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# Investigation on Polymer Based Nano-Silver as Food Packaging Materials

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***Abstract*—**Commercial nanocomposite food packaging type nano-silver containers were characterised using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The presence of nanoparticles consistent with the incorporation of 1% nano-silver (Ag) and 0.1% titanium dioxide ($TiO_2$) nanoparticle into polymeric materials formed into food containers was confirmed. Both nanomaterials used in this type of packaging appear to be embedded in a layered configuration within the bulk polymer. The dimensions of the incorporated nanoparticles were investigated using X-ray diffraction (XRD) and determined by calculation using the Scherrer Formula; these were consistent with Ag and $TiO_2$ nanoparticles in the size range 20-70nm both were spherical shape nanoparticles. Antimicrobial assessment of the nanocomposite container has also been performed and the results confirm the antimicrobial activity of Ag and $TiO_2$ nanoparticles in food packaging containers. Migration assessments were performed in a wide range of food matrices to determine the migration of nanoparticles from the packages. The analysis was based upon the relevant European safety Directives and involved the application of inductively coupled plasma mass spectrometry (ICP-MS) to identify the range of migration risk. The data pertain to insignificance levels of migration of Ag and $TiO_2$ nanoparticles into the selected food matrices.

***Keywords*—**Nano-silver, antimicrobial food packaging, migration, titanium dioxide.

## I. Introduction

SILVER is well-known for its wide-ranging antimicrobial activity against Gram-positive and Gram-negative bacteria (including antibiotic-resistant strains), fungi and certain viruses. The application of silver as an antimicrobial agent has also proved effective when incorporated into a variety of materials including polymers, resulting in nano-silver composite forms in recent years [1].

The application of nanotechnology to the food sector offers potential benefits, including enhancements in production and processing – suggested improvements being consonant with the following preferences; superior food contact materials, quality and freshness monitoring, traceability and product security, sensation, consistency, fat content and nutrient absorption [2]. In fact, nanocomposite food packaging comprises the largest contribution of this technology in the food sector market; the applications of nanotechnology to the sector are only predicted to increase over the next two decades [3].Although in existence for some years now the use of nanocomposite materials has recently gained momentum through their application in consumer products, including commercial packaging [4]. A variety of nanotechnology-derived food ingredients and their additives, as well as materials intended to be placed in close contact with foodstuffs, is already available in a large number of countries and the market for these products is only expected to grow in the future. The antimicrobial material used for food packaging classified into two types, organic and inorganic. Organic antimicrobial materials are frequently less stable at high temperatures compared to inorganic agents. Inorganic materials, for example, metal and metal oxides have attracted scientist over the last decade due to their ability to stand exacting process conditions [5]. A great amount of research has been conducted on the antimicrobial activity of nanomaterial against different types of microorganisms and broadly studied [6]. Combinations of more than one antimicrobial incorporated into packaging have also been used in many packaging material. Microbial growth, enzyme, water activities and change in pigments are the most important factors that affect the quality of fresh fruit and vegetables. By enhancing the packaging material these problems related to these damaging factors are certainly solved [7]. Concomitantly, there is dearth of information about the type, actual use and quantity of nanomaterials in food products, especially from the food industry. Additionally, there has been limited publication concerning the risks associated with ingesting these materials and their effect on the human body [8]. Material in nano-scale has a high surface to volume ratio which has significant consequences in relation to the enhancement of physical and chemical properties of the material. The enhanced physical properties of nanoparticles occur due to an increase in the percentage of atoms at the surface which are available for reaction and bonding with the surrounding environment. Therefore, increases the opportunity for the migration of nano-sized particles into external matrices in close contact with a nanomaterial [9]. By way of approaching the health and safety consequences of the uses of nanocomposite materials in food sector this work attempts to characterise nanocomposite containers which have been specifically manufactured according to nanoparticle polymer incorporation. In the first place, it is important to determine the size of the nanoparticles involved and their distribution in the packaging material, if only to establish whether these match the manufacturers' claims. Furthermore, independent study is also required to establish the efficacy of these nanocomposite products in terms of their readily testable claims – in this case, antimicrobial activity is asserted as a

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benefit of the nanocomposite packaging materials concerned.

## II. Material and Methods

### A. Reagents

All chemicals and reagents used were of analytical grade and high purity. Nonmetallic certified nitric acid ($HNO_3$) was supplied by Fisher Scientific, UK. De-ionised water was purified by a SG Millipore system, Triple Red Laboratory Technology, UK as Ultra purified water (UPW). Nano-silver containers are marketing as antimicrobial containers under commercial name fresh box purchased from Blue Moon Goods, USA. Food samples were supplied by local supermarkets in Middlesbrough, UK.

### B. Characterisation Method

The structure and the surface morphology of randomly selected nano-silver containers were cut from different sides then placed in a crucible and heated in a muffle oven furnace at 550°C for 5-6 hours. The obtained ash was stored in sealed vassals for further analysis [10]. In these analyses, some samples were cut into small sections to analyse the sample from each side and others were cut into small pieces and ground to a powder for further analysis. The morphology, size and shape of each sample was analysed using a scanning electron microscope equipped with EDAX, S-3400N, Hitachi High-Technologies Corporation, Japan. SEM images were obtained at a voltage 20 kV and pressure of 1 torr.

Elemental mapping was performed using EDX in environmental scanning mode, coupled with a Thermo-Noran Vantage light element energy dispersive X-ray detector. Characterisation of all the elements was obtained by X-ray spectroscopy under electron flux. The X-ray diffraction (XRD) analysis was performed using Siemens D500 diffract meter with CuKα radiation at 20 mA° and 40 kV, supported with HBX software to determine the particle size. Diffraction data were collected in the range of 2θ from 20 to 80° at step size of 0.02° and step time of 1s. Thermo gravimetric (TGA) STA 1500 with Infinity pro-thermal Analysis software was used.

The sample analysis was conducted by raising the temperature of the sample gradually and plotting percentage weight against temperature. In this method, the temperature used was 600°C and the sample was performed using commercial packaging polymer (23mg) in 5min [11]. Information about the composition of multi-components, the thermal stability of materials and the amount of moisture in the samples was obtained. This machine was also used to determine the thermal stability of commercial packaging. Transmutation electron microscopy (TEM) attached to Oxford Instruments INCA EDX system at University of Oxford was used for some samples. The particle size distribution obtained using a software package SPSS Inc., Chicago IL attached to TEM. The container ash was prepared, diluting in UPW, (2-3 drops) of the solution on a copper grid and dried at room temperature, after the removal of excess solution using a filter paper.

### C. Migration Assays

Experiments were performed in a temperature and humidity controlled laboratory environment.

Agilent 7500 series, inductively coupled Plasma mass spectrometer (ICP-MS) instrumentation with Octoped Reaction System (ORS), using a high-purity grade (99.99%) Argon as a plasma gas supply.

### D. Samples

Food samples were selected with a range of compositions including; solid, liquid, high fat contain and high acidity, samples are: fresh apples (A), white slice bread (BR), fresh carrot (C), pre-packed soft cheese (CH), modified atmosphere packaging (MAP) milk powder (MP) and fresh orange juice (OJ). The six kind samples were randomly selected, cleaned, each sample type mixed together, cut into pieces $2cm^2$ x $2cm^2$ and (20g) of each sample placed in a container. All packaged samples were sealed using their own lids and stored to eliminate light variation in thermostatically controlled oven capable of maintaining a temperature of 40°C ±1°C for either 7 or 10 days, following the migration test procedure of Regulation (EU) No 10/2011[12]. Identical tests were carried out using conventional containers were used during migration assessment as controls for each sample, as appropriate, purchased from local supermarkets. The same procedure was applied with the conventional containers to compare with the nano-silver containers [13]. During each measurement random samples of all six food types were prepared for the migration assessment.

### E. Extraction Procedure

The migration measurements were carried out in two stages 7 and 10 days, following the incubations of the samples in sealed containers at 40°C. The samples were removed from the incubator and left to cool for few minutes at room temperature [14]. Each individual food material (whole sample) was weighed, placed in a crucible and heated to dryness at 105°C for several hours in an electric fume furnace. This was followed by cooling in a dry atmosphere for 40min. The sample was carbonised using a Bunsen burner, before heating again to 550°C for several hours in a muffle oven furnace until ash formed. The sample was cooled in a dry atmosphere for 40min and stored under aseptic conditions. Triplicate and certified reference samples were prepared at the same time including the controls [15].

### F. Acid Digestion Method

The obtained ash (3.0g) was dissolved in (20mL) non-metallic concentrated $HNO_3$ solution with anti-bumping chips and heated slowly in water bath to constant volume (5-10mL) and filtered. The samples were diluted to $1\mu gL^{-1}$ by UPW and later with 2% $HNO_3$.

To avoid contamination, all glassware (vessels and flasks) were immersed in freshly prepared 2% v/v $HNO_3$ for 24 hours, prior to rinsing thoroughly with doubly de-ionised water and dried in a dust free area before use [16].

*G.Antimicrobial Assessment Procedure*

Nano-silver antimicrobial container used in migration assays was investigated in order to determine the limits of nanoparticles as antimicrobial agents. Clean containers were sprayed with 70% ethanol and rinsed thoroughly with de-ionise sterilised water and dried at 60°C.The samples used in this assessment consisted of carrot sample which was cleaned, peeled, washed with sterilised distilled water, dried; cut to small pieces, weighed (20g) before placing in nano-silver containers and conventional containers.

All samples were sealed and incubated at 35°C for 10 days including the controls [17]. Total count plate was employed every 24 hours. Each sample was weighed (10g) were homogenized in (90mL) of saline primary 1/10 dilution [18]. A standard method protocol of ISO 4833 (2003) was followed with the primary dilution (1mL) being serially diluted to 10-5 and included in the nutrient agar, 5 different dilutions and 2 plates per dilution being prepared. Duplicate samples were prepared for all assessments and incubated at 37°C ±1°C for 72 hours. Colonies were counted by visual inspection [19]. Results were converted to their base 10 logarithm. Plates with 25-250 colonies were counted. Plates with more than 250 colonies were deemed Too Numerous to Count–TNTC. Plates with less than 25 colonies were deemed Too Few to Count – TFTC [20].

## III. Main Findings and Discussion

*A. Morphology Structure*

The information provided from the supplier presented in Table I with a photographic image of the commercial box in Fig. 1, indicated that the nano-sized of silver used. The technical information regarding the nanoparticles used in the product was limited from the manufacturer; therefore, an investigation was carried out to identify the element composition of the product, the particle size, and the amounts of nanoparticles as well as whether the nanoparticles coated onto the surface or embedded inside the polymer matrix. The characterisation of container revealed that the nanomaterial used as antimicrobial agents are two types Ag nanoparticles and $TiO_2$ nanoparticles. The polymer samples without calcinations were characterised using EDX and SEM, $TiO_2$ nanoparticles were identified as flake-like structures spread out within the polymer in some places and Ag nanoparticles in other places, as it shown in Table II spectrum 1 and 2 prior calcinations.

Qualitative analysis confirmed the presence of Ag and $TiO_2$ nanoparticles on the bulk of the polymer by EDX spectra as shown in Fig. 2. The structure of nano-silver containers after calcinations was observed using a SEM, the sample first scanned to confirm the metal with EDX elemental mapping at the same time, the image of that region of the nanoparticle obtained. Ag nanoparticles were found unaided in some places and mixed with $TiO_2$ in others and the particle size measured at 20-70nm as shows in Fig. 3.

Furthermore, the analysis of the nano-silver container after calcination has shown that the $TiO_2$ nanoparticles appear to be integrated into the Ag nanoparticles layers present at some locations in the nanocomposite and also occurring on their own in other regions, EDX results indicates that the percentage of Ag nanoparticles to be 10 times that of the $TiO_2$ nanoparticles present in the bulk polymer. These results were confirmed with the analysis of the container ash ample using ICP-MS and the concentration of silver was $1mgL^{-1}$, whilst Ti concentration was $0.1mgL^{-1}$

TABLE I
COMMERCIAL PROPERTY FOR NANO-SILVER CONTAINER PACKAGING

| Property | Container |
|---|---|
| Material | PE |
| Type | Fresh Box |
| Usage | Home food storage |
| Feature | Odour and air impermeable |
| Hardness | Solid |
| Processing type | Unknown |
| Transparency | Semi transparent |
| Place of origin | USA |
| Brand name | Antimicrobial |
| Model number | Unknown |
| Colour | Transparent |
| Particle size | Unknown |
| Conc. of nano Ag | Unknown |
| Rate of $Ag^+$ releases | Unknown |
| Structure of particle | Unknown |
| Classification | Nano |
| Product testing Information | KOTRIC-CC |


Fig. 1 Commercial antimicrobial fresh box label

TABLE II
ELEMENTS PRESENT WITHIN NANO-SILVER POLYMER CONTAINER PRIOR AND POST CALCINATION (WT %)

| Elements | Prior calcinations | | Postcalcinations | |
|---|---|---|---|---|
| | Spectrum 1 | Spectrum 2 | Spectrum 1 | Spectrum 2 |
| Ti | 0.11 | - | - | 0.46 |
| Ag | - | 1.20 | 4.98 | 4.97 |

Following numerous examinations, focusing on many different sides on the surfaces of the nanocomposite before calcination, Ag and $TiO_2$ nanoparticle layers were found incorporated within the bulk polymer. However, neither Ag nanoparticles nor $TiO_2$ nanoparticles were applied as a coating on the container polymer surface.

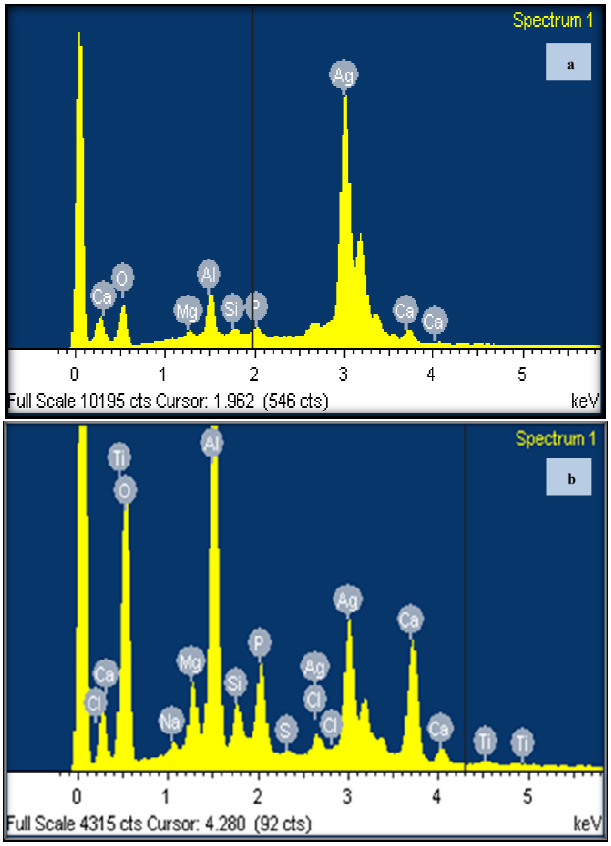


Fig. 2 EDX spectrum of elements present in antimicrobial container, (a) Ag nanoparticles only before calcination and (b) Ag nanoparticles integrated with $TiO_2$ nanoparticles after calcination

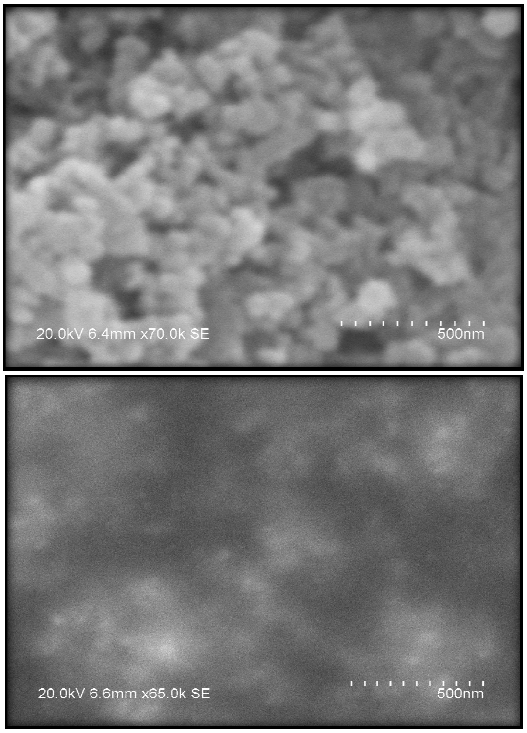


Fig. 3 SEM images of Ag and $TiO_2$ nanoparticles in antimicrobial container at 500nm magnifications

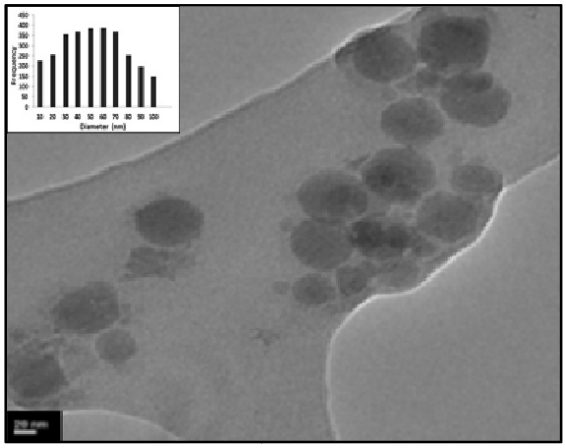

Fig. 4 TEM image **of** Ag nanoparticles (light colour**)** and $TiO_2$ nanoparticles (dark colour) in antimicrobial container at 30nm magnifications with the particle distribution histogram

SEM images with EDX elemental mapping indicated the intercalation of nanoparticles in the nanocomposite. The polymer layers were characteristic of randomly distributed Ag and $TiO_2$ nanoparticles with some evidence of aggregation of these particles apparent. This suggests the uncontrolled nature of the process by which nanoparticles have been incorporated into the bulk polymer. TEM analysis confirmed the particle size and the shape of both nanoparticles with a frequency distribution of particles measurement was obtained as displays in Fig. 4.

XRD patterns of nano-silver container as presented in Fig.5, revealed that characteristic of small particle size within the range 20-70nm, However, aggregation is apparent due to the fact that sized particles around100nm were observed following XRD and SEM characterisation; particle size was calculated also using Scherrer Formula [21].

$$t = \frac{k\lambda}{\beta \cos\theta}$$

where, is the averaged dimension of crystallites; K is the Scherrer constant, somewhat arbitrary value that falls in the range 0.87-1.0 (it is usually assumed to be 1); λ is the wavelength of X-ray CuKα = 0.15406nm and B is the integral breadth of a reflection (in radians 2θ) is the diffraction angle. Additionally converting the unit of theta to degrees by the following equation;

$$\text{Degrees} = \frac{\text{radians} \times 180}{\pi}$$

XRD pattern also, indicated intercalation of nanoparticles in the nanocomposite polymer. The three major characteristic peaks of container composite particles lied in 2θ value of 38°, 44° and 64° with spaces as 134, 329 and 508 which was corresponding crystal face of (111), (200) and (220) of Ag nanoparticle, while before calcination, the nanoparticle peaks are interacted with polymer matrix only the (200) peak was appeared. The other peaks are related to the $TiO_2$ nanoparticle

peaks, which interacted with Ag nanoparticle peaks at 27° and 36° indicating $TiO_2$ in the rutile phase [22]. The results provide supporting evidence for the polymer captured Ag and $TiO_2$ nanoparticle structure.

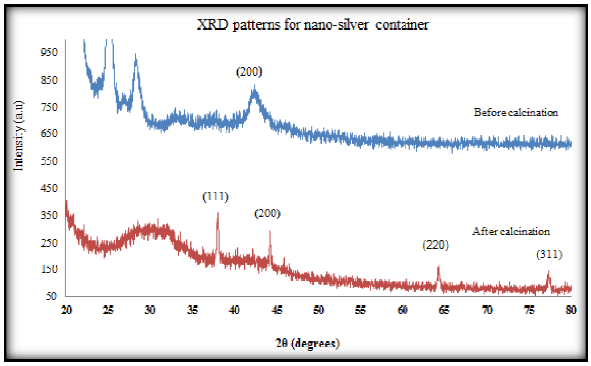


Fig. 5 XRD patterns for Ag and $TiO_2$ nanoparticles in antimicrobial container polymer

Information about composition of multi-component, thermal stability of materials and the amount of moisture in the samples were obtained by TGA analysis. In this term, TGA analysis was performed for containers to confirm the decomposition of the polymer matrix, as in Fig. 6, the polymer did not decompose before reaching a temperature of 250°C and the mass loss was very low. The nanoparticles composite polymer started to decompose beyond 400°C. The residual mass was the mass of silver oxide ($Ag_2O$) and $TiO_2$ indicating that Ag and $TiO_2$ nanoparticle encapsulated in containers and start reacting with oxygen. When the polymer decomposes at about 400°C, the nanoparticles in the polymer matrix were released and reacted with amount of oxygen quickly generated increase of heat resulting in the polymer weight loss by more than 30% at 450°C.

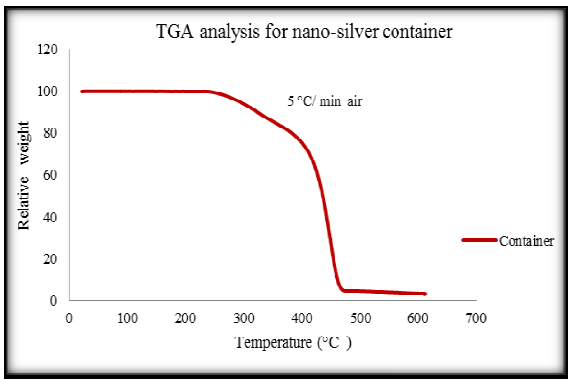


Fig. 6 TGA analysis for antimicrobial container polymer

*B. Migration Assessments Results*

ICP-MS results for all samples examined after 7 and 10 days were incubated at 40°C are presenting in Fig. 7. These results indicated that insignificant levels of Ag and $TiO_2$ nanoparticles are released from nano-silver container. For example, the highest level of Ag nanoparticles released from the packaging into food materials after 7 and 10 days is from the orange juice samples of a value 5.7± 0.02μgL$^{-1}$. In contrast with the original Ag contain in the control samples 0.16 ± 0.01μgL$^{-1}$ and that amount was recorded also from the conventional containers. The second highest is the cheese samples followed by apple samples, whereas, the bread samples had the lowest level. Also for the $TiO_2$, the highest migration levels have been reported from orange juice samples 2.5 ±0.03μgL$^{-1}$ as shows in Fig. 8. However, the migrating quantities of Ag and $TiO_2$ nanoparticles into food samples were less than its allowable concentration 10mgL$^{-1}$ [23]. Therefore, the amount of Ag and $TiO_2$ nanoparticles were found in the selected food samples at as low concentrations as 6μgL$^{-1}$. Method detection limits was measured using spiked samples and was calculated each time as the standard deviation for seven replicate measurements of individual concentrations solution of Ag, Ti near the expected detection limit. MDL is recorder as 0.040859μgL$^{-1}$ and limit of quantifications of 0.13μgL$^{-1}$.

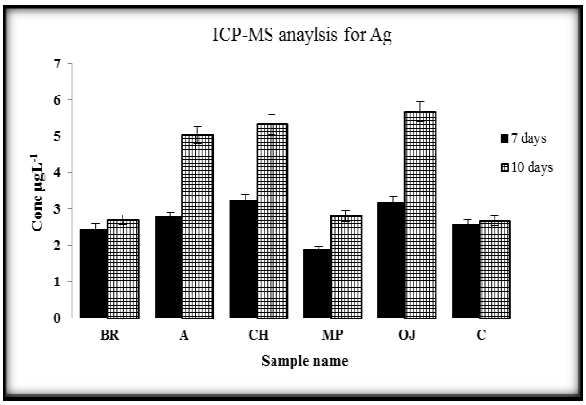


Fig. 7 ICP-MS determination of Ag migration from antimicrobial containers into specified foodstuffs for 7 and 10 days at 40°C

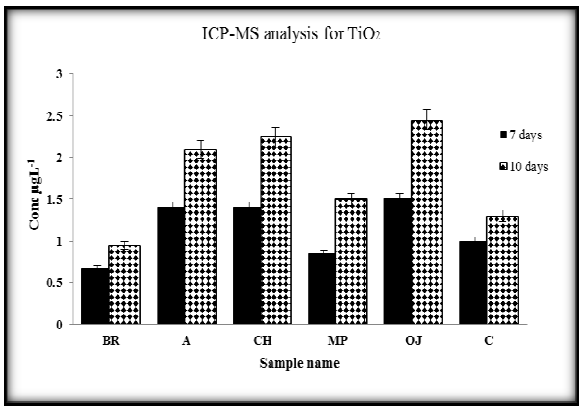


Fig. 8 ICP-MS determination of Ti migration from antimicrobial containers into specified foodstuffs for 7 and 10 days at 40°C

*C. Antimicrobial Activity of Ag and TiO2 Nanoparticles*

The antimicrobial nano-silver packaging investigated in this work shown in Fig. 9; demonstrate the effect of Ag and $TiO_2$ nanoparticles on the microbial growth over time of carrot samples compared with conventional containers. Nano-silver packaging exhibited antifungal activity as demonstrated by

inhibition of the growth of *Penicillium* on the raw samples. Data pertained to the growth antagonistic property of Ag and $TiO_2$ nanoparticles in nano-silver packaging following seven and ten days of storage at 35°C.

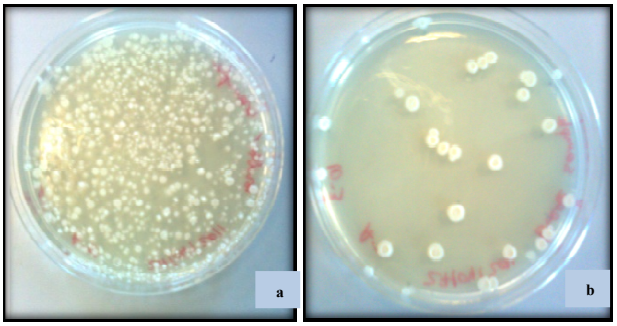


Fig. 9 Total count for carrot sample 72 hours at 37°C (a) conventional container packaging (b) nano-silver container packaging

*D.Decay Rate and Total Plate Count*

The control samples stored using conventional packaging started decaying on day 1 and reached a complete decaying on day 5 at 35°C storage. Conversely little microbial growth was observed during the first six days of storage under identical conditions in nano-silver containers. A significantly lower rate of deterioration was observed up to day 10, due to the antibacterial activity of Ag and $TiO_2$ nanoparticles [24].

The results of the total plate count performed on samples of carrot to characterise the extent of Ag and $TiO_2$ nanoparticles as antimicrobial agents are presented in Fig. 10. The graph provides a comparison between the nano-silver packaging, conventional plastic food containers and the control; where the total plate count corresponded to 3.2 log $CFUg^{-1}$ for food samples stored in the nano-silver packaging and 9.75 log $CFUg^{-1}$ for the control, by day 7.

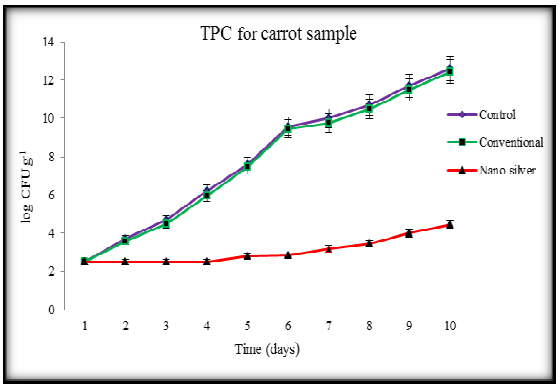


Fig. 10 Total counts for carrot sample stored in different packaging at 35°C for 10 days, values are mean ±SE (n=3) each time statistical significance $p \leq 0.001$

Nano-silver containers show significant activity against the growth of microorganisms compared to conventional food containers, conventional plastic food containers produced similar results to control samples in their original packaging; Samples were compared to their controls over the course of 10 days. Carrot samples were subjected to lactic acid fermentation through the action of a starter culture, *Lactobacillus*.

The safety and stability of food depends on the microorganisms initially present and on their being unable to overcome various biologically undesirable factors in order to multiply, therefore, Ag and $TiO_2$ nanoparticles were able to district the decay only on the top of the samples were no direct contact with the nanoparticles as shows in Fig. 11.


Fig. 11 Photographic images for (a) sample stored in nano-silver container packaging (b) control stored conventional container packaging, at 35°C for 7 days

## IV. Conclusion

This study demonstrated that nano-silver antimicrobial food packaging applications are a novel approach toward the preservation of food and shelf life extension. Characterisation of the commercial nano-silver container revealed that, there were two types of nanomaterial used as antimicrobial agents Ag and $TiO_2$ nanoparticles and not as advertise by the supplier company. The structural morphology showed the intercalation of Ag and $TiO_2$ nanoparticles in the 20-70nm range within the bulk polymer, this giving rise to the observed antimicrobial effect. Some, aggregation is apparent due to the random incorporation of nanoparticles the composite within the polymer. Concentration of the nanoparticles was obtained by ICP-MS analysis of 1% of Ag nanoparticles and 0.1% of $TiO_2$ nanoparticles. Verification of the antimicrobial effect of nano-silver containers has been effected. More detailed investigation of the Ag and $TiO_2$ nanoparticles used in these composites indicates that these are distinctly layered and embedded within the bulk polymer instead of existing as a coating on the polymer surface.

The work performed complete surface intercalations of the food matrices into antimicrobial containers have been achieved and used in the migration assessment; data pertain to insignificance levels of Ag and $TiO_2$ nanoparticles in the selected food matrices which is a far lower than the acceptable levels at $0.01 mgL^{-1}$.

## V. Future Work

Determine the food shelf life of these containers packaging

and its effect on nanoparticles migration into food. In order to justify the safety of these packaging on everyday use, there is a need to identify the nature of the interactions between nanoparticles and their effects on the fundamental cellular processes.

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