Research Article

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Impact of a nanomixture of carbon black and clay on the mechanical properties of a series of irradiated natural rubber/butyl rubber blend

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Abstract: A series of natural rubber/butyl rubber NR/IIR blend loaded with N660 carbon black (CB) and triethoxy vinyl silane treated clay nanoparticles (TCNPs) were prepared using gamma irradiation in the presence of a polyfunctional monomer, trimethylolpropane triacrylate (TMPTA). The effect of incorporating different contents of N660 CB and five parts per hundred of rubber (phr) of treated clay on the mechanical properties of the prepared nanocomposites has been investigated. The addition of TCNP to CB/rubber composites markedly increase their tensile strength due to the increase of the cross-link density. These results indicated that the TCNP may be enclosed or trapped in the occluded structure of CB. The effect of CB and the TCNP content on the tensile strength (σ), elongation at break (ϵ_b , %), and modulus of elasticity (E , MPa) of natural rubber/butyl rubber NR/IIR blend have been investigated. The incorporation of 5 phr of TCNP into 30 phr CB-loaded NR/IIR composites results in the increased tensile strength value by about 60%. Finally, theoretical models were used to interpret the experimental results.

Keywords: rubber, nanocomposites, radiation, mechanical properties, theoretical modeling

1 Introduction

Blending of polymers provides an attractive way for producing new materials and have peerless combinations of properties not available in a monopolymer (1). Co-continuous

polymer blends may have a number of beneficial properties that make it possible to be used in various potential applications (2). Some of the beneficial properties of co-continuous polymeric blends include controlled electrical conductivity, synergistic mechanical properties, or selective permeability (3–5). One of the methods to enhance the mechanical properties of polymeric materials is the incorporation of structure particulate fillers like carbon black (CB), graphite, silica, etc. CB-reinforced filler is the most often used. Composites containing conductive CB dispersed in various polymeric matrixes have been developed and their properties have been studied extensively (6–8).

One of the most ultimate properties of polymeric materials is the possibility of developing their physico-mechanical properties by the manipulation of their design, specifically of their nanoscopic structures. Where combine both of organic and inorganic materials can be formed a nanocomposite with high performance such as hardness, strength, stiffness, and thermal stability, which is different than any other current compounds (9). Since the inorganic fillers have strong reinforcement ability concerning their particle aspect ratio, frequently used particulate inorganic fillers are bentonite and clay mineral (10). When a particular formularization for physicomachanical or engineering applications is chosen, it is very important to distinguish the precept factors concerned with stability and degradation in material planning (11–14). For example, irradiation of polymers causes permanent structural modifications such as crosslinking (15–18), end linking, and chain scission resulting in volatile degradation products that affect the molecular weight distribution (19). Recently, the use of radiation technology in polymer processing received a great deal of interest for numerous reasons, including radiation-induced cross-linking type polymers, low cost of curing or processing, and the green technology. It is recognized that the exposure of these types of polymers to ionizing radiation such as gamma rays and accelerated electrons provides increased stability and ameliorated physicomachanical properties (18,20–23).

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Polyolefins, such as natural rubber (NR) and butyl rubber (IIR) elastomers, are capable of forming intermolecular junctions when subjected to ionizing radiation either in pristine or compounded state (24). These types of materials (polyolefins) have a range of features so that they are widely used in industrial applications. For example, IIR has remarkable gas resistance and moisture (water and steam) permeation. It also has superior resistance to alkalis, certain solvents such as ketones and alcohols, abrasion, and flexing, while NR is widely used where low or normal (not high) oxidizing types of bases and acids are present.

In this paper, polyfunctional monomers, trimethylolpropane triacrylate (TMPTA), was chosen to sensitize radiation vulcanization of NR/IIR rubber blends. The effect of triethoxy vinyl silane (TEVS) treated clay nanoparticles on the mechanical properties of 50/50 NR/IIR blend has been investigated. Due to our familiarity, no investigation or reports were investigated on the effect of treated nanoclays on the mechanical properties of NR/IIR blend loaded with N660 CB that was cured by ionizing radiation.

2 Experimental

2.1 Materials

NR, IIR, and general-purpose furnace (GPF, N660) CB were supplied by Transport and Engineering Co. (TRENCO), Egypt. Highly fine clay (bentonite, BE125) was supplied by Spectrum Chemicals & Laboratory Products, USA. Radiation coagent, namely trimethylolpropane triacrylate (TMPTA, multifunctional monomer, density = 0.936), was supplied by Alnasr Chemicals Co., Egypt. TMPTA was used as multifunctional low molecular weight radiation sensitizer and used without further purification. Triethoxy vinyl silane (silane coupling agent, TEVS) (b.p.: 160–161°C) was obtained from Aldrich Chemical Company Inc., Germany. The basic characteristics of bentonite and N660 are given in Table 1.

2.2 Modification of clay

The modification of clay fillers was done by silylation reaction. The modified clay was prepared using a shear mixer. Firstly, pristine clay was heated at around 130°C in an oilbath heating iron container to remove the moisture

Table 1: Characteristics of bentonite and carbon black

Materials	Parameter	
Carbon black GPF (N660)	Mean particle size (nm)	62
	Pour density (g/cc)	0.47
	Iodine adsorption	26
	DBP ^a adsorption (cc/100 g)	87
	N ₂ surface area (m ² /g)	27
	Ash (% max)	0.1
	Mean particle size (nm)	100
Bentonite (montmorillonite)	Purity	>98%
	Quartz content (crystalline silica)	<2%
	Pour density (g/cc)	2.5–2.6

^a Dibutyl phthalate.

from the clay powder, and then a suitable amount of TEVS (3 wt%) in 100 mL of acetone was used to hydrolyze the reaction under continuous stirring for 1 h. Then, the silylation reaction was carried out by pouring the hydrolyzed TEVS into the clay dispersion under vigorous stirring for 24 h at room temperature. Then, the blend was sheared for 1 h at a shearing temperature of 170°C and a rate of 4,000 rpm. Finally, the modified clay was poured into molds for later experiments. The modified clay was then left in a vacuum oven at 110°C for 24 h. The dry fillers were then ground into very fine powder.

2.3 Compounding and irradiation of the samples

Rubber blends (blend ratio: 50/50 wt%) of NR and IIR were blended using Brabender Plasticorder (Model PLE-330, mixing chamber Model W50-EHT, chamber volume: 50 cm³, mixing temperature: 70°C, mixing speed: 40 rpm) for 7 min. Afterward, CB was added and mixed for 3 min and then the treated clay was added into the rubber and was mixed for 3 min and finally TMPTA was added and mixed for 2 min. The sample designations are tabulated in Table 2. The gradient is presented in parts per hundred of rubber by weight (phr). The obtained compound master batch (final mixing) was then passed through a two-roll mill three times. The sheets were compression molded at 5 MPa pressure and 110°C and in an electrically heated press for 3 min to obtain uniform sheets of thickness ≈ 2 mm. The molded samples, in the form of thin sheets, were irradiated at 50 kGy dose (25) by ⁶⁰Co γ-irradiation at a dose rate of 7.75 kGy/h at 40°C. The ⁶⁰Co γ-source model GB150 type B was manufactured by the

Table 2: Sample designation and compounding

Designation	Ingredient (phr)				
	NR	IIR	clay	CB	TMPTA
B0	50	50			4
B10	50	50		10	4
B20	50	50		20	4
B30	50	50		30	4
B50	50	50		50	4
B10/5	50	50	5	10	4
B20/5	50	50	5	20	4
B30/5	50	50	5	30	4
B50/5	50	50	5	50	4
N30	100	0	0	30	4
II30	0	100	0	30	4
N30/5	100	0	5	30	4
II30/5	0	100	5	30	4

AEA, Canada, and located at National Center for Radiation Research and Technology, Cairo, Egypt.

2.4 Measurements of mechanical properties

The stress–strain of the filled irradiated NR/IIR composites were measured using a tensile testing machine, type H10KS, at 5 mm/min displacement speed. Three samples per formulation were tested. The tensile machine automatically gives values of the tensile strength, elongation %, and Young's modulus.

3 Results and discussion

3.1 Morphology and chemical properties of CB and clay nanoparticles

Transmission electron microscope (TEM) and scanning electron microscope (SEM) provide accurate information about the distribution of nanomixture CB and clay components in internal rubber blend structures. Figure 1a shows the SEM image of clay having peel morphology and layers that give the clay ability to intercalate with CB, which can easily substantiate inside the rubber matrixes. Figure 1b and c show the SEM and TEM images of CB, respectively. The CB appears in spherical shape (nanoscale less than 50 nm) and there is tendency to aggregate structures, as shown in Figure 1c. Interestingly, in Figure 1c, the appearance of the CB structure is found to be more aggregated and collapsed; the powder sample is used in

the SEM technique while suspension particles are used in the TEM technique. In Figure 1d, it is observed that there is very good distribution of both CB particles and NC particles and are intercollected well on the rubber blend. This is possibly due to the small size of clay associated with CB particles. In this case, the reinforcement effect of CB is due to well dispersion of CB in the rubber matrix. More precisely, the increased addition of clay enhances the possibility of CB itself to get inserted within the rubber chains. The surface of CB/nano clay rubber composites is very smooth. Figure 1e shows the FTIR of clay and its modification; as seen in the FTIR, the peak of the OH groups located at 3,150/cm was shifted to 3,282/cm and became wider after the modification process. This confirms that the modification process of clay has taken place.

3.2 Effect of CB loading on the mechanical properties

The stress–strain measurements are most important to determine the characteristics of elastomers. The elastic energy stored in an elastomer as a result of distortion or deformation under the influence of an applied stress is of great interest for scientists. The stress–strain characteristics of radiation cross-linked NR/IIR blend are illustrated in Figure 2, as a function of the GPF CB content. The tensile strength (σ), elongation at break (ϵ_b , %), and modulus of elasticity (E , MPa) obtained from Figure 2 are presented in Table 3. The modulus of elasticity was obtained from first few points of each curve. E and σ of the NR/IIR blend increased with the increasing GPF content due to the strong polymer chains/CB filler interactions and/or between filler and filler. In fact, the molecular mobility decreases with increase in the reinforcing filler loading and leads to the formation of physical bonds between incorporated fillers and the polymer chains. On the other hand, the presence of filler particles decreases the elongation at break gradually, as expected, because it restricts the macromolecular chain elongation of the rubber matrix (26).

3.3 Effect of nanoclay on the mechanical properties

The effect of TCNP loading on the mechanical properties of rubber-CB composites was investigated using montmorillonite, which was mixed with the GPF filled at 5 phr loading. The stress–strain curves are shown in Figure 3, which elucidate

Figure 1: (a) SEM photomicrograph of clay and (b) CB. (c) TEM photomicrograph of CB, (d) SEM photomicrograph of the CB/clay blend rubber surface, and (e) FTIR of clay and modified clay.

the reinforcing effect of the nanoclay. The mechanical parameters obtained from Figure 3 are presented in Table 3. A pronounced increase in the tensile strength and modulus in clay-filled CB/rubber composites with respect to the samples containing similar doses of CB was observed. The ratio of the σ value of the TCNP loaded composites with respect to that of the CB/composite is always higher than 1. On the other hand, the modulus increases and the elongation at break decreases with incorporation of the nanofiller clay. The incorporation of 5 phr of montmorillonite clay enhances the modulus by 15%, 1%, 40%, and 80% and tensile strength by 17%, 32%, 60%, and 53% for 10, 20, 30, and 50 phr CB

loaded rubber, respectively. In conclusion, the addition of 5 phr of TCNP to 30 phr N660 CB filled NR/IIR (50/50 wt%) sample increased its tensile strength value by about 60%.

3.4 Effect of nature of fillers on the single-phase rubber

As good reinforcement has been obtained as a result of incorporating 30 phr of CB and 5 phr of the treated clay, it is interesting to study the effect of these concentrations on the mechanical properties of both NR and IIR. The

Figure 2: Stress–strain curves of carbon black-filled NR/IIR composites.

Table 3: Mechanical properties of unfilled and filled nanocomposites

Sample	E (MPa)	σ (MPa)	ϵ_b (%)	η (mol/kg)
B0	0.047	1.5	68	797
B10	0.086	10.0	156	1,300
B20	0.1	11.0	132	1,729
B30	0.15	12.7	109	2,303
B50	0.2	15.0	98	3,100
B10/5	0.099	11.7	142	1,565
B20/5	0.11	14.6	132	1,824
B30/5	0.211	20.4	105	3,399
B50/5	0.36	22.9	81	6,104
N30	0.113	21.4	214	2,224
I130	0.095	14.5	188	1,553
N30/5	0.375	31.9	113	6,207
I130/5	0.178	17.2	117	2,907

Figure 3: Stress–strain curves of TCNP-filled carbon black/rubber composites.

stress–strain curves of 30 phr GPF and 30 phr GPF and 5 phr of the treated clay-filled NR are shown in Figure 4. The values of ϵ_b (%), σ (MPa), and E (MPa) are reported in Table 3. The addition of 5 phr of TEVS-modified nanoclay into 30 phr CB-filled NR increases the tensile strength from 21.4 to 31.9 MPa (49% increase) and modulus from 0.11 to 0.37 MPa (236% increase). The elongation at break decreases from 214% to 113% with the addition of modified nanoclay. On the other hand, the addition of 5 phr of treated clay into 30 phr N660-filled IIR improves the tensile strength from 14.5 to 17.2 MPa (18% increase) and modulus from 0.095 to 0.178 MPa (87% increase), while the elongation at break decreases from 188% to 117%. These results indicate that the long-chain silane modifiers facilitate the rubber chains to intercalate. The organoclay interact well with both polar NR and nonpolar IIR. It is well known that the mechanical properties depend mainly on polymer–filler and filler–filler interactions (27).

3.5 Crosslinking density (η)

Physical qualification of cross-linked nanocomposites can be characterized by determining its volume average cross-link density. The average cross-link density (η) of elastic materials can be determined from mechanical or swelling investigations. The cross-linking density values of the IIR, NR, and their blends loaded with different fillers have been calculated by using the relation (28):

$$\eta = \frac{F}{2 A_0 \rho_p RT \left(\lambda - \frac{1}{\lambda^2} \right)} \quad (1)$$

Figure 4: Stress–strain curves of different rubbers containing various fillers.

where $\sigma = F/A_0$, $\lambda = \varepsilon + 1$ is the extension ratio, ρ_p is the density of the tested sample, R is the universal gas constant, A_0 is sample cross-sectional area, and T is the absolute temperature. The cross-linking density values are calculated and presented in Table 3. The cross-link density of the NR/IIR blend increased with increasing GPF content due to strong polymer/CB filler interactions (which is the main responsible factor in reinforcement mechanism). On the other hand, the cross-link density increases with the addition of 5 phr of treated clay into the matrix. The incorporation of TCNP enhances the cross-link density with respect to the conventional CB-loaded composites at different CB contents. The ratio of the cross-link density of the nanocomposite containing TCNP to that of the CB-loaded composites is always higher than 1. TCNP may be trapped in the occluded structure of CB, thus increasing the cross-link density. Thus, both CB particles and TCNP contribute to the higher cross-link density. Moreover, NR loaded with 30 phr of black (N660) has a higher cross-link density compared with IIR sample loaded with similar content of CB. Also, the incorporation of 5 phr of treated clay enhances the cross-linking of both samples.

3.6 Theoretical modeling

3.6.1 Young's modulus

The mechanical properties of filler–rubber composites are influenced by various parameters such as filler type and concentration, filler orientation, filler–matrix interaction, filler–filler wettability, and the filler aspect ratio. A number of theories and equations have been developed in the literature to anticipate the properties of the polymer composites. The optimum mechanical properties of the composite are strongly dependent on filler–matrix interactions (29).

The mechanical behavior of composite materials was described by different theories in terms of various parameters. Einstein, Guth, Sato-Furukawa, and Quemeda are the most famous theoretical models selected to describe the mechanical behavior of the particulate filler–matrix systems (30,31). These models are mainly applied for the theoretical calculations of the physicomaterial properties of spherically shaped fillers reinforced polymer composites. Einstein's equation that was mainly applied in the cases of entire adhesion and highly dispersed filler particles has the form (32):

$$E = E_m (1 + 2.5 V_f) \quad (2)$$

where E_m and E are the Young's modulus of the nonfilled and filled matrix, respectively, and V_f is the filler volume fraction. This equation suggests that the reinforcing action or stiffness of the filler is independent of the filler particle size. The equation shows that the volume occupied by the filler is independent of the size of the filler particles, i.e., the volume occupied by the filler rather than its weight is the dominant variable. This model also postulates that the filler is much more rigid than the host material chains.

The originally developed equation of Einstein's theory, which explains rubber reinforcement, is due to the Guth and Smallwood equation. This equation is suitable to describe the behavior of rigid spherical filler and has the form:

$$E = E_m (1 + 2.5 V_f + 14.1 V_f^2) \quad (3)$$

This equation takes into consideration the antiparticle (filler–filler) interactions at higher filler concentrations (33).

For discontinuous blend polymer systems that incorporated with spherical, rigid articulated fillers exhibit some adhesion, and the Quemeda equation (Eq. 4) (34) could be applied to evaluate the E value of the composition. The usual form is:

$$E = \frac{E_m}{(1 - 0.5KV_f^2)} \quad (4)$$

where K is an adjustable coefficient introduced to account for the filler–filler interactions and their aspect ratio. For composites filled with nanoparticles, K is taken as 2.5 (30).

The theoretical prediction based on the data created with polymer composites loaded with spherical particles is the Thomas equation:

$$E = E_m(1 + 2.5V_f + 10.05 V_f^2 + 0.00273 \exp(V_f)) \quad (5)$$

The previous theoretical empirical relationships are correlated with the obtained data and are graphically represented in Figure 5a and b. Experimentally determined values of the corresponding modulus values versus V_f for CB-loaded NR/IIR blends are plotted in Figure 5a. It can be seen that the experimental results are well in agreement with the Thomas relation (Eq. 5).

Figure 5b shows that the experimental values of modulus for treated-clay-incorporated CB/rubber nanocomposites have significant positive deviations compared with the calculated theoretical values. All these predictions did not give a clear explanation for the increase of E values for the compositions containing TCNP. These predictions assume that any interaction operative would only be physical. The enhancement of the modulus for

Figure 5: (a) Theoretical and experimental values of Young's modulus of CB-loaded NR/IIR blends and (b) the effect of TCNP loading.

compositions containing TCNP may not be attributed simply to the introduction of inorganic filler into the rubber matrix.

3.6.2 Tensile strength

The value of tensile strength of filled polymers is a characteristic that is complicated to predict as it depends on the polymer type and filler interfacial bonding as well as the factors mentioned above (Figure 6). Tensile strength is the force required to exert a uniaxial extension of a sheet of material to the point where it breaks. Specifically, the tensile strength is the maximum magnitude of force stress that is applied to a material until it breaks. Elastomeric materials, such as NR/IIR blend, have a yield point, which means that the strength at break and ultimate strength are not the same.

Figure 6: (a) Theoretical and experimental values of the tensile strength of CB-loaded NR/IIR blends and (b) the effect of TCNP loading.

A simple model for the determination of tensile stresses for unfilled and filled polymers was suggested by Turcsanyi et al. (35):

$$\sigma = \frac{1 - V_f}{1 + A V_f} \sigma_m f(V_f) \quad (6)$$

where σ_m and σ are the tensile strength of unfilled and filled polymers, respectively. This model describes the composition dependence of the tensile strength. The value of $A = 2.318$ for face-centered cubic packing, while $A = 2.318$ for a hexagonal close packing (35). After applying Eq. 6 to various polymer/filler systems, it was best described by an exponential function. The resulting expression was (35):

$$\sigma = \sigma_m \frac{1 - V_f}{1 + 2.5 V_f} \exp(BV_f) \quad (7)$$

where B is a fitting parameter associated to the interfacial properties.

Moreover, extensive works have been reported by several researchers, including Nielsen (36), Piggot and Leidner (37), and Nicolais and Narkis (N-N model) (38). All theories postulate the relationship between the tensile

strength and the filler volume fraction (V_f). Nicolais and Narkis suggested that the area fraction depends on the volume fraction to the two-thirds power:

$$\sigma = \sigma_m(1 - KV_f^{2/3}) \quad (8)$$

where K is a fitting parameter and depends on the attractive adhesion between pristine matrix and the filler particles; a low value of K means better the adhesion. The K value is found to be ≈ 1.2 for the extreme case of weak adhesion (39).

In Figure 5a and b, the models used for tensile strengths were compared with the experimental values. The samples loaded with different volume fractions of N660 CB are presented in Figure 5a. while those loaded with treated clay are presented in Figure 5b. The experimental results show considerable positive deviations. This obviously shows the reinforcing ability of both CB and TCNP clay in the NR/IIR blend matrix.

4 Conclusion

In this work, blends of natural rubber/butyl rubber NR/IIR 50/50 nanocomposites containing different doses of general-purpose furnace GPF CB and TCNP were prepared by melt mixing process. The blend ratio of rubber phases (NR/IIR, 50/50 wt%) and the amount of TCNP (5 phr) were kept constant. The samples were then cross-linked using gamma irradiation in the presence of a radiation coagent, trimethylolpropane triacrylate (TMPTA). The mechanical properties of the prepared composites have been discussed in terms of fillers type and concentration. The cross-link density of the NR/IIR blend increased with increasing GPF content due to strong interactions between polymer chains and the CB filler. The incorporation of 5 phr of TCNP into CB-loaded NR/IIR composites results in the increased tensile strength and modulus of the nanocomposite matrix. The addition of 5 phr of TCNP to the sample containing 30 phr of CB increased its tensile strength value by about 60%. Finally, theoretical models were used to interpret the experimental results.

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