

RADIATION PROCESSING OF ACTIVE BIODEGRADABLE GREEN NANO COMPOSITE MATERIALS FOR PACKAGING PURPOSES

Hassan A. Abdel-Rehim, El-Sayed A. Hegazy, and Ahmed Raafat.

National Center for Radiation Research and Technology NCRRT, Atomic Energy Authority, Cairo, Egypt P. O. Box 29, Nasr City, Cairo, Egypt.

Abstract

Clean and green reduction process of silver ions and graphene (GO) into nanosilver metal and graphene (GR) nanosheets respectively was achieved via gamma irradiation. The efficiency of gamma radiation to reduce silver ions and graphene oxide (GO) was investigated using UV-vis spectroscopy. Effects of gaseous atmosphere type, dispersion pH value, capping agent type and irradiation dose on GR nano-sheets formation were investigated. The presence of capping agent such as sodium carboxymethyl cellulose (CMC) or cellulose acetate is proven to be crucial. The obtained GR nanosheets and nanosilver metals are characterized using atomic force microscopy (AFM), transmission electron microscopy (TEM), Fourier transform infrared spectrometry (FT-IR), X-ray diffraction (XRD) as well as thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC). Effectiveness, simplicity, reproducibility, and low energy consumption are the merits of using the Gamma radiation technique. Furthermore, the capping agent is eco-friendly and the dispersion is stable for months at room temperature. This approach can open up large-scale production of GR nanosheets and nanosilver metals.

The prepared Nano-silver can be mixed with different natural polymer like CA to form Nano-composite films. The excellent physical properties of CA did not affect by adding Ag. The ionizing radiation has un-significant effect on the properties of CA-Ag nano composites films. The CA-Ag nano composites possess biological activity towards different microorganisms. On other hand graphene or graphene oxide dispersions might be of interesting for producing biological active packaging films. Go as nanofillers has used for fabrication of a biocomposite with chitosan. The significantly improved in Chitosan /Go nano composites physical properties, including mechanical property, electrical conductivity, and structural stability, was demonstrated. Properties of the CA-Ag and Chitosan /Go nano composites suggest their uses as active eco-friendly food packaging materials.

1. Introduction

Most materials currently used for packaging are non-degradable, generating environmental problems. Several biopolymers have been exploited to develop materials for eco-friendly food packaging. However, the use of biopolymers has been limited because of their usually poor mechanical and barrier properties, which may be improved by adding reinforcing compounds (fillers), forming composites. Most reinforced materials present poor matrix–filler interactions, which tend to improve with decreasing filler dimensions. The use of fillers with at least one nanoscale dimension (nanoparticles) produces nanocomposites. Nanoparticles have proportionally larger surface area than their microscale counterparts, which favors the filler–matrix interactions and the performance of the resulting material. Nanocomposites, defined as polymers bonded with nano-particles to produce materials with enhanced properties, During the processing stage, there is a possibility of re-aggregation where the particles clump together. If this happens, the creation of the nano-composite is un-successful. Compatibility between the nano-fillers and the polymer substrate may cause issues as well,

depending on how they interact with each other. Certain nano-fillers need to be prepared so they can perform well with the substrate. Besides nano-reinforcements nanoparticles can have other functions when added to a polymer, such as antimicrobial activity, and, biosensing, etc.

Research continues into other types of nanofillers (i.e., silver metals and carbon nanofiller), allowing new nanocomposite structures with different improved properties that will further advance nanocomposite use in many active diverse packaging applications. The rapid use of nano-based packaging in a wide range of consumer products has also raised a number of safety, environmental, ethical, policy and regulatory issues. The main concerns stem from the lack of knowledge with regard to the interactions of nano-sized materials at the molecular or physiological levels and their potential effects and impacts on consumers health and the environment. Research and development in the field of active and intelligent packaging materials is very dynamic and develops in step with the search for environmentally friendly packaging solutions. In this context, the design of tailor-made packaging is a real challenge, and it implies the use of reverse engineering approaches based on food requirements and not just on the availability of packaging materials any longer. Nanotechnologies are expected to play a major role, taking into account all additional safety considerations and filling present packaging needs. The present work dealing with preparation of cellulose acetate /Ag and Chitosan /graphene oxide active nano-composite films for packaging purposes (1,2).

2. Experimental

2.1.Preparation of GO

GO is prepared from natural graphite powder according to Hummers and Offeman method (3). 1.5 g of graphite powder is mixed well with 35 g of H₂SO₄ in 500 ml beaker for 0.5 h and then 0.75 g of NaNO₃ is added to the mixture under stirring. The resulting mixture is cooled to 0 °C and then put into ice bath during the slow addition of 4.5 g of KMnO₄ (solid) under vigorous stirring. Keep stirring for further 2 h after complete addition of KMnO₄. After then, the mixture is warmed to ~35 °C and stirred for 0.5 h. 70 ml of water is added slowly under stirring producing large exotherm to ~98 °C. Keep this temperature for 15 min by external heating then cool the mixture to room temperature and add another amount of water (250 ml) and 3 ml of 30% H₂O₂ producing another exotherm and yellowish brown dispersion of GO is obtained. GO is isolated and washed many times with 5% HCl to remove SO₄⁻² ions, and ultrapure water to remove Cl⁻ ions, Successively by centrifugation at 4000 rpm for 45 min and the drying at 60 °C for 3 h.

2.2.Gamma irradiation of GO dispersion

Samples are irradiated with the ⁶⁰Co Indian irradiation facility gamma rays at a dose rate (4.0) KGy/h. The irradiation facility was constructed by the National Center for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority (EAEA).

First, disperse 40 mg of pre-prepared pristine GO in 120 ml of ultrapure H₂O using ultrasonic probe for 10 min. to get clear yellowish brown colloidal dispersion. Second, prepare 0.1% (w/v) solutions of CMC, EHEC, PVA and Glucose and mix 40 ml of each with 60 ml of GO colloidal dispersion under mild stirring for 15 min. Samples of each composition are different doses (10, 20, 30, 40, 50 KGy) at different PH values and in presence or absence of air. GR is separated from highly stable dispersions via ultra centrifugation at 15,000 rpm for 30 min. and dried under vacuum at 60 °C for 3 h for further characterization.

3. Results and discussion

Interest in the use of active and intelligent packaging systems for food products has increased in recent years. Active packaging refers to the incorporation of additives into packaging systems with the aim of maintaining or extending food product quality and shelf-life. In the present work nano-silver metal and graphene nano-sheets prepared by ionizing radiation were incorporated into some natural polymer to produce active biodegradable packaging materials.

3.1. Preparation of Antibacterial CA, containing nano Ag for food packaging

Stable and highly dispersed nanosilver metal was prepared by mixing cellulose acetate with AgNO_3 (1:1wt/wt) in acetone as a solvent and irradiated the solution with Gamma rays at 30K Gy. Ionizing radiation reduces silver ions to nanosilver metal that distinguishes with yellowish brown color. The prepared Ag nano particles capped in CA do not aggregate or precipitate and they highly disperse for long time. The average size of The prepared nanosilver were determined using Dynamic light scattering (DLS) and transmission electron microscope TEM. The average size of the prepared nano-silver was found to be around 8 nm Fig. 1.

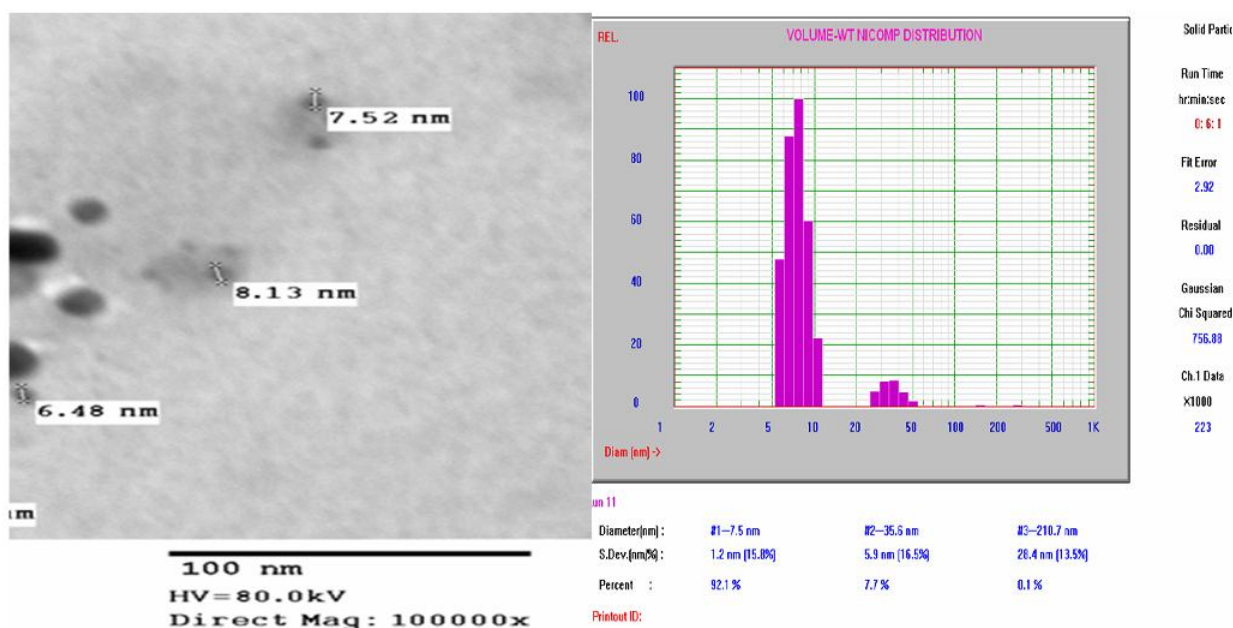


Fig. 1. TEM and DLS of the prepared Ag nano particles capped in CA.

The most frequently used approach to prepare dispersion of silver nanoparticles attached in polymer matrices involves the entrapment of silver cations from polymer chains followed by reduction with gamma rays. This method presents two advantages compared to the simple mixing of the two components and the polymerization in the presence of pre-synthesized silver nanoparticles. Firstly, the template role of the host macromolecular chains for the synthesis of nanoparticles helps improve the dispersion of nanoparticles inside the polymeric matrix, and also partially prevents the formation of aggregates. Secondly, the template role that the polymer chains, leads to reduced size of nanoparticles with a narrow size distribution and well defined shape as shown in the Fig. 2.

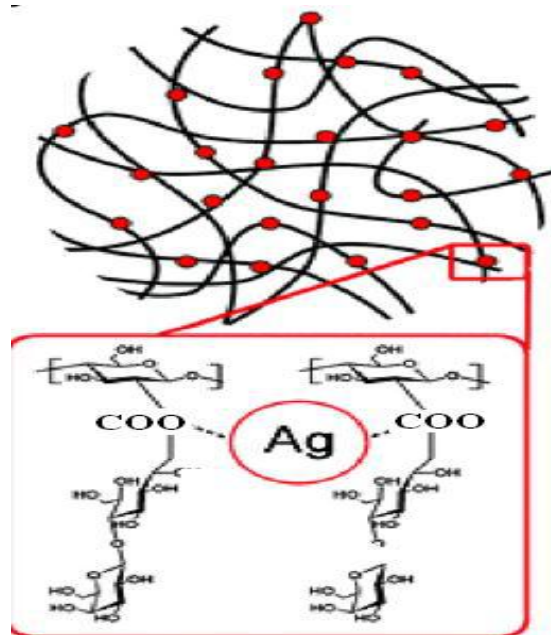


Fig. 2. mechanism of formed stable silver nanoparticled capped with CA.

3.2.Preparation of AC-Ag nanocomposite films

Cellulose acetate was dissolved in acetone and mixed with different amount of Nano-silver prepared by irradiation in the presence of capping agent. The mixture solution was poured in Petri dish and left to dry at 25°C. The color of prepared Nano composite films is change from colorless to brown. As the Ag increases, the intensity of film color increases. Fig 3

3.3.Effect of Nano-silver on the structural of CA film

The structure and properties of pure CA film and CA-Ag composite films were studied. FTIR revealed that there no change in the chemical structure of CA film after composing with nanosilver metals. Meanwhile, . Xrd date shows that the presence of Ag at relatively high concentration (3%) alters the crystallinity of CA. Fig. 4 Mechanical properties of CA composites of different Ag content were investigated. Slight improvement on tensile strength of CA-Ag composite films was archived if compared with that for pure CA.Table1.

3.4.Effect of gamma rays on the properties of CA-Ag nanocomposite

CA-Ag Nano composites of different Ag contents were exposed to ionizing radiation at different irradiation doses. The irradiated samples were characterized using ESR, FTIR Mechanical testing. ESR measurement revealed that the radicals that form during the irradiation at (30kGy) decayed and /or recombined after 6hr after irradiation process . Consequently, it was expected that the irradiated film keep unchanged if storing after irradiation treatment for long time. Insignificant effect on the mechanical property and structure of irradiated CA-Ag Nano composite was also observed .

The biological properties of Ag-CA nano composite of different silver contents towards gram positive and gram negative bacteria was investigated. It was observed that theca/Ag composite films of different Ag contents possessed antimicrobial activity property against gram negative and gram positive bacteria Fig 5.

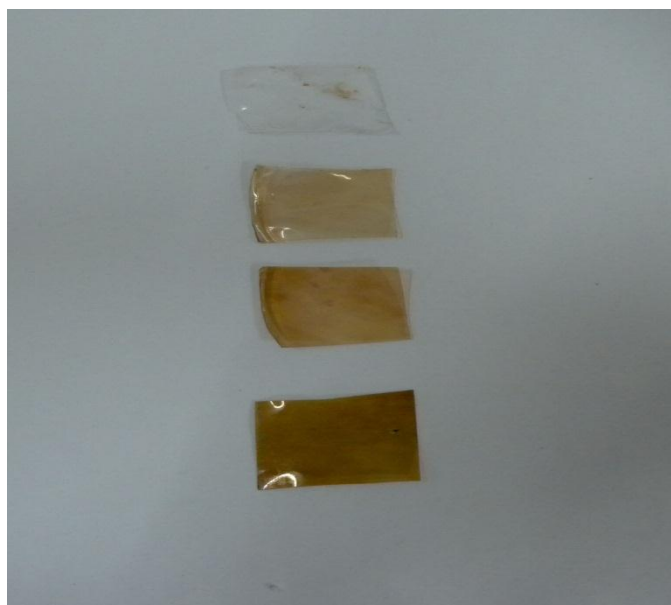


Fig. 3. change on CA colore after composing with different amount of Ag

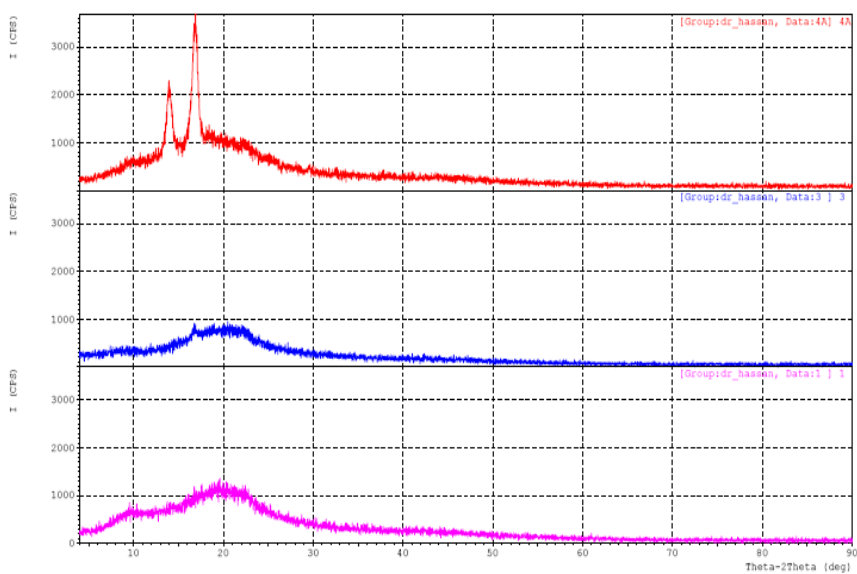


Fig. 4. Effect of Ag capped by CA using Gamma rays on the structure and crystallinity of CA.

TABLE 1. MECHANICAL PROPERTY OF CA AND CA/AG NANOCOMPOSITE FILMS AT DIFFERENT CONCENTRATION OF AG

	Tensile MPa	elongation %
CA Black	34	8
CA + 1% Ag	36	6
CA + 2% Ag	35	5
CA + 3% Ag	37	8



Fig. 5. The biological properties of Ag-CA nano composite of different silver contents towards gram negative bacte

3.5.Migration of nano-silver from Ag-CA nano composite film

Release of Ag from CA was investigating. The film was soaked in distilled water for interval times up to 72 h and the amount of Ag release was determined. It was found that the amount of Ag release after 24h is very limited and does not increase significantly by time. On the other hand, the Release of Ag from CA film (prepared in thee presence of 5%PEG400) was relatively high if compared with that prepared in absence of 5%PEG400. The results assumed that the hydrophobicity and rigidity of CA restrict the incorporated Ag to move and release outside the films.

3.6.Green synthesis of highly stable graphene nano-sheets using Gamma radiation

Clean and green reduction process of graphene oxide (GO) into graphene (GR) nanosheets was achieved via gamma irradiation. The efficiency of gamma radiation to reduce GO into

GR nanosheets was determined using UV-vis spectra. Capability of gamma rays for reduction of GO at different atmospheres and pHs was investigated

At pH 7, GO dispersion saturated with air or N₂ were gamma irradiated at dose of 50 KGy. The color of irradiated GO dispersion saturated with nitrogen gas changed from yellowish brown to dark one. Meanwhile, no significant change on the color of dispersion saturated with air was observed. UV-vis spectra confirm this observation as the absorption peak at 278 nm was recorded only for the irradiated dispersion saturated with N₂ gas Fig. 6. the apparent peak at 278 nm can be attributed to GR .

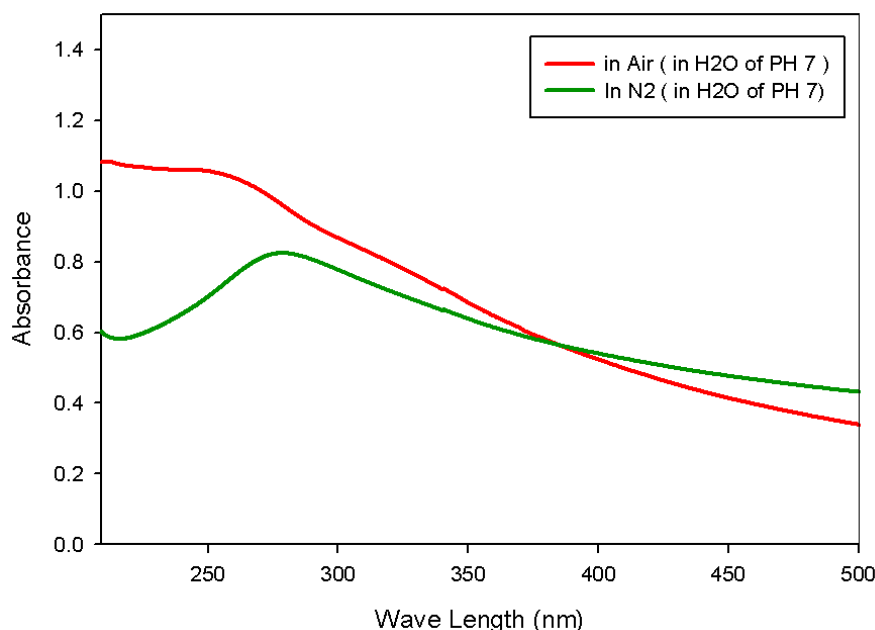
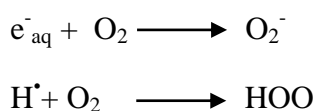


Fig. 6. UV-vis spectra show the effect gaseous atmosphere-type on reduction process of GO into GR at irradiation dose of 50 KGy at PH 7 in absence of capping age.

This behavior can be explained by assuming that in N₂-saturated dispersions at PH 7, the reaction takes place with each of (solvated electrons e⁻_{aq}, OH[•] and H[•]). In absence of OH[•] scavengers, a competition between Oxidizing species (OH[•]) and reducing species (solvated electrons e⁻_{aq} and H[•]) is established and low concentration of GR is formed. This justifies the weakness in UV absorption peak at 278 nm. But in air-saturated dispersions at PH 7, the reactive species are OH[•] and the couple O₂^{-•} / HOO[•] (superoxide radical anion / perhydroxyl radical) and this couple is originated by scavenging reducing species (solvated electrons e⁻_{aq} and H[•]) with O₂ (4):



The presence of such oxidizing species restricted the GO reduction and may aid in further oxidation of GO.

The irradiation process for GO dispersions saturated with nitrogen was carried out at different pHs and the yield of formed GR was determined using UV-vis spectra Fig. 7. It can be seen that at low pH 2.5 the reduction of GO does not occur. As the pH value increases, the

intensity of peak at 279 nm increases. This means that the reduction of GO by ionizing radiation takes place at high PH value.

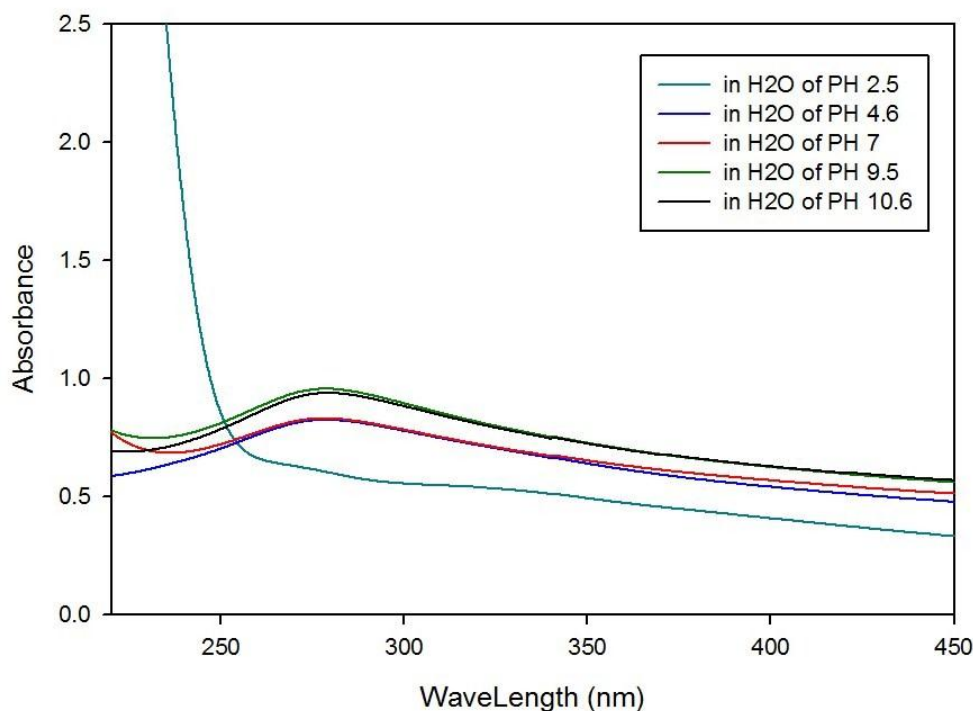
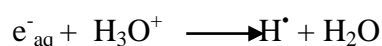


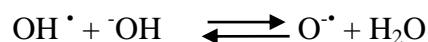
Fig. 7. UV-vis spectra of GO dispersed in N_2 -saturated H_2O of different PHs irradiated at 50 KGy.

In case of strong acidic medium PH 2.5, nearly equal amounts of OH^\bullet and H^\bullet only are present. This is due to that solvated electrons (e^-_{aq}) are converted into H^\bullet by reacting with hydroxonium ions (5):



As a result, no change occurred to GO dispersion of PH 2.5 after radiation.

The small increase in the intensity of UV-vis absorption spectra in alkaline (PH 9.5, 10.6) than that in slightly acidic (PH 4.6) and neutral (PH 7) conditions suggests that a little more efficient reduction occurred. This change is due to the appearance of less reactive oxidizing species O^\bullet instead of more reactive OH^\bullet due to the reaction (5):



The yield of GR obtained from N_2 -saturated GO dispersions via ionizing radiation is very low. In addition, the stability of GR dispersion is limited as the obtained GR nanosheets aggregated and participated by time. Thus, capping agent was required to enhance the yield of highly dispersed GR and sustain its stability. Therefore, different types of capping agents such as CMC, EHEC, Glucose and PVA were used. Fig. 8 show the UV-vis spectra of GO irradiated in the presence of the previous capping agents.

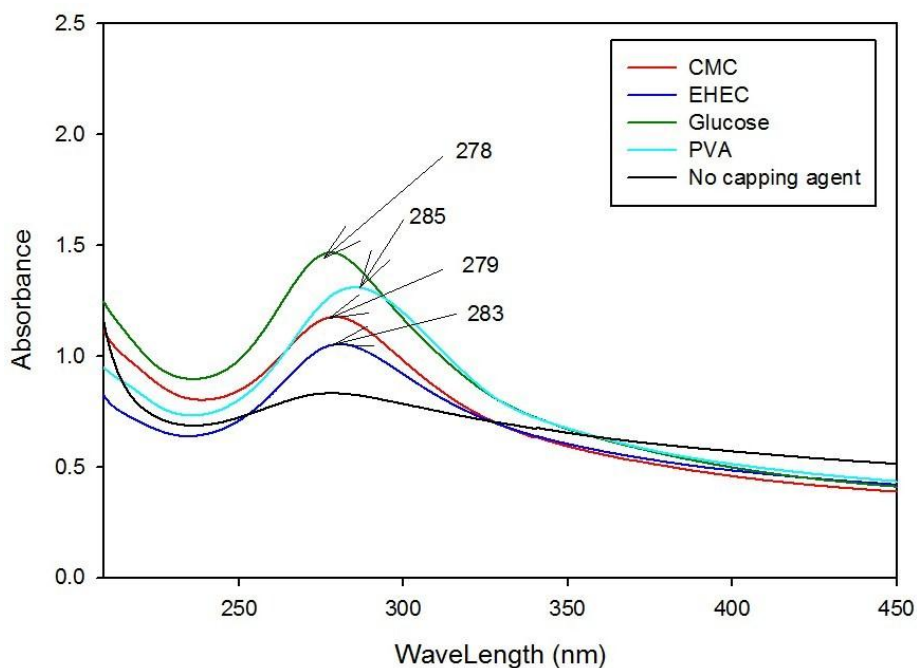


Fig. 8. UV-vis spectra of N_2 -saturated GO dispersion using different capping agents (CMC, EHEC, PVA and Glucose) solutions of PH 7 irradiated at 50KGy.

The intensity of GR characteristic peak for GO dispersion irradiated in the presence of different capping agents is much higher than that for N_2 -saturated GO dispersion irradiated in absence of a capping agent. The intensity and maxima of the peak is varied according to the nature of the capping agent used. The highest GR yield obtained when Glucose was used. However the natural polymer (EHEC) gives lower GR yield than Glucose but it gives more efficient reduction. PVA is the best one from reduction efficiency and yield points of view, but the synthetic polymer as PVA is not eco-friendly. Thus, CMC was selected as capping agent because it is naturally occurring polymer for green synthesis of Gr and resulted in efficient reduction of GO into GR with reasonable yield.

From the previous results we can assume that Fig. 9 represents the mechanism of producing stable GR from GO using gamma radiation. During the irradiation process, CMC consumes the produced oxidizing species and degraded into low molecular weight leaving the reducing species to interact with GO. As a result high yield of efficiently reduced GO is obtained. On the other hand, the produced low molecular weight CMC is adsorbed on the hydrophobic surface of GR nanosheet and stable dispersed hydrophilic GR nanosheets were formed.

GO dispersions were exposed to different doses. It was observed that the color of dispersion changed with irradiation dose. Fig. 10 shows gradual changes in color of GO dispersed in air-saturated CMC solution of PH 7 and its corresponding UV-vis spectra show shifting with the increase in radiation dose. Before gamma irradiation, GO dispersion appears to be yellowish brown and absorbs UV at 247 nm, but after irradiation at dose 10 KGy the color of GO dispersion becomes dark brown and UV absorption peak is red-shifted to 266 nm. With the increase in radiation dose the dispersion color becomes darker and shifts to higher wave length.

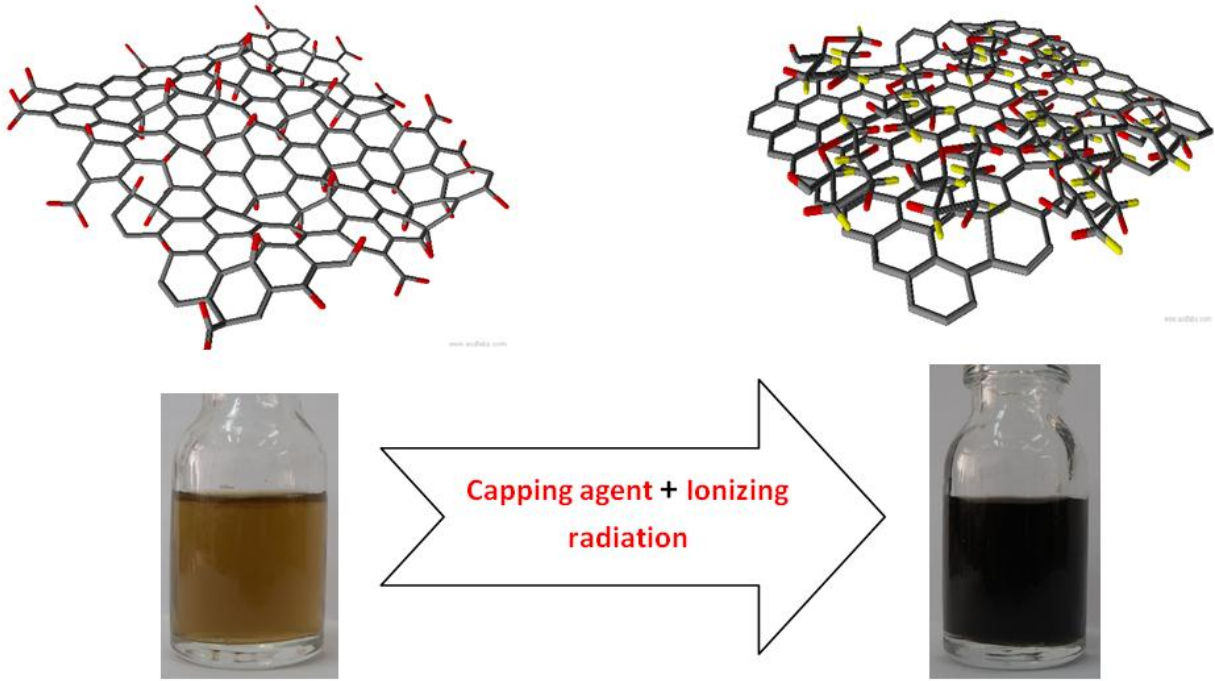


Fig. 9. Illustration of the preparation of GR via gamma irradiation in presence of CMC as capping agent and air atmosphere at PH 7.

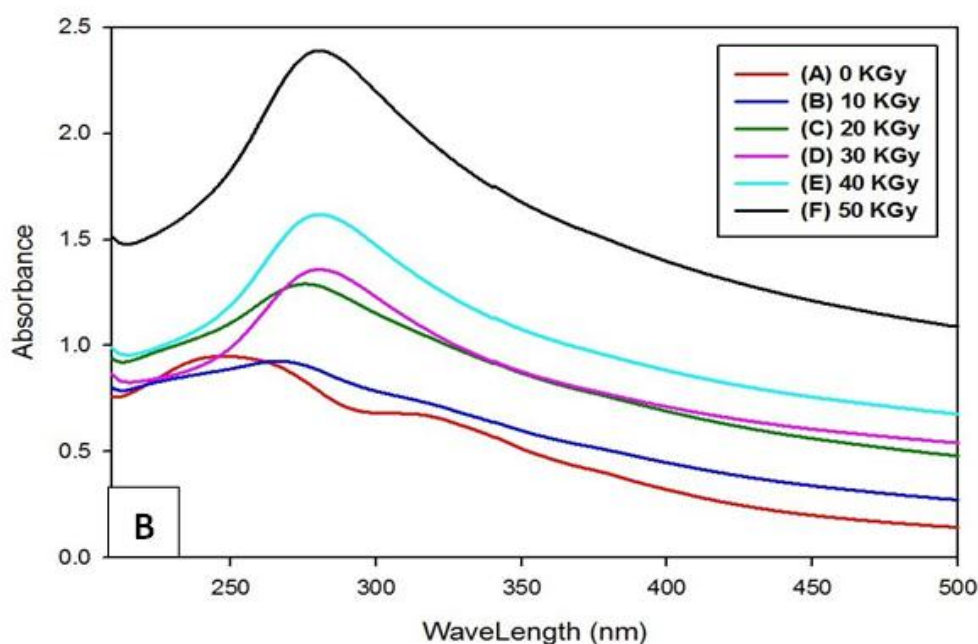
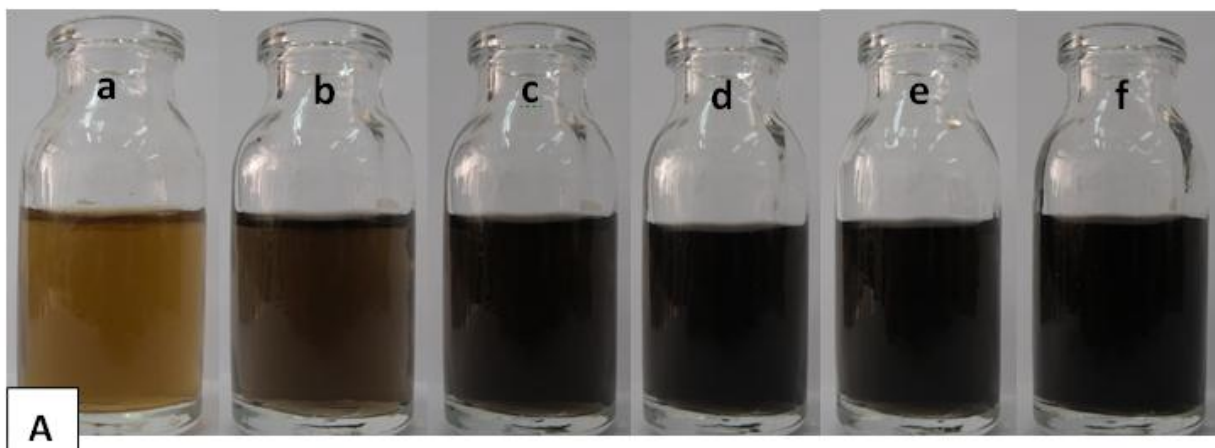


Fig. 10. (A) Photographs of (0.1 mg/mL) GO dispersion before (a) and after (b-f) gamma irradiation at doses (10-50 KGy) in air-saturated CMC solution of PH 7. (B) The corresponding UV-vis absorption spectra showing the change as a function of radiation dose.

By further increasing in irradiation dose more than 30 KGy where dispersion absorbs at 280 nm no red shift is observed but there is an increase in absorption in the whole spectral region indicating the increase in concentration of GR formed. This suggested that GO is reduced into GR and electronic conjugation within the GR sheets is gradually restored (6).

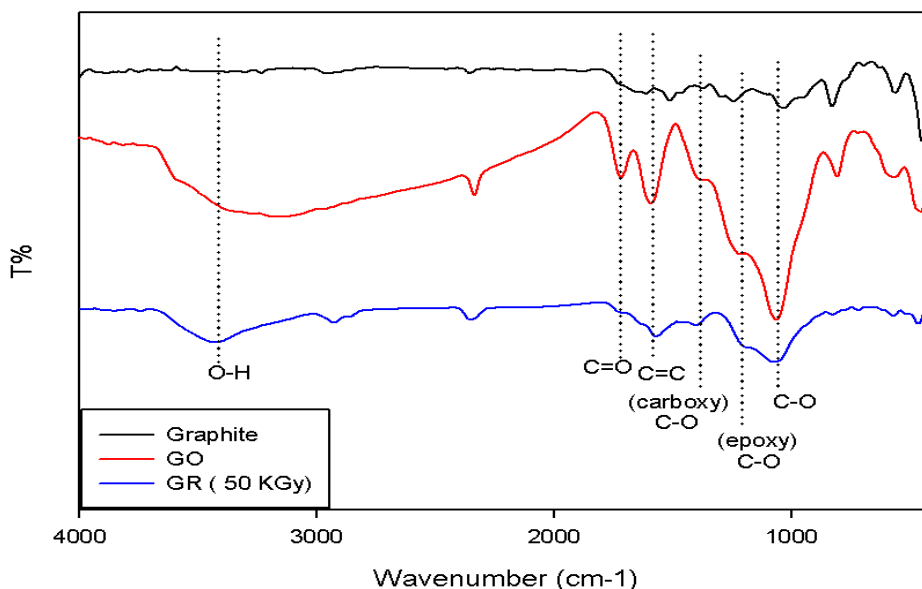


Fig. 11. FT-IR spectra of Graphite, GO and GR obtained at radiation dose of 50 KGy.

FTIR spectroscopy (Fig. 11) can confirm the formation of GR using gamma irradiation in presence of CMC as capping agent and air atmosphere at PH 7. The FT-IR spectra of graphite shows no characteristic peak of oxygen-containing functional groups, but in case of GO, characteristic peaks appear for O-H (3414cm^{-1}), C=O (1722 cm^{-1}), aromatic C=C (1600 cm^{-1}), carboxy C-O (1390 cm^{-1}), epoxy C-O (1214 cm^{-1}) and C-O (1060 cm^{-1}) (54;55). After irradiation of GO at 50 KGy a dramatic vanishing in GO characteristic peaks happens confirming the conversion of GO into GR.

Important information about the change in crystal structure can be obtained via comparing XRD patterns of pristine Graphite, GO and GR formed at 50 KGy in presence of CMC as capping agent and air atmosphere at PH7. As shown in Fig. 12 pristine graphite has crystalline structure with inter-planner distance ($d= 0.34\text{ nm}$), but GO has damaged crystalline (amorphous) structure with wider inter-planner distance ($d= 0.88\text{ nm}$) indicating introduction of oxygen-containing functional groups to carbon layers. For GR formed at 50 KGy, instead of the peak at 10° of parent GO a new very broad peak appears at 22° with ($d= 0.41\text{ nm}$) suggesting the efficient reduction of GO into GR and formation of single graphene sheets which are randomly ordered in the powder form.

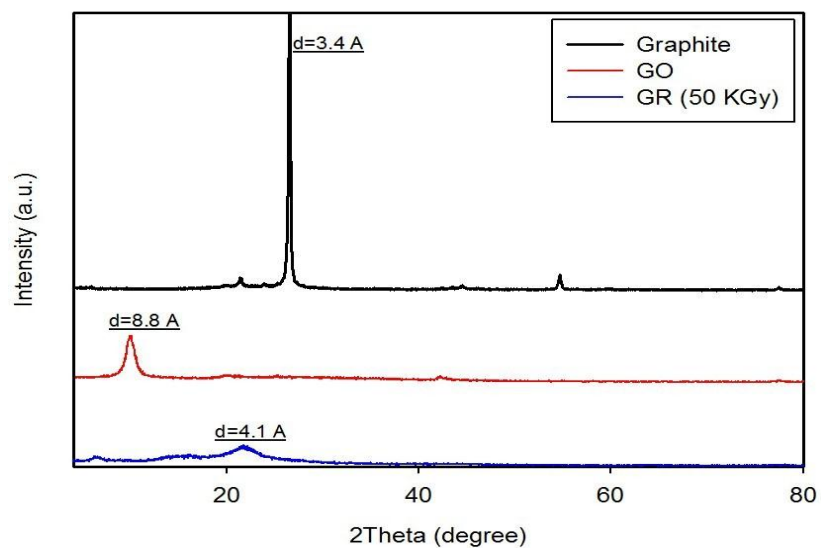


Fig. 12. XRD pattern of pristine Graphite, GO and GR formed at 50 KGy in CMC solution in presence of oxygen at PH7.

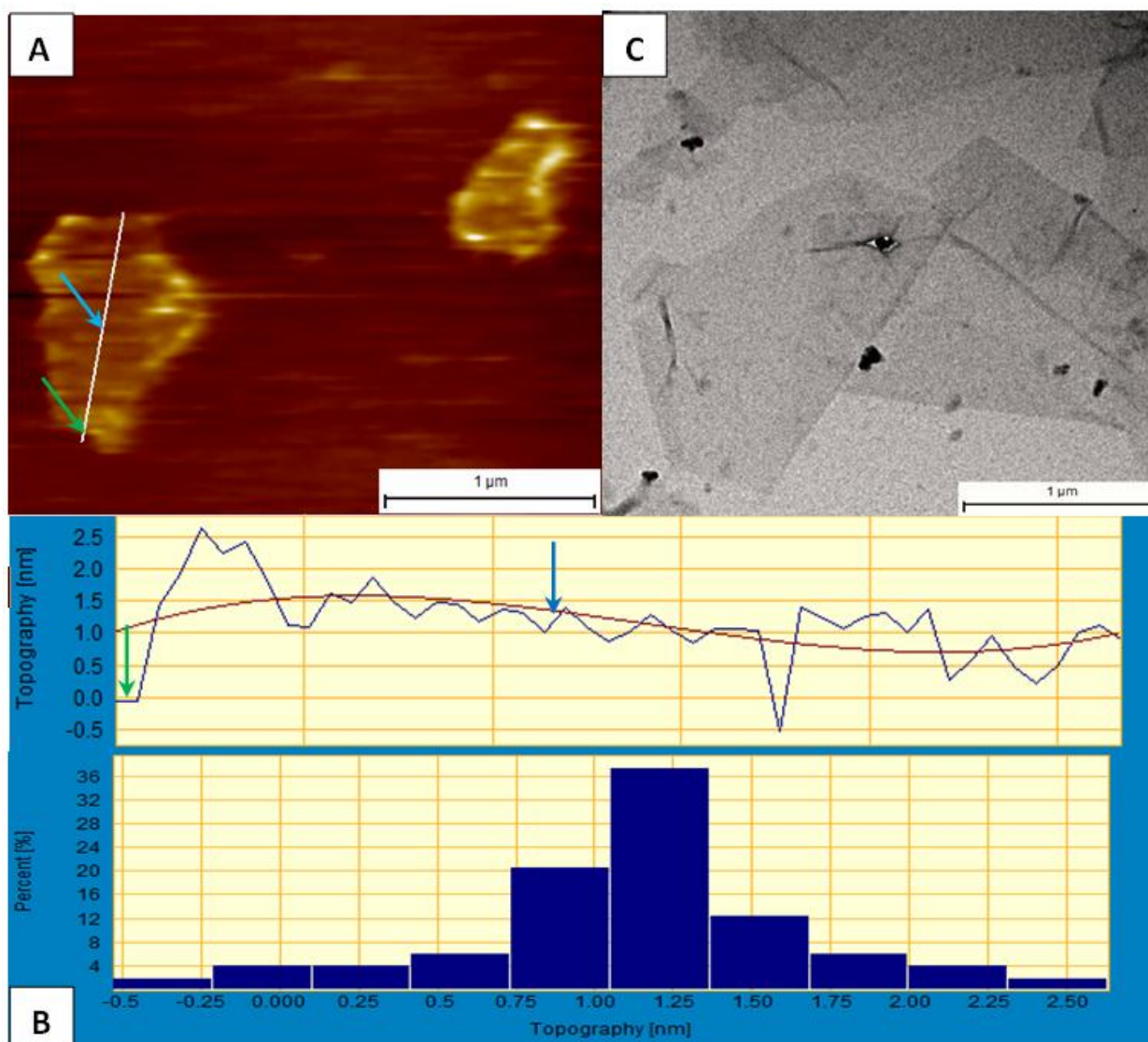


Fig. 13. (A) AFM image of GR nanosheet obtained via gamma irradiation of GO dispersed in air-saturated CMC solution at dose of 50K Gy. (B) height profile along the line shown in the AFM image beside its corresponding topography distribution. (C) Typical TEM image of GR nanosheets.

Fig. 9 (8) (missing?) shows a typical AFM image of GR nanosheets obtained by drop-casting method on a freshly cleaved mica surface. The average thickness of GR nanosheet is about 1.25 nm as shown from the height profile in Fig. 13 (B). This thickness of GR nanosheets is greater than the ideal thickness of single GR sheet (0.35 nm) and this is attributed to the capping agent that affects greatly thickness. Fig. 13 (C) shows TEM image of GR nanosheets with lateral dimension more than 1 μm. some corrugations are present in GR sheets.

3.7. Preparation of chitosan/Go-nanocomposite films

Trails has been made to prepare graphene -chitosan nano-composite for possible use as antimicrobial packaging materials. Graphene oxide and -chitosan were mixed at different ratios using ultrasonic probe for 10 mins. The mixture was poured in a Petri dish and left to

dry. The color of the chitosan films change from pale yellow to dark and the intensity of the color increases with increasing GO content (Fig. 14).

A mechanical property of CA composite of different GO contents was investigated. The tensile strength of graphene oxide -chitosan nano-composite film improves significantly if compared with pure chitosan. As the amount of GO increases the tensile strength of composite film increases. Table 2.

The water uptake of the composite films was determined. It was found that the ability of chitosan -GO nano-composite film to adsorb water is reduced if compared with that of pure chitosan. Meanwhile, the treatment with 1% NaOH solution for 30min significantly decrease the swelling % for both of chitosan and chitosan -GO nano-composite films table 3.



Fig. 14. Change in color of chitosan film when mixed with GO.

TABLE 2. MECHANICAL PROPERTIES OF CHITOSAN COMPOSITE OF DIFFERENT GO CONTENTS

Polymer type	Un-irradiated		Irradiated 25kGy	
	Yield MPa	Yield%	Yield MPa	Yield%
chitosan	33	30	31	32
Chitosan +1%GO	41	16	42	11
Chitosan +3%GO	47	11	49	11
Chitosan +5%GO	55	7	54	5

TABLE 3. WATER UPTAKE OF CHITOSAN AND CHITOSAN /GOCOMPOSITE

Type of polymer and treatments	Swelling %
Pure chitosan	200
Chtiosan/3%GO	122%
Pure chitosan after treated with 1% NaOH for 30min	115%
Chtiosan3%GO after treating with 1% NaOH for 30min	71%

References

Silvestre C, Duraccio D and Cimmino S., Food packaging based on polymer nano-materials Progress in Polymer Science 2011 in press

J. H. Han, Antimicrobial packaging systems, innovations in food packaging.2005 Elsevier LTD

Hummers W, Offeman R.Preparation of graphitic oxide. J Am Chem Soc 1958; 80(6):1339

EMMI SS, TAKCS E. Water remediation by the electron beam treatment. In: Spothem-Maurizot M, Mostafavi M, Douki T, Belloni J, editors.RADIATION CHEMISTRY- from basics to applications in material and life sciences.EDP Sciences; 2008

BUXTON GV. An overview of the radiation chemistry of liquids. In: Spothem-Maurizot M, Mostafavi M, Douki T, Belloni J, editors.RADIATION CHEMISTRY- from basics to applications in material and life sciences.EDP Sciences; 2008

Li D, Muller MB, Gilje S, Kaner RB, Wallace GG. Processable aqueous dispersions of graphene nanosheets. Nat Nano 2008 Feb;3(2):101-5