are added to latex, the surfactant anions displace a part of protein molecules and get adsorbed on the rubber particles. The surfactants retained on rubber during coagulation play a major role on the cure characteristics, mechanical properties and ageing characteristics of the recovered rubber. Better cure characteristics as revealed from a higher level of vulcanization are obtained for gum and carbon black filled compounds for NR prepared by immediate coagulation in comparison with the conventionally coagulated NR. Better mechanical properties and solvent ageing resistance are also observed. Carbon black filled vulcanizates give a higher modulus, tensile strength, hardness and significantly higher abrasion resistance as compared with conventional rubber vulcanizate. The compression set and heat build-up characteristics are comparable. The improvement in mechanical properties and solvent resistance obtained for the NR prepared by the new process is attributed to the surfactants retained in rubber, higher level of vulcanization and better dispersion of filler.

Keywords: Carbon black, Latex, Mechanical properties, Surfactant.

INTRODUCTION

NR latex is a colloidal dispersion of rubber particles in an aqueous medium obtained from latex vessels of *Hevea brasiliensis* tree. The dry rubber content of latex generally varies from about 28 to 42 per cent. In addition to rubber, latex contains non- rubber ingredients like proteins (2-2.5%), sugar (1-1.5%) resin (1-2%) and ash (0.7-0.9%). These non rubber ingredients play a major role in the colloidal stability of latex and in cure and mechanical properties of the recovered rubber. The composition of non-rubber ingredients change after latex leaves the tree and the obvious consequence of this is the coagulation of latex within a few hours of tapping. This is called spontaneous coagulation. Normally rubber is recovered from latex by a slow coagulation process after the addition of coagulants like formic acid, acetic acid, sulphamic acid *etc.* Earlier reports show that the process of spontaneous coagulation, which occurs in the absence of added coagulants, can be accelerated by addition of suitable surfactants (Van Gils, 1947; Blackley, 1997; Cockbain, 1952). The mechanism of this is believed to be due to displacement of the protective layer of proteins by added

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surfactant anions followed by their interaction with divalent metal ions like magnesium present in latex.

Hence sensitization of latex with surfactants could reduce the coagulation time of latex by the conventionally used acid coagulants. By using suitable surfactants the non rubber constituents retained in rubber could also be adjusted so that rubber of improved cure characteristics and mechanical properties could be obtained. This paper presents the work on the raw rubber, cure and mechanical properties of natural rubber obtained by surfactant sensitized coagulation of NR latex.

EXPERIMENTAL

Fresh natural rubber (NR) latex having a DRC of 35-38 per cent was obtained from Rubber Research Institute of India. The surfactants used were of commercial grade fatty acid soaps.

Surfactant sensitized coagulation of NR latex

NR latex was mixed with the quantity of surfactant required for sensitization to quick coagulation was prepared as reported earlier (Alex *et al.*, 2003; 2013). The surfactant used was higher fatty acid soap. The latex was then diluted to a dry rubber content (DRC) of 20 per cent and coagulated by addition of 10 per cent acetic acid. It was noted that a higher amount of acid was required for quick coagulation of surfactant sensitized latex as compared to conventional slow coagulation. The coagulum was washed free of acid and dried at 70 °C in a laboratory oven. NR prepared as per the conventional method was used as control.

Raw rubber properties

Initial plasticity (P_0) and plasticity retention index (PRI) were determined using Wallace Rapid Plastimeter as per the standard procedure. The acid value was expressed as number of milligrams of caustic potash required to neutralize the acids present in extract from 100 g of rubber. For this, acetone extract from about 10 g of rubber was dissolved in 100 mL ethyl alcohol and titrated with 0.1 N KOH using phenophthalin as an indicator. Other tests were carried out as per relevant international standards.

Cure behavior, mechanical properties and solvent resistance

The vulcanization characteristics were determined using ACS1 based formulation (Table 1) and the mechanical properties are evaluated based on a conventional tread formulation (Table 2). The cure characteristics of rubber compounds were determined using moving die rheometer (Rheotech MD) at 150 °C. The rubber obtained was compounded using a laboratory model mixing mill and vulcanized to optimum cure time in a hydraulic press.

Table 1. **Formulation and cure characteristics of ACS1 based mixes**

Ingredients	NR sensitized coagulation	NR conventional coagulation
Natural rubber	100	100
ZnO	6	6
Stearic acid	0.25	0.25
Sulphur	3.5	3.5
MBT *	0.5	0.5
Parameters	Cure characteristics at 150 °C	
Torque Max. dN.m	3.15	2.59
Torque Min. dN.m	0.19	0.55
Optimum cure time, min	25.11	23.36
TS_1	8.23	8.51

* Mercaptobenzothiozole

Table 2. **Formulation and cure characteristics of carbon black filled mixes**

Ingredients	NR sensitized coagulation	NR conventional coagulation
Natural rubber	100	100
ZnO	5	5
Stearic acid	2	2
Antioxidant TDQ [1]	1	1
HAF black	40	40
Aromatic oil	4	4
CBS [2]	0.75	0.75
Sulphur	2.5	2.5
Parameters	Cure characteristics at 150 °C	
Torque Max. dN.m	14.93	10.15
Torque Min. dN.m	0.57	0.62
Optimum cure time, min	13.05	9.01
TS_1	2.20	2.07
TS_2	2.77	2.57

1. 2,2,4-trimethyl 1, 2, dihydroquinoline
2. N- cyclohexyl benzthiazyl-2-sulphenamide

The other mechanical properties were determined as per the relevant ASTM standards. Solvent resistance was carried out using ASTM fuel C at room temperature by measurement of per cent weight of fuel absorbed for various immersion periods.

Scanning electron microscopy (SEM) studies

This was conducted using Hitachi SEM (model 2400). The tensile fractured surfaces and the abraded surfaces where sputter coated with gold within 24 h of testing and examined under SEM.

Atomic force microscopy (AFM) studies

Atomic force microscopy studies were conducted at ambient conditions with a scanning probe microscope 5500 (Agilent Technologies, USA). Etched silicone probes with stiffness of 40 N/m were used in this study. Imaging was performed in oscillatory mode at different tip – samples forces by varying A_0 (amplitude of free oscillating probe) and A_{sp} (set point amplitude). In the oscillatory mode, the AFM probe is driven to oscillation at its resonant frequency and damping of the cantilever's amplitude due to tip-sample force interactions is employed for surface imaging. The change in cantilever amplitude from A_0 to A_{sp} is used for the feedback that tracks surface topography. Flat faces on the samples were prepared with an ultramicrotome RMC (Tucson, AZ). Cutting of the rubber sample was performed with a diamond knife at a temperature of -100 °C. Freshly prepared samples were used for imaging.

RESULTS AND DISCUSSION

1. Effect of surfactants on coagulation of latex

It was observed that addition of surfactants resulted in immediate coagulation of fresh latex when used at a definite concentration. Earlier reports show that soap coagulation of latex was possible by different types of vegetable oil soaps (Van Gills, 1947). On addition of fatty acid soaps to latex they cause displacement of proteins and get strongly adsorbed on rubber particles. In this way the protein stabilized latex gets transformed into a soap stabilized system. On addition of acids to surfactant treated latex the adsorbed surfactant anions react with acid to form un-dissociated surfactants, and deprive the latex particles of stabilizers. As a consequence, latex coagulates immediately (Blackley, 1997).

2. Raw rubber properties of rubber

As observed from Table 3, the raw rubber properties of the rubber obtained by surfactant sensitized coagulation showed a

higher acetone extract, acid number, and lower P_0, PRI and Mooney viscosity in comparison with conventionally coagulated NR. These observations reveal that some non-rubber ingredients that are acidic are retained on rubber through the added surfactant. Resins, quabrachitol and steroids along with organic acids, are known to be extracted by acetone.

Earlier studies show that the carbonyl group of free fatty acids such as stearic, oleic and linoleic acids and their methyl esters increase the rate of oxidation of polyisoprene.

Table 3. **Raw rubber properties**

Parameters	Modified	Conventional
Volatile matter , %	0.7	0.7
Acetone extract, %	4.5	1.9
Acid number	1178	144
Mooney viscosity	77	84
Initial plasticity (P_0)	39	47
Aged plasticity (P_{30})	29	40
Plasticity retention index (PRI)	74	85

Oleic and linoleic acids exhibit synergistic pro-oxidant activity. (Arnold and Evans, 1991). The lowering of PRI could be attributed to the formation of higher fatty acids from the surfactant added to effect modified coagulation of latex. As the fatty acids are plasticizers of rubber they reduce Mooney viscosity and initial plasticity.

3. Vulcanization characteristics

The cure characteristics of the mixes are given in Tables 1-2. The rubber recovered from surfactant sensitized coagulation showed better overall cure characteristics. It had a higher level of crosslinking which is attributed to the surfactants retained on rubber. In carbon black filled mixes there is a higher level of crosslinking which is also expected to be due to activation of cure by uniformly dispersed surfactant retained.

As an activator of vulcanization ZnO requires sufficient amount of fatty acids which convert it into rubber soluble form. Though NR contains a certain amount of these acids it is usually insufficient. Therefore their contents are adjusted to the required level by addition of commercial stearic acid (Franta, 1989). It is expected that the retained surfactants act as cure activators.

4. Mechanical properties and solvent resistance

Carbon black filled NR vulcanizates based on rubber obtained by surfactant sensitized coagulation recorded a higher modulus, tensile strength and elongation at break. Heat-build up and compression set values were comparable to that of control (Table 4). The improvement in mechanical properties is attributed to the formation of

Table 4. **Mechanical properties of carbon black filled vulcanizates**

Parameter	NR sensitized coagulation	NR conventional coagulation
100% Modulus, MPa	3.6	2.5
200% Modulus, MPa	9.4	6.8
300% Modulus, MPa	16.7	13.1
Tensile strength, MPa	28.4	27.4
Elongation at break, %	440	420
Hardness, Shore A	66	58
Resilience, %	58	58
Compression set, 22h/70°C,%	21	20
Heat build-up, T,°C	21	20
Din abrasion loss, mm^3	84	126

higher level of crosslinks and other interactions involving filler and rubber. Fatty acids have a considerable effect on vulcanization kinetics and interaction with fillers. It is expected that there is better polymer filler interaction involving uniformly dispersed fatty acids derived from the surfactants, though the actual mechanism is not clear from this study.

It is noted that there was a significantly improved abrasion resistance. There are reports that use of higher dosage of stearic acid in tread formulation enhanced the abrasion resistance. In this study it is inferred that fatty acids are formed during vulcanization from added surfactant and it acts as lubricant, reducing the abrasion loss (Gelling, 1992; Joseph *et al*., 2003).

It is observed that there is improved solvent resistance for NR vulcanizates based on rubber obtained by surfactant sensitized coagulation (Fig. 1). The fuel used was ASTM D 471 reference fuel C which is a mixture of isooctane: toluene, 50: 50 (v/v). The modified

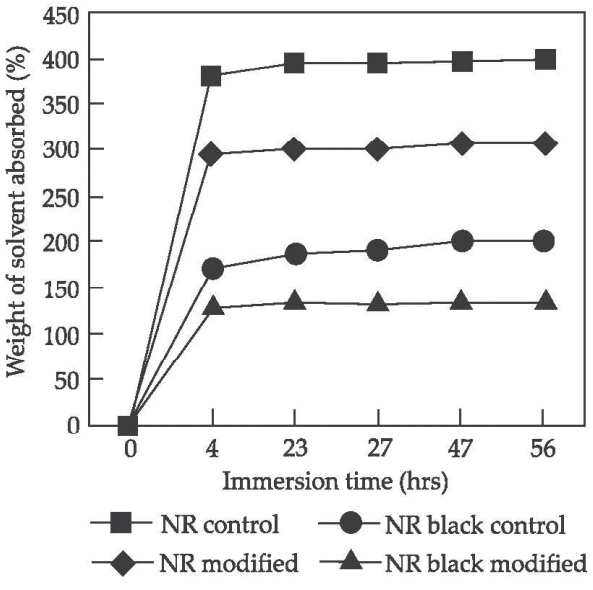

Fig. 1. Amount of ASTM Fuel C absorbed by NR prepared through conventional and fatty acid soap sensitized method

rubber contains higher fatty acids formed from the surfactants added during coagulation of latex. These are more polar in nature compared to the solvent used and this leads to a lower solvent uptake compared to the control NR mixes that have only much lesser proportion of higher fatty acids.

5. Scanning electron microscopy (SEM) studies

The scanning electron microscopy data was taken to analyze the abraded surface and tensile fracture surface to understand the nature of the rubber matrix. The SEM photographs of the tensile fracture surfaces of NR vulcanizates prepared using rubber obtained by modified coagulation (sample A) and rubber obtained by conventional coagulation (sample C) are shown in Figure 2. Both samples showed several broad fracture paths. At low magnification (200 x), it is seen that the modified sample had shorter fracture paths which indicated fracture deviation while the conventional NR had longer fracture paths and also smoother surface. An idea of nature of the surfaces is evident at higher magnifications. In 1000x and 3000x magnifications NR prepared in the conventional way appeared smoother and there were signs of material removal while the modified sample showed a rougher surface. Earlier reports show that the presence of curved short tear lines and roughness on tensile fracture surfaces indicated rubber matrix of higher tensile strength (Mathew *et al*., 1982). The rubber prepared by surfactant sensitized coagulation had a higher tensile strength as shown in Table 4.

The SEM photographs of the abraded surfaces of NR vulcanizates prepared using rubber obtained by modified coagulation (sample A) and rubber obtained by

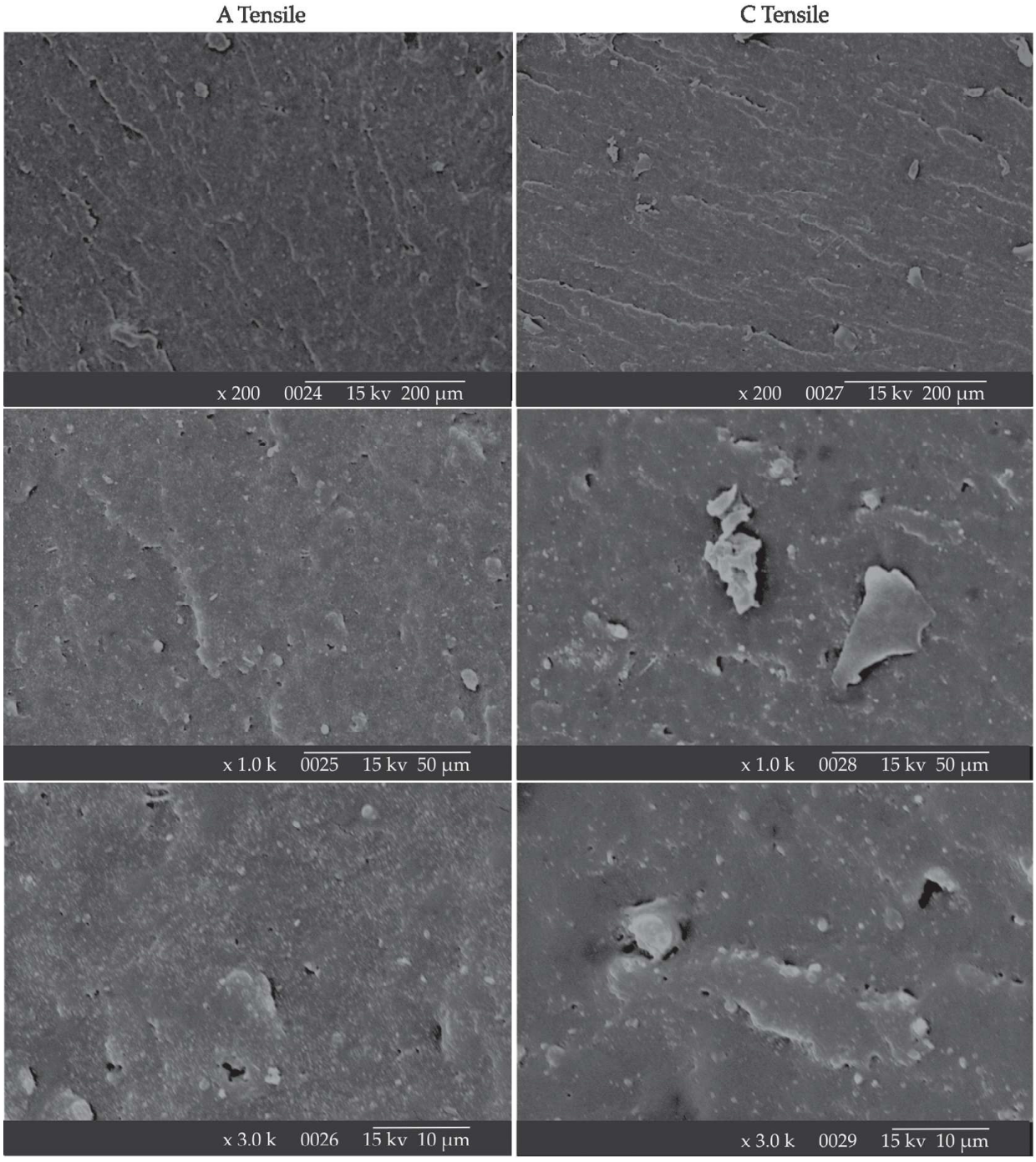

Fig. 2. The SEM photographs of the tensile fracture surfaces of NR vulcanizate prepared using rubber obtained by modified coagulation (sample A) and rubber obtained by conventional coagulation (sample C) at different magnifications (200 x, 1000 x and 3000 x)

conventional coagulation (sample C) are shown in Figure 3. At lower magnification it is evident that both samples showed ridge formation. More information about the ridges is observed at higher magnifications (1000 x and 3000 x) The ridge pattern was comparatively wider for NR vulcanizates prepared in the conventional way. At high

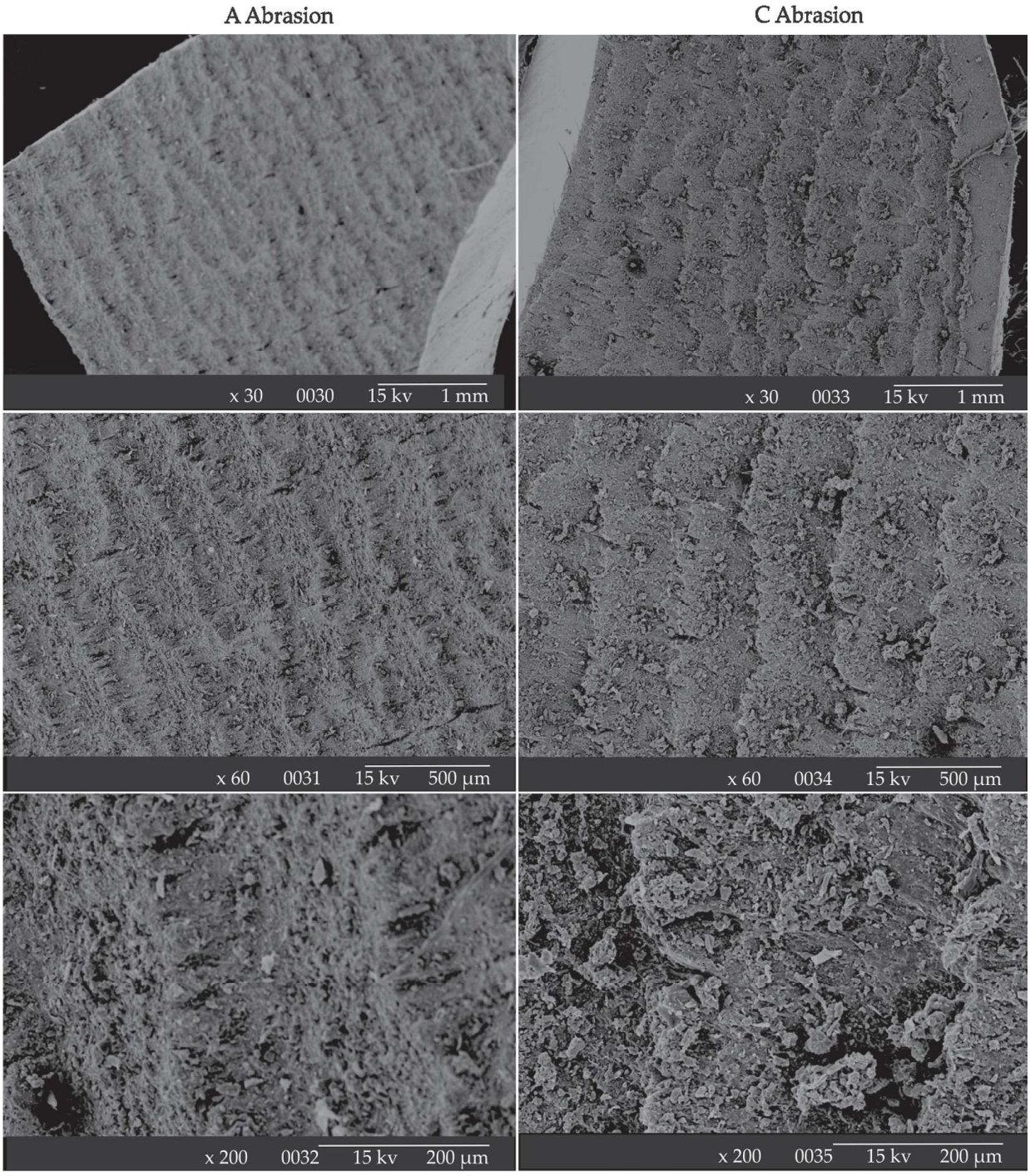

Fig. 3. The SEM photographs of abraded surfaces of NR vulcanizate prepared using rubber obtained by modified coagulation (sample A) and rubber obtained by conventional coagulation (sample C) at different magnifications (200 x, 1000 x and 3000 x)

magnification (3000x) the presence of ridges was not observed on the abraded surface of rubber prepared in the conventional way while the rubber prepared by modified coagulation showed presence of ridges. Earlier reports show that during abrasion of rubber there is ridge formation, and the changes in the nature of ridges along with

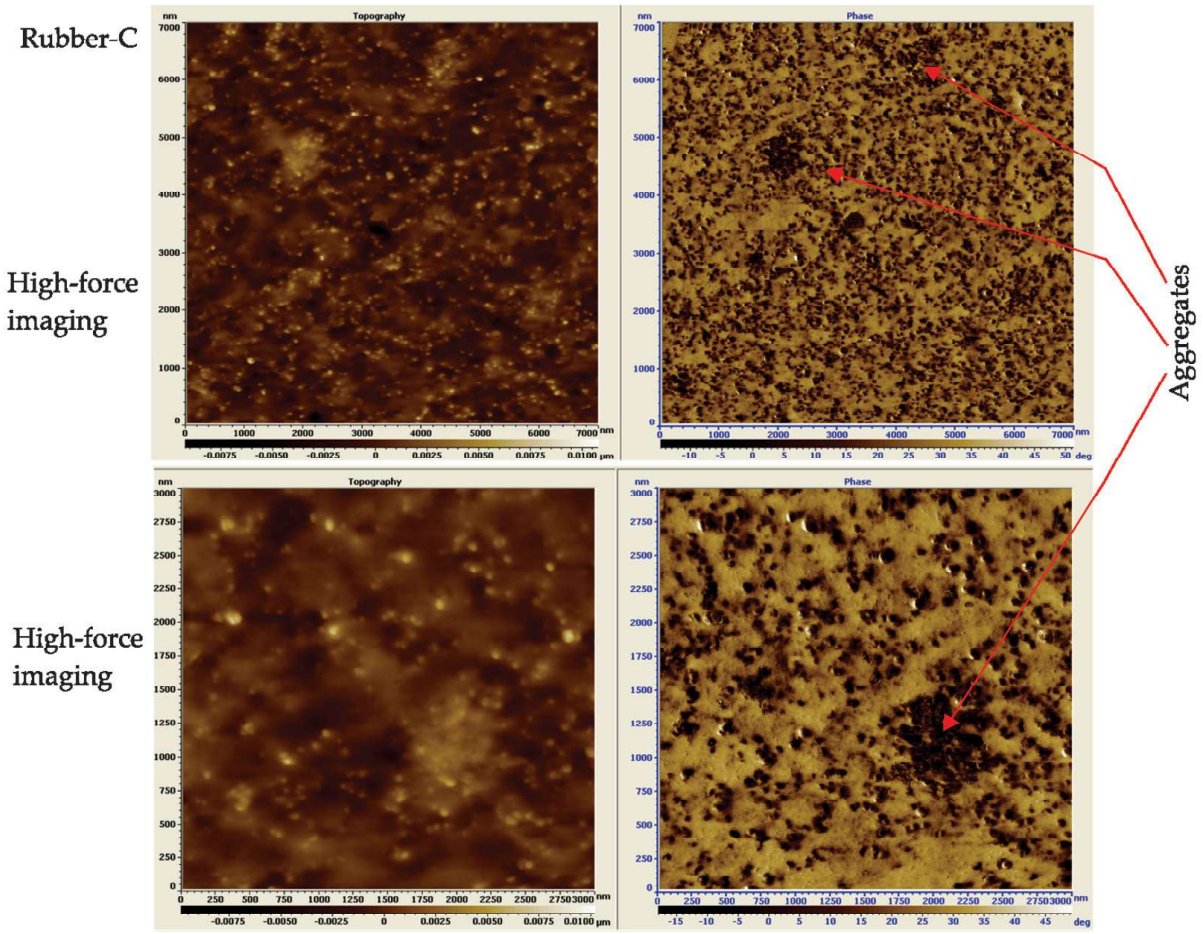

Fig. 4. High force topography and phase images of carbon black filled NR vulcanizates prepared using NR obtained through conventional coagulation taken at two portions on ultramicrotomed sample

evidences of material removal could indicate the mechanism of abrasion resistance. Fine pattern for the ridges along with less material removal indicated higher abrasion resistance **(**Bhowmick *et al*., 1981; Nayek *et al*., 2005). Comparatively very high abrasion resistance was observed for rubber prepared by surfactant sensitized coagulation (Table 4). As discussed earlier, fatty acids can act as lubricant and reduce abrasion loss (Gelling, 1992).

6. Atomic force microscopy (AFM) studies

The height and phase images of the surface of sample C (prepared from rubber obtained by conventional coagulation) and sample B (prepared from rubber obtained by modified coagulation) of the fresh faces of the samples obtained using an ultramicrotome are shown in Figures 4- 6.

As a general observation dispersion of carbon black as nanoparticles is observed for both samples. Sample C contains little number of aggregates from topography images as marked. Phase images also show that there are aggregates which appear as lumps.

Generally topography images account for differences in height and more information on fine features of the

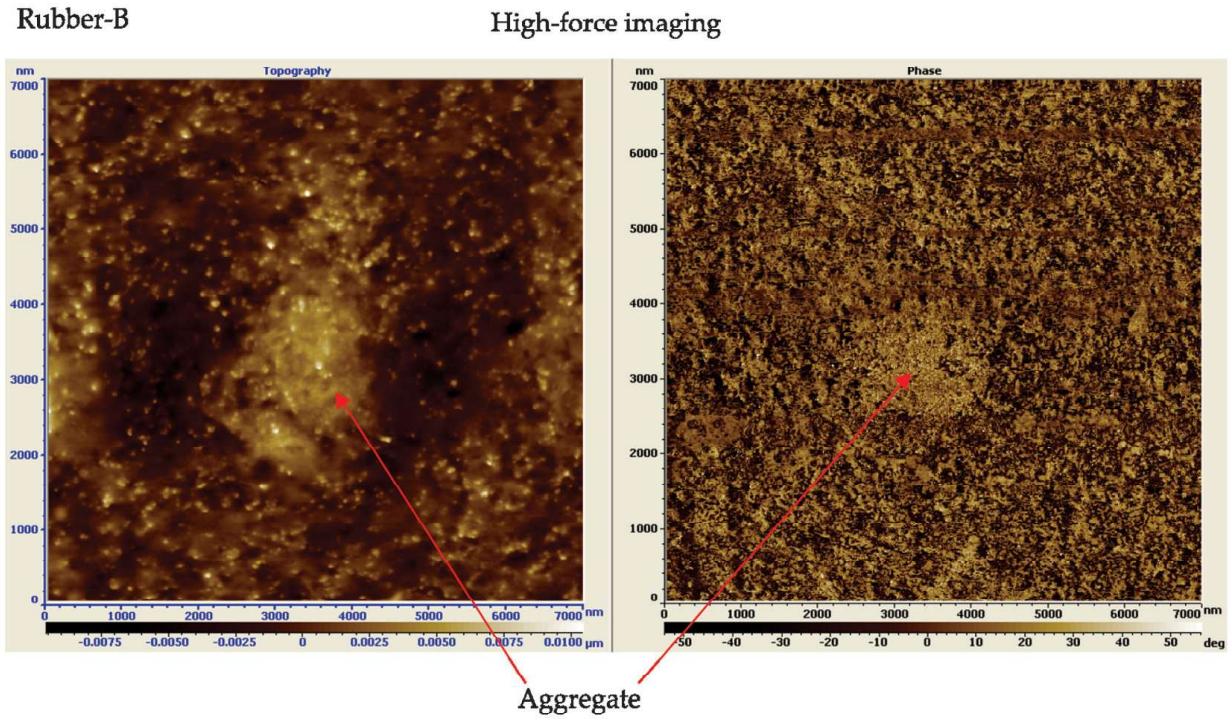

Fig. 5. High force topography and phase images of carbon black filled NR vulcanized prepared using NR obtained through modified coagulation

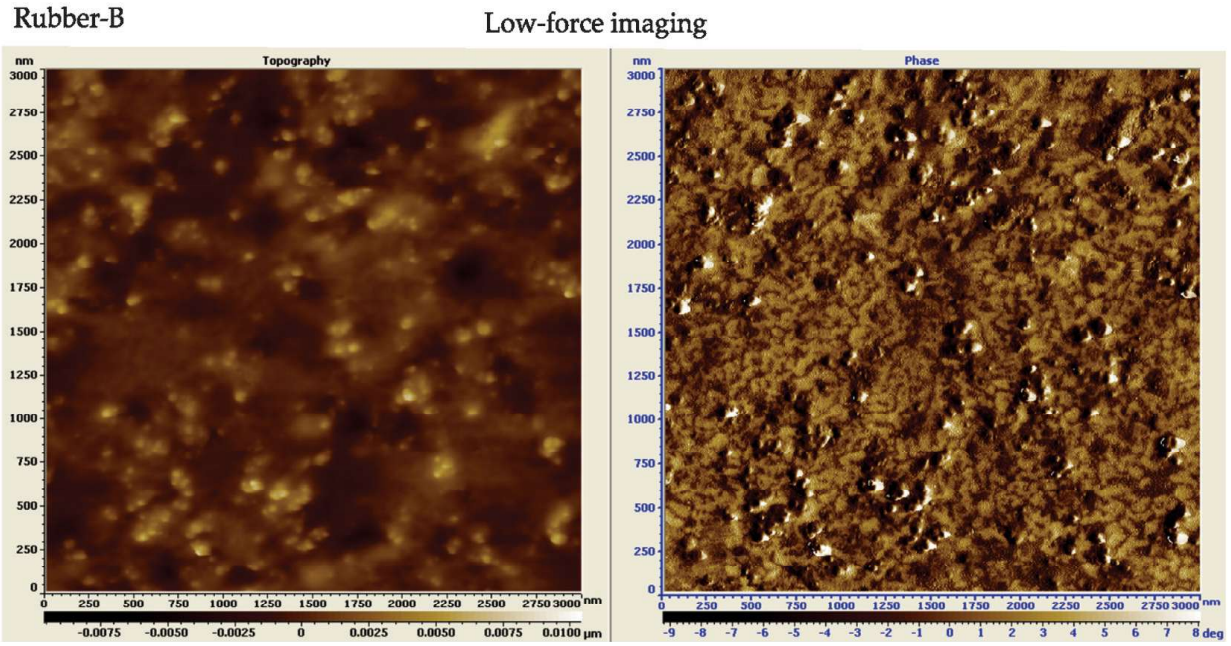

Fig. 6. Low force topography and phase images of carbon black filled NR vulcanizates prepared using NR obtained through modified coagulation

aggregates is obtained from phase images. It is known that during analysis, the AFM probe is driven to oscillation at its resonant frequency and damping of the cantilever's amplitude due to tip-sample force interactions is employed for surface phase imaging while the change in cantilever amplitude is used to track surface topography. The former gives more information on the nature of aggregates.

Sample B also shows some level of aggregation as seen from topography image. In phase image as it highlights edges it provides clearer observation on the edges of the aggregate. As observed from phase image edges appear less prominent, appear to be like a smear and seem to be distributed rather homogeneously. Low force imaging is known to give more relevant images and the small tip - sample contact area that accompanies low force imaging offer better image resolution. The low force AFM images of sample B also reveal homogeneous dispersion of carbon black in rubber matrix.

Thus on comparison it is observed that nature of aggregation of nanoparticles is more as lumps for sample C as compared to sample B. Earlier results show that AFM images could be used to determine the size of aggregates and diameter of single particle of carbon black (Niedermeier *et al*., 1994; Wang *et al*., 2005).

The plasticizers in general help in the incorporation of fillers and they are likely to cause lower level of filler dispersion, caused by the lower shear forces experienced during mixing if the quantity used is high. From AFM studies it is observed that the filler aggregation is lower for rubber prepared by modified coagulation process. The hydrocarbon portion of the fatty acid soaps formed during vulcanisation is soluble in rubber and it is expected that the degree of solubility of this portion is one of the factors that influence the mechanical properties of rubber. Wider molecular weight distribution of hydrocarbon chain of the surfactant process additive results in a lowering of melting point and easy dispersion in rubber. High polarity functional groups tend to reduce the solubility in rubber somewhat and give the product more activity as a surface lubricant. But they have the advantage that they provide an attraction for polar fillers improving the dispersion of such fillers in the rubber compound (Christopher, 2001).

Carbon blacks have functional groups such as hydroxyl, carboxyl, ketone and aldehyde on their surface and it is expected that there can be some interactions of filler with the polar groups of the surfactants added to latex.

CONCLUSION

The coagulation of NR latex in presence of acids is accelerated by addition of small quantities of anionic surfactant. A proportion of the surfactants added to latex gets adsorbed on rubber particles and are retained in rubber after coagulation. The surfactants retained on rubber activate the vulcanization and enhance the filler dispersion thereby improving the mechanical and solvent ageing characteristics of recovered rubber. The carbon black filled rubber vulcanizates based on rubber obtained by modified coagulation show significantly higher abrasion resistance mainly due to the lubricating action of the fatty acids formed in rubber.

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