

# Formation of Silver Nanoparticles in Natural Rubber Matrix

N. H. H. Abu Bakar<sup>1</sup>, J. Ismail<sup>1,\*</sup>, M. Abu Bakar<sup>1</sup>

*Nanoscience Research Laboratory,*

*<sup>1</sup>School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia*

\* To whom correspondence shall be addressed,  
Email: [dchem@usm.my](mailto:dchem@usm.my); Tel: 604-6577888; Fax: 604-657 4854;

## Abstract

Metallic silver nanoparticles were formed in natural rubber matrix via photo reduction of films cast from natural rubber latex containing silver salt. The particles formed are discrete spherical silver nanocrystals with a size range of 4.8 to 10 nm and narrow size distribution, as confirmed by TEM and XRD analysis. The particle size depends on the time of exposure to light. The presence of protein in natural rubber may be responsible for the formation of these discrete particles in the natural rubber matrix. This paper reports the findings.

*Keywords: Natural rubber matrix; Silver nanoparticles; Nanocomposites*

## 1.0 Introduction

The morphology and size of metal nanoparticles are influenced by various factors such as the reducing agent and stabilizer used as well as the matrix or environment in which they are formed. Many researches have studied the synthesis of metal particles in order to obtain metal nanoparticles with desired shape and sizes, for it is well known that these factors affect the properties of the resulting nanocomposites [1, 2].

Various polymers have been employed as stabilizers or matrix as they provide the nanoparticles with conducive environment for stability by preventing them from

oxidation and coalescence [3]. Studies on the size and shape of noble metal nanoparticles in different matrices have been carried out, for instance, the synthesis of silver nanometals in polyvinylpyrrolidone (PVP) [4], hyperbranched polyurethane (HP) [5] and polyacrylonitrile (PAN) [6]. It has been found that spherical silver nanoparticles were formed in all three polymers. However the average size of the silver nanoparticles varied in each case. This shows that while the matrices can act as stabilizers their effectiveness as a stabilizer varies.

Reports on the syntheses of metal nanoparticles in renewable polymers are few. Among the natural polymers that have been used as stabilizers or matrices for metal nanoparticles are chitosan [7] and cellulose [8]. To date, there has yet been any research involving metal nanocrystals synthesized in natural rubber (NR). Natural rubber latex is a creamy colloid, which has been used widely in industries such as for adhesives, gloves, and latex based health care products. The latex particles with sizes ranging between 0.2 to 2 microns consists mainly *cis*-1,4-polyisoprene surrounded by a thin membrane of proteins and lipids. Silver-protein complexation is well known and in the case of natural rubber latex it may offer some potential as a stabilizer for metal nanoparticles. Thus, we carried out investigations to study the growth and morphology of silver nanocrystals in natural rubber film cast from its latex. For the purpose of comparison, studies were also carried out in films by solution casting using latex systems such as deproteinized natural rubber (DPNR) latex in which particles are stabilized with sodium dodecyl sulfate (SDS), NR latex containing SDS, and bovine serum albumin (BSA) solution. Here, we report the results of the above studies.



## 2.0 Experimental

Natural rubber and deproteinized natural rubber latexes of 60% dry rubber content (DRC) were provided by BARD Malaysia Sdn. Bhd. and SUMI Rubber Malaysia respectively. Both latexes were centrifuged at 5613 g using a Kubota Model 5800. The cream phase was then separated and diluted to 30% dry in order to obtain clean latex, which was used to prepare the metal nanocomposite films. Bovain albumin serum with a concentration of 10mg/ml was purchased from Promega, Madison, USA and was used without further purification.  $\text{AgNO}_3$  was obtained from Johnson Matthey Materials Technology, UK.

Typically, 1 g of clean latex was diluted with 20 ml of distilled water before adding 0.005 g ( $2.94 \times 10^{-5}$  mol) of  $\text{AgNO}_3$ . The mixture was homogenized for duration of 30 minutes followed by casting on a microscope glass substrate and dried overnight in an oven at 50 °C. The resultant films were subjected to a UV light to reduce the silver ions. A 250 W high intensity mercury lamp with a wavelength of less than 300 nm was used as a light source. The above procedure was repeated for the DPNR and NR stabilized with 5 % (wt/v) SDS. As for albumin serum, the same quantity of silver salt was homogenized with appropriate volume of the solution, then cast and dried to finally obtain thin films. These samples are used for structural and spectroscopic measurements.

Silver nanoparticles were measured using JEM-1230 Transmission Electron Microscope operating at 20kV. Films were prepared on copper grid mesh by placing a drop of latex-salt mixture on a carbon-coated copper mesh grid and allowed to dry under conditions described above. Appropriate time of exposure to UV light was used in the studies of reduction of silver ion in natural rubber matrix. On the other hand,

XRD analysis was carried out using a SIEMENS D5000 X-ray Diffractometer with a Cu – K $\alpha$  radiation monochromatic filter in the 2 $\theta$  range of 20° – 80°.

### 3.0 Results and Discussion

In the present work, silver nanoparticles were formed in dried films after exposure to UV light. Figure 1 shows typical silver nanoparticles formed in the natural rubber matrix. The nanoparticles are spherical in shape and exhibit a narrow size distribution. However, they are less homogeneously dispersed in the matrix. The occurrence of particles seems to be confined at the interstitial region of the fused latex particles that form the film matrix. The population density of discrete nanoparticles is higher than in other regions suggesting good stabilizing property of NR that could be due to the protein and lipids present on the surface of the rubber particles.

The silver nanoparticles for all samples studied are characterized by XRD technique. Typical metallic silver XRD spectrum is shown in Figure 2 where only silver peaks are observed. These peaks are indexed to the (111), (200), (220) and (311) planes representing the face centered cubic (fcc) phase of silver as reported elsewhere [9].

Figure 1

Figure 2

The size of silver nanoparticles changes with the time of exposure and the salt concentration. Table 1 summarizes the particle sizes of the silver nanocrystals obtained after different exposure times for NR containing  $1.4 \times 10^{-3}$  M of AgNO<sub>3</sub> as well as at different concentrations of silver salt. The average size of the particles



decreases with increasing time of exposure but increases with silver salt concentration.

#### Table 1

The role of protein on the formation of silver nanoparticles may be important in the present NR-silver nanocomposite as suggested by the above results. The silver ions may have complexed with the protein molecules found on the rubber surfaces during mixing and drying. In dried films the silver ions are immobilized as complexes and reduced to nanocrystals upon exposure to UV light. This gives rise to the apparently high concentration of the silver nanoparticles in the region where the rubber particles coalesce and interdiffuse to form continuous matrix. The silver nanoparticles are stable even after six months suggesting the stabilizing property of NR.

The above results are significant for NR as it relates to the presence of protein in the rubber latex. This motivates us to continue our investigation on the formation of silver nanoparticles in a system without protein using DPNR latex under similar conditions. DPNR latex is one in which practically all proteins have been removed and is stabilized by SDS. Figure 3 shows the TEM micrograph of the metallic silver particles in DPNR matrix. Apparently, aggregates of silver metals are observed in the composite films instead of discrete nanoparticles. It is further noted that the aggregates increase in size according to time of exposure from 20 minutes (Figure 3(a)) to 90 minutes (Figure 3(b)). It was also noted that a small number of discrete nanoparticles occur in the vicinity of the aggregates. The results suggest that DPNR is not an effective stabilizer. However, the role of protein could not be interpreted due to the presence of SDS on the surface of rubber particles, which could have caused

interference on effects associated with the absence of protein. To understand the occurrence of aggregates we used clean natural rubber latex in which 5 % (wt/v) SDS was added and again the reduction reaction was carried out under the same conditions. The TEM results show the formation of silver metal aggregates, similar to that observed in DPNR. This is shown in Figure 4. The results suggest that in the presence of SDS additive, with or without protein, aggregation of silver is dominant. Thus it may be concluded that in NR latex, SDS influences the formation of aggregates and in its absence, protein is responsible for the formation of spherical silver nanoparticles.

Figure 3

Figure 4

The unique role of protein is further demonstrated in another study in which reduction of silver was carried out in a neat protein environment. Here BSA (the only protein available during the time of this study) was used as a model protein to simulate  $\alpha$ -globulin of which is known to be present in NRL.  $\alpha$ -globulin has chemical properties similar to that of albumin but its molecular weight is generally higher [10, 11]. Proteins have amino acids such as histidine, cysteine, aspartic and glutamic acid, which act as binding sites for transition metal salts [12]. Figure 5 show the micrographs of silver nanoparticles formed under the influence of metal–neat albumin interaction at 20 and 90 minutes of exposure. All conditions remain the same and the particles formed are spherical in shape, time dependent and have a narrow size distribution. They are homogeneously dispersed in the matrix. Typical average sizes are  $4.2 \pm 1.7$  and  $8.8 \pm 4.6$  nm after 20 and 90 minutes exposure respectively. The silver nanoparticles increase in size with time of exposure in contrast to the behaviour in NR matrix. A possible explanation for the reverse trend in the neat



protein environment may be due to the absence of hindrance to the mobility of the silver particles caused by NR molecular chains. The mechanism for the formation of spherical silver nanoparticles has been reported elsewhere [13]. The nanoparticles are stabilized in a matrix, which is entirely attributed to the protein. Previous study has also shown that protein can interact with metal surface via  $\text{-NH}_2$  [14] as well as  $\text{-SH}$  [15] that exist in albumin. However the manner of interaction is not fully understood. It has also been reported that silver, like gold is expected to show high interaction with amino groups due to its large complexation constant for noble metal amines [16]. The results demonstrate the effect of protein and may provide explanation on the role of protein in natural rubber on the formation of silver metal nanoparticles.

Figure 5

Figure 6

In this work, the occurrence of simultaneous photo-oxidation of NR during reduction and formation of silver nanoparticles is also noted. This is a critical reaction as it affects degradation of NR and therefore poses a challenge to the study and development of NR-Ag nanocomposites. Experimental evidences of such changes are demonstrated by the FTIR and gel permeation chromatography (GPC) measurements. Shortening the time of exposure is a practical way to minimize NR oxidation while reduction to metallic silver is still accomplished. Figure 6 illustrates the spectra of NR and NR - Ag composites showing the effect of UV exposure. It is evident that photo-oxidation is not significant comparing NR - Ag for 3 minutes exposure (b) to NR (a) while NR - Ag after 90 minutes of exposure has significant photo-oxidative effects. The molecular mass of NR before and after 3 and 90 minutes of exposure time respectively confirm this and are presented in Table 2.

Following this, besides its role as stabilizer the FTIR study also showed that albumin is resistant to UV light suggesting the photo stability of protein in general. Furthermore the silver-protein interaction leading to spherical silver particles could also immobilize protein molecules in the natural rubber matrix. This phenomenon is of technological importance to natural rubber applications associated with latex based products especially in the health care sectors. While the main interest of our study is to increase understanding on the formation metal nanocrystals in natural rubber matrix where protein is concerned, it is equally important to study other methods of silver ion reduction that offer minimum oxidation of NR and maximum capability to stabilize nanocrystals. Ongoing investigation is looking into these aspects.

#### Table 2

### **4.0 Conclusion**

Silver nanoparticles have been formed in NR films by reduction of silver salt via UV exposure. The particles are metallic silver nanocrystals with average sizes of less than 10 nm and time dependent. The protein present in natural rubber latex is believed to play an important role in the growth and stabilization of the particles. Aggregates of nanoparticles of metallic silver are observed in DPNR and NR containing surfactant SDS.

### **Acknowledgements**

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Appendix

Figure 1

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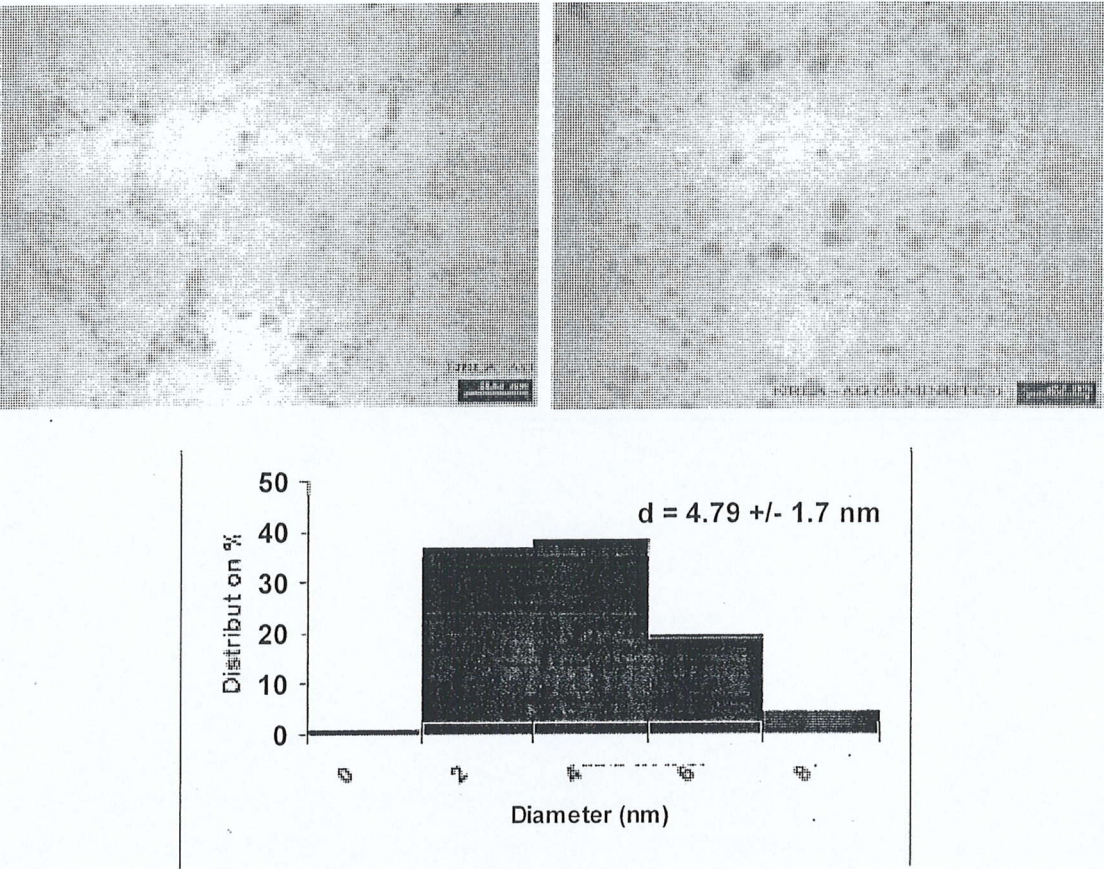


Figure 2

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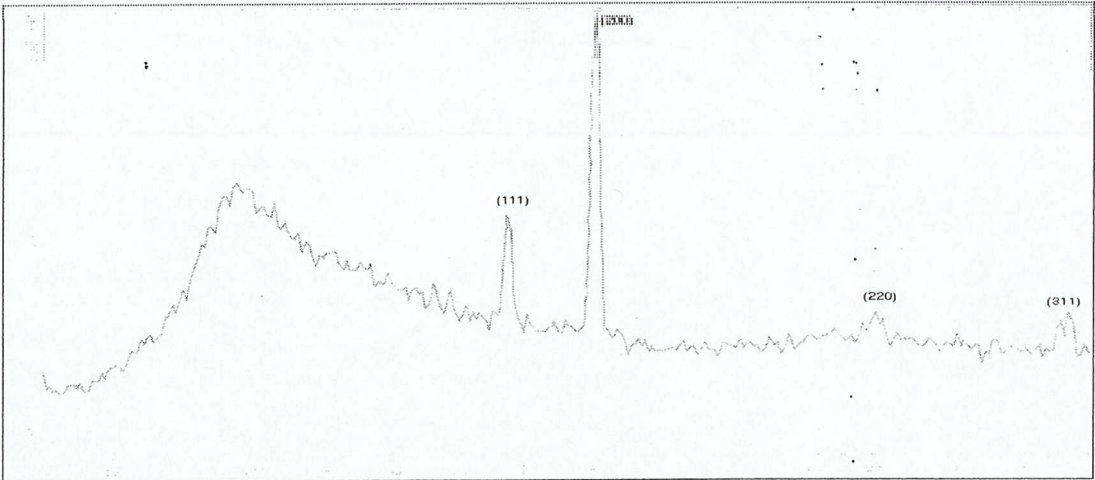
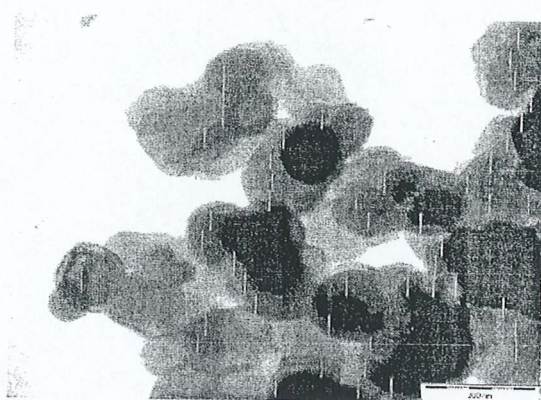
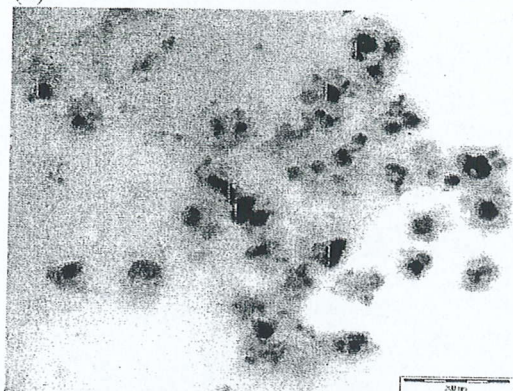




Figure 3

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(a)



(b)

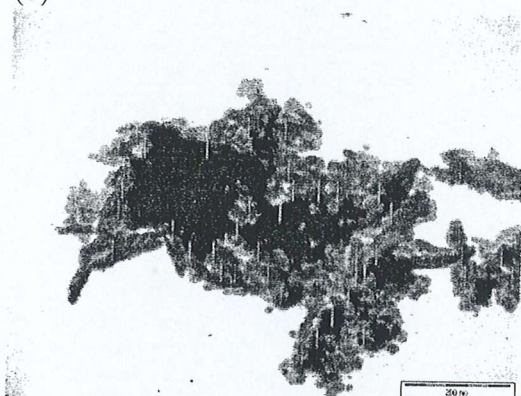
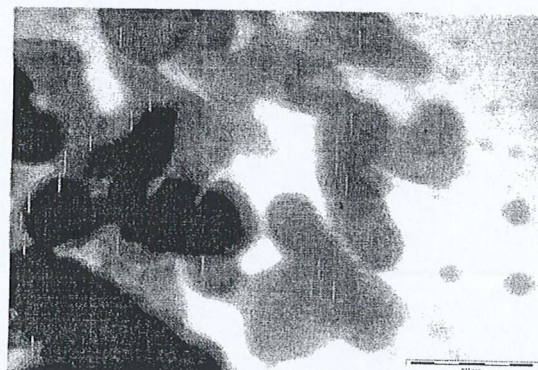
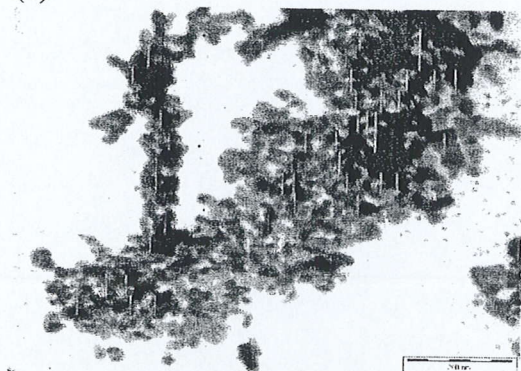


Figure 4

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(a)



(b)

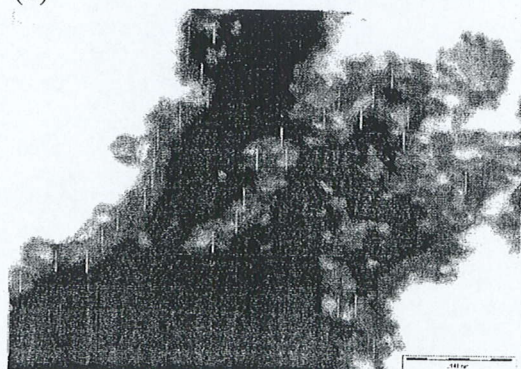




Figure 5(a)

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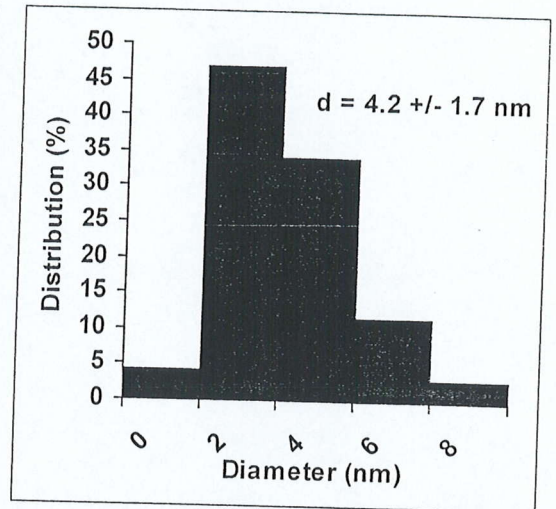
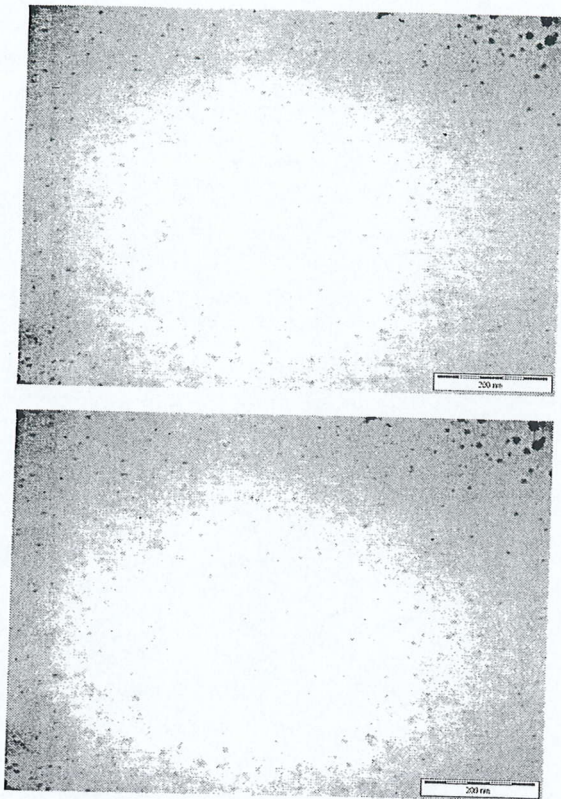
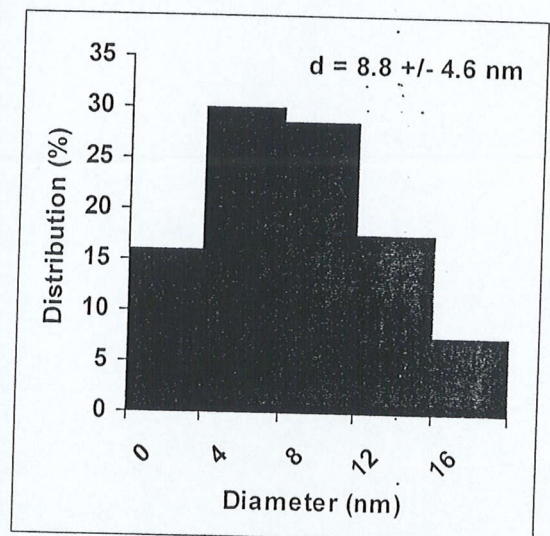
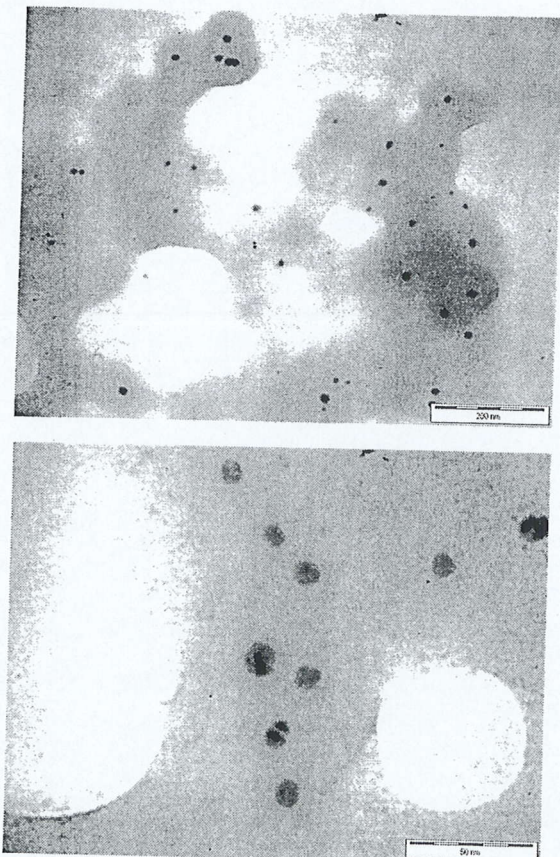


Figure 5(b)



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## Figure Captions

- Figure 1:** TEM images and size distribution of silver nanoparticles in NR – Ag films after 90 minutes of UV exposure.
- Figure 2:** XRD spectrum of NR–Ag composite film after 90 minutes of UV light exposure.
- Figure 3:** TEM images of silver aggregates in DPNR–Ag films after (a) 20 minutes and (b) 90 minutes of UV exposure.
- Figure 4:** TEM images of silver aggregates in NR - SDS films after (a) 20 minutes and (b) 90 minutes of UV exposure.
- Figure 5a:** TEM micrographs and size distribution of silver nanoparticles in albumin – Ag after 20 minutes of UV exposure.
- Figure 5b:** TEM micrographs and size distribution of silver nanocrystals in albumin – Ag samples 90 minutes of UV light exposure.
- Figure 6:** FTIR spectra of (a) NR and NR-Ag after exposure with a UV light for (b) 3 minutes and (c) 90 minutes.

Tables

**Table 1:** The average size of silver nanoparticles in NR–Ag films at various UV exposure times and different AgNO<sub>3</sub> concentrations.

UV Exposure Time (Min)	AgNO <sub>3</sub> (10 <sup>-3</sup> M)	Average Particle Size (nm)	Standard Deviation
20	1.40	7.4	3.5
60	1.40	5.2	3.0
90	1.40	4.8	1.7
90	0.84	4.6	1.2
90	1.96	8.0	2.6
90	2.52	9.7	3.1

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**Table 2:** Molecular weight of NR after various UV exposure times.

Conditions	Mw
No UV exposure	830000
3 minutes UV exposure	840000
90 minutes UV exposure	400000

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