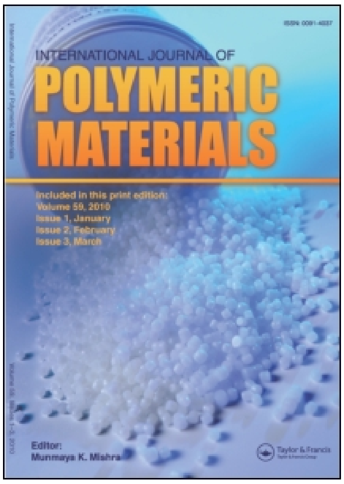

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Natural Rubber-Carbon Nanotube Composites through Latex Compounding

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Natural rubber (NR)-based nanocomposites have been prepared with single-walled carbon nanotubes (SWNTs) through a latex stage mixing method. SWNTs were dispersed in water through ultrasonication and stabilized by the subsequent addition of a surfactant. The stabilized aqueous dispersion of SWNTs was mixed with NR latex and the effect of nanofiller on the flow properties of NR latex was investigated. Casting the compounded latex followed by curing gave good quality composite films with significantly improved mechanical properties. For example, the tensile strength and modulus of the composite film containing 2.0 phr (parts per hundred parts of rubber) SWNTs were, respectively, 56% and 63% higher in relation to pure NR. Electrical percolation threshold concentration of SWNTs in the NR matrix was found to be 1.5 phr. Thermogravimetric analysis indicated that the thermal stability of NR remains unaffected by the presence of SWNTs at low concentrations.

Keywords carbon nanotubes, conductivity, mechanical properties, nanocomposites, natural rubber

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INTRODUCTION

Natural rubber (NR) is a high molecular weight polymer of isoprene (2-methyl 1,3-butadiene). It is commonly obtained from the latex of the *Hevea brasiliensis* tree and is the oldest known rubber and the most versatile one for fabrication into rubber products [1]. The high and reversible deformability of natural rubber is of great industrial importance. However, its initial modulus and durability are low, and an additional reinforcing phase is required for practical use [2–4]. Carbon black and silica particles have been extensively used for this purpose [5–8]. In addition, $CaCO_3$, ZnO, MgO, and talc have also been used [9–12]. The influence of these particulate fillers on the deformability of the polymer was earlier considered to be purely hydrodynamic. However, later it was proven that specific interactions between the filler and matrix are very important in imparting the reinforcement [13].

Nanoparticles have been recently used to reinforce elastomers including natural rubber. For example, Stephen et al. have studied the properties of nanocomposites of layered silicates with natural rubber and carboxylated styrene butadiene rubber and their blends [14]. Liu et al. have studied the structure and properties of natural rubber-organoclay nanocomposites prepared by grafting and intercalating method in latex [15]. Indeed, There are other reports in the literature regarding the preparation and characterization of natural rubber-based nanocomposites with various nanofillers [16].

Single-walled carbon nanotubes (SWNTs), the long thin cylinders of carbon, are considered to be unique for their size, shape and remarkable physical and electrical properties. Since their discovery in early 1990's by Iijima [17], considerable effort has focussed on producing functional composite materials with SWNTs [18]. This is because of their outstanding characteristics like high Young's modulus, electrical and thermal conductivity, stiffness, flexibility, large aspect ratio, and chemical inertness [19]. Their mechanical properties, coupled with relatively low density, make SWNTs ideal candidates for weight-efficient structures and for the same reason they are considered to be the ultimate reinforcement in polymer composites. However, the effective utilization of SWNTs in composite applications depends on the ability to disperse them homogeneously throughout the matrix without destroying their integrity [20]. Furthermore, good interfacial bonding is required to achieve load transfer across the filler-matrix interface, a necessary requisite for improving the mechanical properties of the composites. Several recent reports describe the preparation and properties of SWNT-based nanocomposites with elastomers as matrix materials [21]. For example, in a particularly impressive report by Kueseng and Jacob, they have mentioned the mechanical properties of natural rubber-carbon nanotube nanocomposites [22]. They prepared the nanocomposites by incorporating carbon nanotubes in a solution of rubber and subsequently evaporating the solvent. Their report claims that the initial modulus increased by up to 50% relative to pure NR at a nanotube concentration as low as 1.5 phr.

So far there have been no reports in the literature regarding the preparation of natural rubber-SWNT nanocomposites through latex stage mixing. This is studied here, and the effect of incorporation of SWNTs on the mechanical, thermal and electrical conduction characteristics of natural rubber is hereby reported.

EXPERIMENTAL

Materials

Natural rubber latex (dry rubber content (DRC) = 60%, Total Solids Content (TSC) = 61.2%) was purchased from Njavallil Latex, Cochin, India. SWNTs were purchased from CarboLex Inc. (Lexington, USA). They were prepared by an arc discharge method and the average diameter of an individual tube is 1.4 nm and the length in the range of 2–5 μm. Sodium dodecylbenzenesulphonate ($C_{18}H_{29}NaO_3S$, hereafter referred as NaDDBS) was purchased from Loba Chemie. Sodium dodecylsulphate ($C_{12}H_{25}NaO_4S$, hereafter referred as SDS) was purchased from Sisco Research Laboratories. Poly(vinyl alcohol) (PVA) was supplied by Fluka. Isooctyl phenoxy polyethoxy ethanol (commercially known as Criton X-100) and sodium benzoate (C_6H_5COONa) were obtained from Central Drug House. Other compounding ingredients were of commercial grade.

The recipe for NR latex compounding is given in Table 1. Aqueous dispersions of ZnO, ZDC and sulphur (50%) were prepared by ball milling, using stainless steel jars and ceramic balls. These dispersions contain small amounts (~4 wt%) of Sodium methylenebisnaphthalene sulphonic acid (commercially known as Dispersol F), which helps to prevent reagglomeration of the dispersed particles. Potassium oleate was prepared by mixing stoichiometric amounts of potassium hydroxide (dissolved in water) with oleic acid at 75°C.

Table 1: Formulation for NR latex compounding.

Ingredients	**Amount (g)**
Centrifuged latex (60% DRC)	167.0
50% ZnO dispersion	1.0
50% ZDC dispersion	2.0
50% Sulphur dispersion	3.0
10% KOH solution	1.0
10% Potassium oleate solution	1.0
20% Vulcastab VL* solution	1.0

*Vulcastab VL-Polyethylene oxide condensate.

Preparation of the Nanocomposites

Natural rubber latex was compounded as per the formulation given in Table 1. Carbon nanotube dispersions have been prepared using a mechanical probe sonicator (13 mm, VibraCell Processor VC 750, operating at 40% of the maximum power 750 W) by sonicating aqueous suspension of nanotubes for 20 min. Subsequently, the surfactant dissolved in water has been added and further sonicated for 20 min. The nanotube dispersions have been mixed with the compounded latex at various compositions so as to result in SWNT concentrations of 0.5–2.0 phr in NR, and stirred well using a magnetic stirrer for ~30 min so as to achieve uniformity. The samples were cast onto flat glass trays, dried and subsequently cured.

Rheological Experiments

Rheological experiments of the latex systems were carried out using a Haake Viscotester (model VT 550). Coaxial cylinder sensors were used for the measurements. The experiments were done at 25°C over a range of shear rates. Effect of temperature on the viscosity was also studied for two selected compositions.

Mechanical Properties

Dumbbell shaped tensile and angle tear specimens were punched out from the vulcanized sheets and the mechanical properties of NR-SWNT nanocomposites were studied using a Shimadzu Universal Testing Machine (UTM, model-AG1) with a load cell of 10 kN capacity. The gauge length between the jaws at the start of each test was adjusted to 30 mm and the measurements were carried out at a cross-head speed of 500 mm/min. Average of at least six sample measurements represents each data point.

Electrical Conductivity

The room temperature D.C. electrical conductivity of the samples (rectangular strips of dimensions 40 × 15 × 1.8 mm) was measured using a Keithley Nanovoltmeter using a standard four-probe electrode configuration.

Thermal Stability

Thermogravimetric analyzer (TGA Q-50, TA Instruments) was used to study the effect of SWNTs on the thermal stability of NR. Approximately 5 mg of the samples were heated at a rate of 20°C/min from ambient to 700°C. The chamber was continuously swept with nitrogen at a rate of 60 mL/min.

RESULTS AND DISCUSSION

The physical adsorption of surfactants/long chain polymers on SWNTs offers an attractive solution to prevent their agglomeration in solution. The advantage of this method is that it does not involve covalent or ionic interactions on SWNTs [23]. The surfactant or the polymer can either thread themselves onto or wrap themselves around the surfaces of SWNTs and will disrupt the van der Waals interactions which cause SWNTs to aggregate into bundles [24]. The effect of use of these kinds of surfactants has been reported elsewhere [25].

To evaluate the competing stabilization characteristics of SWNT-dispersions, the dispersing power of five different surfactants, sodium dodecyl benzene sulphonate (NaDDBS), sodium dodecyl sulphate (SDS), polyvinyl alcohol (PVA), isooctyl phenoxy polyethoxy ethanol (Criton X-100) and Sodium benzoate has been explored. The first step toward stabilization was to find appropriate concentration ratios of nanotubes to the surfactant. To this end, nanotubes were suspended in water with various surfactant concentrations and sonicated for 20 min. A ratio was reckoned suitable when the nanotubes dispersed and did not reaggregate after sonication. The optimum ratio of nanotubes to the surfactant varied from 1:2 to 1:10 by weight for different surfactants. The SWNT-NaDDBS dispersion was by far the most stable; it remained dispersed for at least six weeks. The optimum ratio in the case of NaDDBS was 1:5. Apparently, most of the surfactant in suspension adsorbed onto the nanotube surfaces as neither sedimentation nor aggregation of the nanotube bundles was observed in this case. By contrast, we were unable to prepare nanotube dispersions that are stable with other additives. It is readily observed that the NaDDBS-nanotube dispersion is homogeneous, whereas the rest contain coagulated bundles of tubes at the bottom of their respective

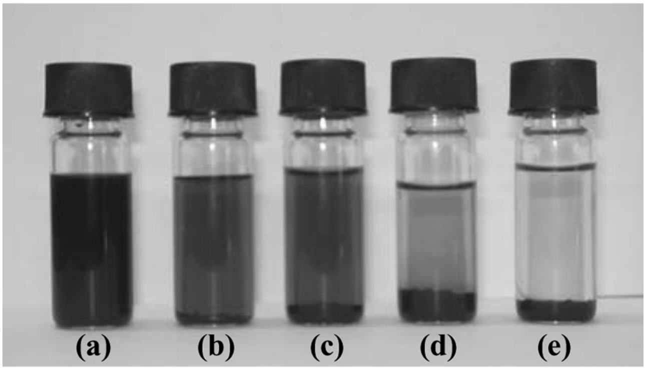

Figure 1: Vials containing aqueous dispersions of SWNTs in (a) NaDDBS, (b) SDS, (c) PVA, (d) Criton X-100, and (e) sodium benzoate (Photograph taken after six weeks of the sample preparation).

containers (Figure 1). Tube stabilization depends on the surfactant molecules that lie on the tube surface parallel to the cylindrical axis. It is assumed that the alkyl chain groups of a surfactant molecule adsorb flat along the length of the tube instead of the diameter. It has been reported that NaDDBS disperses the tubes better than SDS because of its benzene rings, and Criton X100 because of its slightly longer alkyl chain [26].

The properties of natural rubber-SWNT nanocomposites prepared through latex compounding assisted with ultrasound (+surfactant) treatment are summarized in the following sections. Flow properties of the latex compounds are also investigated.

Rheology of Latex Compounds

Rheological behavior of latex compounds is industrially important as far as the manufacturing of latex goods is concerned. There have been many literature reports regarding the rheological properties of various latex systems [27,28]. Understanding the flow behavior of lattices having fillers can even help to study the matrix-filler interaction. In this section, rheological behavior of natural rubber latex containing various amounts of carbon nanotubes is reported with reference to shear rate, concentration of nanotubes and temperature of testing.

Figure 2 presents the plots of viscosity versus shear rate measured at 25°C for the latex compounds at three selected composition of SWNTs. As expected, the viscosity of lattices increases as a function of filler loading over the entire range of shear rate studied. This is attributed to the uniform dispersion of carbon nanotubes, which in turn provides effective polymer-filler interaction, or in other words, reinforcement that occurred in the system in the presence of carbon nanotubes. A higher viscosity reduces the colloidal movement of the latex particles and hence improves colloidal stability. It is also observed from

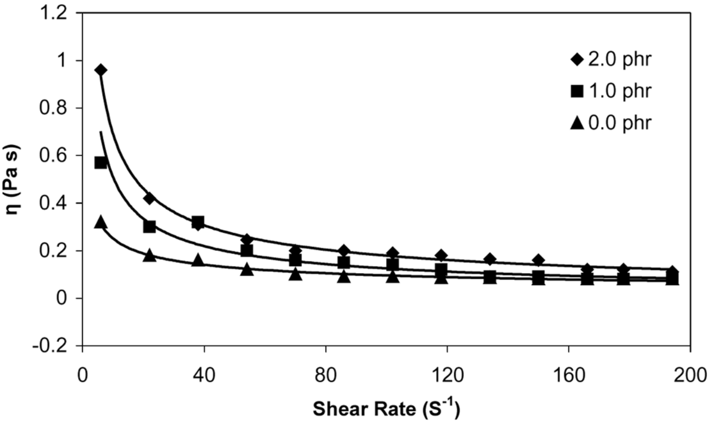

Figure 2: Effect of shear rate on the viscosity of NR-SWNT latex compounds.

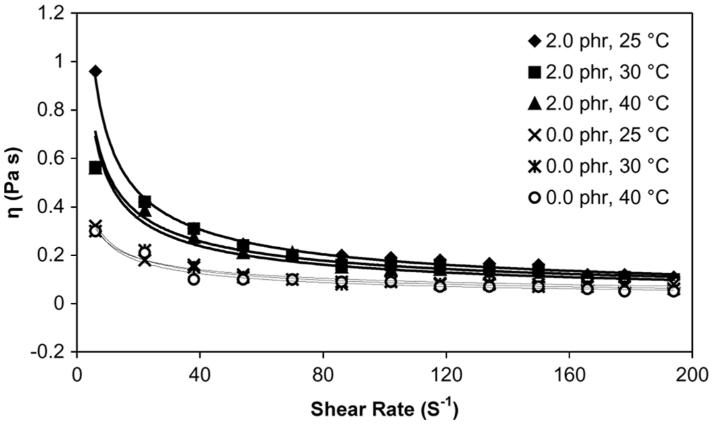

Figure 3: Viscosity vs. shear rate plots at different temperatures.

the figure that the viscosity of the SWNT-reinforced NR latex samples decreases with increase shear rate, representing pseudoplastic nature or, in other words, shear thinning behavior. This effect is more predominant in the case of samples with high filler loadings.

Figure 3 shows the effect of temperature on the viscosity of the latex systems. It is noticeable that the viscosity of the samples decreases with temperature over the entire range of shear rate tested, the effect of which is more predominant in the case of NR-SWNT system than pure NR latex system. These results are in agreement with those reported by Stephen et al. [14] who studied the rheological behavior of latex systems of natural rubber containing layered silicates as nanofillers.

Mechanical Properties

Mechanical properties of our NR-SWNT nanocomposite samples prepared through latex compounding are summarized in Table 2. It is evident from the results that SWNTs significantly increase the strength and modulus of natural rubber. For example, the tensile strength of NR increases by around 56%

Table 2: Mechanical properties of NR-SWNT nanocomposites.

Concn. of SWNTs (phr)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tear strength (N/mm)
0	23.4	1.80	1495.6	32.3
0.5	24.1	1.85	1494.8	32.7
1.0	29.3	1.97	1371.5	34.1
1.5	32.3	2.31	1106.1	37.3
2.0	36.5	2.95	1065.6	41.9

with a nanotube concentration as low as 2.0 phr. The tensile modulus (at 300% elongation) of the NR-SWNT nanocomposite at this concentration is roughly 63% higher than that of pure rubber. However, the elongation at break of the matrix reduces with increasing nanotube loading due to stiffening of the elastomer matrix. Tear strength is also higher by around 30% as compared with pure rubber at SWNT fractions as low as 2.0 phr.

These results are in agreement with those reported by Atieh et al. who dissolved both the nanotubes (by sonication) and the rubber in toluene to prepare the NR-MWNT nanocomposites [29]. Their paper reports a significant improvement in tensile strength and modulus of natural rubber. Varghese et al. also adopted the latex compounding method to prepare natural rubber-based nanocomposites with layered silicates [30]. They observed that the nanocomposites exhibit significant enhancement in mechanical properties and thermal stability relative to pure natural rubber.

Although the mechanisms are not fully understood, there is a general agreement about the basic processes contributing to the reinforcement of filled elastomers [31–33]. In addition to the expected increase in the modulus resulting from the inclusion of rigid filler particles in the soft matrix, another contribution arises from the filler-rubber interactions, leading to additional crosslinks in the network structure. The improved reinforcement observed in NR-SWNT nanocomposites is due to the interaction between SWNTs and the rubber matrix. An essential condition for this interaction is an efficient dispersion of the nanofillers in the matrix, which is accomplished through surfactant-assisted sonication and subsequent latex stage mixing. A good interface between SWNTs and the rubber matrix supports the material to withstand stress. Since SWNTs are extremely strong materials compared to other types of fillers, they are good candidates as nanofillers. Under a load, the matrix distributes the force to SWNTs, which carry most of the applied load.

The mechanical properties of the nanocomposites given in Table 2 indicate that SWNTs are indeed effective in reinforcing natural rubber when incorporated at the latex stage at low loading levels through surfactant-assisted sonication.

Electrical Conductivity

Electrical conducting properties can be imparted to insulating polymers by dispersing electrically conducting particles that may form a conducting network through the sample at concentrations exceeding a certain minimum value called the percolation threshold. This approach reduces the manufacturing and maintenance costs of components as compared with those previously coated with an antistatic paint. The technology is also relevant to other applications where static electrical dissipation is needed such as computer housings or exterior automotive parts. Though carbon black is traditionally

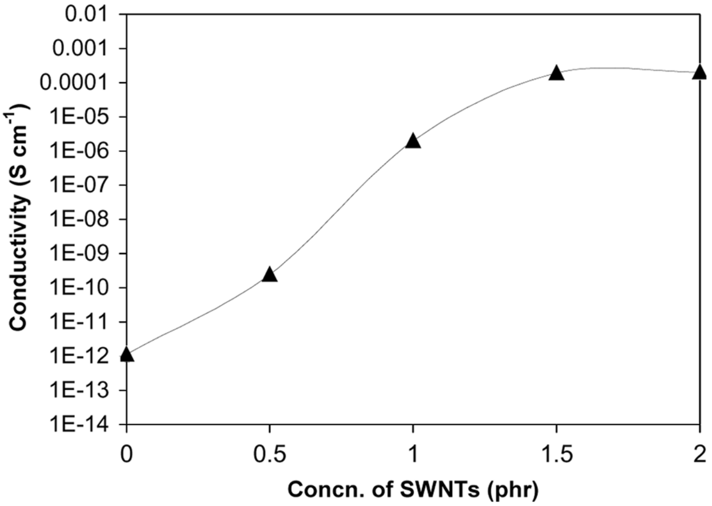

Figure 4: Electrical conductivity of NR-SWNT nanocomposites.

used as the conductive filler, the small diameter and the large aspect ratio of SWNTs has enabled achievement of very low percolation threshold concentrations, presumably depending on the quality of their dispersion. The room temperature D.C. electrical conductivity results of our NR-SWNT nanocomposites are given in Figure 4. It is obvious from the figure that SWNTs are effective in imparting electrical conductivity to the insulating rubber matrix.

The conductivity of pure natural rubber is of the order of $10^{-12}\,\mathrm{S\,cm^{-1}}$. At concentrations exceeding 1.0 phr, the conductivity surpasses the antistatic criterion ($10^{-8}\,\mathrm{S\,cm^{-1}}$) of thin films, with an order of magnitude of $10^{-6}\,\mathrm{S\,cm^{-1}}$ and reaches percolation with a value above $10^{-5}\,\mathrm{S\,cm^{-1}}$ at SWNT fractions exceeding 1.5 phr. These results are in good agreement with literature reports that are concerned with the carbon nanotubes-induced electrical conductivity in various insulating polymer matrices [34]. It is also well known that the percolation threshold is sensitive to the polymer matrix in which the nanotubes are dispersed [35]. This effect is due to the enhanced role of interfacial properties in the case of nanocomposites.

Thermal Stability

The effect of nanoparticles on the thermal stability of various polymers has been reported elsewhere [36,37]. Since the thermal stability of elastomer-based composites is critical as far as their application potential is concerned, we have investigated the effect of carbon nanotubes on the thermal stability of natural rubber. TGA plots of pure NR and NR-SWNT nanocomposites prepared through latex compounding are given in Figure 5. The results

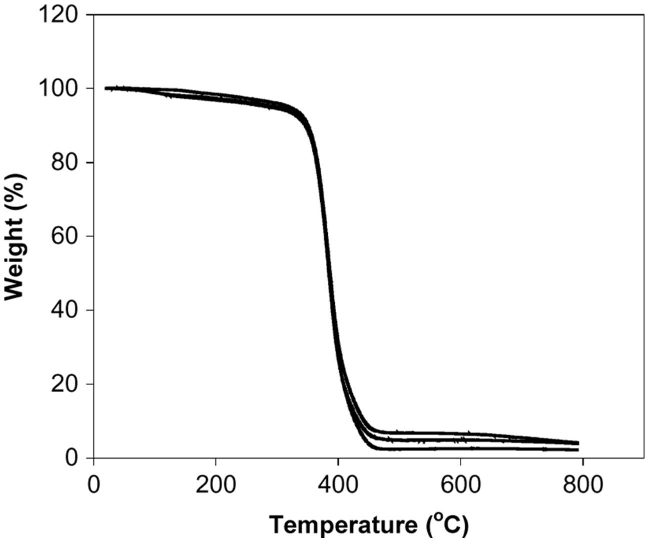

Figure 5: Temperature dependence of the weight loss characteristics (TGA) of pure NR (lowest curve) and NR-SWNT nanocomposites (1.0 and 2.0 phr).

indicate that the presence of SWNTs at low weight fractions has no significant effect on the thermal stability of natural rubber.

CONCLUSIONS

Natural rubber/single-walled carbon nanotube composites have been prepared through latex compounding. SWNTs dispersed in water through ultrasonication and stabilized with an added surfactant were found to uniformly mix with natural rubber latex. Rheological characterization of the carbon nanotubes-filled NR latex samples revealed that they exhibit a pronounced shear thinning behavior. SWNTs were found to provide effective reinforcement to the NR matrix at very low loading levels when incorporated at the latex stage followed by the latex compounding and subsequent curing. They were also found to impart electrical percolation to the insulating NR matrix at low weight fractions. The thermal stability of natural rubber remained unaffected with SWNTs at concentrations of up to 2.0 phr.

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