Radiation Preparation and Characterization of Grafted Polyethylene Coated Polypropylene Loaded with Silver Nanoparticles for Antibacterial Application

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ABSTRACT

In this study, polyethylene coated polypropylene (PE-co-PP) non-woven fabric was grafted with acrylic acid (AAc) monomer by using gamma radiation technique then loaded with silver nanoparticles (Ag NPs). Two factors affecting the grafting process, concentration of monomer and radiation dose, were studied. The structure of the grafted fabric before and after loading with Ag NPs was characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscope (SEM). The morphology of all grafted fabrics showed a noticeable change due to incorporation of Ag NPs. Moreover, the mechanical properties of all fabrics in terms of tensile strength and elongation at break (%) were studied. The incorporation of Ag NPs in the grafted fabrics was confirmed by X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The grafted PE-co-PP fabrics loaded with AgNPs demonstrated an excellent antibacterial activity against the tested bacteria, *Escherichia coli* and *Staphylococcus aureus*.

KEYWORDS

Grafting; Gamma Irradiation; Silver Nanoparticles; Antibacterial.
INTRODUCTION

It is well established that grafting is an ideal and efficient technique for attaching polymer chains containing desired chemical groups via covalent bonding. Continuous efforts have been made to improve physico-chemical properties of polymers by grafting technique both by conventional chemical grafting technique (Wu et al., 2003) and by radiation grafting (Princi et al., 2005).

Radiation-grafting has many advantages over other conventional methods because it does not require the use of catalyst nor additives to initiate the reaction. It has been shown to be a good method for the functionalization and development of smart polymeric materials (Pino-Ramos et al., 2016).

Polyethylene coated polypropylene (PE-co-PP), as a synthetic non-woven fabric, is considered as an industrial important fabric. It consists of spun bonded polypropylene (PP) coated with a layer of impervious polyethylene (PE). They are generally hydrophobic synthetic non-toxic and non-stimulated fabrics. Moreover, they have good laminating properties, high degree of anti-dust and can effectively protect the human skin. The hydrophilicity of these synthetic fibers can be improved by applying, grafting or surface coating with suitable hydrophilic ingredient to be used in different applications (Abo El-Khair et al., 2013). On the other hand, the synthetic fabrics and their blends involved in various applications, provide excellent substrates for bacteria growth because they are contaminated easily with microorganisms under the appropriate environmental conditions (Borkow and Gabbay, 2008 & Gao and Cranston, 2008). Therefore, in recent years research works have shown interest in developing antibacterial fibers by incorporation of metal nanoparticles such as silver nanoparticles which has a good antibacterial activity. Fabrics with antibacterial ability can be used in various applications such as clothing, underwear, ladies tights, shoe linings, armbands, sleeping bags and toys for children. Metal nanoparticles were extensively used as antibacterial agents towards many pathogens (Jayaramudu et al., 2013; Varaprasad et al., 2013; Raghavendra et al., 2015).

Silver nanoparticles were extensively studied because of their potential anti-bacterial properties results from the large contact areas with microorganisms (Kolya et al., 2015). Since the antibacterial activities of silver nanoparticles are strongly dependent on their sizes and shapes, silver particles possess physicochemical and biological properties on the nanoscale because of their modifications of biological fictionalization (Parak et al., 2003; Hemant et al., 2012).

The addition of metal-based particles into polymers is a versatile route to take advantage of their strong antimicrobial properties producing novel bio-cide materials and allowing a further extension of the range of applications. Although there are several researches related with metal nanoparticles incorporated into different polymer matrices (Gunawan et al., 2011). Further research is needed to support the development of bioactive polymeric materials in order to be used in hospital equipment or in prostheses, avoiding for example hospital acquired infections. In this context, we stress technologies based either on commercial matrices with embedded metal nanoparticles or on polymer/metal coatings, as they can be easily implemented at industrial scale or in implant materials, respectively (Humberto, 2015). In this study, PE-co-PP non-woven fabric was grafted with acrylic acid and then loaded with silver nanoparticles using gamma radiation. The properties of the grafted loaded non-woven fabric with AgNPs were analyzed by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy(SEM), X-ray diffraction (XRD), thermo gravimetric analysis(TGA), and antibacterial activity against gram positive and gram negative.
Experimental and Characterization Techniques

Materials

PE-coated-PP non-woven fabric, diameter of 13 µm, was provided by Kurashiki Textile MFG, Osaka, Japan. A laboratory grade AAc monomer with purity 99% from Merck (Germany) was used as received. Silver nitrate (AgNO₃), molecular weight, M.W. 169.87, purchased from Sigma – Aldrich, USA.

Radiation grafting of acrylic acid onto PE-co-PP non-woven fabric

Mutual radiation grafting method was used to graft acrylic acid monomer with different concentrations (5, 10, 15, and 20%) onto polyethylene coated polypropylene non-woven fabric. Pieces of dried fabric (Wo) were completely immersed in grafting solution of suitable concentration in a glass tube. The samples in glass tube were then irradiated in gamma chamber at different doses (30, 50, 70 and 100 kGy). The grafted samples were then washed thoroughly with hot distilled water to remove unreacted monomer and surface homopolymer. The grafted samples were extracted in boiling water to constant weight. The grafted sample was dried in vacuum oven at 50°C and weighed (Wᵣ). The grafting yield (%) was determined gravimetrically using the following relation:

\[ \text{Graft yield} \% = \left( \frac{Wᵣ - W₀}{W₀} \right) \times 100 \]

Loading of grafted fabric with silver nanoparticles (Ag NPs)

One wt% of AgNO₃ solution was prepared by dissolving 1 g of AgNO₃ in 100 ml of distill water. Then Grafted fabrics were immersed in 100 ml of AgNO₃ solution for 72 h then irradiated by γ – irradiation dose 50 kGy (1.64 kGy/h) at the National Center for Radiation Research and Technology, Cairo, Egypt. Afterwards, samples were rinsed with water and dried at 40°C for 40 min.

Characterization techniques

Water absorption (%)

In this process, the grafted samples were immersed in distilled water for 24 h at room temperature. The samples were then removed, blotted on absorbent paper and quickly weighed. The percent of water absorption was calculated using the following relation,

\[ \text{Water absorption} \% = \frac{(W₂ - W₁)}{W₁} \times 100 \]

Where W₁ is the initial weight of the grafted fabric, and W₂ the final weight of the grafted fabric after being immersed in water and blotted.

Tensile Mechanical Properties

Mecmesin, (Model 10-I) UK, equipped with software is used, Crosshead speed of 50 mm/min. In this all mechanical parameters were directly calculated. The samples for tensile measurements were dumbbell shaped having width of 4 mm and length of 50 mm. The recorded value for each mechanical parameter is the average of five measurements.

IR spectroscopic analysis

FTIR spectrophotometer model Mattson 100, made by Unicam, (UK) was used for FTIR measurements over the range 500–4,000 cm⁻¹.

X-ray diffraction

XRD was used to identify the silver nanoparticles into the (PE-co-PP)-co-AAc/Ag non-woven fabric. These measurements were carried out on a Shimadzu (Kyoto, Japan) X-ray diffractometer (XRD-6000 model) equipped with an X-ray tube (Cu target), and using a voltage of 40 kV and a current of 30 mA.

Transmission electron microscopy (TEM)

TEM was performed with a JEOL 100CX JEM operating at 80 kV. It is used to determine the size
of iron nanoparticles inside the polymeric matrix. To image the Ag nanoparticles on the TEM, finely ground polymer samples were dispersed in 1 mL of ethanol and then they sonicated to get a dispersed solution. Approximately 10–20 μL of this solution was dropped onto a 3 mm copper grid, which was then dried at room temperature. Finally, the copper grid was inserted into the transmission electron microscope.

**Thermogravimetric analysis (TGA)**

TGA studies were carried out using a TGA-30 apparatus (Shimadzu, Kyoto, Japan), at a heating rate of 10°C/min. in air, over a temperature range from room temperature to 600°C. Duplicate runs of the TGA thermograms of some starch/clay composite films were performed to check the reproducibility of the thermal data.

**Scanning Electron Microscope (SEM)**

The surface morphology of the Ag/grafted non-woven fabric in comparison with the ungrafted non-woven fabric was examined by SEM. The micrographs were taken with JSM-5400 instrument manufactured by Joel, Japan.

**Antibacterial activity testing**

Disk diffusion test according to Kirby-Baur method (Singh et al., 2014) was applied to identify the bacterial effect, through the measurements of bacterial broth was add over solidified nutrient agar and swapped over the surface with cured medical swap. The samples were placed in the Petri-dishes and then incubated for 24 hr at 30-32°C. The inhibition zone was then measured in cm from one side of the square sample. Both positive and negative bacteria were tested viz. Escherichia coli and Staphylococcus aurous.

**RESULTS AND DISCUSSION**

Acrylic acid was grafted on the surface of PE-co-PP non-woven fabric using gamma irradiation technique. The extent of radiation grafting is a function of many variables experimental such as monomer concentrations and irradiation dose. Therefore, effect of various experimental parameters onto grafting yield was investigated in order to optimize the experimental parameter to get desired grafting extent.

**Effect of monomer concentration**

The effect of monomer concentration on degree of grafting (%) was investigated keeping constant ratio of weight of substrate to volume of grafting solution. Figure (1) shows the effect of monomer concentration (%) on the degree of grafting (%). From this figure, it was found that the degree of grafting (%) increases with increasing monomer concentration at constant irradiation dose (50kGy). Higher degree of grafting (%) was expected at higher monomer concentrations. This increase may be due to the increase of free radicals formed on the AAc monomer in the bulk of the substrate. Also, the high monomer concentration at the grafting sits favors propagation of growing chain, consequently increasing the grafting yield.

**Effect of irradiation dose (kGy)**

Figure (2) shows the effect of irradiation dose (kGy) on the degree of grafting (%). From this figure, it was found that the degree of grafting (%) in-
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Increases with increase irradiation dose (kGy) up to 100 kGy. Grafting occurs through the formation of free radicals sites by the effect of gamma radiation, on the polyethylene coated polypropylene non-woven fabric backbone from which grafting occurs. Therefore, generally the increase of degree of grafting (%) may be attributed to the increased number of free radicals formed on both the polymer backbone and the monomers (Sayeda et al., 2006).

Water absorption (%)

Since non-woven fabric is hydrophobic in nature, thus the addition of acrylic acid imparts hydrophilic character to this fabric. Therefore, the water absorption of grafted non-woven fabric was measured. Figure (3) shows the effect of Grafting yield (%) on water absorption (%) of grafted non-woven fabric. From this figure, it was found that water absorption (%) increases with increasing the grafting yield (%). For example, water absorption increases from 18% for ungrafted non-woven fabric to 868% for grafted fabric (grafting yield 145%). The improvement in water absorption of non-woven fabric which occurred after grafting is due to the presence of poly (acrylic acid) chains along the backbone of non-woven fabric. This is because this fabric is hydrophobic in nature and poly(acrylic acid) possesses a high hydrophilic character. Moreover, the opening up and disruption of the non-woven fabric structure, caused by grafting, facilitates the absorption and diffusion of water molecules. In addition, the relative proportion of polar linkages in the non-woven fabric chains is increased by the introduction of more polar groups provided by polyacrylic acid (Abo El-Khair et al., 2013).

Mechanical properties

Figure 4 shows the tensile strength (TS) and elongation (%) at break of (ungrafted and grafted) non-woven fabric with different grafting yield (%). From this figure, it can be seen that the T.S of grafted non-woven fabric increases with the increase of grafting yield (%). The increase of tensile strength may be due to the increase in crosslinking density as the grafting yield (%) increases. Moreover, the increase of T.S of the grafted fabric indicates the presence of some interaction between the nonwoven fabric and PAAC during the irradiation processes. On the other hand and as expected, the elongation values at break have in counter a systematic decrease with the increase of grafting yield (%).
PE-co-PP non-woven fabric is an inert polymer, doesn’t have any polar groups. The grafting with acrylic acid creates a –(COOH)– polar group which makes it ready to react with silver ions to form a polymer used as antibacterial fabric. Several experiments were carried out to study the characterization of these non-woven fabric loaded with Ag NPs.

**Characterization of the grafted PE-co-PP fabrics and loaded with Ag NPs**

**IR spectroscopy**

The FT-IR spectra of ungrafted PE-co-PP fibers, grafted PE-co-PP fibers with acrylic acid, grafted PE-co-PP fibers with acrylic acid loaded with Ag NPs is shown in figure 5. The ungrafted non-woven fabric bands at 2915, 2848, 1463, and 719 cm⁻¹ were responsible for deformation vibrations of CH-groups. The grafted fabrics show new bands around 1700 cm⁻¹ due to carbonyl group (C=O) characteristic of the group COOH as shown in figure 5. Also, this figure shows an absorption band (broad peak) beginning at 3330 cm⁻¹ due to the –OH stretching of the carboxylic acids present in AAc monomer. The presence of these new bands in the spectra confirms the grafting process. Moreover, an increase of the grafting yield leads to an increase in the intensity of these bands. However, in figure 5 the broad peak of OH disappears in the spectrum of Ag loaded non-woven fabric, thus indicating the binding of Ag with O of the OH group which resulting from grafting of AAc.

**X-ray diffraction (XRD) analysis**

The XRD patterns of the ungrafted PE-co-PP fibers, grafted PE-co-PP fibers, and PE-co-PP fibers grafted and loaded with Ag NPs are shown in figure 6. The XRD pattern of ungrafted fabric (figure 6a) shows sharp peaks in the range of 20° to 24° due to the semicrystalline structure of (PE-co-PP) fabric. It is noticed also, that these peaks appeared in all the XRD pattern of both grafted, and Ag/grafted fabrics. For the sample after loading with AgNPs and exposed to a gamma radiation at a dose of 50 kGy, a diffraction peaks characteristic to AgNO₃ NPs appear at 2θ of 38.08, 44.18, 64.6 and 78.3 figure 6 c (Perelshtein et al., 2012). The diffraction peaks of Ag crystal, which has a face-centered cubic structure, are readily identified for the AAc and Ag/grafted fabric irradiated to 50 kGy in figure 6(b, c). These results indicate that the Ag (I) complex ions in the AAc and Ag/grafted fabric were reduced to form Ag metal crystals.
Transmission Electron Microscopy (TEM)

TEM is a good tool to help us monitoring and determining the shape and the size of nanoparticles. Figure 7 shows typical TEM image and particle size distribution of silver nanoparticles prepared by reduction of AgNO$_3$ loaded on the grafted fabrics, by soaking for 24 h, using gamma irradiation as a reducing agent. The nanoparticles are found as dark spherical objects. The size was determined by measuring the diameter of the particles present in the TEM image; the size of the formed Ag NPs is found to be in the range (10-15 nm).

Fig. (7): TEM image of PE-co-PP fibers grafted with acrylic acid and loaded with Ag NPs.

Thermogravimetric analysis (TGA)

TGA thermograms of ungrafted PE-co-PP fabrics, grafted PE-co-PP fabrics and PE-co-PP fabrics grafted and loaded with Ag NPs in the temperature range from 0-600°C are shown in figure 8. The TGA of ungrafted, grafted, Ag-grafted non-woven fabric show three degradation steps attributable to water loss (first step). In the temperature range of 300–500°C all samples have weight loss, which may be attributed to the degradation of side chain groups of non-woven fabric (Feng et al., 2007). From this figure, the thermo stability of Ag-grafted non-woven fabric was higher than that of the ungrafted and grafted fabric in the temperature range (380-500°C). This stability may be due to the formation of stronger hydrogen bonds between the well-distributed nanoparticles with grafted fabric. It is important to mention that the grafting and loading process which is carried out on the non-woven fabric doesn’t affect its thermal stability.

![TGA thermograms](image)

Fig. (8): TGA thermograms of (a) ungrafted PE-co-PP fabrics (b) grafted PE-co-PP fabrics with acrylic acid and (c) grafted PE-co-PP fabrics with acrylic acid and loaded with acrylic acid.

Scanning electron microscope (SEM)

Figure (9) shows the SEM micrographs of ungrafted PE-co-PP fabrics, PE-co-PP grafted fabrics with acrylic acid and PE-co-PP grafted fabrics with acrylic acid loaded with Ag NPs. It can be seen that the fibers of ungrafted non-woven fabric is very indiscernible, flat and smooth. The presence of grafting changes the structural characteristics of the resulting substrate. SEM also confirms the presence of grafted non-woven fabric which exists in the form of anchors, attachments on the surface of non-woven fabric (fig.9). Moreover, it may be observed that after irradiation of grafted fabric for 5 kGy in an AgNO$_3$ solution, some small dots appear on the grafted surfaces (fig.9) which indicate the presence of AgNPs. The aggregation may be due to the lack of surface legends on the AgNPs (Liu et al., 2007). To limit the side effects, low irradiation dose with efficient AgNPs production is preferred for this approach.
Antibacterial activity of Ag-grafted non-woven fabrics

For checking the antibacterial activity, equally weighed of ungrafted, grafted and Ag-grafted non-woven fabrics were subjected to disc diffusion method. The test was carried out on gram positive, gram negative, and fungi. After 18 h of incubation at 37°C, inhibition zone was observed in case of Ag-grafted non-woven fabrics for gram negative bacteria only, while on the other hand there are no effect observed in case of ungrafted, grafted non-woven fabrics for any of tested bacteria and fungi. Figure (10) shows the antibacterial activity picture of ungrafted, grafted and Ag-grafted non-woven fabrics. (PE-co-PP) non-woven fabric was successfully grafted by acrylic acid using gamma radiation. The grafted non-woven fabric absorbs much higher quantities of water than the ungrafted sample. The prepared grafted non-woven fabric with free carboxylic groups incorporated by grafting with acrylic acid was used for the preparation of silver nanoparticles.

The synthesis of Ag NPs by this method resulted with uniform nanoparticles distribution. The resulted grafted fabric loaded with Ag NPs was examined for its antibacterial activity toward various bacteria and fungi. It is concluded that the prepared grafted fabric with Ag NPs have antibacterial activity toward gram negative bacteria only and no effect had been noticed in case of gram positive and fungi.
REFERENCES


التحضير والتوصيف الإشعاعي للبولي ايثيلين المغطى بالبولي بروبلين المطعم والمحمل بذرات الفضية متناهية الصغر لإستخدامها كمضادات للبكتيريا

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في هذا البحث تستخدم إشعاع جاما لتطعيم البولي ايثيلين المغطى بالبولي بروبلين بمونمر الأكريلك وتحميله بذرات الفضية متناهية الصغر. تم دراسة تأثير تركيز المونمر والجرعة الإشعاعية على درجة التطعيم. نسبة امتصاص الماء تزداد بعد عملية التطعيم مما يحسن خاصية الامتصاص للماء للبولي ايثيلين المغطى بالبولي بروبلين المطعم بالأكريلك. تم دراسة خواص البولي ايثيلين المغطى بالبولي بروبلين المطعم والمحم بذرات الفضية متناهية الصغر بالأشعة تحت الحمراء والماسح الإلكتروني وحيد اشعه بالإضافة إلى دراسة استخدام البولي ايثيلين المغطى بالبولي بروبلين المطعم والمحم بذرات الفضية متناهية الصغر كمضادات للبكتيريا.