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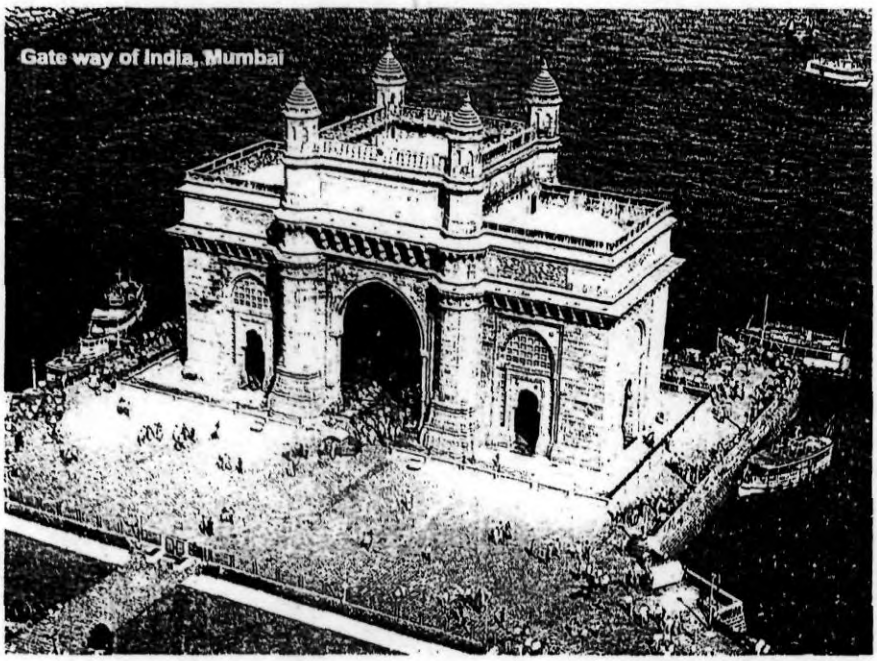

International Rubber Conference & Exhibition

Emerging Trends & Opportunities In Rubber Industry

NOVEMBER 17-19, 2010

Renaissance Hotel & Convention Centre, Mumbai (India)

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Paper : S-01/6

Natural Rubber - Silver nanocomposites : Via a novel route for nanocomposites (EA-087)

Manoj Kurian Jacob*, John Britto I. , Rosamma Alex, and Thomas K.T.

Rubber Research Institute of India, Rubber Board P.O, Kottayam, Kerala-686009, India.
E-mail : manojkjk@yahoo.co.in

Introduction

The inquisitive nature of human minds to engineer novel composite materials with contradicting behaviours has resulted in the blending of extremely different materials like rubber with metals resulting in Rubber Metal Composites. Conventionally the Rubber Metal Composites have been prepared by incorporating commercial metal powders to the rubber matrix.[1-2] Many of these metal powders used to prepare the composite were of micron size dimensions and were added at 5 to 20 phr to the rubber matrix, to impart the desired properties. The past decade has seen significant progress in our understanding of the preparations of nano metals of defined dimensions and specific shapes like nano spheres, nano rods and nano wires etc.[3] This naturally has stimulated research interest in the preparation of various rubber metal nanocomposites. The renewed interest in the above field is due to the fact that metal particles in nano meter scale dimensions can impart novel properties to the composites. As in the case of any other rubber nanocomposites, the dispersion of nano metals in a homogeneous manner within the rubber matrix is a haunting and challenging problem.

Conventionally rubber nanocomposites have been prepared by two strategies. In the first strategy the nano materials are added ex situ to the rubber matrix by melt mixing in a two roll mill or solution mixing in organic solvents.[4] But since the nano material possess high surface area and high surface energy, their addition to rubber matrix often results in aggregation. This leads to a non homogeneous dispersion of the metal within the rubber matrix. In the second strategy nano materials are generated in situ in rubber matrix.[5] But this is always associated with difficulties in removal of the unreacted reactants and byproducts from the final composite. Under these circumstances, we propose a novel route for the preparation of the rubber nanocomposites. In this method the nano metal is coated on a carbon black and then introduced to the rubber matrix using the conventional two roll mill. In the present paper we have demonstrated the above concept by the preparation of nano silver loaded carbon black with very low loading of the nano silver from 0.01% to 0.08%. This was followed by the preparation of rubber silver nanocomposites with various rubber curatives using a two roll mill. The cure characteristics, mechanical and dynamic properties of the nanocomposites have been characterized. The interesting results obtained in the above study have been discussed in the present paper.

Experimental Method

Natural rubber (ISNR 5) is used as the matrix. Fillers and other ingredients are of commercial grade. The nano silver suspension used for the study has been prepared in the laboratory by modifying existing protocols.

1. Preparation of the nano silver suspension and its characterization.

An aqueous 1 mM silver nitrate solution containing 1 mM trisodium citrate is irradiated in the gamma chamber 5000 unit (Co^{60}) at a dose rate of 2.0 Kgy / hr for 3 hours. The nano silver suspension is characterized using U.V. Spectrophotometer, Dynamic Light Scattering (DLS) and Transmission Electron Microscope (TEM).

2. Preparation of Silver loaded carbon black N330

The required amount of nano silver suspension is added to aqueous slurry of carbon black N 330. The mixture is dried in an air oven at 70 ° C until a constant weight is achieved. In this study N330 coated with 0.01 to 0.08 % nano silver have been prepared. XRD pattern of the silver loaded carbon black was recorded on a shimadzu diffractometer using Cu-Kα radiation operated at 50 kV and 100mA at 2θ range 30-80°.

3. Preparation of the Rubber–Silver nanocomposites.

Natural rubber (ISNR 5) is mixed with various rubber curatives as shown in **Table 1.** The carbon black N330 with 0.01 to 0.08 % nano silver loading is used to prepare the nanocomposites, RSnC 1 to 4. The composites are prepared in a two-roll mill (150 –300 mm).

Table 1 : Formulation of the mixes

Ingredients	Control	RSnC1	RSnC2	RSnC3	RSnC4
ISNR 5	100	100	100	100	100
Stearic Acid	2	2	2	2	2
Zinc oxide	5	5	5	5	5
HSL	1	1	1	1	1
N330	40				
0.01Silver@N330		40			
0.02Silver@N330			40		
0.04Silver@N330				40	
0.08Silver@N330					40
Naphthenic oil	7	7	7	7	7
Sulphur	2.5	2.5	2.5	2.5	2.5
CBS	0.7	0.7	0.7	0.7	0.7

4. Cure characteristics of the nanocomposites

The compounds are cured up to their optimum cure time (t90) at 150°C using a Moving Die Rheometer as per ASTM D 5289. The sulphur /CBS cure behavior of the control and nanocomposites with various loading of nano silver is evaluated.

5. Evaluation of mechanical and dynamic properties of the nanocomposites

Tensile properties of the composites are measured using Universal Testing Machine ('Zwick' UTM Model 1474) at a crosshead speed of 500 mm/min at 25 ° C

as per ASTMD 412-80. For ageing studies, tensile specimens of the samples are kept in an air oven at 100° C for three days. The tensile strength of the aged samples is determined, after conditioning the aged sample for 24 hrs.

The heat build up of the composites is evaluated using the Goodrich Flexometer using ASTM D 623- 93. The temperature sweep experiment of the composites is carried out using the DMA and the tan delta at 60°C is found out as per ASTM D 5279.

Results and Discussion

The gamma irradiation of the aqueous silver salt solution resulted in a clear yellow solution. The surface plasmon resonance (SPR) spectra of the nano silver suspension is recorded using the U.V. spectrophotometer and is shown in Figure 1. The peak extended from 320 nm to 500 nm and the maximum of the peak is observed at 400 nm. As per the previous studies, this clearly indicates the formation of nano silver particles.[6] The particle size is determined using DLS and TEM as shown in Fig. 2 and 3 respectively. The average particle size is observed around 15 nm by DLS and around 25 nm by TEM.

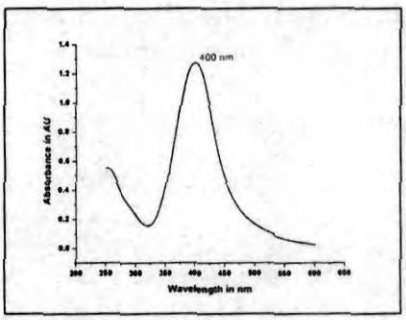

Fig. 1 : SPR spectra of the synthesized citrate capped nano silver

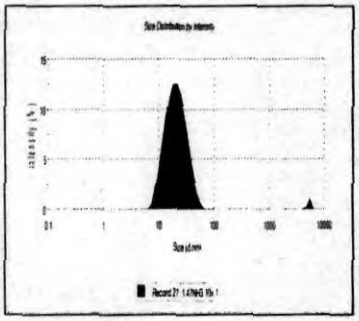

Fig. 2 : Particle size distribution of citrate capped nano silver by DLS

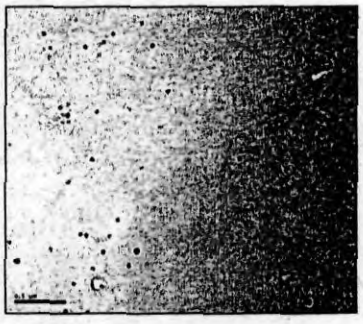

Fig.3 : TEM image of the citrate capped nano silver

The next stage is the preparation of silver loaded carbon black. For this the aqueous nano silver solution is treated with aqueous slurry of carbon black. After mixing for various time intervals, the supernatant is subjected to U.V. analysis. The absence of SPR spectra in the supernatant after 1 hr mixing, confirmed that the transfer of the nano silver from the aqueous phase to the carbon black phase is quantitative. The mixture is dried at 70 ° C in an air oven till a constant weight is obtained. In the present paper the loading of nano silver on carbon black is varied from 0.01 to 0.08%. The XRD pattern of the dried powder is shown in **Figure 4**. This pattern showed distinct diffractive peaks at 2θ values of 38, 44, 64 and 77° which confirmed the presence and crystalline nature of nano silver on carbon black.

The cure curves of the vulcanizate are as shown in **Figure 5**. The cure characteristics of the composites are given in **Table 2**. The rheometric torque for the nanocomposites is found to be higher than that of the control. The torque value for the nano composites containing 0.01 and 0.02 % nano silver loaded carbon black increased by around 20 % as shown in **Fig 6**. Further increase in the nano silver loading was

found to decrease the torque. The optimum cure time for the nano composite RSnC1 was almost the same as that of the control. With increasing content of nano silver the optimum cure time increased. The nanocomposites RSnC1 and2 with 0.01 and 0.02% nano silver loaded carbon black showed higher cure rate than that of the control. This is evident from the higher rate of increase in torque in the cure curves. But in nanocomposites RSnC4 and RSnC8, with higher concentration of nano silver, the cure rate of composites is found to be slower than that of the control.

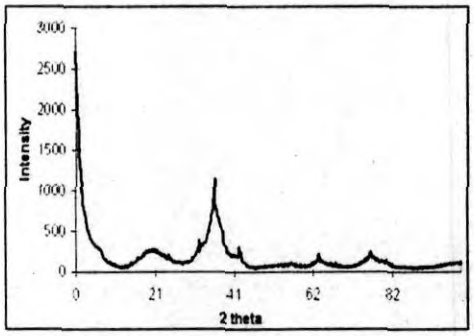

Fig.4 : The XRD pattern of nano silver loaded N 330

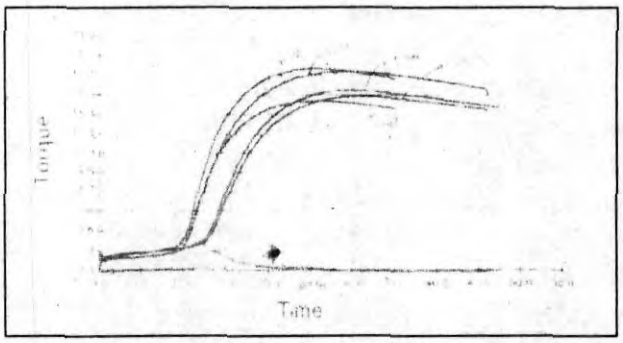

Fig.5 : The cure curves marked 0.01, 0.02, 0.04, 0.05 represent composites RSnC1, RSnC2, RSnC4, RSnC8 respectively along with control cure curve.

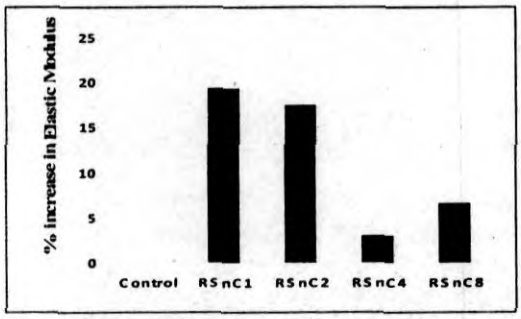

Fig. 6 : Percentage increase in elastic modulus of nanocomposites

Table 2 : Analysis of rheometric curve

	MH	ML	t100	t90	ts2
Control	**16.6**	**1.25**	**26.75**	**17.89**	**9.71**
RSnC1	**19.9**	**1.27**	**24.96**	**17.91**	**8.2**
RSnC2	**19.5**	**1.30**	**28.10**	**20.08**	**10.37**
RSnC4	**17.1**	**1.35**	**30.84**	**22.54**	**13.16**
RSnC8	**17.7**	**1.36**	**29.56**	**22.00**	**12.79**

The tensile strength and elongation at break of the nano composites and control is as shown in **Fig 7 and 8** respectively. The results obtained are comparable in both unaged and aged nanocomposites to that of the control. This confirmed that the presence of nano silver dosenot affect the ageing of the composites. The dynamic properties like heat build and tan delta @ 60° C of the nanocomposites and control are tabulated in **Table 3**. Interestingly the nanocomposites exhibited lower heat build up and lower tan delta.

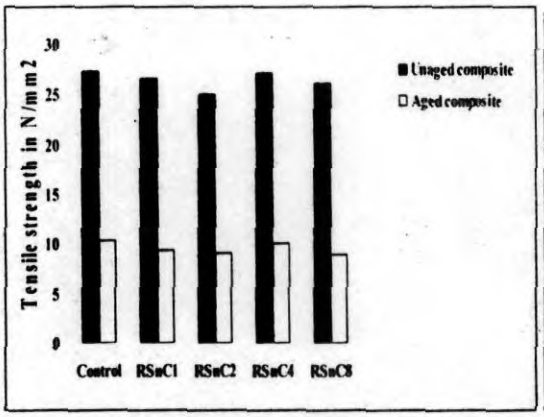

Fig. 7 : Tensile strength of the nanocomposites & control

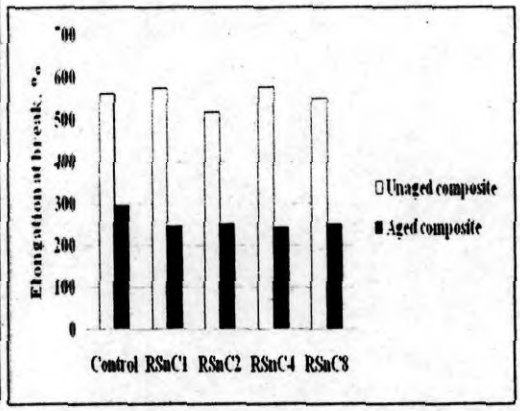

Fig. 8 : Elongation at break ,% of the nanocomposites & control

Table 3 : Tan delta and Heat build up of the composites

Sample	Tan delta @60°C	Heat build up
Control	0.07050	15
RSnC1	0.06436	14
RSnC2	0.05978	13
RSnC4	0.05304	09
RSnC8	0.05316	09

Summary

In the present paper nano silver has been prepared using gamma irradiation and coated on carbon black. Rubber Silver nanocomposites are prepared using silver coated carbon black and curatives in a two roll mill. The cure studies showed that the nanocomposites exhibited up to 20% increase in elastic modulus. The presence of nano silver did not affect the ageing behavior of the nanocomposites. Interestingly the nanocomposites exhibited lower tan delta and heat build up even at very low percentage incorporation of nano silver.

Acknowledgement

The authors acknowledge Dr. Benny George, Shri Madhusoodanan and Dr. Siby Varghese of RRII for helpful suggestions.

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