RADIATION VULCANIZATION OF NATURAL RUBBER LATEX LOADED WITH CARBON NANOTUBES

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Abstract: The radiation vulcanization of natural rubber latex (NRL) has been carried out with 150 keV electrons beam with the presence of carbon nanotubes. The NRL/CNTs were prepared by using solving casting method by dispersing carbon nanotubes in a polymer solution and subsequently evaporating the solvent. The load of the carbon nanotubes in the rubber was varied from 1–7wt%. Upon electron beam irradiation, the tensile modulus of the nanocomposites increases with the increase of carbon nanotubes content up to 7wt%. The nanotubes were dispersed homogeneously in the SMR-L matrix in an attempt to increase the mechanical properties of these nanocomposites. The properties of the nanocomposites such as tensile strength, tensile modulus, tear strength, elongation at break and hardness were studied.

Keywords: Carbon nanotubes, Nanocomposite, Natural rubber, Radiation vulcanization

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1. INTRODUCTION

Research on new materials technology is attracting the attention of researchers worldwide. Developments are being made to improve the properties of the materials and to find alternative precursors that can confer them desirable properties. Great interest is recently being shown in the area of nanostructured carbon materials that are attaining considerable commercial importance since the discovery of buckminsterfullerene, carbon nanotubes and carbon nanofibers. In this context, carbon nanotubes (CNTs) exhibit unique mechanical, electronic and magnetic properties, which have been the subject of a large number of studies (1–3). CNTs are probably the strongest substances that will ever exist with a tensile strength greater than steel but with only one-sixth of its weight (4). Iijima discovered, for the first time, carbon nanotubes using the arc discharge method (5, 6). Subsequently, other methods have been used such as laser vaporization (7) and catalytic chemical vapor deposition of hydrocarbons (8–10). Since carbon–carbon covalent bonds are among the strongest bonds in nature, a structure based on a perfect arrangement of these bonds oriented along the axis of nanotubes would produce an exceedingly strong material. Nanotubes are strong and resilient structures that can be bent and stretched into shapes without catastrophic structural failure in the nanotube (11, 12). The Young’s modulus and tensile strength rival that of diamond (1 Tera Pascal and ~200 Giga Pascal, respectively) (13–16). This fantastic mechanical strength allows these structures to be used as possible reinforcing materials. Just like current carbon fiber technology, it is expected that CNTs could provide the polymer matrix a better comprehensive performance due to their unique and excellent mechanical and physical properties. Various nanocomposite materials with high ability for absorbing the applied load were developed (17, 18). Initial experimental work on carbon nanotube-reinforced rubber has demonstrated that a large increase in effective modulus and strength can be obtained with the addition of small amounts of carbon nanotubes. However, comparing the many studies on the applications of CNTs in other polymers, there are fewer works dealing with the applications of CNTs in rubbers for reinforcement (19–24). Currently, the natural rubber (NR) vulcanized has a wide range of properties of great interest from a technological point of view, such as mechanical, damping, dynamic fatigue resistance, heat and age resistance, low temperature flexibility, compression set, swelling resistance and electrical properties (25–29). It has been recognized that the filler and polymer play an equally important role in governing the rubber properties. Carbon black fillers are functional materials or components that have a significant effect on rubber performances and properties by the changes of the morphology and the increase in polymer-filler
interaction. They are used to achieve the level and range of properties to provide an adequate amount of reinforcement such as tensile strength, abrasion resistance and tear resistance. They are most often looked upon as quality enhancing and not as cost-cutting materials. In order to achieve a high level of reinforcement, the amount of carbon black filler loading has to be increased substantially, and it is not possible to enhance all of these properties to the same optimal degree (30–35).

The vulcanization is a process that transforms the predominantly thermoplastic or raw rubber into an elastic or hard ebonite-like state. This process is also known as “crosslinking” or “curing” and involves the association of macromolecules through their reactive sites. The key chemical modification is that sulfide bridges are created between adjacent chains, as shown in Figure 1 (36).

The crosslinking imparts various properties to rubber. It improves its tensile strength, becomes more resistant to chemical attack and is no longer thermoplastic. It also makes the surface of the material smoother, prevents it from sticking to metal or plastic chemical catalysts and renders it impervious to moderate heat and cold. In addition, it is a good insulator against electricity and heat. These attractive physical and chemical properties of vulcanized rubber have revolutionized its applications. This heavily cross-linked polymer has strong covalent bonds, with strong forces between the chains, and is therefore an insoluble and infusible thermosetting polymer (36).

Natural rubber is sticky and nonelastic by nature. Crosslinking is a reaction of polymers to form a three-dimensional network. Crosslinking of rubber results in the vulcanization which makes it more elastic. When the NR is irradiated by high energy radiation, hydrogen atoms of the trunk chain, mainly of methylene group’s proportional to double bonds, are ejected and radical sites are formed, and these radical sites are combined into C-C crosslink (see Figure 2).

The addition of NR radicals to unsaturated C=C bond provides formation of crosslinks. However, the radiation crosslinking efficiency of NR is not high. This is believed to be due to the loose packing of NR molecules with the cis structure and the presence of methyl group (36).

The most important vulcanization agent for rubber is sulfur. Various concentrations of sulfur are used to manufacture different kind of rubber compounds. For every 100g of rubber, a dosage of 0.25–5.0g of sulfur is

![Figure 1. Vulcanization — formation of sulfide bridges between adjacent chains (36).](image-url)
used for the preparation of soft rubber goods, while for hard rubber compounds the sulfur concentration is 25.0–40.0g. The rubber compounds produced with a dosage of 5.0–25.0g have poor strength and elastic properties and are of less importance for most applications. For conventional vulcanization, one uses 1.5–2.5g sulfur with 0.5–1.0g accelerator. If the content of the accelerator is increased, the sulfur content has to be decreased to achieve the same crosslink density, as a result of which the crosslinks with low sulfur content are formed. The sulfur used for the vulcanization process should be at least 95% pure (ash content < 0.5%) devoid of SO₂ (37). The vulcanization specifications usually require accelerator systems that have insufficient scorch safety, toxic materials, short vulcanization times or high processing temperatures; one often needs to retard the initiation of vulcanization (scorch time) to ensure sufficient processing safety (39).

Radiation technology has emerged as one of the foremost techniques for the processing of polymer materials. It has been an area of enormous interest in the last few decades. Irradiation can induce reactions in polymers, which may lead to polymerization, crosslinking, degradation and grafting. Crosslinking is a reaction where polymer chains are joined and a network is formed. Natural rubber can be crosslinked by irradiation. When a polymer is subjected to high energy radiation such as gamma rays and accelerated electron beams, it may undergo various effects such as formation of free radicals, formation of hydrogen and low molecular weight hydrocarbon, increase in saturation, formation of C – C bonds between molecules, cleavage of C – C bond (chain scissoring), breakdown of crystalline structure, coloration and oxidation, all of which can lead to crosslinking or degradation of the polymer depending on its structure and irradiation conditions. Most polymers fall into two distinct classes: the ones which crosslink and the ones which degrade. Table 1 shows the classification of some polymers into the two groups when the polymer is irradiated at ambient temperature in a vacuum. In the presence of oxygen, oxidative degradation might occur (37).

The radiation vulcanization of NR latex (RVNRL) is an emerging technology in which radiation is used in place of sulfur in the...
conventional prevulcanization process for the manufacture of dipper NR latex products. This technique has been under investigation since the late 1950s (37). The main components of NR latex are NR and water. Radiation vulcanization of NR latex involves radiation-induced cross-linking of macroscopic particles of NR dispersed in the aqueous medium. Upon radiation, both NR molecules and water molecules absorb radiation energy independently (38). The radiolysis products of water are diffused into NR particles and react with NR molecules. The OH radicals, H radicals and hydrated electron formed are involved in the radiation induced crosslinking of NR latex. The products obtained have noticeable advantages over the conventionally vulcanized natural rubber latex due to the absence of the carcinogenic nitrosamines derived from the common accelerators of the sulfur vulcanized natural rubber latex. Due to radiation decomposition of NR latex proteins, the amount of extractable proteins in RVNR is greater than in conventional sulfur vulcanizate (39, 40).

To the best of our knowledge, no reports on standard Malaysian rubber latex/carbon nanotubes nanocomposites exist in the literature. In this work, results on the preparation and mechanical studies of standard Malaysian rubber latex (SMR-L)/multi-walled carbon nanotubes nanocomposites are presented. The properties such as tensile strength, tensile modulus and elongation at break are also reported.

2. EXPERIMENTAL

2.1. Production of Carbon Nanotubes

High purity multi-walled carbon nanotubes were produced by using a chemical vapor deposition technique. The procedure of the production of CNTs was reported by Muataz et al. (41). The produced carbon nanotubes were characterized by using Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM).

2.2. Preparation of Carbon Nanotubes/SMRL Nanocomposites

The carbon nanotubes were added to standard Malaysian rubber latex (SMR-L) as nanofiller. The preparation of the nanocomposites was carried out by a solvent casting method using toluene as a solvent.

The first phase involved the dissolution/dispersion of CNTs in toluene in order to disentangle the nanotubes that typically tend to cling together and form lumps, which become difficult to process. The required quantity of carbon nanotubes was added to a specific amount of toluene.
The solution was further sonicated using a mechanical probe sonicator (Branson sonifier) capable of vibrating at ultrasonic frequencies to induce an efficient dispersion of nanotubes. For this study, CNT solutions, containing CNTs in various weight ratios, were prepared.

The added amounts of the carbon nanotubes were 1, 4 and 7 wt% of 50 grams of the total weight.

i) 1 wt% (0.5 g) of CNTs in 50 ml of toluene solution
ii) 4 wt% (2.0 g) of CNTs in 50 ml of toluene solution.
iii) 7 wt% (3.5 g) of CNTs in 50 ml of toluene solution.

In the second stage, the rubber was dissolved in toluene and the desired weight ratio obtained by dissolving 50 g of rubber in 600 ml of solvent. The final step involved the thorough mixing of the solutions prepared in the first and second stages, resulting in a solution consisting of a good blend of nanotubes in the rubber. The solution was then poured onto a plate and the toluene evaporated to afford the nanocomposite samples.

2.3. Radiation Vulcanization of the Carbon Nanotubes/SMRL Nanocomposites

About 22–23 g of CNT/SMR-L nanocomposite samples were molded using Labtech hot and cold press under high pressure of 14.7 MPa at 150°C for 8 minutes. The samples were compression molded into uniformly flat sheets of 140 mm × 140 mm × 1 mm. They were cut according to BS6746 standards with 1 mm thickness measured using a micrometer gauge and were irradiated using a 3 MeV electron beam accelerator at a dose of 150 kGy. The acceleration energy and beam current were 2 MeV and 2 mA, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Carbon Nanotubes

A high purity of multi-walled carbon nanotubes were achieved with a chemical vapor deposition (CVD) technique. The produced carbon nanotubes were observed by using FE-SEM and TEM. The diameter of the produced carbon nanotubes were varied from 20–40 nm with the average diameter at 24 nm, while the length of the CNTs was up to few microns. Figure 3(a) shows the SEM image of carbon nanotubes at low magnification, and figure 3(b) shows the SEM image of carbon nanotubes at high magnification. From the SEM observation, the product is pure and only carbon nanotubes were observed.
TEM was carried out to characterize the structure of nanotubes (Figure 4). To prepare TEM samples, some alcohol was dropped on the nanotubes films, then these films were transferred with a pair of tweezers to a carbon-coated copper grid. It is obvious from the images that all the nanotubes are hollow and tubular in shape. In some of the images, catalyst particles can be seen inside the nanotubes. TEM images indicate

**Figure 3.** SEM Images of carbon nanotubes at (a) at low resolution (b) at high resolution.

**Figure 4.** TEM Images of carbon nanotubes (a) at low resolution (b) at high resolution.
that the nanotubes are of high purity, with uniform diameter distribution and contain no deformity in the structure. Figure 4(b) shows the High Resolution Transmission Electron Microscope (HRTEM) of the carbon nanotubes and that a highly ordered crystalline structure of CNT is present.

3.2. Effect of CNTS on the Stress-Strain Value of SMRL with and without Radiation Vulcanization

The results obtained for the mechanical strength of the nanocomposites of rubber with different percentages (1, 4 and 7wt%) of pure carbon nanotubes compared to natural rubber of SMRL are shown in Figure 5. The stress-strain curve indicates that the strength of the rubber nanocomposites at 7wt% of CNTs is approximately 6 times that of natural rubber.

The tensile strength increased significantly as the amount of CNTs concentration increased. The general tendency was that the strain level decreased and the stress level increased by the addition of CNTs, which

![Stress/Strain (Without vulcanization)](image)

**Figure 5.** Stress/Strain curve of SMR-L with different percentage of CNTs without vulcanization.
appears to play the role of reinforcement. Under load, the matrix distributes the force to the CNTs, which carry most of the applied load. The observed reinforcing effect of CNTs makes them good candidates as nanofillers.

The results obtained for the mechanical strength of the nanocomposites of rubber compared to natural rubber of SMR-L with an irradiation dosage of 150kGy are shown in Figure 6. The strength of irradiated nanocomposites of rubber with 7wt% of CNTs is almost 1.8 times that of irradiated natural rubber. The radiation vulcanization has a marked effect on the tensile strength of the nanocomposites. However, the effect of the addition of CNTs in increasing the tensile strength is not significant, and the CNTs appear to play the role of an additive in the rubber only. If we compare the stress-strain curve of an irradiated CNT/SMRL with that unirradiated at 7wt%, the strength increases almost 6 times; if we compare irradiated CNT/SMRL with the blank rubber the strength increases 38 times due to the crosslinking of the carbon atoms in the rubber with carbon nanotubes.

As the tensile strength increases for both irradiate and unirradiate nanocomposites, the elongations are expected to drop as shown in Figures 5 and 6. However, the elongation of unirradiate nanocomposites seems to be less affected compared to irradiate nanocomposites, which show considerable drops in elongation up to 50%.

Figure 6. Stress/Strain curve of SMR-L with different percentage of CNTs at 150kGy irradiation dosage.
3.3. Effect of CNTS on the Young’s Modulus of SMRL with and without Radiation Vulcanization

The stiffness measured of an isotropic elastic material is called Young’s modulus (E). It is also known as the Young modulus, modulus of elasticity, elastic modulus (though Young’s modulus is actually one of several elastic moduli such as the bulk modulus and the shear modulus) or tensile modulus. It is defined as the ratio of the stress over the strain in which Hooke’s Law holds. This can be experimentally determined from the slope of a stress-strain curve created during tensile tests conducted on a sample of the material (42).

Young’s modulus, $E$, can be calculated by dividing the tensile stress by the tensile strain:

$$E = \frac{\text{tensile stress}}{\text{tensile strain}} = \frac{\sigma}{\varepsilon} = \frac{F/A_0}{\Delta L/L_0} = \frac{FL_0}{A_0\Delta L}$$

where $E$ is the Young’s modulus (modulus of elasticity), $F$ is the force applied to the object, $A_0$ is the original cross-sectional area through which the force is applied, $\Delta L$ is the amount by which the length of the object changes and $L_0$ is the original length of the object.

The Young’s Modulus of the nanocomposites with and without radiation vulcanization normalized with that of the pure matrix (SMR-L) is presented in Figure 7. As shown in Figure 7, the Young’s Modulus values increase with the increase in CNTs content in both cases, leading to an increase in the degree of stiffness of the nanocomposites. Both nanocomposites exhibit the same trend with increasing CNTs content. This clearly indicates that the intercalation of CNTs into the SRML layers has improved the compatibility of the two materials and resulted in increase in tensile strength.

3.4. Effect of CNTS on the Energy Absorption of SMRL with and without Vulcanization

Figure 8 shows the toughness of the CNT/SMRL nanocomposites with and without radiation vulcanization and considers the amount of energy required to fracture the material. Since strength is proportional to the force needed to break the sample, and strain is measured in units of distance (i.e., the distance the sample is stretched), then strength times strain is proportional to force times distance which in turn equals to energy.

$$\text{Strength} \times \text{strain} \sim \text{force} \times \text{distance} = \text{energy absorption}$$

The samples with 1, 4, and 7wt% showed a general trend of increase in stiffness with an increase in energy, which was 0.17, 0.328, and 0.395 J,
respectively, compared with that of pure natural rubber (0.09 J) for unirradiated samples. For irradiate samples the energy absorption was 3.3376, 3.5225 and 4.1840 J, respectively, compared with that of irradiated natural rubber (3.1612 J). The same phenomenon was observed for the energy absorption as function of the CNTs. If we compare the energy absorption curve of an irradiated CNT/SMRL with that unirradiated at 7wt% the energy required to fracture the sample is almost 11 times, while if we compare irradiated CNT/SMRL at 7wt% with the blank rubber the energy required to fracture the sample increase 47 times due to the crosslinking of the carbon atoms in the rubber with carbon nanotubes. This can be attributed to the reinforcing property of carbon nanotubes, which in turn increases the strength of the rubber.

4. CONCLUSION

In summary, we have demonstrated the successful fabrication of nanocomposites consisting of standard Malaysian rubber latex (SMR-L) with 1–7wt% of multi-walled carbon nanotubes. Carbon nanotubes
were applied as an interface nano-reinforcement in advanced commercial carbon/rubber composite. This is the first attempt such a work is reported. The preparation of the nanocomposites was carried out by a solvent casting method with toluene as a solvent. It is clear shows that the maximum stress of pure SMR CV60 is 0.2839 MPa. With the addition of 1wt% of CNTs to the unirradiated rubber, the stress level for the nanocomposite material increased from 0.2839 MPa to 0.56413 MPa. Addition of the CNTs to the natural rubber increased the stress level gradually as shown in Figure. At 7wt% of CNTs, the stress value obtained reached 1.7 MPa which is 6 times that of pure natural rubber. The result indicates that by increasing the amount of CNTs into the rubber, the ductility decreased and the material become stronger and tougher but at the same time more brittle. The clear trend observed here is that as the nanotube amount increases, the fiber breaking strain decreases. The physical and mechanical properties of radiation-induce crosslinking of natural rubber CNTs composites improved due to the presence of nanosized CNTs in the natural rubber matrix. It is clear shown that by using radiation process at 150 kGy there is tremendous increase in the mechanical properties of the SMRL with CNTs. If we compare the stress-strain curve of an irradiated CNT/SMRL with that

Figure 8. The toughness as a function of wt% of CNTs with and without radiation vulcanization.
unradiated at 7wt%, the strength increases almost 6 times. If we compare irradiated CNT/SMRL with the blank rubber the strength increases 38 times due to the crosslinking of the carbon atoms in the rubber with carbon nanotubes.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the King Fahd University for Petroleum and Minerals (KFUPM) and International Islamic University Malaysia (IIUM) for their support of this study.

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