# SYNTHESIS AND CHARACTERIZATION OF ANTIMICROBIAL POLYMER CONTAINING SILVER NANOPARTICLES

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## ABSTRACT

*Various types of polymers are currently used for making indirect restorations for rehabilitation of patient in dentistry. Most of these lack inherent antimicrobial property. The aim of this study was to develop and characterize antimicrobial polymer by impregnation with silver nanoparticle which besides serving its primary function also possess antimicrobial property. This study was conducted during MSc, Dental material programme, year 2010-11 in School of Engineering and Material Sciences, Queen Mary, University of London, UK under supervision of Professor Pankaj Vadgama. For this purpose polydimethylsiloxane(PDMS) based poly ether urethane(PEU) was selected to synthesize antimicrobial polymer. In methodology ultraviolet visible spectroscopy was used to detect size and shape and interaction of matrix with nanoparticles. Thermogravimetric analysis was employed to determine the thermal stability, degradation pattern, absorption of moisture and inorganic content .Contact angle measurements were carried out to determine the wettability and hydrophilicity of the material. X-ray diffraction was conducted to determine crystallinity, particle size and phase identification. The uv-vis spectroscopy results showed the presence of silver nanoparticles. Contact angle measurement of the composite material indicated that wettability of the material improved with the addition of silver. XRD analysis confirmed the presence of nanoparticles.*

**Key Words:** *Silver nanoparticles, Biomaterial, Nanocomposite.*

## INTRODUCTION

The polymers with antimicrobial properties are required in many areas but they are particularly desirable in health care, hygiene and food packaging. Antibiotics and biocides can be used to develop antimicrobial polymer but they are toxic to human health and ecosystem.[1] Since the emergence of multidrug resistant micro organisms and ever increasing trend of health care cost, researchers are trying to introduce new antimicrobials agents which are effective against drug resistant bacteria, economically cheaper and which can be easily incorporated into polymers having wide range of applications[2].

There have been number of studies reported in the literature about the coating and impregnation of antimicrobials into different polymers such as tricolsan, surfactants antibiotics, quaternary ammonium compounds etc.[3] Among the different antimicrobial agents investigated so far silver nanoparticles and ions are considered the most promising antimicrobials agent active against wide range of microorganisms and non toxic to cells.[4] Recently due to its unique physiochemical and medicinal properties there is renaissance in exploring its antimicrobial potential.

Polyurethane is a versatile class of polymer and is being used in fabricating maxillofacial prosthesis[5], water tubing, tubing for air water syringe, tubing for hand pieces[6], and also patented as orthodontic appliances, prosthetic dentures, myofunctional appliances and dental composite resin. Besides this the medical and surgical applications of polyurethane include fabrication of catheters, implants, vascular grafts and drug delivery system.[7]

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Silver is a white shiny metal found extensively in the environment. It also exists in human body entering into body through airborne particles, traces in diet and drinking water but has limited traces value.[8] For almost 2000 years silver is known to have antimicrobial efficacy.[9] It has been suggested that nano size metal particle exhibit unique physical properties which are different from ionic form and bulk material. AgNPs are generally smaller than 100nm and contain about 15000-20,000 atoms.[10]

Mechanism of action of silver on microorganisms is unclear. However according to structural and morphological changes in bacterial cell possible mechanism has been suggested. The effect of silver ions on bacteria can be observed by the changes resulting by the reaction of silver ions with cell components. When the silver ions enter the cell the DNA loses the ability to replicate silver ions also deactivate proteins by reacting with thiol group. Mechanism of action of silver nanoparticle is similar to that of silver ions and possesses bactericidal effects rather than bacteriostatic effect. The nanoparticle penetrates inside the bacterial cell by attaching to their cell membrane. It interacts with proteins present in the bacterial cell wall and phosphorous containing compounds such as DNA affecting respiratory chain and cell division.[11] The shape of the nanoparticle also affects the efficiency of nanoparticle against microorganism. Truncated triangular silver nanoparticle with a (111) lattice plane displayed the most effective antimicrobial activity when compared with spherical and rod shaped nanoparticles.[12] Truncated triangular particle exhibit antimicrobial activity with silver content of 1ug while about 12.5ug is needed for bacterial inhibition by spherical nanoparticles.[11]

Silver ionic compound incorporated into polymer show rapid and effective response but there is not a sustained release over a long period of time which limits their efficacy for short term applications. In contrast to silver compounds elemental silver provides sustained release of silver ion exhibiting antimicrobial activity[13].The objective of this study was to develop a method to synthesize polyurethane/silver nanoparticle composite and to characterize this composite films containing different concentration of silver nanoparticles in terms of their physical, thermal, chemical properties and wettability.

## METHODOLOGY

Silver nanoparticles were synthesized by dissolving silver nitrate salt into dimethyl formamide (DMF).Four samples of 10%,5%,1% and 0.5% of silver nanoparticles in DMF were prepared. Each sample was stirred for about five minutes in order to dissolve $AgNO_3$ salt. Before making polyurethane/AgNPs composite four samples of polyurethane in tetrahydrofuran (THF) were prepared. 0.90g, 0.95g, 0.99g and 0.995g of polyurethane were weighed and 25ml of tetrahydrofuran was added to each sample to make four samples. Samples were then stirred on a magnetic stirrer for one hour until all of the PDMS-PEU was dissolved into THF. After preparation of solution of polyurethane in THF, solution of $AgNO_3$ in DMF was added to the polyurethane solution to make films of 10%, 5%, 1% and 0.5% $AgNO_3$ respectively then the solution was stirred for about five minutes. One sample of 10% $AgNO_3$ in PDMS-PEU was prepared to be used as a control.

Films of about 0.1-1mm thickness were prepared by casting from solution. Films were cast on petridishes. Petridishes were covered for 36 hours to avoid environmental contamination and to allow for controlled evaporation of THF. The polymer films were removed from petridishes and placed on Teflon sheet for heat treatment. Color change was observed in the samples. The color of the samples changed from translucent to silver colour which indicated further reduction of silver salts to elemental silver.

## CHARACTERIZATION

X-ray diffraction is a conventional technique for determination of crystallographic structure and morphology. Each individual constituent exhibit characteristic diffraction intensity distinct from other constituents. There is increase in intensity with the increase in amount of constituent. The x-ray diffraction data were collected for PDMS-PEU/AgNPs composite using Simens D500 diffractometer using Cu-Ká radiation.

Thermogravimetric analysis measure the change in weight of material as function of temperature and environment and gives information related to thermal decomposition of material or their stability in different environment. In this study TGA Q 500 (TA instruments 530) with auto sampler was used to determine the thermal decomposition of PDMS-PEU/ AgNPs composite material. The samples were heated at a con-

stant rate of 20C/min in an inert atmosphere containing nitrogen gas from 20-1000C. In order to do TGA analysis films were cut into small pieces of about 50mg.

Uv-vis spectroscopy is the most widely used technique for structural characterization of silver nanoparticle[12]. In order to determine the size, shape of the nanoparticles and interaction of nanoparticle with the surrounding matrix, ultraviolet visible spectroscopic analysis was conducted. Contact angle was measured by a contact angle rig (CAM200,KSV Instruments, Helsinki, Finland) equipped with a video recorder that collected one image per second. Image analysis was performed with CAM 200 Software. Water was used as wetting agent. For each sample four readings were taken by using sessile drop method. The samples were cut into 8 mm × 1 cm dimension.

## RESULTS

Silver nanoparticles were synthesized by dissolving silver salts into N,N dimethyl formamide (DMF). It was noted that the colour of the solution changed in about five minutes. The colour becomes yellow initially and gradually darkened with the passage of time. Colour change indicates the reduction of silver salts by DMF. After the synthesis of films heat treatment was carried out, it was observed that the colour of the films changed from whitish yellow to brownish silver. The colour change of the film indicated further reduction of salt into nanoparticles. Stretching of the films manually indicated that the film possess adequate mechanical strength.

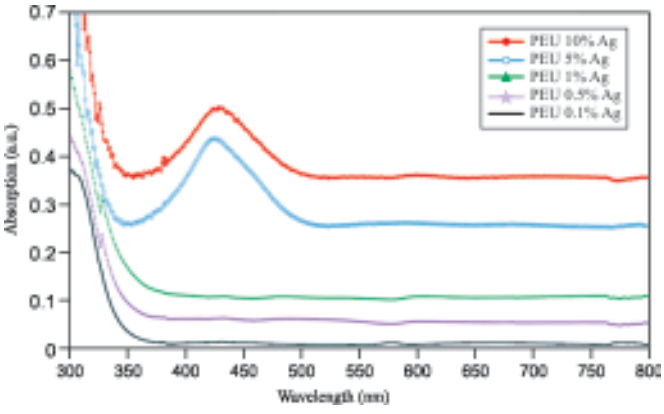


Fig. 1: Uv-vis spectroscopy of PDMS-PEU/Ag composite films

Ultraviolet visible spectroscopic analysis (Fig. 1) showed no surface plasmon resonance absorption peaks for the samples containing 1%, 0.5% and 0.1% silver nitrate. However samples containing 10% and 5% silver nitrate exhibited absorption peak centered at 430nm wavelength.

The wettability of the composite was analyzed by contact angle measurement(Table 1) The contact angle for neat PDMS-PEU was 96.35° where as contact angle value for the sample containing 10%,5%,1% and 0.5% AgNO3 was about 73°,76°,71° and 80° respectively (Table 1). Decrease in contact angle measurement was observed after the addition of silver to polyurethane but there was no significant difference in contact angle value among from samples loaded with different concentration of silver. Hydrophobicity of material decreases with decrease in contact angle value. The addition of silver to polyurethane results in decrease in hydrophobicity leading to improved wettability of the material.

TABLE 1: WATER POLYMER SURFACE CONTACT ANGLE MEASUREMENTS OF PDMS-PEU /SILVER NANOPARTICLE COMPOSITE WITH WATER

| Sample | Contact angle values |
|---|---|
| Control Sample | 96.35 |
| 10% AgNO3, PDMS-PEU | 72.105 ± 1.5 |
| 5% AgNO3,PDMS-PEU | 76.64 ± 0.75 |
| 1% AgNO3,PDMS-PEU | 70.99 ± 0.73 |
| 0.5% AgNO3,PDMS-PEU | 73.53 ± 1.76 |

X-ray diffraction analysis displayed from diffraction peaks 32.25,38.23,44.43,64.63 corresponding to (111) (200) and (220) planes indicated face centered cubic crystalline silver phase where as the two peaks at 2 theta 32.25 and 64.50 correspond to (111) and (311) planes indicating the presence of cubic crystalline silver oxide. The strong and the sharp peak suggest highly crystalline silver particles in the sample where as polymer is represented by broad peak of low intensity. It is also noted that reflection of 5% and 10% loading PDMS-PEU samples are very similar to each other. XRD analysis of samples indicated the presence of two phase silver nanoparticles and silver oxide beside polymer phase. Furthermore size of the nanoparticles can be calculated by using Scherrer equation.

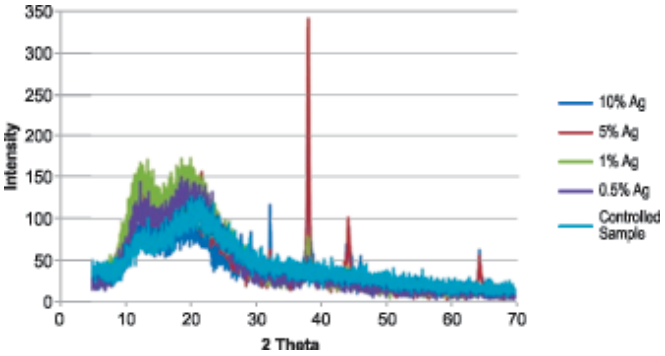


Fig. 2: XRD analysis of PDMS-PEU/Ag composite films

Thermogravimetric analysis (TGA) indicated that the material is stable up to 300°C. (Fig 3) Beyond this temperature limit the material exhibited 60 to 80% weight loss. Furthermore there was no further decline in weight percentage in loaded samples beyond 450 to 500°C. The difference in remaining weight percentage of individual loaded samples corresponds to the quantity of the silver added. There was complete structural decomposition and evaporation of the polymer at 450 to 500°C.

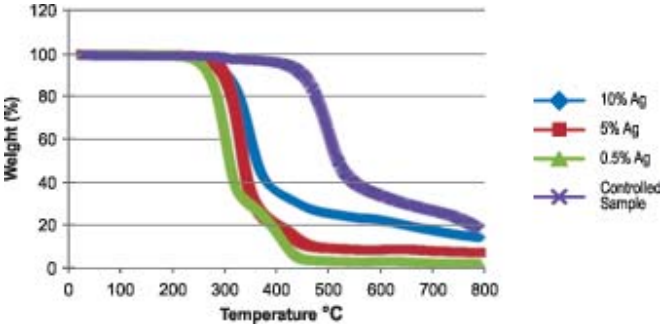


Fig. 3: TGA curve of PDMS-PEU/Ag composite films

## DISCUSSION

Ultraviolet visible spectroscopic analysis provides information about the size, shape and the interaction of silver nanoparticles with the surrounding matrix. As shown in (Fig1) the samples containing 10% and 5% Ag exhibit absorption peaks centered at about 430 nm indicate spherical shape of particle.[14,9] No absorption peaks were observed for samples containing 1%, 0.5%, and 0.1%. This might be due to extremely low concentration of nanoparticles. Tailing effect is also observed in the SPR band extending up to 800nm which indicates broad size distribution for these particles which are confirmed by findings in the XRD analysis.[14] The broad peak in the 5% Ag containing sample indicate large particle size of of AgNPs this is in agreement with previous study which demonstrates that with the increase in diameter the peak plasma resonance shifts to a longer wavelength and broadens.[15]

Contact angle measurements (Table 1) indicated that the surface contact angle decreased with the addition of silver to the polymer. In order to achieve effective release of drug from the polymer hydrophilic surface is desirable. The release of silver ions from antimicrobial polymer is based on three elementary processes. The entry of water molecules into the composite material, chemical reaction between water molecule and silver resulting in production of silver ions and release of silver ions from the material into the environment. Composites possessing less crystallinity and high water uptake leads to more release of silver ions[16]. The contact angle measurement of pristine PDMS-PEU shows less hydrophilic surface indicating less water uptake. However with the incorporation of silver nanoparticles the contact angle measurement decreases indicating increases in hydrophilicity which will result in improving water uptake by the polymer. This indicates that the incorporation of silver nanoparticles improves wettability of the PDMS-PEU based films.

TGA analysis (Fig 3) shows that unfilled PDMS-PEU has more thermal stability and there is loss in thermal stability with the addition of silver to it. However the figures shows that by changing the concentration of silver does not influence the thermal stability up to 300°C because in all composite films there is sudden weight loss occurring at above 300°C. This indicates that PDMS-PEU/Silver composite is stable up to 300°C and fulfills the requirements for most of the medical and dental applications. Furthermore it can be noted from the graphs that there is no further decrease in weight percentage of the sample with increase in temperature beyond 450°C. This weight percentage left behind correspond to the weight of the silver added to the sample indicating that almost complete structural decomposition of the polymer occurs at about 450C leaving behind the silver particles only.

The four diffraction peaks obtained at angle 2 theta 32.35, 38.23,44.43 and 64.60(Fig2) corresponding to (111),(200) and (220) planes and are related to

the face centered cubic (fcc) crystalline silver phase of the sample. While the two diffraction peaks obtained at an angle 2 theta 32.35 and 64.60 correspond to (111) and (311) planes in the crystal to the cubic crystalline phase of the silver oxide phase of the sample. The strong and sharp peaks suggest the formation of highly crystalline silver particles in the nanoscale structure.[13] The narrow peak indicates the large size of the particles which confirms the findings determined in uv-vis spectral analysis[17]. The size of the particle can be calculated by Scherrer formula. The diameter of the particles ranges from 22nm to 48nm determined by the Scherrer formula.

## CONCLUSION

A new method of synthesis of silver nanoparticles was introduced. The results of some of the tests conducted indicate that this material could be used for dental and biomedical application. There is scope for improvement and potential for advanced studies based on these findings. It would be useful if the material is further investigated to determine its silver release properties, biocompatibility, radiopacity, mechanical and biological properties.

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