

## Toward “Rubbery” Nanoparticles

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**ABSTRACT:** The synthesis of electrically Conducting Natural Rubber (CNR) nanoparticles from natural rubber (cis 1, 4 polyisoprene) by a simple chemical doping technique is reported for the first time. Much before the establishment of conjugation as a precondition for polymers to be conducting a typical nonconjugated polymer like cis 1,4 polyisoprene was shown to develop intrinsic conductivity on doping. However, the possibility of developing conducting nanoparticles of natural rubber by doping has never been explored. Doping of natural rubber solution with Antimony pentachloride is found to lead to the formation of nanosized rubber particles with improved thermal stability and lower degradation characteristics than that of pristine rubber. Transmission electron microscopy and Dynamic Light Scattering experiments revealed a highly uniform dispersion of the particles with sizes in the range of 4 nm. The doped nanoparticles are found to retain “rubbery” properties of natural rubber and therefore these can be rightly termed as Rubber Nano particles. The development of nanoparticles of rubber assumes great significance in that it would lead to hitherto unknown applications for natural rubber in micro applications-like sensors, and optoelectronics devices to macro applications such as compatible reinforcing fillers for elastomers and plastics to replace conventional fillers like carbon particles. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 100–105, 2013

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### INTRODUCTION

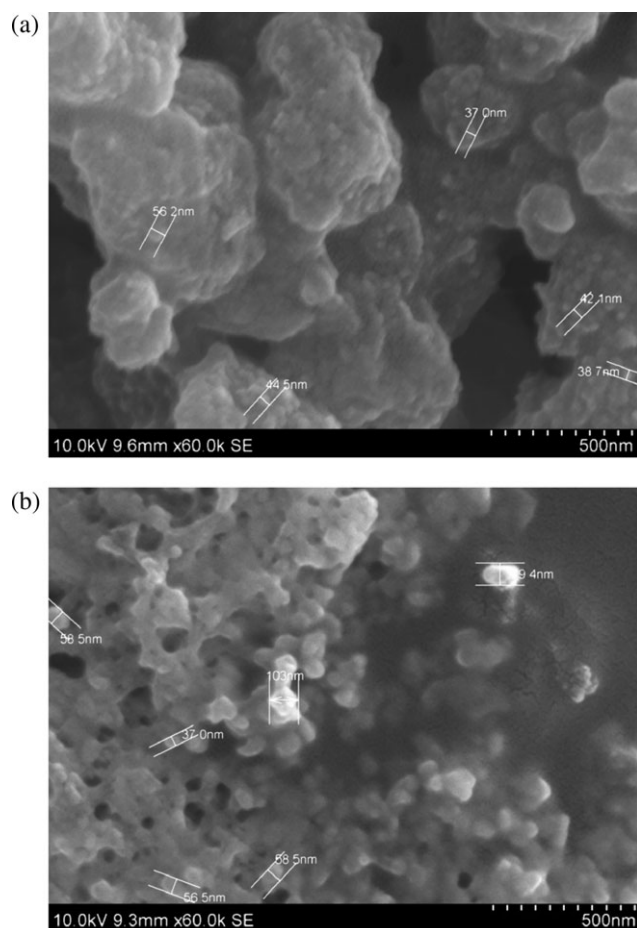
Natural rubber (cis1,4 polyisoprene) is a polymer of isoprene (2-methyl-1, 3-butadiene) in the form of folded polymeric chains which are joined in a network structure<sup>1,2</sup> having high degree of flexibility. Natural rubber (NR) and other members of the elastomer family are known for their high value of electrical resistivity and perceived as highly insulating polymer. However Thakur<sup>3</sup> in 1988 reported that conductivity of natural rubber could be increased by about tenfold upon doping with iodine. This was surprising as it has been widely believed<sup>4,5</sup> that only polymers with conjugated back bone could be made conducting by doping and natural rubber is a typical nonconjugated polymer. However, successive studies<sup>6,7</sup> indicated that the doping of NR consists of a two stage reaction in which rubber attains a conjugated structure by a double shifting process followed by the formation of charge transfer complexes. Although the doping of natural rubber thin films by lewis acids such as SbCl<sub>5</sub> were also reported there are no reports available so far on the possibility of developing conducting nanoparticles by such doping.

In this report the formation of conducting nanoparticles of natural rubber by solution doping with reflux boiling technique

using a Lewis acid, SbCl<sub>5</sub> as dopant is revealed for the first time. Detailed studies of the conducting nanoparticles are made by optical, electrical and thermal techniques. Through this method aqueous dispersions of rubber particles with sizes less than 5 nm are made possible. These rubber nanoparticles promise tremendous application potential such as in sensors, radiation resistant nanocomposites, transparent conducting films, etc. The bulk form of these nanoparticles has the potential to be used in rubber composite industry as a replacement for fillers like carbon. As the natural rubber nanoparticles are seen to retain the original properties of natural rubber with the added advantages of nano size, thermal and mechanical stability, and most importantly electrical conductivity, they can prove to be cost effective and compatible filler for natural rubber composites.

### EXPERIMENTAL

The natural rubber used for this study is Indian Standard NR, grade 3 (ISNR 3) with a number average molecular weight of  $3 \times 10^5$  collected from Rubber Research Institute, Kottayam, India. The dopant Antimony pentachloride (Aldrich) and the



**Figure 1.** (a) Scanning Electron Micrograph of CNR nanoparticles before dispersion. (b) Scanning Electron Micrograph of CNR nanoparticles after dispersion.

solvent Carbon tetrachloride (Merck) are purchased from local suppliers and used for the study without further purification.

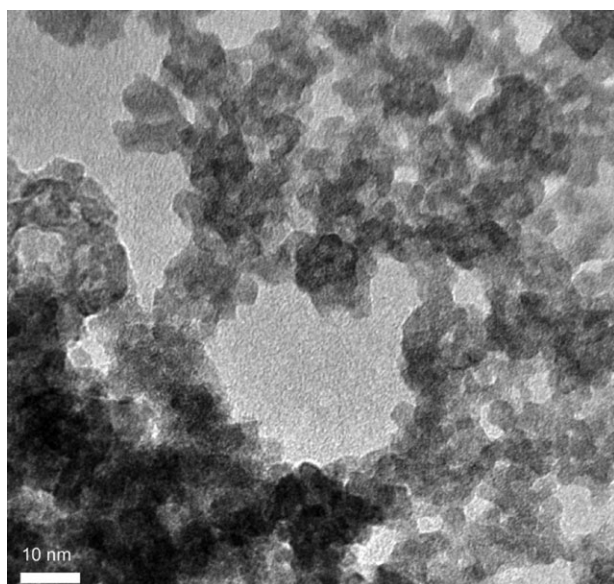
As the first step, 0.408 g (6mmol per monomer unit) of natural rubber is completely dissolved under nitrogen in 27 mL of anhydrous Carbon tetra Chloride ( $\text{CCl}_4$  - Merck) in a round bottom flask equipped with a stirrer and a dropping funnel. A solution of  $\text{SbCl}_5$  (1.5 mL) dissolved in  $\text{CCl}_4$  (4.7 mL) is added to the dropping funnel. The  $\text{SbCl}_5$  solution is added drop wise into the natural rubber solution at room temperature. Here, NR: Dopant mol ratio is maintained as 1 : 1. During the doping process the color of the solution changes from brown to black. The entire process is carried out under vigorous stirring and it is continued for another 5 h under nitrogen atmosphere. The experiment is repeated with reflux boiling technique using a three-necked flask fitted with a stirrer, reflux condenser, and a dropping funnel. When the drop wise addition of the dopant is completed, the mixture is boiled under reflux for 6 h with stirring. The mixture is then cooled and the reaction is arrested by the addition of ethanol. The precipitate is filtered out with suction in an atmosphere of nitrogen and washed thoroughly with  $\text{CCl}_4$  several times to flush out the excess and unreacted  $\text{SbCl}_5$  if any. The dark black precipitate is then dried under vacuum at

303 K for 48 h followed by grinding in a mortar to get a black fine powder of conducting rubber. The experiment is repeated by varying the elastomer: dopant mol ratio (1 : 2 and 1 : 3), doping period (3, 9, 12, and 15 h), and doping temperature (283, 323, 343, and 373 K). SEM micrographs of the finely ground aggregates as well that dispersed in deionized water are obtained with a Hitachi SU 660 Variable Pressure Field Emission Scanning Electron Microscope. Stable suspensions of the rubber nanoparticles are formed by centrifuging the rubber aggregates in deionized water in the presence of SDS as surfactant at a speed of 12,000 rpm followed by centrifuging the supernatant of the first centrifuge at the same rpm. The particle size of this suspension is evaluated using a JEOL make HRTEM (Transmission Electron Microscope) instrument. Particle sizes distribution is also measured using a Malvern make Dynamic Light Scattering (DLS) equipment. For measuring electrical properties aggregates are made into pellets of ASTM standard using a hydraulic press unit. The electrical conductivity of the pelletized samples is measured using Keithley 6514 Electrometer, and Keithley DMM 2000. Temperature dependence of electrical conductivity is measured using a cryostat fitted with temperature controller. Thermal characteristics of the samples are carried out with a Mettler-Toledo make Differential Scanning Calorimeter (DSC) and Perkin Elmer make Differential Thermogravimetric Analyser (DTA). Optical absorption spectra and Fourier Transform Infrared Spectroscopy (FTIR) of the samples are taken using Avantes UV/Vis spectrophotometer in the range 200–900 nm and Nicolet 5700 FTIR Spectrometer, in KBr medium, in the range 400–4000  $\text{cm}^{-1}$  respectively. XRD studies are conducted by Bruker AXS D8 advance photometer XRD with Cu  $K\alpha$  radiation.

## RESULT AND DISCUSSION

The Figure 1(a,b) shows the scanning electron micrographs of CNR rubber powder, and water dispersed aggregates before centrifuging. Strong aggregation of the nanoparticles are observed in both case. However, aggregates of sizes down to 50 nm are clearly visible [Fig. 1(b)] for particle dispersion in water.

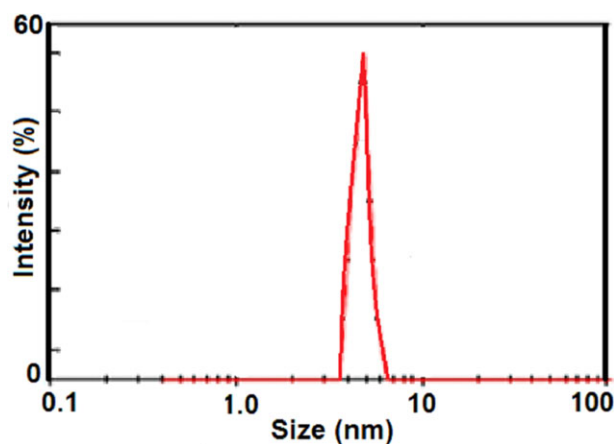
As mentioned in the earlier section, finely dispersed suspension of CNR nanoparticles in deionized water is obtained only after the dispersion is aggressively stirred for 4 h followed by ultrasonication for 30 min in a bath and then centrifuging twice at 12000 RPM. The residue of the first centrifuge is removed and the supernatant is again centrifuged to get stable water dispersions. Ethanol, methanol, isopropanol, benzene, etc. are also found to be good dispersion media for these nanoparticles. However, optimum particle dispersion is obtained in deionized water. The dispersion obtained after first centrifuge is not stable with the appearance of residual particles in the bottom in a few minutes. However, the dispersion after second centrifuging stayed for months together without the appearance of any residue. Figure 2 shows the TEM image of the nanoparticles from this water dispersion. Average particle sizes of about 4 nm are visible. Particle distribution obtained from the DLS experiment (Figure 3) is also found to be about 4.5 nm.



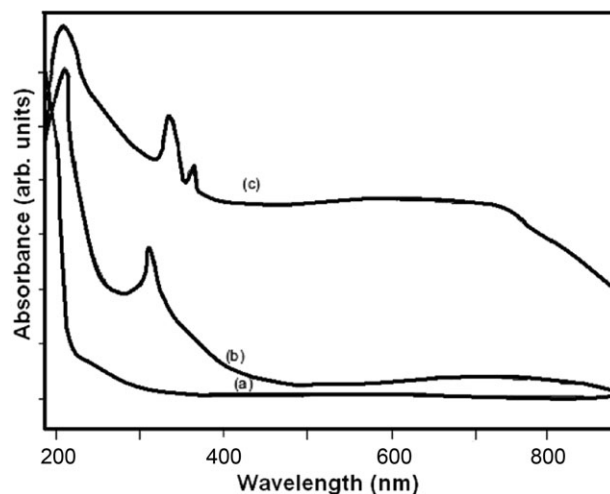
**Figure 2.** HRTEM image of suspended CNR nanoparticles in deionized water. Average particle size is about 4 nm.

The UV/Vis spectra of the pristine natural rubber and CNR nanoparticles (Figure 4) show that while the pristine cis 1,4 polyisoprene does not absorb in the visible domain  $\text{SbCl}_5$  treatment makes polyisoprene to absorb strongly in the visible region probably due to<sup>7</sup> the formation of various conjugated sequences ( $-\text{CH}=\text{CH}-$ ) in the polyisoprene chains. The peaks formed in the range 300–400 nm could be attributed to the charge transfer excitation of the complex that are formed upon doping. As dopant concentration is increased the absorption edges extend to longer wave lengths.

This is because of the higher density of the conjugated structures. Consequently charge transfer excitation energy decreases. At higher doping levels broad absorption bands extending to the near infrared region are observed. This absorption is



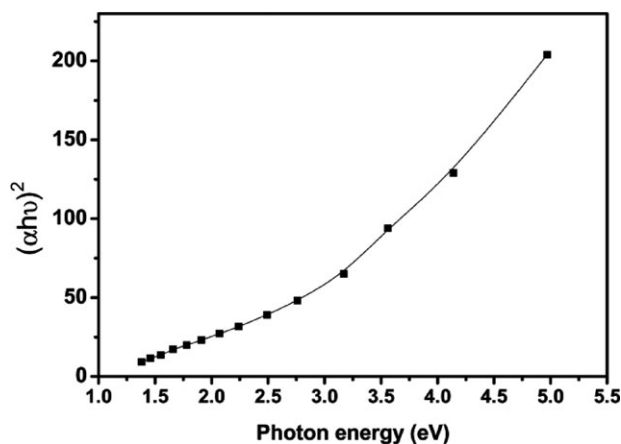
**Figure 3.** Size distribution of CNR nanoparticles in water dispersion from (4.73) nm for 100% peak from Dynamic Light Scattering. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



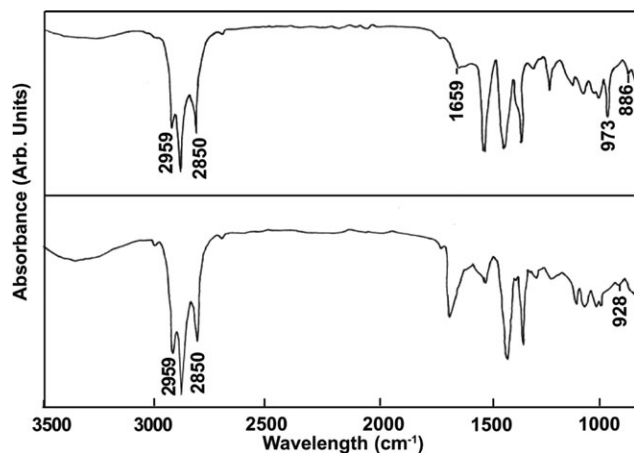
**Figure 4.** Optical absorption spectra of (a) Natural Rubber in the pristine state. (b) Natural Rubber doped with  $\text{SbCl}_5$  (1 : 1 ratio), and (c) Natural Rubber doped with  $\text{SbCl}_5$  (1 : 2 ratio).

essentially due to the formation<sup>9</sup> of stronger charge transfer complexes. It can be suggested<sup>7</sup> that short conjugated sequences of five to six  $\text{C}=\text{C}$  bonds get introduced<sup>9</sup> in to the cis 1, 4 polyisoprene chains where the presence of electron releasing substituent forming a key factor in the generation<sup>7</sup> of conducting complexes. The color of the CNR nanoparticles must be originating<sup>10</sup> from the absorption of the oxidized polymer. The optical band gap ( $E_g$ ) can be obtained from the absorption coefficient ( $\alpha$ ) measurement. The optical band gap ( $E_g$ ) is estimated by the extrapolation of the linear portion to  $(\alpha h\nu)^2 = 0$  in the  $h\nu$  versus  $(\alpha h\nu)^2$  plot shown in Figure 5. This is found to be 2.25 eV. It is observed that the band gap decreases from 5.8 eV (for pristine NR) to 2.25 eV for doped ones, which confirms the formation of conjugated sequences of double bonds in polyisoprene backbone.

The introduction of conjugation along the backbone of CNR nanoparticles is further confirmed by analyzing the FTIR spectra [Figure 6(a,b)] of the pristine natural rubber sample and that of CNR nanoparticles. The band corresponding to the stretching

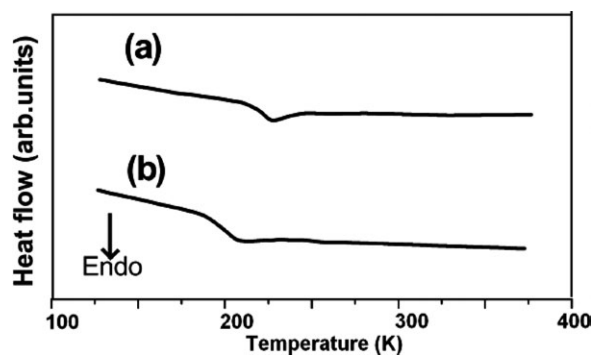


**Figure 5.**  $(\alpha h\nu)^2$  versus photon energy for CNR nanoparticles.



**Figure 6.** FTIR spectra of Pristine state natural rubber (top), and CNR nanoparticles (bottom).

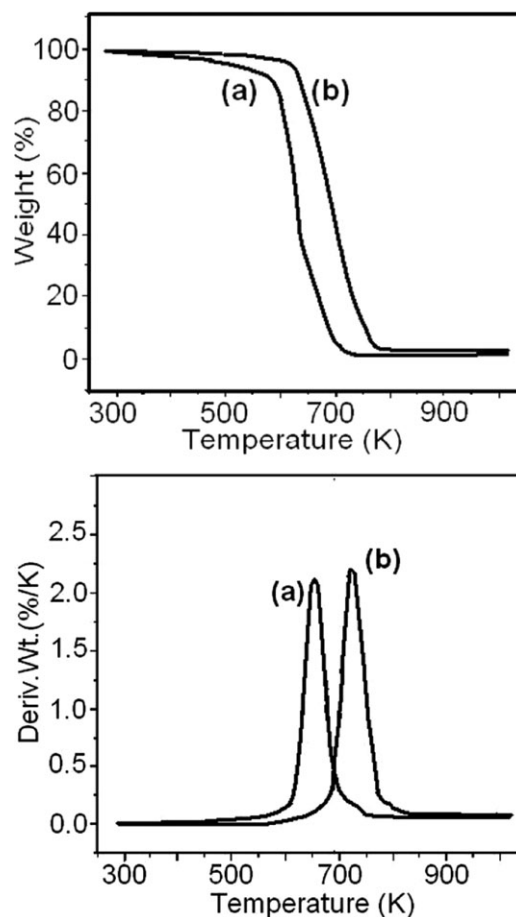
vibrations of isolated (C=C) bonds of pristine polyisoprene chains at  $1658\text{ cm}^{-1}$  is seen to shift to higher frequencies upon doping. The changes in the spectra are consistent with the addition of  $\text{SbCl}_5$  to (C=C) bonds along the polyisoprene backbone. The characteristic bands of pristine natural rubber at  $973\text{ cm}^{-1}$  and  $886\text{ cm}^{-1}$  due to the stretching vibration of  $\text{CH}_2$ <sup>11</sup> are disappeared and a new band at  $928\text{ cm}^{-1}$  is appeared in the spectrum of nanoparticles. This new band can be attributed to the rocking vibrations of newly formed (C-Cl) bond. The strong asymmetrical and symmetrical stretching of methyl group vibrations preset in the natural rubber are observed<sup>12</sup> near  $2959\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$ , respectively. Spectra of all the rubber materials which contain methyl groups should show two distinct bands occurring at around  $2950\text{ cm}^{-1}$ . The first band resulting from asymmetrical stretching mode in which two C-H bonds of methyl group are extending while the third one is contracting. The second band arises from symmetrical stretching in which all the three C-H bonds extend and contract in phase. Both samples show methyl and ethyl group vibrations and OH stretching vibrations at around  $3400\text{ cm}^{-1}$  which are attributed<sup>6</sup> to polymeric hydroxyl groups irrespective of their compositions. All these indicate that the CNR nanoparticles retain the general structural aspects of pristine natural rubber on doping.



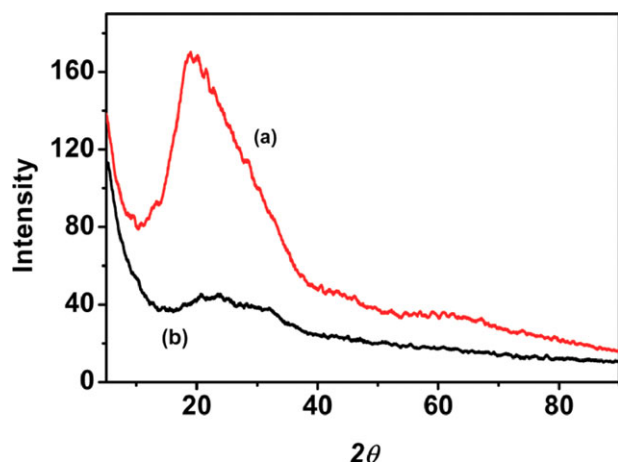
**Figure 7.** The DSC thermograms of Pristine natural rubber and CNR nanoparticles.

Thermal stability and degradation properties of the CNR nanoparticles are investigated using DSC and TGA. DSC thermograms of the pristine natural rubber and the CNR nanoparticles are shown in Figure 7. The glass transition temperature ( $T_g$ ) is evaluated as the peak point of the heat flow versus temperature curve. The thermogram of pristine natural rubber shows a glass transition peak at 210 K whereas for CNR nanoparticles the glass transition peak is at 230 K. It has been suggested that the transition is due to freezing of the segmental mobilities of the micro Brownian type which leads to a marked changes of all kinds of properties. This increase in  $T_g$  indicates that<sup>11,13</sup> for the fusion of the particles in the system more heat is required. This shift in the glass transition temperature towards a higher value is a typical evidence of the enhancement of thermal stability of the CNR nanoparticles compared to pristine natural rubber.

The thermogravimetry analysis of the pristine natural rubber and CNR nanoparticles are shown in Figure 8(a,b). The gravimetric analysis (TGA) and the derivative thermogravimetry (DTG) curves are recorded in the course of heating from room temperature to 973 K. The TGA and DTG behaviour of pristine NR are well known.<sup>14</sup> The thermal degradation of natural rubber usually shows two characteristics regions of weight loss. The



**Figure 8.** (a) TGA and (b) DTG curves of Pristine NR and CNR nanoparticles.



**Figure 9.** XRD pattern for (a) Natural Rubber in the pristine state. (b) CNR nanoparticles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

main weight loss region occurs in the temperature range of 470–670 K with degradation onset at around 580 K. This main degradation is due to oxidation resulting in the formation<sup>15</sup> of aldehydes, ketones, etc. The second region of degradation is comparatively very small and occurs around 700 K. This has been attributed<sup>14</sup> to a slow decomposition of the polymer chains and highly crosslinked polymer waste. The TGA curve obtained in this study [Figure 8(a)] also is a smooth weight loss curve with a similar dominant weight loss region and onset.

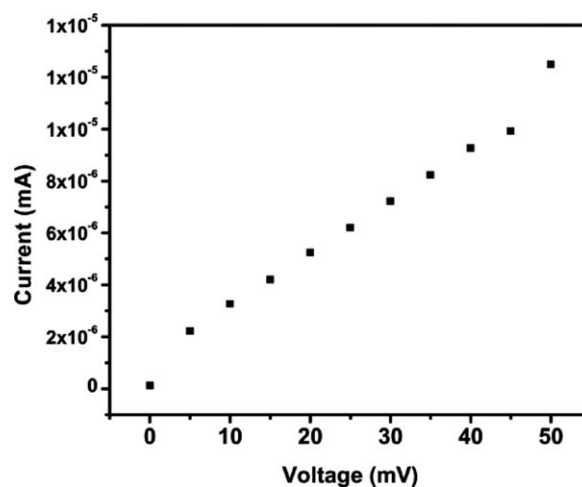
However, only a very weak shoulder at about 700 K is seen in this case for pristine rubber. This is expected as we have used high quality hydrocarbon rubber with no significant amount of crosslinked polymer wastes. The DTG curves [Figure 8(b)] also show similar trends and a very weak second shoulder is visible in the case of pristine rubber in this case also. This indicates that the degradation is more or less a one step reaction. For the CNR nanoparticles, the TGA and DTG curves move toward higher temperatures indicating an improved thermal stability for the CNR nanoparticles. While the profile for DTG peaks for both pristine and doped rubbers are similar, there is a discernible increase in the full-width at half height of the DTG curve which indicates that the CNR nanoparticle degradation occurs more slowly. Further the more or less similar profile of TGA and DTG curves of both pristine and CNR nanoparticle indicates that the nanoparticles retain their rubbery characteristics.

The X-ray diffraction patterns of the pristine Natural Rubber and CNR nanoparticles are illustrated in the Figure 9. The XRD pattern of pristine natural rubber has displayed the typical behavior of a fully amorphous polymer. A broad hump is located at around  $2\theta = 18^\circ$ , which is characteristic<sup>16</sup> of natural rubber. The doped rubber particles also show a similar hump at the same position but with reduced intensity. This formation of a hump with reduced intensity points to the formation of certain degree of cross linking in the rubber due to doping. It would be appropriate to note at this point that an earlier study<sup>10</sup> on iodine doping of rubber indicated the formation of cross links on doping. The observed increase in  $T_g$  for CNR

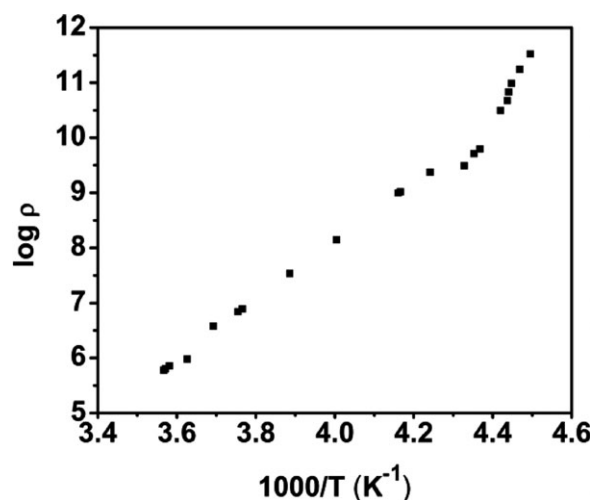
nanoparticles in the DSC study as reported elsewhere in this article also points to the formation of cross links in the rubber structure by doping. The formation of high intensity hump on rubber structure in the XRD pattern can be attributed to the anisotropic X-ray scattering due to the anisotropy<sup>16</sup> in the molecular orientation in natural rubber. The formation of cross links on doping may create a disoriented proportion of amorphous chains due to the heterogeneity of cross links and this may be the reason for the decrease in scattering intensity observed in the case of CNR nanoparticles. Thus the XRD studies along with the DSC data serve to confirm the formation of cross links, though random and in a low degree, in the CNR nanoparticles.

Electrical conductivity studies on the CNR nanoparticles confirmed the indications of optical studies on the formation of conjugated sequences in the rubber back bone on doping. Figure 10 shows the Current-Voltage (I–V) characteristics of the CNR nanoparticles which gives a bulk resistance of about 50 Mega Ohms. This shows that consequent to doping at room temperature, an increase in the electrical conductivity by about 10 orders is taking place. The linear behavior of the curve suggests the ohmic nature of the conductivity. During the process of doping the color of the natural rubber solution is turned from colorless to black, which indicated<sup>7</sup> the presence of conjugated sequences in the polymer backbone. It is seen that the dopant ratio, doping period and doping temperature have not much significant role in the yield and conductivity of the synthesized CNR nanoparticles. However there is a slight increase in the yield and conductivity for those particles synthesized by reflux doping.

The development of intrinsic electrical conductivity in nonconjugated polymers like rubber is explained<sup>6</sup> in the back drop of the requirement of a conjugated structure for a polymer to be made by doping. In rubber-like polymers it has been shown that doping initiates a two stage process in which the first step of the reaction initiates conjugation by a double bond shifting sequence followed by the formation of charge transfer complexes. The temperature dependence of electrical conductivity



**Figure 10.** I–V characteristics for CNR nanoparticles.



**Figure 11.** Variation of resistivity with temperature for CNR nanoparticles.

provides a direct insight into the conduction mechanism as shown in Figure 11.

It can be seen that the resistivity of CNR nanoparticles decreases with increasing temperature. This implies that charge transport in this system includes an intersite hopping mechanism.<sup>5</sup> Although appreciable linearity is observed in the region, 280–240 K, a nonlinearity in the temperature-resistivity sets in below this region. The observed discontinuity at 230 K here can be attributed to a phase transition that is occurring in the CNR nanoparticles at this temperature. It is interesting to note that DSC studies had indicated a glass transition for CNR nanoparticles at 230 K, and the discontinuity in  $\log \rho - 1/T$  curve at 230 K can, therefore, rightly be attributed to the glass transition occurring at this temperature.

## CONCLUSIONS

Nanoparticles of natural rubber of sizes ca 4 nm are successfully synthesized for the first time by a simple doping of natural rubber. These particles are found to be electrically conducting and also their thermal characteristics showed increased thermal stability and degradation resistance. The potential applications of rubber nanoparticles range from diverse areas of organic elec-

tronics to a compatible filler for natural as well as other rubber composites.

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