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Mechanical properties of nr latex- nano silica composites

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Nanosilica is used as filler and is separately incorporated into the latex matrix and the corresponding nano composites are prepared by co-vulcanization method. The mechanical properties are measured and compared with the corresponding macroscopic latex-silica composites. The study reveals that there is a remarkable increase in the properties when Nanosilica is used as filler in the latex matrix due to the improved latex-nano particle interaction and better homogeneity in the distribution of nano particles in the latex matrix. The effects of nanolayer reinforcement are manifested in terms of reduced swelling by solvents and higher modulus values in the latex-nano particle composites. Differential scanning calorimetry (DSC), Thermo gravimetric Analysis (TGA) and tunneling electron microscopy (TEM) are done for characterisation studies.

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1. Introduction

Cross linked rubber compounds show improved mechanical properties if filled with active fillers like carbon black or precipitated Silica where reinforcement is governed by Hydro dynamic effects and physi-or chemisorption of elastomer chain at the filler surfaces [1]. A novel class of fillers are nano silica and nano clay which attains unique properties. In contrast to silica fillers in polymer metrics where matrix-filler and filler-filler interaction can be controlled by surface modification with silanes, in nanosilica having fine particles size distribution is generated in situ through the mixing process which results to change aggregate structure. The second feature of the nanosilica is their anisotropic nature which leads to filler networking at much lower loading levels than for isotropic carbon black or silica or clay fillers [2] and also gives rise to pronounced hysteresis in rubber nanocomposites. Moreover nanocomposites usually exhibit improved performance properties compared with conventional composites owing to their unique phase morphology and improved interfacial properties. For these reasons, nanostructured organic-inorganic composites have attracted considerable attention from both a fundamental research and an application point of view [3, 4].

2. Experimental

Centrifuged latex containing 60% DRC was used for the study. All water insoluble compounding ingredients except nonox styrenated phenol (SP) were prepared as 50% dispersions using a ball mill. The Nonox SP was prepared as 30% emulsion as described in chapter 2. The stabilizers potassium hydroxide and potassium oleate were prepared as 10% solutions is water. 40% silica filler dispersion was also prepared.

2.1 Preparation of 20% nanosilica dispersion

5 gm of nanosilica is accurately weighted and taken in a clean 250 c.c beaker. 20gms of distilled water is added followed by 0.05 gm. of dispersal F and 0.05 gm of dispersion stabilising liquid. The ingredients in the beaker were stirred gently and steadily using a magnetic stirrer at 500 rpm for 96 hrs continuously so as to form a uniform dispersion. Then the beaker with the dispersion was kept open for 24 hrs. to expel all the bubbles and air entrapped in the dispersion. The formulations of different latex compounds are given in Table l and Table 2. The centrifuged latex was taken in a beaker and deammoniated to 0.2 percent ammonia content. Then it was stabilised by adding potassium hydroxide and potassium oleate solutions. The vulcanising agent (sulphur), accelerator (ZDC) and activator (ZnO) were added as dispersion. Antioxidant (Nonox styrenated phenol) was added as emulsion. The contents were stirred gently to attain homogeneity. Thus the base latex compound was prepared.

Table 1. Formulations of the base latex compound.

Ingredients	Unfilled
NR Latex	167
10% KOH	1.0
10% Pot. Oleate	1.0
50% ZnO	1.0
50% ZDC	2.0
50% Sulphur	2.0
30% Nonox SP	3.0

The precipitated silica dispersion of 2.5 phr, 5 phr, 7.5 phr and 10 phr of 40% conventional silica dispersion was added separately to the respective base latex compounds. Similarly 0.2 phr, 0.4 phr,0.6 phr, 0.8 phr, 1.0 phr of 20% nanosilica dispersion was incorporated separately into the respective base latex compounds and homogenised.. Maturation was given and the latex films of the base latex compound, silica and nanosilica filled latex compounds were cast on the glass trays in each case.

Table 2. Formulations of the latex filled nano composites.

Ingredients	Parts by weight (wet) gm								
	Latex-silica composites				Latex silica nano-composites				
NR Latex	167	167	167	167	167	167	167	167	167
10% KOH	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
10%Pot. Oleate	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
50% ZnO	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
50% ZDC	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
50% Sulphur	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
30% Nonox SP	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Silica	2.5	5.0	7.5	10	-	-	-	-	-
Nanosilica	-	-	-	-	0.2	0.4	0.6	0.8	1.0

2.2 Optimum cure time of the latex compounds

The base latex films were dried at room temperature for 24 hrs. They were kept in an air oven at 110 ^{0}C for deferent times varying from 25 to 40 minutes to take them to different cure levels. Dumbbell shaped tensile pieces were punched out of these sheets and tensile properties were measured, using a Schimadsu universal testing machine. The cure time of the sample which gave the maximum tensile strength was taken as the optimum cure time.

After drying for 24 hrs, the base latex film, the silica, and nanosilica latex films were vulcanised at 110 °C upto the optimum cure time. The covered samples were then cooled and dumbbell specimens were cut out of the sheets for tensile testing. The tensile strength, the elongation at break, and the modulus of the vulcanisates were measured using a Schimadsu 5 KN universal testing machine at an extension rate of 500 mm/min as per ASTM standards. Angular test specimens were punched out of the moulded sheets and the tear strength of the selected vulcanisates was also measured on the Schimadsu 5KN UTM.

The swelling index of the samples of base latex compound, silica and nano silica filled latex compounds were determined by equilibrium swelling in toluene according o the following equation

$$\text{Swelling index} = \frac{\text{swollen weight - de swollen weight}}{\text{Initial weight}}$$

The thermogravimetric analysis (TGA) of the samples of silica and nanosilica filled compounds were carried out in a Q-250 thermal analyser in nitrogen atmosphere at a heating rate of 10 °C/min as per the ASTM standards. The differential scanning calorimetry (DSC) curves of the samples of silica and nanosilica filled compounds were carried out on a Q -100 model instrument at a heating/cooling rate of 10 °C/min. under nitrogen atmosphere as per ASTM standards. Tunnelling electron microscopic photographs of latex silica and latex nano silica composites were taken by a TEM 2500J model instrument.

3 Results and discussion

3.1 Variation of tensile properties

Fig. 1 shows the variation of tensile strength of the base latex vulcanisation with different cure times at a temperature of 110 °C. The tensile strength of the vulcanisate increase with cure time. The maximum tensile strength is obtained on for the vulcanizate having a cure time of 28 minutes, which is taken as the optimum cure time at 110 °C.

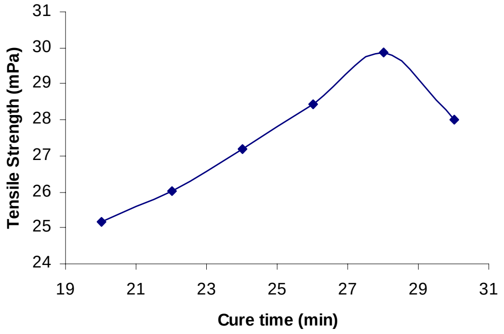

Fig. 1. Variation of tensile strength of the base latex compound.

Figs. 2 and 3 shows the variation of tensile strength of the silica filled and nanosilica filled NR latex vulcanizates with the amount of the filler respectively. In the case of silica filled NR latex vulcanizates it is found that the tensile strength slightly increases initially, and then decreases continuously with the amount of the filler. It may be due to the poor latex-filler interaction and also due to the non uniformity in the filler distribution. But in the case of nanosilica filled NR latex vulcanizates, the tensile strength increases gradually and reaches a maximum and then slightly decreases. It is noted that maximum tensile strength is observed at a low level of nanosilica filler loading (0.8 phr. of 20% dispersion) compared to the silica filler loading (2.5 to 10 phr of 40% dispersion) used in the study.

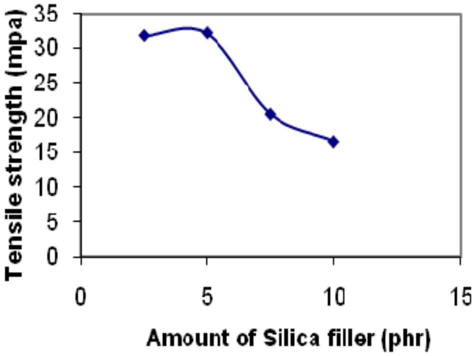

Fig. 2. Variation of tensile strength of latex-silica composites with the amount of silica.

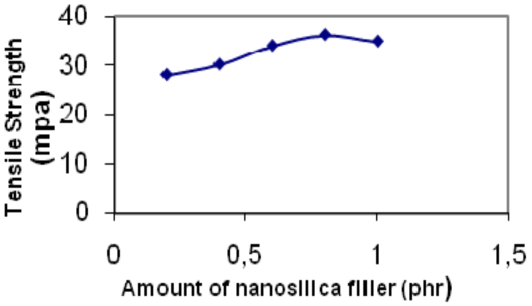

Fig. 3. Variation of tensile strength of latex-silica nanocomposites with the amount of nanosilica.

The remarkable increase in tensile strength of nanosilica filled NR latex vulcanizates compared to the tensile strength of the ordinary silica filled NR latex vulcanizates may be due to the more homogeneous distribution of the nanosilica in the latex compounds and also due to the improved latex-nanosilica interaction. Moreover the unique phase morphology and improved interfacial properties are also responsible for the better performance properties of the latex-silica nano composites compared to the conventional composites. [5-9]. Figs. 4 and 5 describe the variation of elongation at break of the silica filled and nanosilica filed NR vulcanizates with the amount of filler respectively. The elongation at break is found to decrease continuously with the amount of silica filler in the case of NR latex-silica conventional composites. This also may be due to the poor latex-silica interaction and also may be due to the non uniformity in the filler silica distribution. But in the case of NR latex-nano silica composites the elongation at break steadily increases and reaches a maximum value and then decreases. The maximum value of elongation at break is noticed at a low level of nanosilica filler loading (0.8 phr of 20% dispersion of the filler) compared to the silica filler loading (2.5 to 10 phr of 40% dispersion of the silica).

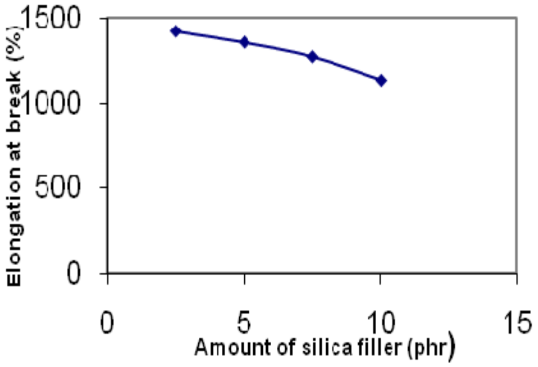

Fig. 4. Variation of Elongation at Break of latex-silica composites with the amount of silica.

The increase is elongation at break of NR latex-nanosilica composites may be due to the more uniform homogeneous distribution of nanosilica in the latex matrix and also due to the improved latex-nanosilica interaction. Besides, the unique phase morphology and improved interfacial properties are also responsible for the improved performance properties of the latex- nanosilica composites compared to the conventional latex-silica composites.

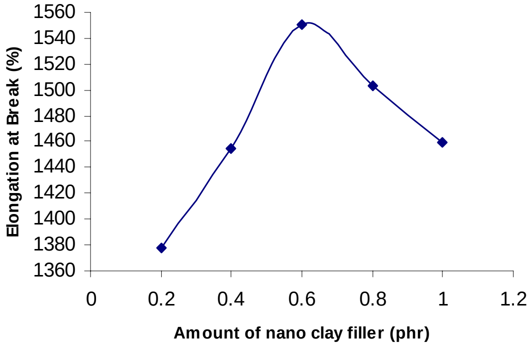

Fig. 5. Variation of Elongation at Break of latex-silica nano composites with the amount of nano silica.

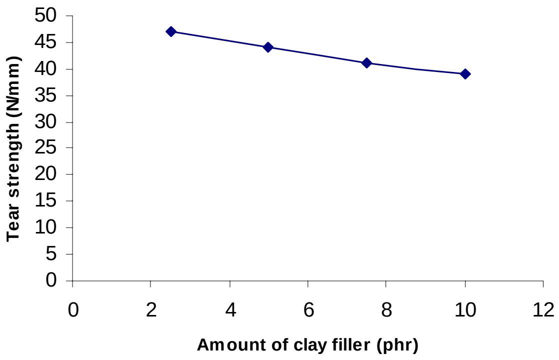

Fig. 6. Variation of tear strength of the latex-silica composites with the amount of silica filler.

Fig. 6 shows the effect of different dosage of the filler, silica on the tear strength of the conventional latex-silica composites. Here also the tear strength continuously reduces with the amount of the silica in the latex as in the case of tensile properties. Fig. 7 gives the variation of tear strength of the nanosilica filled NR latex vulcanzates with the amount of the nanosilica. In this case also, even at the very low nanosilica filler loading of 0.6 phr, the tear strength is found to be higher due to the unique phase morphology and the improved interfacial properties of the latex-nanosilica composites compared to the latex-silica conventional composites. Moreover higher latex-nanosilica filler interaction in the latex-silica nano composites and the more uniform nanosilica distribution which in turn due to the more uniform surface area of the nanosilica filler compared to the conventional latex-silica composites again shows that, nano composites exibit improved performance properties compared with conventional composites.

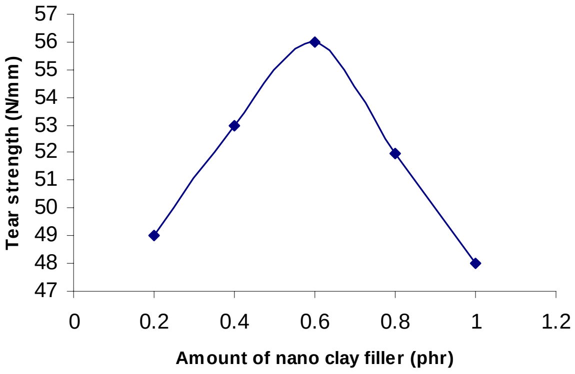

Fig. 7. Variation of tear strength of the latex silica nano composites with the amount of nano silica filler.

3.2 Evaluation of modulus and swelling index

Table 3 shows the variation of the modulus and the swelling index values of the latex-silica composites, and Table 4 shows the variation of the modulus and the swelling index values of the latex-nanosilica composites. The modulus values are found to be higher for the latex-nanosilica compounds compared to the latex-silica conventional composites. The increased modulus values shown by the latex-nanosilica vulcanizates may be due to the higher latex-nanosilica interaction and also due to the more uniform nanosilica distributions. In the case of swelling index values, the latex-nanosilica composites show, lower values due to the reduced swelling by solvents compared to the conventional latex-silica composities. This depicts that the addition of nanosilica restricts swelling due to more latex-nanosilica attachment compared to the latex-silica attachment in the conventional composites. Figs. 8 and 9 show the DSC curves of the NR Latex-silica Nanocomposite, and NR latex-silica conventional composite respectively. It is noticed that since the peak area, and hence the delta H value is more [10-12] in the case of NR latex-silica nanocomposites indicating a high crystallization rate of the nanocomposite compared to the conventional Latex-silica composite.

Table 3. Variation of Modulus and Swelling Index of latex-silica composites with silica filler loading.

Silica Filler Loading (Phr)	Modulus (%)	Swelling Index
2.5	1.51	1.89
5	1.71	2.04
7.5	1.81	2.41
10	1.94	2.52

The TGA traces of NR latex-silica nanocomposites and NR latex-silica conventional composites are shown in figures 10 and 11 respectively. It is found that the thermal stability of the latex matrix is improved by the nanocomposite formation. For a particular range of temperature Latex-silica nanocomposite shows higher thermal stability [13] due to the lower weight of the loss of the nanocomposite at this temperature range compared to the conventional nanocomposite.

Table 4. Variation of Modulus and Swelling Index of latex-Silica Nano Composites with nanosilica filler loading.

Nano Silica Filler Loading (Phr)	Modulus (%)	Swelling Index
0.2	2.12	1.72
0.4	2.45	1.54
0.6	2.82	1.49
0.8	2.64	1.58
1	2.34	1.79

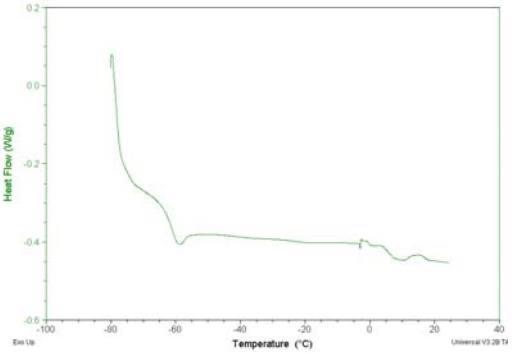

Fig. 8. DSC Curve of latex – silica composite.

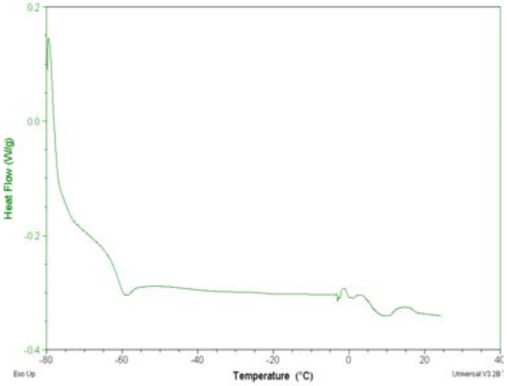

Fig. 9. DSC Curve of latex –silica nano composite.

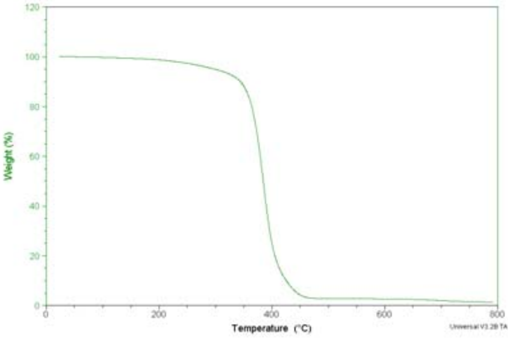

Fig. 10. TGA trace of latex – silica composite.

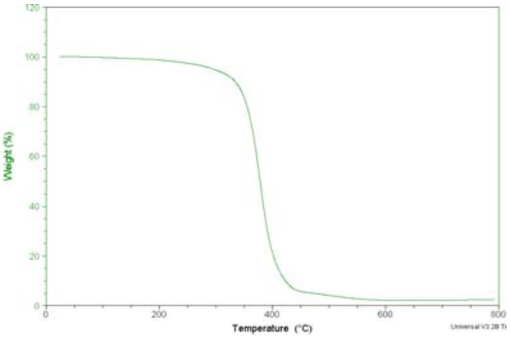

Fig. 11. TGA Trace of latex-silica nano composite.

Fig. 12 and 13 shows the TEM photographs of latex silica and latex nanosilica composite respectively. Latex nano silica photograph shows better homogeneity and better filler interaction and uniform distribution throughout the latex matrices. This also supports the enhancement of the mechanical properties of the latex nano silica composites.

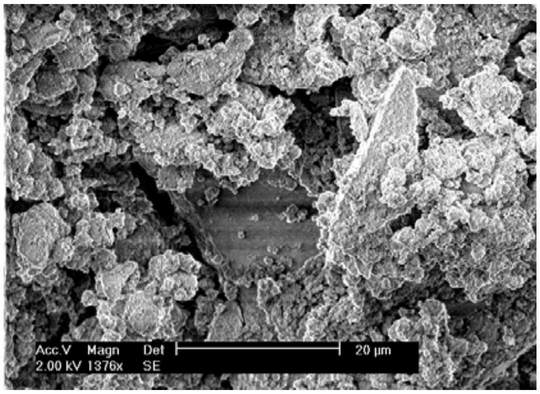

Fig. 12. TEM photograph of latex silica composite.

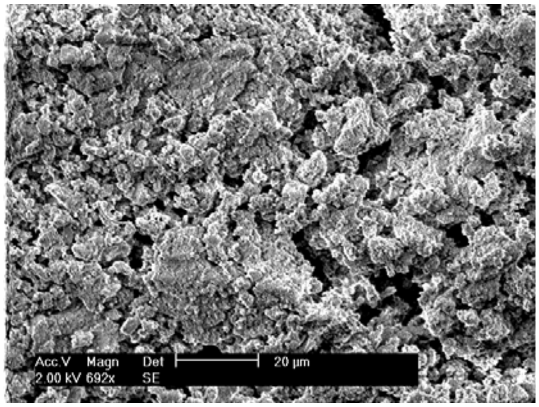

Fig. 13. TEM photograph latex silica nano composite.

4. Conclusions

The study shows that the silica nanoparticle distribution in the NR latex matrix affects the mechanical properties. The following conclusions can be drawn from the study.

1. The exfoliations of organically modified nanosilica in the latex greately improves the mechanical properties of the matrix through the reinforcement provided by the silicate nanolayers.
2. The effects of nanolayer reinforcement are also manifested in terms of reduced swelling by solvents, and higher modulus values.
3. Lesser amount of nanosilica (0.6phr of 20% nanosilica dispersion) is only required for the better mechanical properties compared to the amount of silica (up to 10 phr of 40% silica dispersions) in the conventional latex-silica composites.

4. The mechanical properties of the conventional latex-silica composites continuously decreases with increase in the amount of silica filler.
5. The NR latex-silica nanocomposites are more thermally stable.

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