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RESEARCH ARTICLE

DEGRADATION BEHAVIOUR OF NANO SILICA AND NANO TITANIA FILLED NATURAL RUBBER LATEX NANOCOMPOSITES

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The shelf-life of natural rubber latex products are highly dependent on various environmental factors. To improve the quality as well as performance, fine particle dispersions are employed in their formulations. The degradation behaviour of silica (SiO_2) and Titania (TiO_2) nanoparticles incorporated natural rubber latex (NR) nanocomposites against various degrading agents *viz.* thermal, γ-radiation, UV radiation and chlorination were studied. The properties such as tensile strength, elongation at break and modulus were recorded after exposing the latex films to various degrading environments. Compared to the gum vulcanizates, addition of nano SiO_2 and nano TiO_2 improved the tensile strength even after ageing. Enhanced UV resistant properties were noticed for nano titania latex composites from mechanical property measurements. Nano SiO_2 (0.3 phr) imparted maximum tensile strength after chlorination.

Keywords: Degradation, Mechanical properties, Nano SiO_2, Nano TiO_2, Natural rubber, UV radiation

INTRODUCTION

Natural rubber (NR) exhibits unique mechanical properties due to highly stereo regular microstructure resulting from its high molecular weight (Wang, 1998). However, its resistance to heat, oxygen and ozone is poor due to the presence of large number of double bonds in the chemical structure (Nwanorkh and Enyiegbulam, 1998). Degradation of NR can be affected by a variety of factors such as elevated temperatures, light, humidity, impurities, radiation, chemicals *etc.* The shelf-life of rubber products are dependent on such environmental factors.

Natural rubber on prolonged exposure to heat undergoes thermo-oxidative degradation, which in turn adversely affect the properties. When NR products are exposed to UV radiation, free radicals are produced. These free radicals abstract H atom from poly-isoprene chains thereby producing more free radical sites in the chain. These alkyl free radicals react with oxygen in atmospheric air to produce hydroperoxides. The free radical chain reaction process continues until entire rubber gets degraded (Peethambaran and Kuriakose, 1989). Light ageing in rubber can be retarded by adding UV resistant materials

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and by the use of antioxidants which will inhibit any subsequent oxidation. Chlorination, a process commonly used in the manufacture of powder-free gloves, may have detrimental effects on the mechanical and barrier properties after exposure to elevated temperatures (Walsh *et al.,* 1999). Crack generation, discoloration and poor heat resistance were observed for NR latex films after chlorination (Ho and Khew, 1999). Degradation of NR by gamma radiation is also a serious issue, where it is used for sterilization purpose.

It would be quite interesting to study the effect of nanofillers on degradation resistance of NR latex films. Development of nanocomposites consisting of TiO_2 and SiO_2 nanoparticles in polymeric matrix is positively perceived now-a-days (Rejinders, 2009). TiO_2 is a well-known inorganic material with good optical and photo catalytic properties. Due to high refractive index and excellent light scattering capacity, it is effectively served as a white pigment in latex industry. Besides, it provides better protection against UV light. Incorporation of TiO_2 nanoparticles in to polymer matrix results improved thermal stability and mechanical strength (Wu *et al.,* 2008; Chatterjee and Islam, 2008). Natural rubber/silica (NR/SiO_2) nanocomposite with a SiO_2 loading of 4 wt% was developed by latex compounding technique (Li *et al.,* 2006). The resulting nanocomposites showed enhanced thermal resistance. Several publications are available regarding the reinforcement of natural rubber with nanofillers (Varghese and Karger-Kocsis, 2003; Meera *et al.*, 2009; Kueseng and Jacob, 2006; Anand *et al.*, 2010). The ageing properties of NR and filled rubber vulcanizates are studied by various authors (Baker, 1988; Gorton, 1989; Rohana Yahya *et al.*, 2011; Zakir Hossain *et al.,* 2010; Kosikova *et al.*, 2007; Mathew *et al.,* 2013).

The oxidation process requires contact between rubber and oxygen which normally can occur at the surface of the product. The diffusion of oxygen in to the bulk of the rubber is a slow process; consequently, oxidation is confined to the surface of thick articles whereas latex based thin articles suffer more from the effects of oxidation (Lewis, 1987). The major reactions operating under accelerated ageing conditions are polymer chain scission, cross-linking and cross-link breakage.

The main objective of the present study is to analyze the effect of ageing conditions including thermal, chlorination, UV and γ-radiations on the mechanical properties of NR latex vulcanizates filled with nano TiO_2 and nano SiO_2. The mechanical properties of latex vulcanizates containing different filler content were compared with the gum (unfilled) vulcanizate. The swelling index

Table 1. **Details of the filler dispersions**

Material	Particle size	Concentration
Nano silica dispersion	Particle size < 250 nm	Silicon dioxide -20 wt % in water, Purity - 99.99 %
Nano titanium dioxide dispersion	Particle size <100 nm	Titanium (IV) oxide, mixture of rutile and anatase – 33 to 37 wt % in water, 99.9 % trace metal basis

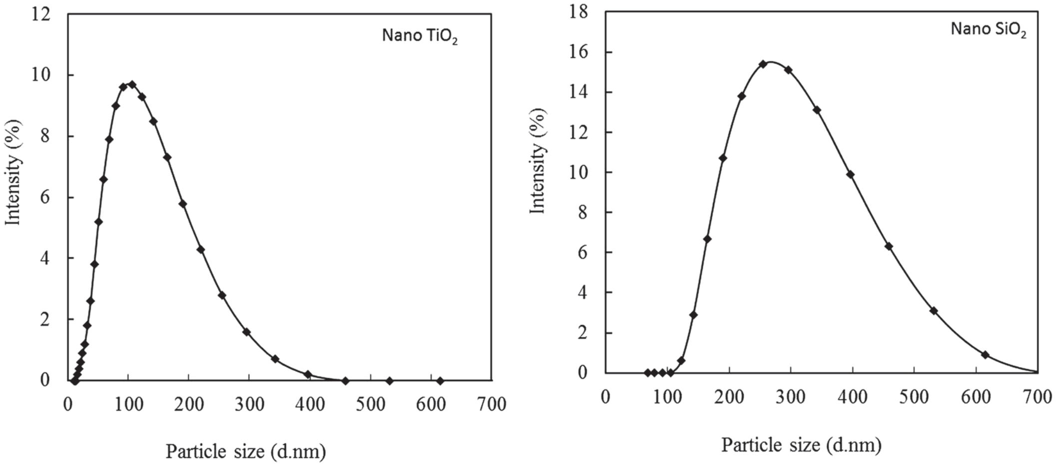

Fig. 1. Particle size distribution of nano titania (TiO_2) and nano silica (SiO_2) dispersions

and cross-link density of all the vulcanizates prior to keep before ageing atmosphere was also measured.

MATERIALS AND METHODS

Centrifuged natural rubber latex (high ammonia type) with 60 per cent dry rubber content conforming to IS 5430 was collected from Pilot Latex Processing Centre of Rubber Research Institute of India, Kottayam, India. Nano silica dispersion and nano titanium dioxide dispersion were procured from Sigma Aldrich. Table 1 shows the details of the filler dispersions used. Particle size distribution of filler dispersions are shown in Figure 1. Dispersions of the other compounding ingredients were prepared by conventional ball milling method. Latex compounding formulations are given in Table 2.

Before adding the compounding ingredients, the total solid content of the latex was maintained at 55 per cent. The compounded NR latex was matured for 24h at room temperature.

Preparation of latex films

The compounded NR latex was mixed with varying amount of nano SiO_2 and nano TiO_2 dispersions and gently stirred for getting uniform distribution. The compounded latex was then poured on glass trays (inside dimensions 13 cm x 10 cm x 2 mm) and films were casted. Drying of the latex films were carried out at 45^{0}C in an air oven.

Table 2. **Formulation of the latex compound**

Ingredients	Dry weight (phr)
60% Centrifuged latex (High ammonia type)	100
10% Potassium hydroxide solution	0.20
20% Potassium laurate solution	0.10
50% Sulphur dispersion	1.5
50% ZDEC* dispersion	1.0
50% Zinc oxide dispersion	0.5
20% Nano SiO_2 dispersion	Variable
37% Nano TiO_2 dispersion	Variable

*Zinc diethyldithiocarbamate

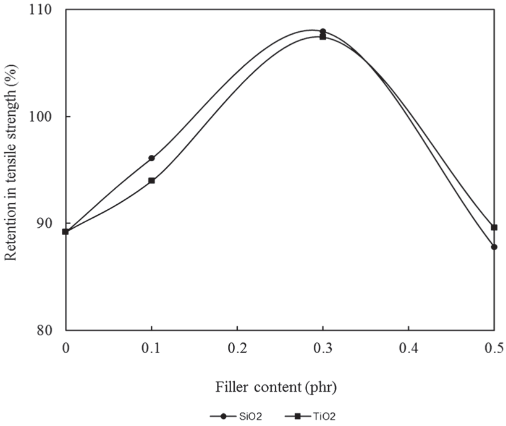

Fig. 2. Percentage retention in tensile strength of nanocomposites after thermal ageing

Post vulcanization was carried out at 100^{0}C for 1h to ensure maximum strength to the composite films. The vulcanized latex films are designated as G, T1, T3, T5, S1, S3 and S5. G represents gum vulcanizate whereas T and S denote nano TiO_2 and nano SiO_2 filled vulcanizates respectively. The numbers (1, 3, 5) indicate vulcanizates containing 0.1, 0.3 and 0.5 phr filler respectively.

The extent of vulcanization for the compounded latex films was determined using swelling index measurements. It was determined by immersing a small portion of the composite film in toluene for 48h and measuring the increase in the weight.

The swelling index can be calculated using the equation:

$$\text{Swelling index (Q)} = \frac{W_2-W_1}{W_1}$$

where W_1 and W_2 are the initial and swollen weights of the latex films respectively.

The variation of swelling index for vulcanized natural rubber specimens can be broadly classified as follows: unvulcanized (>15), lightly vulcanized (7-15), moderately vulcanized (5-7) and fully vulcanized (<5) (Sasidharan *et al.*, 2005).

The cross-link density of filler (nano SiO_2 and nano TiO_2) incorporated latex vulcanizates were calculated using the equation (Flory and Rehner, 1943),

$$\nu = \frac{1}{2M_C}$$

$$M_C = \frac{\rho_r V_s \phi^{1/3}}{\ln[1-\phi] + \phi + x\phi^2}$$

where M_c is the molecular weight between the cross-links.

where ρ_r is the density of the polymer, V_s is the molecular weight of solvent (toluene) and χ is rubber-solvent interaction parameter (0.391).

Table 3. **Swelling index and crosslink density of vulcanized latex films**

Samples	Swelling index	Cross-link density (x 10^5) (moles.cm^{-3})
G	4.119	5.618
T1	4.142	5.562
T3	4.084	5.987
T5	3.944	6.246
S1	4.141	5.454
S3	3.973	5.975
S5	3.485	6.561

The swelling indices and cross-link density of vulcanized latex films are given in Table 3.

Degradation studies

Thermo gravimetric analysis (TGA) was conducted using a thermogravimetric analyzer (Perkin Elmer TGA 4000) in N_2 atmosphere at a heating rate of 10 °C min^{-1}.

Dumb-bell shaped specimens were aged at 70 °C for 7 days in a hot air circulated oven. Elongation at break, modulus at 100 per cent elongation and percentage retention in tensile strength of the films were measured. The percentage retention in tensile strength was calculated as follows (Setua and De, 1983).

$$\text{Retention in tensile strength (\%)} = \frac{\text{Tensile strength after ageing}}{\text{Tensile strength before ageing}} \times 100$$

For UV degradation studies, radiation from a UV chamber (PHILIPS TLD 30W HOLLAND) was used. The UV source used consists of two fluorescent tubes each having a capacity of 15W. The dumb-bell shaped specimens were kept on a glass plate which is fixed at the middle of the chamber horizontally with the radiation source. Both the sides of the samples were simultaneously exposed to the UV radiation for about 48h and mechanical properties were estimated.

The optical photographs of the UV aged samples were recorded using a Leica DIAPLAN microscope (Leica QWin).

Dumb-bell shaped test specimens were irradiated with γ-rays from a ^{60}Co radiation source. The samples were irradiated to different levels *i.e.,* 30, 50 and 100 kGy. The dose rate was 1.06 kGy/h in air at room temperature. The mechanical properties of the gum and the composite films were measured after irradiation.

Chlorination was carried out in a closed vessel by immersing the latex films in 0.1 per cent chlorine solution for 3 min. After chlorination the product was washed in dilute ammonia solution (1%) and there after in water and then dried. The mechanical properties of the films were measured thereafter.

The tensile properties were measured using ZWICK (Model 1474) universal testing machine. For every sample, five specimens were tested and the average is calculated.

RESULTS AND DISCUSSION

The particle size distribution curves of silica and titania nanoparticles are displayed in Figure 1. The average particle size (Z-average) of nano TiO_2 and nano SiO_2 dispersions are 84 nm and 297 nm respectively. For nano TiO_2, 49.8 per cent of the particles showed size < 100 nm and 50.2 per cent showed size in the range of 100-500 nm. In the case of nano SiO_2, majority of the particles (94.5 per cent) showed size in the range 100-500 nm. Particles having size below 100 nm was absent in the case of nano SiO_2.

Swelling studies

The swelling indices of the gum and the composite latex films are shown in Table 3. The cross-link density of the sample is related to swelling index. In comparison with the gum vulcanizates, swelling indices of the filled vulcanizates are lower and the reduction is more pronounced at higher filler loadings. This indicates that the extent of vulcanization is higher in the filled specimen than the virgin specimen. Among all, vulcanized latex films incorporated with 0.5 phr nano silica dispersion exhibited the lowest swelling index value. The cross-link densities of filled systems (Table 3) are higher compared to gum sample and are

Table 4.**Weight % retention of gum and nanocomposite samples at various temperatures**

Temperature (^{0}C)	wt.% retained						
	Gum	T1	T3	T5	S1	S3	S5
250	96.7	97.2	97.1	96.9	97.2	96.2	96.3
300	94.4	95.1	95.2	95.0	95.1	93.7	94.0
350	89.8	89.7	90.1	87.2	90.1	84.6	87.3
400	32.8	33.1	35.5	27.8	36.2	28.9	31.6
450	3.6	4.3	5.1	4.0	5.3	4.2	6.7
500	1.3	2.1	3.0	2.9	3.1	2.4	4.8

more pronounced at higher filler loading (0.5 phr). The presence of high surface area nanoparticles and their homogeneous distribution in the rubber matrix provides more hindrance to the solvent molecules thereby improving the solvent resistance capacity.

TGA studies

The percentage weight of NR/TiO_2 and NR/SiO_2 nanocomposites retained at various temperatures is determined from TGA studies and is given in Table 4. The thermal stability of the composite is proportional to the weight retained at particular temperature. Latex composites containing nano TiO_2 and nano SiO_2 imparts better thermal stability to the vulcanizates. At 500 ^{0}C, the weight per centage retained for 0.1, 0.3 and 0.5 phr nano TiO_2 filled composites were 2.14, 2.98 and 2.94 respectively, whereas it was 3.05, 2.41 and 4.79 for nano SiO_2 filled composites. For gum vulcanizate it was only 1.33.

Effect of thermal ageing on mechanical properties

In rubber compounds, high temperature causes two competing reactions- cross-link formation and chain scission. This will affect the mechanical properties of the composites. The variation in tensile strength, elongation at break (EB) and modulus of the NR latex nanocomposites can be explained based on these processes.

The percentage retention of tensile strength of NR/TiO_2 and NR/SiO_2 nanocomposites after thermal ageing is shown in Figure 2. After ageing at 70 ^{0}C for 7 days, the retention in tensile strength values of both the composite increases (107%), which is much higher than (89%) the retention of the gum vulcanizate. High retention in tensile strength value has been attained for the composites with the addition of 0.3 phr filler. Further increase in

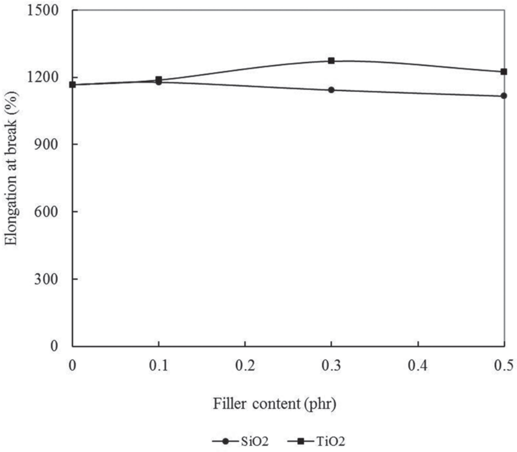

Fig. 3. Effect of filler content on elongation at break of nanocomposites after thermal ageing

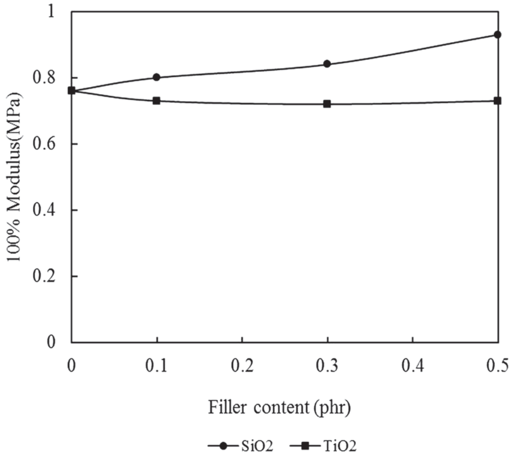

Fig. 4. Effect of filler content on modulus (M100) of nanocomposites after thermal ageing

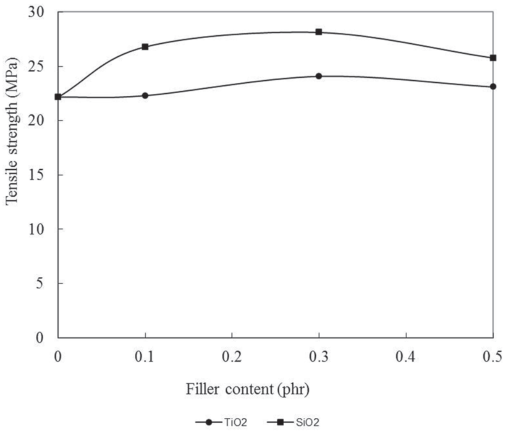

Fig. 5. Effect of filler content on tensile strength of nanocomposites after chlorination

filler concentration (*i.e.* 0.5 phr) causes reduction in tensile strength. A slight reduction in tensile strength was observed for SiO_2 filled systems at higher loadings. This might be due to the adsorption of sulphur on the surfaces of the silica particles. Due to this adsorption, sulphur available for cross-linking will be minimum which leads to monosulphidic linkages. Further, the strain induced crystallization of rubber will be hindered by high filler content and may affect the strength (Wang *et al.*, 2005).

The flexibility of rubber composites can be expressed using the parameter elongation at break (EB). Variation of EB of thermally aged latex nanocomposites with filler content is given in Figure 3. At higher filler loadings, NR/TiO_2 nanocomposites showed higher EB compared to NR/SiO_2. Highest EB (1272) was registered for latex vulcanizates containing 0.3 phr nano TiO_2. For NR/SiO_2 nanocomposites, EB value has decreased with increase of SiO_2 content. This reduction is due to stiffening of the matrix. Also, the improved adhesion of nano SiO_2 restricts the mobility of NR chain thereby causing reduced elongation. As more cross-links are formed, the segmental mobility of the rubber chain decreases. This also leads to a gradual reduction in EB for NR/SiO_2 nanocomposites.

Figure 4 illustrates the variation of M100 (modulus at 100 per cent elongation) of aged nanocomposites with filler loadings. Modulus changes are directly associated with changes in the original cross-link structure, such as main chain scission and cross-link modifications (Rohana Yahya *et al.*, 2011). NR/SiO_2 nanocomposite exhibited higher modulus than NR/TiO_2 and it increases with increase in filler content whereas the M100 of NR/TiO_2 nanocomposites did not affected by TiO_2 content. Incorporation of 0.5 phr nano SiO_2 resulted highest M100 (0.93 MPa) after ageing. The increase in modulus with SiO_2 content is due to the reinforcing action of the filler. These data clearly indicates that nano TiO_2 and nano SiO_2 can impart better thermal stability to NR. It has been reported that on loading with TiO_2 pigment and china clay, good retention of tensile strength, modulus and EB were obtained for RVNRL films after thermo oxidative ageing (Jaimon Kurian, 2002).

Effect of chlorination on mechanical properties

Chlorination is a method used for de-proteinization and sterilization of medical latex goods including gloves, catheters, surgical tubings etc. Chlorination technique allows not only the removal of allergenic proteins but also gives improved donnability to the product.

Figure 5 displays the effect of nanoTiO_2 and nano SiO_2 on tensile properties of NR latex composite films after chlorination. The high strength of gum vulcanizate is due to strain induced crystallization. It has been found that tensile strength increases with increase of nanofiller content and reaches the maximum when the filler content is 0.3 phr. Significant increase in tensile strength for NR/SiO_2 nanocomposites is due to the addition of high surface area SiO_2 nanoparticles which will be in contact with rubber causing high stress transfer between rubber matrix and SiO_2 particles. Further increase in filler concentration causes reduction in tensile strength. Among the two, SiO_2 filled vulcanizates exhibited higher tensile strength than TiO_2.

It can be seen in Figure 6 that latex vulcanizates containing nano SiO_2 showed a steady increase in M100 with filler content. Maximum modulus of 0.91 MPa was obtained for the composite with 0.5 phr nano SiO_2. On the other hand, nano TiO_2 incorporated latex composites gave the maximum modulus of 0.78 MPa, which is slightly higher than the M100 of gum vulcanizate. The increase in modulus with increasing filler levels was more marked for SiO_2 than TiO_2.

Effect of UV light on mechanical properties

NR hydrocarbon produces free radicals by absorbing energy from UV radiation in the region 290-350 nm (Carlson *et al.*, 1979). During UV irradiation chain scission may

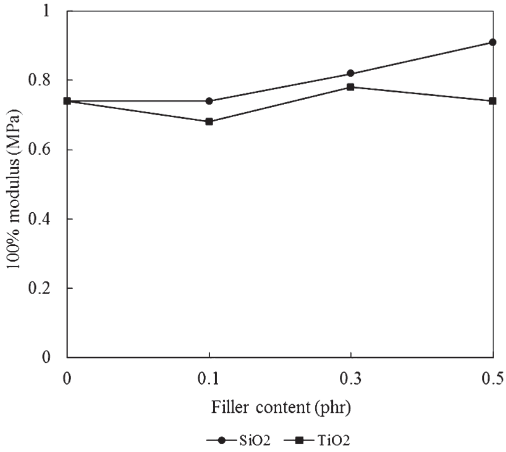

Fig. 6. Effect of filler content on modulus (M100) of nanocomposites after chlorination

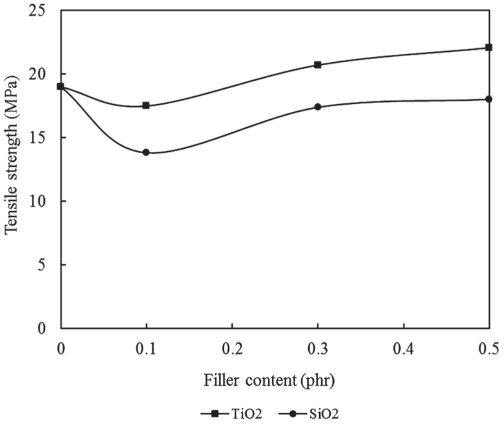

Fig. 7. Effect of filler content on tensile strength of nanocomposites after UV ageing

occur as a result of the following reactions (Gowariker *et al.*, 1996)

$$\text{Polymer} \xrightarrow{\text{hõ}} R^*$$

$$R^* + O_2 \qquad RO_2^*$$

$$RO_2^* + RH \qquad ROOH + R^*$$

$$2\ RO_2^* \qquad \text{Non radical products}$$

Figure 7 depicts the variation in tensile strength of NR/SiO_2 and NR/TiO_2 nanocomposites after exposure to UV light for 72h. An increase in tensile strength was observed with nano TiO_2 filled samples than nano SiO_2 filled systems, with filler loadings. This indicates the better UV resistance capacity of TiO_2 based nanocomposites. Optical photographs of the UV aged latex composites containing 0.5 phr filler (nano SiO_2 and nano TiO_2) incorporated films are shown in Figure 8. After 72h of UV irradiation, micro-cracks can be observed in NR/SiO_2 nanocomposites. The drop in tensile strength could be attributed due to the formation of surface cracks resulting in earlier sample rupture. However, for both the composites containing 0.1 phr nano fillers, slight drop in tensile strength is observed. It has been presumed that reduction in tensile strength for NR/SiO_2 nanocomposites is expected to be due to the presence of OH^- groups, co-ordinatively unsaturated metal atoms, free radicals present on the surface of the filler etc. (Bryk, 1991).

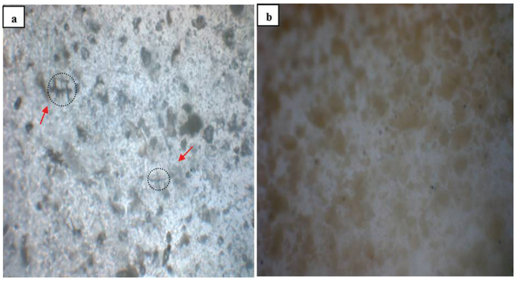

Fig. 8. Optical photographs of UV aged latex vulcanizates containing a) 0.5 phr nano SiO_2 b) 0.5 phr nano TiO_2

Effect of gamma radiation on mechanical properties

Effect of radiation dose on tensile strength of nano filler incorporated (0.3 phr) latex vulcanizates is shown in Figure 9. The tensile strength of gum vulcanizate is initially high (25 MPa) and it decreased to 21 MPa after γ-irradiation (30kGy). Further increase in radiation dose did not affected the tensile strength. NR/TiO_2 nanocomposite showed a higher tensile value of 23 MPa when exposed to 50 kGy radiation dose. Upon irradiation, different type of functionalities present on the surface of TiO_2 may take part in physical and chemical bond formation at the interface between TiO_2 and rubber. In the case of SiO_2 filled nanocomposites, tensile strength increases with increase in radiation dose. Moreover, the trend observed here are in accordance with earlier reports for other rubber composites (Khalid *et al.*, 2010). This shows that, mechanical properties of NR/SiO_2 and NR/TiO_2 latex nanocomposites on exposure to γ-radiation are highly dependent on filler type and its surface characteristics.

CONCLUSIONS

Incorporation of nano particles of silica and titania improved the degradation resistance of NR latex films. Retention in tensile strength was observed for the composites with 0.3 phr filler addition after thermal expansion. Silica nanocomposites exhibited better strength after chlorination. There is no colour change for the composites upon chlorination. The UV resistance capacity was found to be better for NR/TiO_2

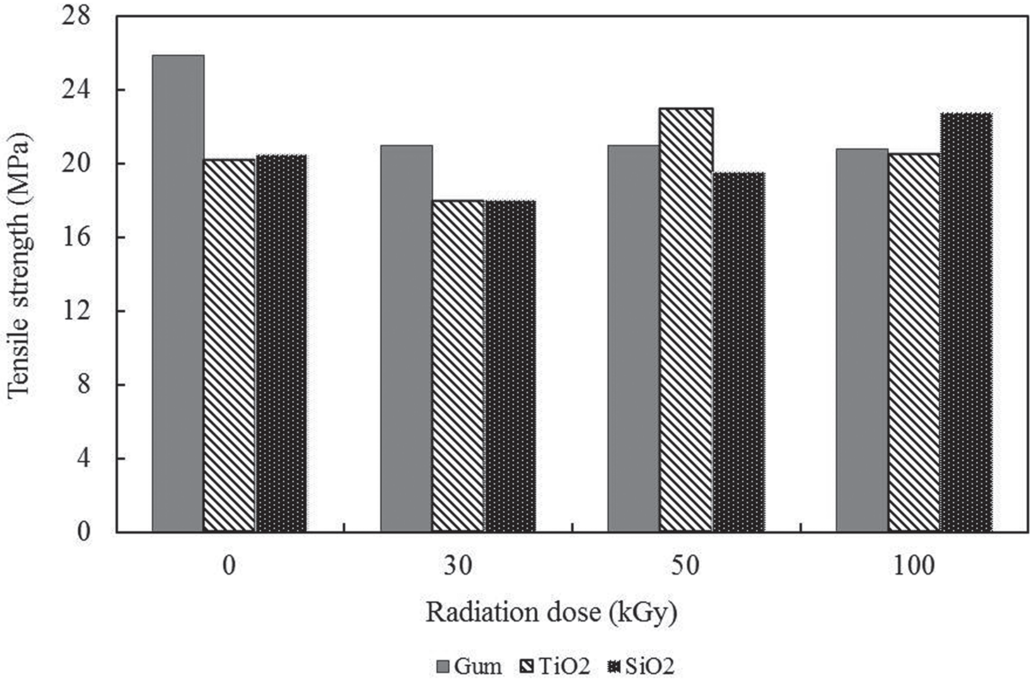

Fig. 9. Variations of tensile strength with γ radiation

nanocomposites. The reduction in tensile strength for NR/SiO_2 nanocomposites upon UV irradiation is due to the formation of micro-cracks on the surface of the films. In the case of SiO_2 filled nanocomposites, tensile strength increases with increase in radiation dose. A progressive increase in modulus of NR/SiO_2 composites with filler dosage can be attributed to more cross-link formation as evident from low swelling index values.Thus, the addition of nano silica and nano titania in natural rubber latex can result in products having improved shelf-life.

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