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SILVER NANOCLUSTERS AND NANOFRACTALS IN NATURAL RUBBER MATRIX

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ABSTRACT

Silver nanocrystals were synthesized in natural rubber matrix via UV irradiation technique. A high intensity UV light with a wavelength below 300 nm was used to reduce the silver ions in the natural rubber matrix. Silver ions ($AgNO_3$) were reduced in two different natural rubber environments i.e film and colloid. The resulting silver nanocrystals obtained were compared in terms of the morphology and particle size distribution investigated using transmission electron microscopy (TEM). Studies showed that small silver nanoparticles were obtained in natural rubber – silver (NR - Ag) films while nanofractals were formed in the NR – Ag colloids. XRD analysis confirmed the face centered cubic (fcc) structure of the silver crystals.

INTRODUCTION

Materials manufactured from polymers containing noble metal nanoparticles have received tremendous attention in the past few years. Synthetic as well as natural polymers such as PMMA[1] and chitosan[2] have been used as stabilizers and matrices. Natural rubber latex or also known as cis - 1, 4 – polyisoprene is a natural colloid obtained from the tree *Hevea Brasiliensis*. Due to its excellent properties and renewablity, it has been widely used in manufacturing industries such as tyres and gloves[3]. In an effort to broaden the use of this polymer in other fields, the first step was taken in implanting nanosized metal particles in films cast from the latex as well as stabilizing them in natural rubber colloid.

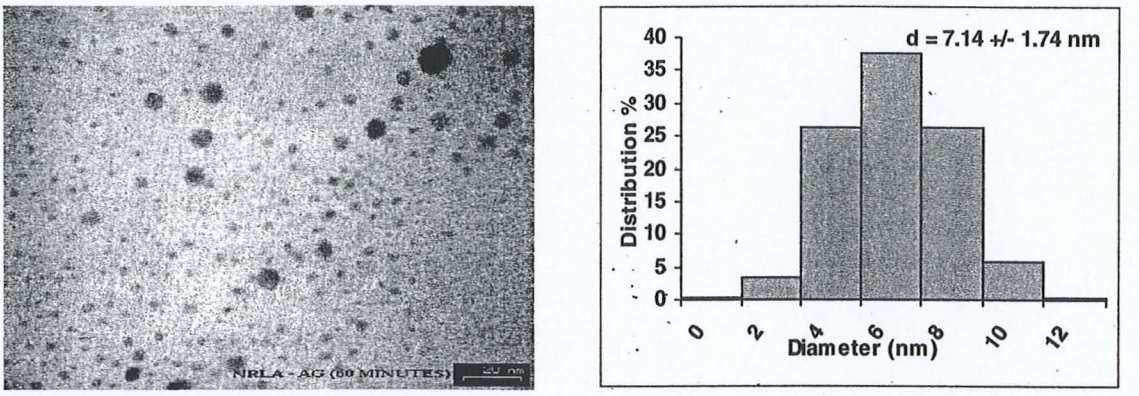
Nanosize noble metals display various properties compared to its bulk material. Different methods have been widely investigated in order to control the size of the nanocrystals formed. Among them are chemical reduction[4 - 5] and irradiation techniques[6]. Here, we discuss the formation of silver nanoclusters in natural rubber matrix, synthesized by UV irradiation.

MATERIALS AND METHODS

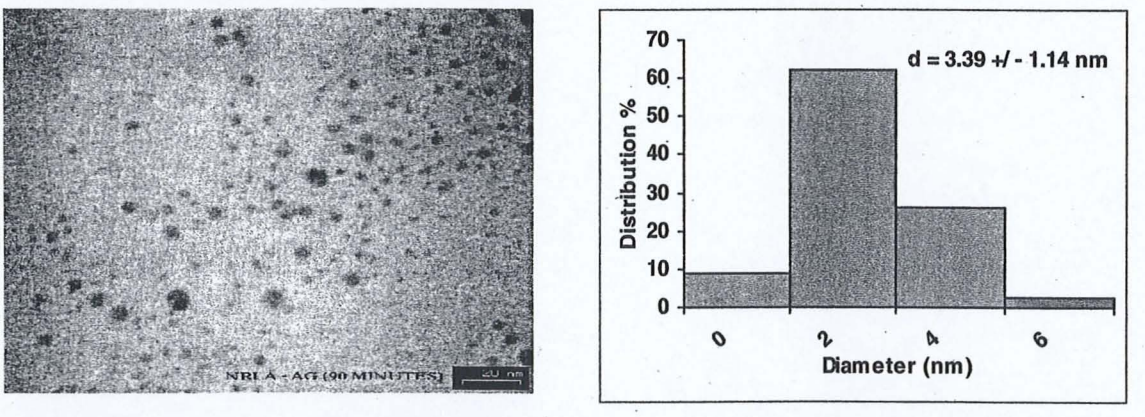
Natural rubber latex, a gift from BARD (Malaysia) Sdn Bhd, was centrifuged at 5613g using a Kubota Model 5800 centrifuge. The cream phase was separated and diluted to 30% DRC with doubly distilled water to obtain clean natural rubber latex. Following this, 1 g of the clean latex was weighed and diluted with 20 ml of distilled water. This colloid was then added with 2.94×10^{-5} mol of silver nitrate ($AgNO_3$) (Johnson Matthey, U.K.) and subsequently, the mixture was homogenized for 30 minutes.Two samples were prepared for TEM analyses. An aliquot of the homogenized mixtures above was diluted five folds with water. A drop of the diluted colloid mixture was then placed onto a carbon coated copper grid and dried at 50°C. The grid was then irradiated with the UV light followed by TEM analysis. To another aliquot, the homogenized mixtures were UV irradiated prior to the placement on the copper grid. Upon drying, the sample was subjected to TEM analysis.XRD analysis was also carried out on the samples. The patterns were obtained using a SIEMENS D5000 X–ray Diffractometer in the 2θ range of 20 – 60°.

RESULTS AND DISCUSSION

Small spherical silver particles were synthesized when NR – silver (NR - Ag) films were irradiated with a UV light. Figure 1a – b shows the TEM micrographs and size distribution histograms after 20 and 90 minutes of irradiation. The average particle size at both UV irradiation times is 7.39 ± 3.50 and 4.79 ± 1.70 nm respectively. It can be seen that a narrower size distribution was obtained after 90 minutes. This proves that the silver particle size reduces with increasing irradiation time.



(a)



(b)

Figure 1: TEM images of silver nanoparticles embedded in natural rubber films after (a) 20 and (b) 90 minutes of UV irradiation.

In contrast, when a mixture of NR – Ag ion colloid was irradiated, fractals were obtained. These structures were the result of silver cluster aggregation, based on the following reaction[7],

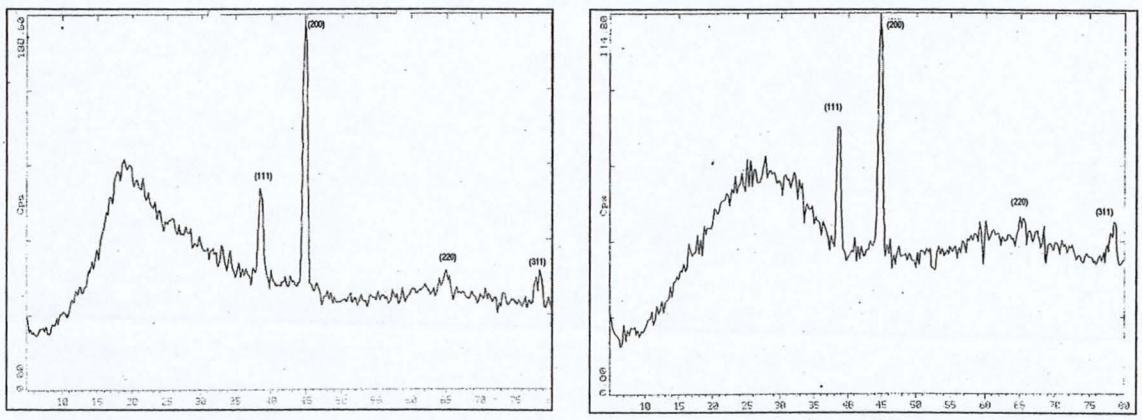
$$Ag^{+} \xrightarrow{\text{irradiation}} \text{Ag clusters} \xrightarrow{\text{aggregation}} \text{fractal morphologies}$$

This growth phenomenon occurs due to non-equilibrium growth and molecular anisotropy[8]. It has been reported that factors such as solvents[9] and absorbates[10] play a role in fractal growth. However, that is not the case here. Both systems contain the same amount of rubber and silver. Due to this, we can conclude that the fractals may be a result of rapid hitting and sticking of the silver nanocrystals, which can occur in the colloids, compared to the films. The fractal

dimension D = 1.67 is in agreement with the diffusion – limited aggregation model[11,12]. The TEM micrographs of the fractals are shown in Figure 2 at two different magnifications.

Figure 2: TEM Images of NR – Ag Colloids After 90 Minutes UV Irradiation

Finally, XRD analysis was carried out to observe the nature of the nanoparticles. XRD patterns of the samples exposed to UV irradiation in films as well as in colloid systems are typical of the silver crystals as presented in Figure 3a – b. Both patterns clearly demonstrate that the peaks are assignable to the (111), (200), (311) and (222) planes of face centered cubic (fcc) silver crystals. These are similar to those reported by Yongchun Zhu et al.[13].



(a) (b)

Figure 3: XRD Patterns for (a) Natural Rubber – Silver Film, (b) Natural Rubber – Silver Colloid.

CONCLUSION

In summary, it has been shown that it is possible to synthesize silver nanocrystals with different morphologies even with the same materials. Spherical silver nanoparticles with an average size of 4.79 ± 1.70 nm in films after 90 minutes of irradiation were able to be firmed. On the other hand, nanofractals with a fractal dimension of 1.67 were obtained in NR – Ag colloids.

ACKNOWLEDGEMENT

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