



Preparation and Characterization of Novel Poly(MMA-co-GMA)/Ag Nanocomposites for Biomedical Applications



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THE current work aims at preparation of novel nanocomposite materials based on polymerization of methyl methacrylate (MMA), glycidyl methacrylate (GMA), monomers and silver nanoparticles (Ag-NPs) for biomedical applications. The fabricated poly(MMA-co-GMA)/Ag nanocomposites were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and FT-IR spectroscopy. The XRD and FT-IR spectra results confirmed the formation of the poly(MMA-co-GMA)/Ag nanocomposites with silver in nanoform. Furthermore, SEM indicated that the Ag-NPs had well dispersion in polymer matrix. Moreover, the prepared nanocomposites were displayed good enhancement in the thermal stability after addition of (Ag-NPs) by different ratios during polymerization process. Additionally, the antimicrobial activity of the synthesized poly(MMA-co-GMA)/Ag nanocomposites against *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans* and *Aspergillus niger* as representatives for gram positive, gram negative bacteria, yeast and fungi were investigated. Thus, poly(MMA-co-GMA)/Ag nanocomposites were concluded as good candidates for biomedical applications.

Keywords: PMMA; PGMA; Silver nanoparticles; nanocomposites; antimicrobial properties; SEM; XRD; FT-IR.

Introduction

During the last decades, nanotechnology science is interesting for many researchers in different fields. Nano-science is a promising technology that connects different field of science including physics, biology, and chemistry concerning medical and industrial applications. Applications related to utilization of nanotechnology have grown the variety of methods adopting synthesis of nanomaterials including but not limited to chemical, physical and biological processes but it can be hybrid methods employed for synthesis of different types of nanoparticles (NPs) [1].

Glycidyl methacrylate (GMA) copolymers have many applications in biologies, electronics as well as paint application and synthesis of thermal energy storage materials [2-5]. GMA is a reactive monomer has both vinyl and epoxy functions, which meets the requirements for post-polymerization modification. Also, it is cheap reagent and extensively used in the industrial production of functional methacrylic epoxy resins for coatings and adhesives [6]. The GMA is a very beneficial monomer for different applications due to the ability of the epoxy group to undergo ring-opening reactions with different nucleophiles [4].

Correspondingly, the copolymer of (MMA-co-GMA) has been used as a compatibilizer

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in some polymer blends [7]. Terpolymers of methacrylate-glycidyl methacrylate-ethyl acrylate were used as compatibilizer for poly-butylene terephthalate /acrylonitrile-butadiene-styrene blends (PBT/ABS) and nylon6/ABS blends where the dispersed phase of PBT/SAN blends did not display any roughening [8,9].

Alkyl methacrylate-based crosslinked polymers containing pendant epoxy functionality are significantly applied in coatings, molding and as mediator for bioactive materials [10,11]. The physico-mechanical investigation of polyalkylmethacrylate-GMA revealed promising results reflecting better mechanical properties of hydroxy-functional methacrylate/GMA copolymers after crosslinking the epoxy pendant groups [12].

Silver nanoparticles (Ag-NPs) display good antimicrobial efficiency against bacteria and eukaryotic microorganisms, so it played a major role in the field of nanotechnology and nanomedicine [13-15]. Silver is particularly important because of its characteristic properties such as high conductivity, antibacterial and catalytic activities beside the chemical stability. In recent decades, Ag-NPs have been applied in catalysis, electronics, optics and other fields due to their unique optical, electrical, and magnetic properties depending on their particle size. Currently, Ag-NPs are applied mostly as antibacterial and antifungal agents in many application directions such as bioengineering, biotechnology, textile and water treatment in addition to many consumer products based on silver [16-18].

In the current work we are keen to prepare poly(MMA-co-GMA)/Ag nanocomposites based on methyl methacrylate (MMA), glycidyl methacrylate (GMA) monomers and silver nanoparticles (Ag-NPs), then the prepared poly(MMA-co-GMA)/Ag nanocomposites were characterized using FT-IR, XRD, SEM and antimicrobial investigation. In the next context, poly(MMA-co-GMA) will be denoted as PMMA/GMA.

Materials and Methods

Materials

Glycidyl methacrylate, methyl methacrylate monomer and acrylic acid (AA) from Sigma-Aldrich (USA) were used without further purification. Potassium persulfate, sodium lauryl sulfate (SDS), silver nitrate and citric acid were purchased from S.D. Fine-Chem Ltd.

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Methods

Preparation of PMMA/GMA/Ag nanocomposites

It was carried out as follows; in a 250 ml 3-necked flask, fitted with a reflux condenser, containing 85 ml of distilled water and 0.167 g of sodium lauryl sulfate (SDS) as emulsifier. After that, 8.5g of methyl methacrylate monomer was added followed by the addition of 1g of glycidyl methacrylate monomer and 0.7g of acrylic acid and 0.167g of sodium acetate to adjust pH equal 6 then emulsified for 10 min using homogenizer at 5000 rpm. Then silver nitrate (0.5, 1, 3, 5 wt%) based on monomer concentration was added, then citric acid (1 mole /1 mole of silver nitrate) were added. Potassium persulphate as initiator (0.1g) was used to starting the polymerization process. Finally, the mixture was stirring using mechanical stirrer at 500 rpm at the 80°C for 5 hrs. The prepared co-polymer was precipitated using acetone then filtered and dried at 60°C, and then the final precipitate was grinded using mortar to be ready for using.

Characterization

Powder XRD (Rigaku, Miniflex X-ray diffractometer ME 14848DO4 with CuK α radiation source, $\lambda = 1.5418 \text{ \AA}$, Japan) was used to characterize the prepared PMMA/GMA/Ag nanocomposites where samples were positioned in a vertical configuration (transmittance) for data collection and the d-spacing was calculated by using Bragg's equation. Also, Tescan VEGA-II, USA, scanning electron microscope (SEM) operated at 20 kV was used to characterize the surface properties and morphology of PMMA/GMA/Ag nanocomposites. The thermal behavior was investigated with the aid of a Perkin Elmer thermogravimetric analyzer (TGA) operated under nitrogen atmosphere and at a heating rate of 10°C/min.

Antimicrobial evaluation

The disc agar plate method was used to assess the antimicrobial activity of PMMA/GMA/Ag nanocomposites. The microorganisms were supplied by the culture collection center, Microbial Chemistry Department, NRC, Egypt. The prepared PMMA/GMA/Ag nanocomposites discs of 0.5 cm diameter were positioned on the surface of agar plates seeded with the microbes used for the investigation. The agar plates were incubated for 24 h at the suitable temperature of each test organism. PMMA/GMA/Ag nanocomposites were investigated against various

microbial strains, i.e., (*Staphylococcus aureus*), gram negative (*Escherichia coli*) bacteria, yeast (*Candida albicans*) and fungi (*Aspergillus niger*). The bacterial and yeast microbes were grown on a nutrient agar medium (DSMZ1) of the following ingredients (g/l): Peptone (5.0), Meat extract (3.0), Agar (20.0), distilled water (1000.0 ml) and the pH to 7.0. The fungal microbes were grown on Czapek-Dox medium (DSMZ130) consisting of (g/l) sucrose (30.00), NaNO_3 (3.0), $\text{MgSO}_4 \times 7 \text{H}_2\text{O}$ (0.50), KCl (0.50), $\text{FeSO}_4 \times 7 \text{H}_2\text{O}$ (0.01), K_2HPO_4 (1.0), agar (18.0) and distilled water (1000.0ml). The pH was adjusted to 7.2 and the cultures of the test microbes were diluted by sterilized distilled water to 107 - 108 cells/ml. After that, 1ml of each was immersed in 250 ml of solid agar medium in 1L-Erlenmeyer flask then poured in 10 cm diameter Petri dishes (25 ml). Discs of 5 mm diameter were placed on the surface of previously infected agar plates with the test microbe and incubated for 24 h at 37 °C for bacteria and yeast but for 48 h at 30 °C for fungus.

Results and Discussion

FTIR spectra

FT-IR spectra of PMMA/GMA/Ag nanocomposites were presented in Fig. 1 where the C=C characteristic peak at 1638 cm^{-1} almost disappeared indicating the nearly complete copolymerization of MMA/GMA monomers. Also, the C=O characteristic peak at 1729 cm^{-1} was shifted to a higher value at 1740 cm^{-1} in PMMA/GMA/Ag nanocomposites spectrum. The intensity of CH absorption peak at 2996.84 cm^{-1} and

2952.48 cm^{-1} was relatively improved indicating some interaction between Ag-NPs and the polymer matrix. In addition, the six spectra of PMMA/GMA/Ag nanocomposites with the various Ag-NPs loads are nearly the same with the difference only in the intensity of the peaks.

Structure and Morphology

The morphological properties of the prepared PMMA/GMA/Ag nanocomposites with different concentrations of Ag-NPs were evaluated using SEM. The development of Ag-NPs distribution is significant and subsequently, the good dispersion of Ag-NPs results in an essential enhancement in the properties of the fabricated PMMA/Ag nanocomposites. Figure 2 showed that the fabricated Ag-materials were of a mean size of about 10 nm i.e. laying in the nanometer scale. Ag-NPs were dispersed in PMMA/GMA/Ag nanocomposites and led to well significant results on the various characteristics of PMMA/Ag nanocomposites such as thermal and antimicrobial properties.

Homogeneous dispersion of Ag-NPs is preferred to avoid the formation of crack creativities in the PMMA nanocomposites. In order to think about the influence of Ag-NPs in the PMMA matrix loaded (0.5, 1 and 3%wt) on the distribution and the dispersion of the Ag-NPs as nanofiller in the PMMA/GMA/Ag nanocomposites matrix, scanning electron microscope (SEM) was used to evaluate the dispersion of Ag-NPs in the nanocomposite matrix. From Fig. 2 it clears that from EDX analysis that the Ag-NPs present in PMMA/GMA/Ag nanocomposites in all

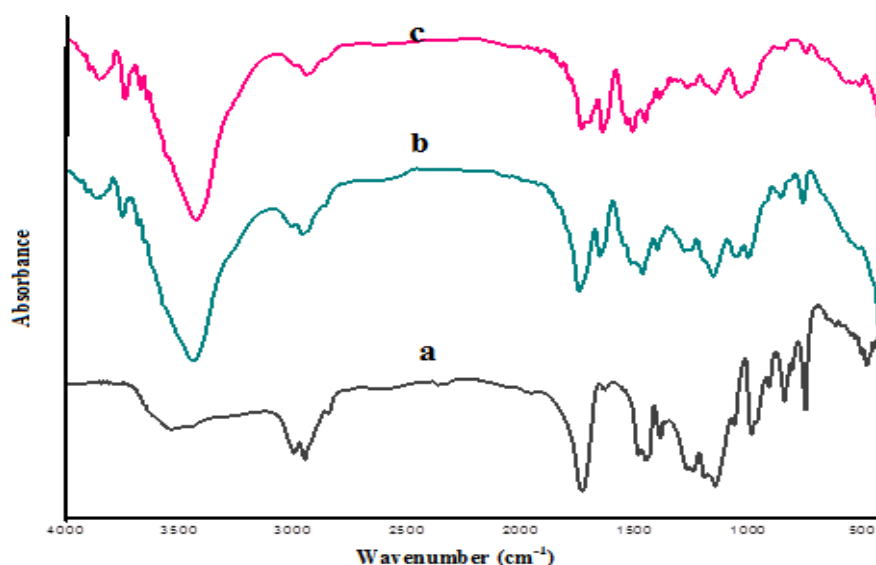


Fig. 1. FT-IR spectra of (a) PMMA/GMA blend, (b and c) PMMA/GMA/Ag nanocomposites with different loads of Ag-NPs (0.5 and 1%), respectively

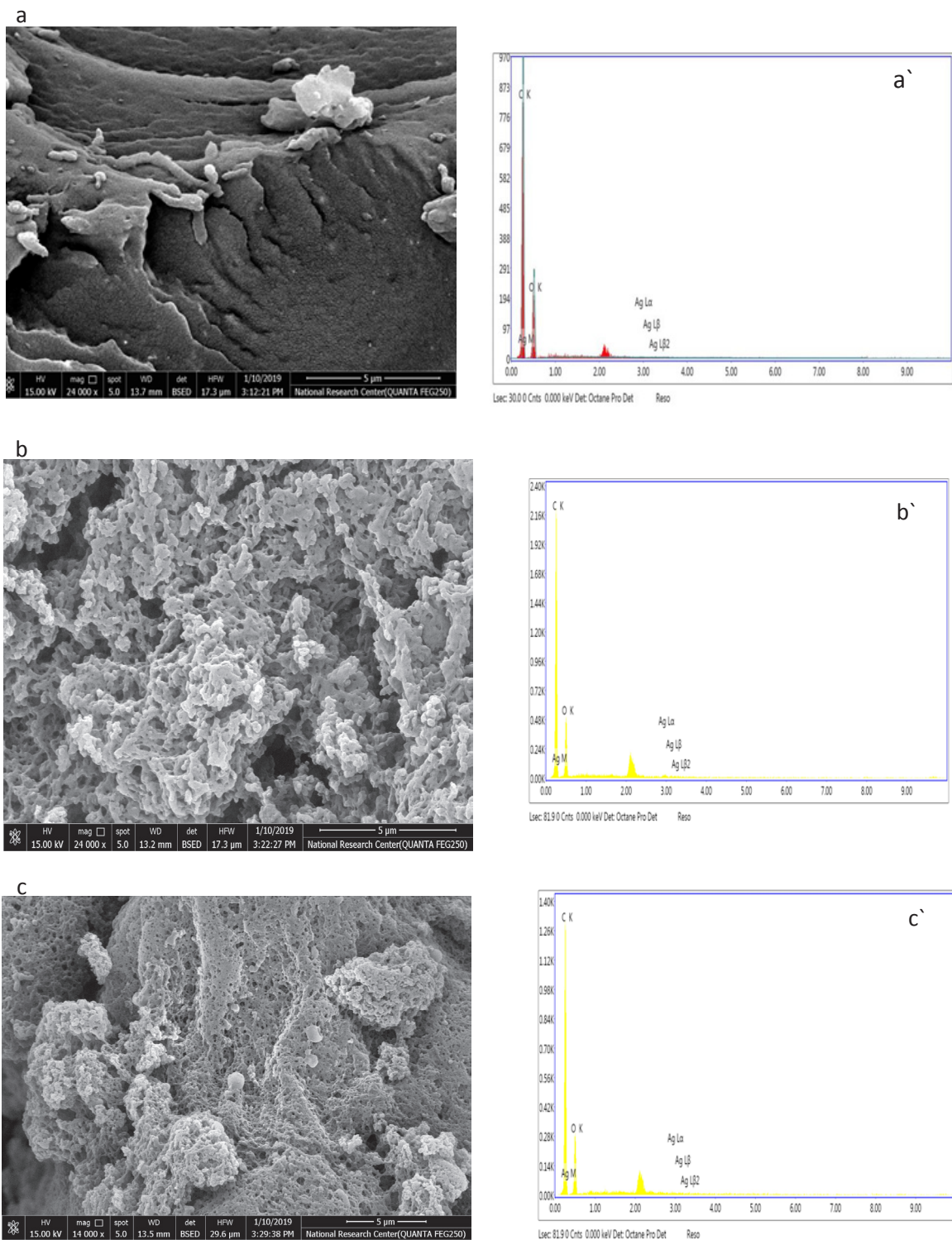


Fig. 2. SEM image of PMMA/GMA/Ag nanocomposites of different loads of Ag-NPs (0.5, 1 and 3 %) a, b and c, respectively, and their corresponding EDX (a', b' and c').

concentrations which prove the formation of Ag-NPs in the copolymers matrix.

X-ray diffraction pattern of the prepared PMMA/GMA/Ag nanocomposites

Figure 3 represents the XRD pattern of Ag-NPs, PMMA/GMA blend and PMMA/GMA/Ag nanocomposites with different loadings of Ag-NPs (0.5 and 1% Ag-NPs). The Ag-NPs were fabricated using solvo-thermal method in this method ethanol was performances as a reaction medium. The X-ray diffraction pattern of the obtained Ag-NPs is shown in Fig. 3 for 2θ diffraction angles between 10 and 70 displays most attributed peaks that related to the planes (100) at $2\theta=30.6^\circ$, (002) at $2\theta=34.44^\circ$, (101) at $2\theta=36.25^\circ$, (102) at $2\theta=47.42^\circ$, (110) at $2\theta=56.57^\circ$, (103) at $2\theta=62.86^\circ$ in addition to (112) at $2\theta=67.93^\circ$. The result gets from XRD demonstrated the high similarity of the largest part of diffraction peaks of the prepared Ag-NPs with the packed orthorhombic structure and agree with the stated JCPDS data.

While the XRD pattern of PMMA/GMA blend displays that there are no significant peaks but there is a peak at $2\theta = 13.5^\circ$ that is relative to the crystalline polymer structure. Moreover, the XRD pattern of PMMA/GMA/Ag nanocomposites loaded by different concentrations of Ag-NPs (0.5 and 1%) was illustrated in **Fig. 3** that exhibited the existence of Ag-NPs into the polymer matrix in all Ag-NPs loadings that confirmed the good formation of PMMA/GMA/Ag nanocomposites. Additionally, the intensity of Ag-NPs peaks in PMMA/GMA/Ag nanocomposites was increased on increasing the Ag-NPs content in the polymer matrix.

Thermal analysis of the prepared PMMA/GMA/Ag nanocomposites

The thermal properties of the prepared PMMA/GMA/Ag nanocomposites are very necessary and reflected the greatest significant properties of the key studies for different utilizations particularly in packaging applications. Therefore, TGA is essential for the creation and thermal stability of the prepared PMMA/GMA/Ag nanocomposites which displayed in **Fig. 4**. Figure 4 shows TGA of PMMA/GMA blends as well as PMMA/GMA/Ag nanocomposites with various loadings addition of Ag-NPs. The PMMA/GMA blend was attainable through three main steps of thermal degradation. The first step was between $T= 102$ and 230°C , weight loss of around 8wt% was recognized to the vaporization of remaining solvent, and perhaps, a

depolymerization stage was started at weak head-to-head links growing from chain termination via combining of vinylidene chain ends which outcome from disproportionation. The second step was located among 235 and 410°C . Furthermore, adding of Ag-NPs into PMMA/GMA blend enriches the thermal stability of the prepared PMMA/GMA/Ag nanocomposites as shown in **Fig. 4**. A remarkable improvement was detected at greater Ag-NPs loadings when the highest thermal degradation peak rises by approximately 20 K associated to the main peak of PMMA/GMA blend. Correspondingly, the improvement of PMMA/GMA/Ag nanocomposites thermal stability with raising the content of Ag-NPs may be credited the morphological, thermal properties and antibacterial activity of PMMA/GMA/Ag nanocomposites which open great view points for the applications of PMMA/GMA/Ag nanocomposites in different fields especially in biomedical applications.

Antimicrobials activity of PMMA/GMA/Ag nanocomposites

The antimicrobial activity of the fabricated PMMA/GMA/Ag nanocomposites was performed through The Agar Plate Method to recognize the zone of inhibition of the synthesized PMMA/GMA/Ag nanocomposites films. Additionally, these films were examined against G^{+ve} (*Staphylococcus aureus*), G^{-ve} (*Escherichia coli*) bacteria, yeast (*Candida albicans*) and fungi (*Aspergillus niger*). The antimicrobial activities of the fabricated PMMA/GMA/Ag nanocomposites against the bacteria, yeast and fungi were evaluated as shown in Table 1 and Fig. 5.

Figure 5 was displaying a significant increase in the inhibition zone by increasing Ag-NPs content in PMMA/GMA/Ag nanocomposites. Furthermore, the large inhibition zones of PMMA/GMA/Ag nanocomposite films directed against demonstrative strains of Gram-positive (*Staphylococcus aureus*), Gram negative (*Escherichia coli*) bacteria did not show a significant modification with increasing the concentration of Ag-NPs in PMMA/GMA/Ag nanocomposites of low Ag-NPs content as shown in Fig. 5. The inhibition zone was increased by increasing the ratios of Ag-NPs in the PMMA/GMA/Ag matrix. It is predictable that the inhibitory influence of Ag-NPs in contradiction of microorganisms up till now is not completely examined. It has been assumed that DNA misses its duplication ability and cellular proteins come to be deactivated.

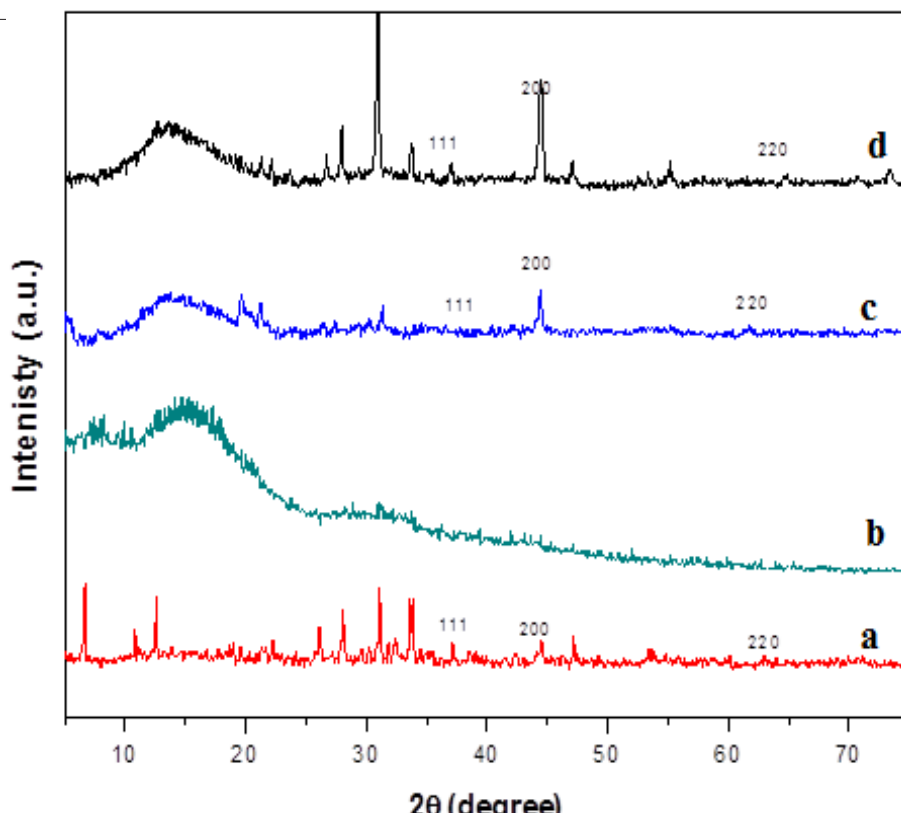


Fig. 3. XRD pattern of (a) Ag-NPs, (b) PMMA/GMA blend, (c) PMMA/GMA/Ag nanocomposites loaded with 0.5%, 1% of Ag-NPs, respectively.

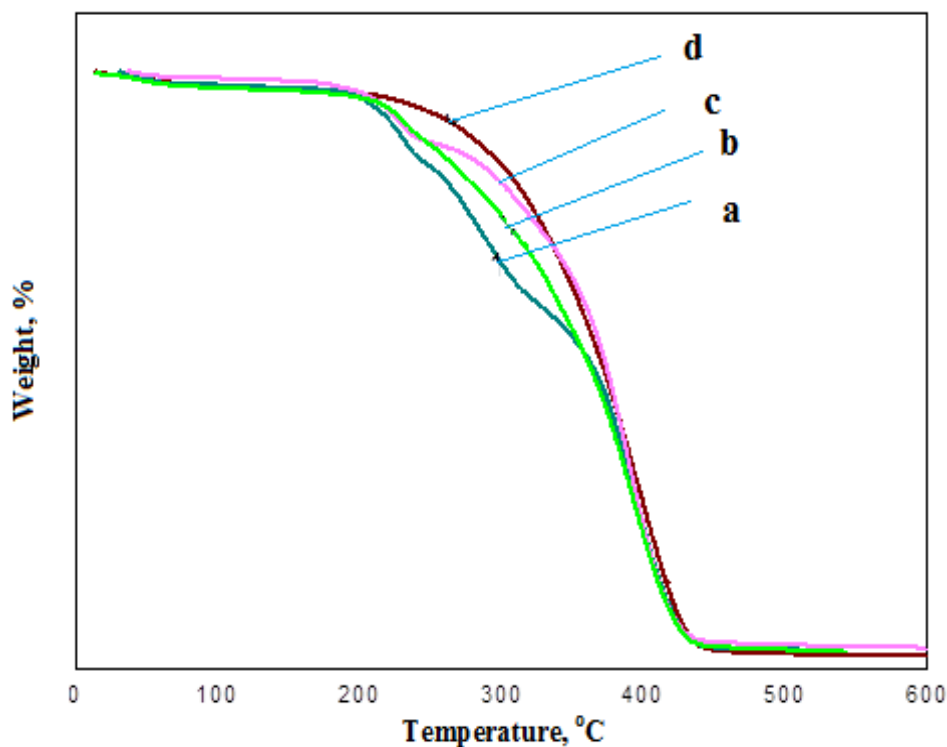
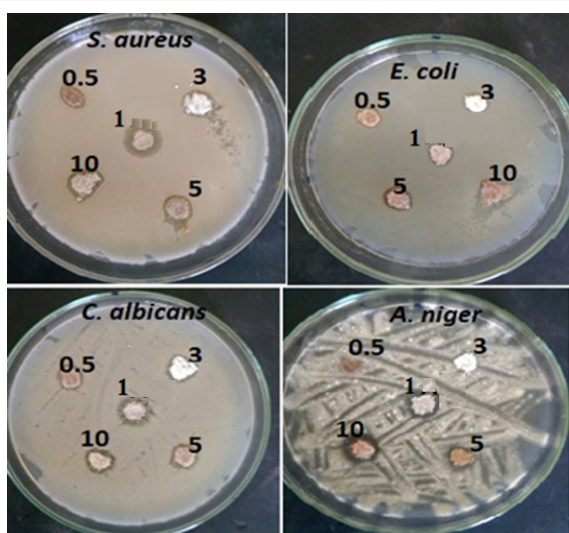


Fig. 4. TGA curves of (a) PMMA/GMA blend, (b, c and d) PMMA/GMA/Ag nanocomposites with different concentrations of Ag-NPs, (0.5, 1, 3 and 3%), respectively.

TABLE 1. Antimicrobial activity of the prepared nanocomposites against different pathogenic bacteria and fungi

Samples	Ag-NPs, Conc., %	Clear zone (ϕ mm)			
		<i>Staphyl. aureus</i>	<i>E. coli</i>	<i>Candida albicans</i>	<i>Aspergillus niger</i>
P M M A / G M A blend	0.0	0.0	0.0	0.0	0.0
PMMA/GMA/Ag	0.5	14	12	15	14
PMMA/GMA/Ag	1.0	16	14	16	16
PMMA/GMA/Ag	3.0	17	14	17	19
PMMA/GMA/Ag	5.0	20	12	19	18

**Fig. 5. The antimicrobial activity of the PMMA/GMA/Ag nanocomposites against gram positive (*Staphylococcus aureus*), gram negative (*Escherichia coli*) bacteria, yeast (*Candida albicans*) and fungi (*Aspergillus niger*).**

Conclusions

In the current work we successfully prepared novel nanocomposite materials based on methyl methacrylate (MMA), glycidyl methacrylate (GMA), monomers and silver nanoparticles (Ag-NPs) for biomedical applications. The prepared polymer nanocomposites were evaluated using X-ray diffraction pattern (XRD), scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FT-IR) as well as the mechanical properties. The data obtained from XRD and FT-IR spectra established the formation of the PMMA/GMA/Ag nanocomposites containing Ag-NPs. Correspondingly; the morphology of the prepared PMMA/GMA/Ag nanocomposites was evaluated using SEM which designated that the Ag-NPs dispersed

well in the prepared nanocomposite matrix. The prepared nanocomposites were demonstrated good the thermal stability after addition of (Ag-NPs). Furthermore, the PMMA/GMA/Ag nanocomposites displayed good antimicrobial activity against gram positive (*Staphylococcus aureus*), gram negative (*Escherichia coli*) bacteria, yeast (*Candida albicans*) and fungi (*Aspergillus niger*) which were considered as good candidate materials for biomedical applications.

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