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Antimicrobial and Thermal Properties of Metal Complexes of Grafted Fabrics with Acrylic Acid by Gamma Irradiation

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ABSTRACT

Cotton, cotton/PET blend and PET fabrics were treated against microbial effect by radiation - induced grafting of acrylic acid followed by metal complextaion with some divalent transition metal ions Co (II), Ni {II) and Cu (II). The microbial resistance was evaluated by testing the mechanical properties of the treated fabrics after burring for one and two weeks in a moist soil reach with microorganisms. Also, the growth of microorganisms was examined by scanning electron microscope (SEM). Moreover, the effect of this treatment on the thermal decomposition behavior was investigated by thermogravimetric analysis (TGA). On the basis of microbial studies, it was found that the metal complexation of the grafted fabrics with acrylic acid enhanced the antimicrobial resistance of the fabrics and the antimicrobial resistance could be arranged according to the metal ions as follows: copper> nickel> cobalt. Also, the thermal stability of different fabrics could be arranged as follow: grafted fabrics complexed with Cu (II) > grafted fabrics complexed with Ni (II) > grafted fabrics complexed with Co (II).

Keywords: Radiation Grafting/ Fabrics/ Antimicrobial Resistance/ Structure Morphology/; Thermal Stability

INTRODUCTION

Textiles for outdoor use are constantly exposed to the influence of microbes, in which the formation of spots and odors are just the perceivable signs of contamination. When fibers are subjected to attack by microbes, specific properties such as tensile strength and impermeability are lost. Textile clothing for work, sports, and military use is particularly susceptible to microbial attack in which soil and perspiration offer ideal living conditions for microbes[(1)]

Heavy metals, in traces, are essential for the proper functioning of all living cells; they are supplied in the form of cations[(2,3)]. Metal-binding agents, by upsetting the balance of metals and in other ways, have proved to be valuable agents of selective toxicity. They are manufactured in vast quantities for this purpose, particularly as fungicides in agriculture.

Recently, it is of interest to propose systematic methods to investigate the metal complex formation during radiation-induced graft copolymerization of vinyl monomers onto polyester micro-fiber materials. A study on the metal complex formation during the radiation-induced graft copolymerization of acrylic acid onto poly(tetrafluoroethylene-perfluorovinyl ether) films was reported[(4, 5, 6)]. It was possible to determine the polymer-metal complexes for various applications as semiconductors beside their performances as cation-exchange membranes. In the present work, an attempt was made to introduce a new antimicrobial treatment based on grafting cotton, cotton/PET blend and PET fabrics with acrylic acid by γ- irradiation technique and metal complexation of the

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grafted fabrics with the metal ions {Co (II), Ni (II) and Cu (II)}.The effect of these treatments on the growth of certain microorganisms representing bacteria was studied. In this regard, the microbial studies involved the measurement of mechanical properties of the treated fabrics after burring for one and two weeks in a moist soil rich with microorganisms and observing the growth of microorganisms by scanning electron microscope (SEM). Moreover, the effect of this treatment on the thermal decomposition behavior was investigated by thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

The used fabrics were plain weave polyester, cotton/polyester blend at a ratio of 30/70 and cotton fabric. All these fabrics were scoured and bleached and were not subjected to any finishing processes. A laboratory grade of acrylic acid (AAc) monomer, Methyl alcohol and ferric chloride were used. All the monomers were used as received without treatment. Metal salts of copper sulfate, cobalt sulfate and nickel sulfate of analytical grade were used.

Gamma Radiation Graft Copolymerization

Irradiation was carried out in the Cobalt-60 gamma cell source (made in Russia) installed at the National Center for Radiation Research and Technology, Cairo, Egypt. The direct radiation grafting method was used, in which the samples of polyester, cotton and cotton/polyester fabrics were introduced in Pyrex test tubes, containing the monomer, solvent and inhibitor and, then the tubes were exposed to different irradiation doses. At the end of the grafting process, the samples were washed thoroughly with hot water to remove the unreacted monomers. The degree of grafting was calculated according to the equation 1.

$$\text{Graft Yield } (\%) = [(Wg - W_o) / W_o] \times 100 \quad (1)$$

Where W_o and W_g are the initial and final weights of the samples.

Synthesis of Metal Complexation of Grafted Fabrics

The different metal complexes of cotton cotton/PET blend and PET grafted fabrics were prepared by boiling in reflux system with aqueous solution containing 3% of the different metal salts under investigation.

Evaluation of Microbial Resistance

The microbial resistance of the treated fabrics was tested by the soil burial test(7). In this method, naturally fertile top soil is placed in a dry wooden box to a depth of at least 13 cm. The soil was brought to the optimum moisture content by gradual addition of water accompanied by mixing. The soil was left for 24 h and then it was sieved through a 6.4-mm mesh screen.

Mechanical Measurements

The buried samples were gently washed and air-dried at room temperature for 24 h before measuring the tensile strength. The mechanical properties including tensile strength and elongation at break were tested at room temperature.

Scanning Electron Microscope (SEM)

The surface morphology of the different fabrics before and after burring in the moist soil was examined by SEM. The micrographs were taken with a JSM-5400 instrument by Jeol, Japan. A sputter coater was used to pre-coat conductive gold onto the surface before observing the microstructure at 30 kV.

Thermogravimetric Analysis (TGA)

The thermal decomposition behavior of the samples was tested by TGA technique using a TG-50 instrument from Shimadzu (Japan) at a heating rate of 10 C^o/min. The data obtained from TGA curves were used to determine the different kinetic parameters.

RESULTS AND DISCUSSION

The different factors which affect the grafting process such as monomer concentration, solvent composition, inhibitor concentration and irradiation dose were studied. The results showed that the best grafting yields onto cotton fabric were by using 30% of AAc monomer, 0.1% inhibitor conc., (90% H2O:10% MeOH) solvent composition and 20 kGy irradiation dose. For cotton/PET blend and PET fabrics, the best grafting yields were achieved by using 50% AAc monomer, 0.2% inhibitor conc.,(20% H2O: 80% MeOH) solvent composition and 20 kGy irradiation dose.

Evaluation of the Antimicrobial Properties of Metal Complexes of Grafted Fabric.

Evaluation by Soil Burial Test.

Mechanical properties may be considered the most important of all the physical and chemical properties of textile material for most applications. The stress-strain test is the most widely used of all the mechanical tests because it is very important practical test. Also, the grafting and metal complexation would eventually cause a change in the tensile mechanical properties of the textile fabrics due to the introduction of side chains and complexation.

Figures 1 and 2 show the tensile mechanical of different metal complexes of graft copolymer of cotton fabrics (12% graft yield) before and after burring in soil for different intervals of time. As shown in Fig.1, the tensile strength of cotton fabrics was not greatly affected by grafting at this extent of graft yield. Also, the metal complexation of the grafted cotton fabrics with cobalt, nickel and copper metals does not affect the tensile strength before burring. As shown in **Fig.1**, the cobalt metal complex of grafted cotton fabrics displayed the lowest microbial resistance among the different metal complexes, in which the tensile strength was decreased by ~71 and 90% after burring for one and two weeks, respectively. On the other hand, the nickel metal complex of grafted fabrics displayed the highest resistance to microbial attack, in which the tensile strength was decreased by ~ 6 and 19 %, respectively. Also, in the case of copper metal complex of grafted fabrics, the tensile strength was decreased by ~ 15 and 52 %, respectively.

As shown in Fig.2, the elongation at break of cotton fabrics was greatly affected by grafting and metal complexation depending on the kind of metals. In this regard, the elongation at break was increased by 51, 16 and 32% after complexation with cobalt, nickel and copper, respectively. Also, it can be seen that the elongation at break of the grafted cotton fabrics with metal complexes was not affected by burring but it tends to increase even after two weeks compared to the complete deterioration of the elongation break of ungrafted cotton. These trends may be attributed to the fact that the formation of complexation will form some kind of coordination bonding and entanglement similar to crosslinking. Upon tension, this semi-network structure withstands and resists tension. It can be concluded that the metal complexation of grafted cotton with different metal ions enhances the antimicrobial properties and the efficiency of the metal ions in the enhancement of the antimicrobial properties can be arranged as follow: nickel > copper > cobalt.

The same trend was noticed in the case of cotton/PET blend and polyester fabrics. The efficiency of the antimicrobial properties can be arranged according to the used metal ions as follow: nickel > copper > cobalt.

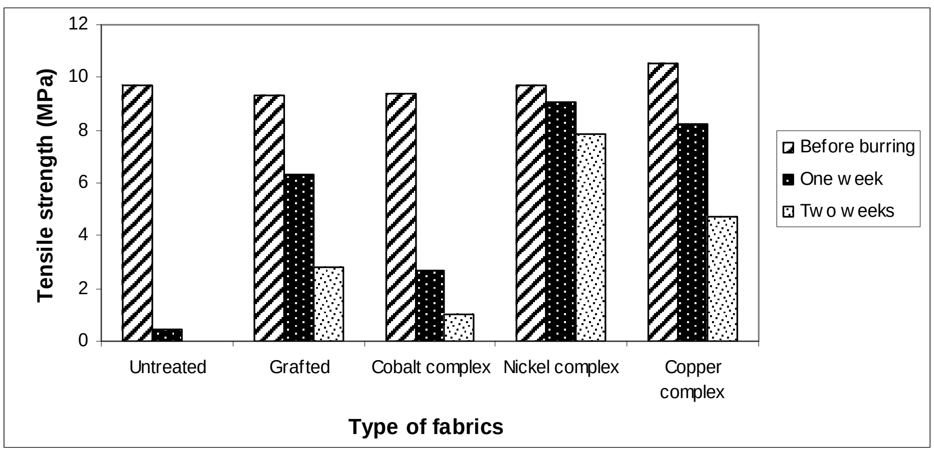


Figure 1. Tensile strength of cotton fabrics grafted with AAc (12%), complexed with Co (II), Ni (II) and Cu (II) metal ions after different periods of soil burial test.

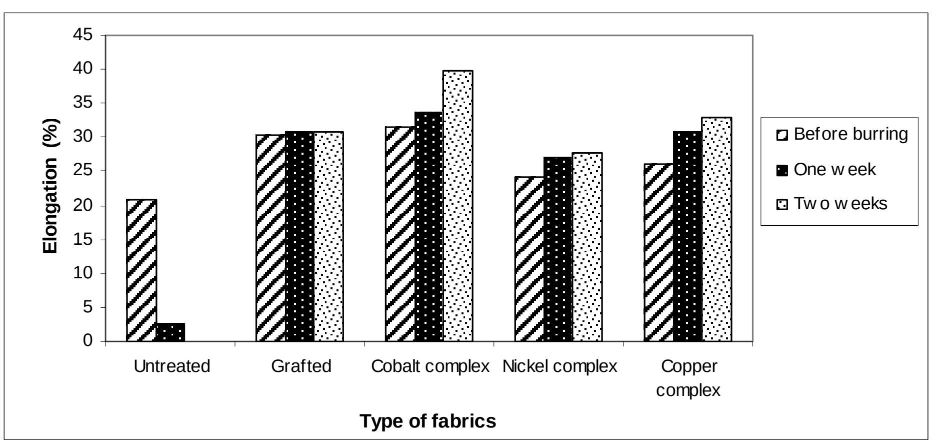
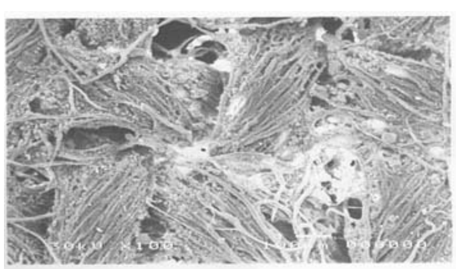


Figure 2. Elongation strength of cotton fabrics grafted with AAc (12%), complexed with Co (II), Ni (II) and Cu (II) metal ions after different periods of soil burial test.

Evaluation by Scanning Electron Microscope (SEM)

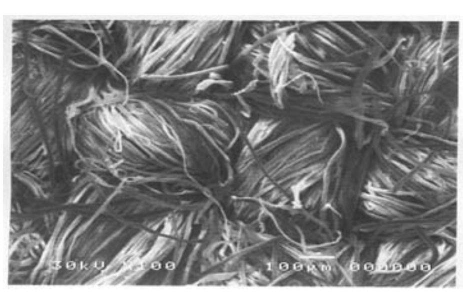
SEM was used to demonstrate the deterioration occurred in the weave structure of fabrics as a result of microbial attack and also to examine the effect of metal complexation on the growth of microorganisms. Therefore, ungrafted and grafted cotton, cotton/PET and PET fabrics were buried in moist soil rich of microorganisms for two weeks. At the end of burring period, the samples were genteelly washed with water to remove the adhered soil on the surface of fabrics and examined by SEM as shown in Figs. 7-9. It is well known that soil offer ideal living conditions for different microorganisms including bacteria, fungi and mildew-rot, which they are strongly attack textiles and may contribute to progressive decomposition and oftenly discoloration of textile materials.

As shown in Fig. 3 (a), the weaving structure of cotton fabrics could not be seen, in which the surface of ungrafted cotton fabric was completely damaged after burring. A different microstructure features can be seen for the grafted fabrics and complexed with Ni (II), Cu (II) and Co (II) ions as shown in Figure 3 (b - d). The treatment prevents the attack of microorganism to the fabrics, in which the weaving structure was not affected and the strings forming the warp and weft directions can be distinguished. The same trend was found in the case of cotton/PET blend and polyester fabrics, but it was found that the untreated polyester has a highly resistant to the attack to microorganisms. In conclusion, few points can be made (1) the ungrafted fabrics may be arranged as follow: polyester > cotton/polyester > cotton. (2) The grafted fabrics and complexed may be arranged as follows: copper>Nickel>cobalt. These trends may be explained based on the metabolism of microorganisms. In this regard, copper is essential for the growth of microorganisms rather than cobalt. However, if this metal exists in large quantities the metabolism will disturb and consequently the growth will stop.



(a)

(b)



(c)

(d)

Figure 3. SEM micrographs of the surface morphology of cotton fabrics grafted with AAc and its different metal complexes before and after soil burial test for two weeks.

Thermal Decomposition Behavior of Metal Complexes of Grafted Fabrics

Thermal Stability of Grafted Fabrics

The thermal stability of any polymer material is largely determined by the strength of the covalent bond between the atoms forming the polymer molecules. The reported dissociation energy for the different covalent bonds C-H, C-C, C-O, C=O, C=C, and O-H were found to be 414, 347, 351, 741, 611, and 464 kJ/mol, respectively[(8)]. On the basis of these values, the average complete dissociation energy of polyester and cellulose was calculated to be 443.7 and 386.2 kJ/mol, respectively. For cotton/polyester fabric, the average dissociation energy may be calculated to be 417 kJ/mol based on the ratios of cotton cellulose and polyester in the blend. Therefore, it may be concluded that polyester fabrics possess theoretically higher thermal stability than cotton/polyester blend.

Figure 4 shows the initial TGA thermograms of ungrafted cotton, cotton/PET blend and PET fabrics. According to the weight loss and the the thermal stability of the different fabrics can be arranged as follow: PET > cotton/PET blend > cotton. The rate of reaction (dw/dt) or the derivative of the thermogravimetric analysis curve (DTGA) taken from the initial (TGA) for cotton, cotton/PET blend and PET fabrics was plotted against the heating temperatures as shown in Figure 5, in which it can be seen that the maximum value of rate of reaction of different fabrics were 352, 362 and 435^{o}C for cotton, cotton/PET blend and PET fabric, respectively. According to the data from Figures 4 and 5, the different fabrics in terms of thermal stability can be arranged as follow:

PET > cotton/PET blend > cotton.

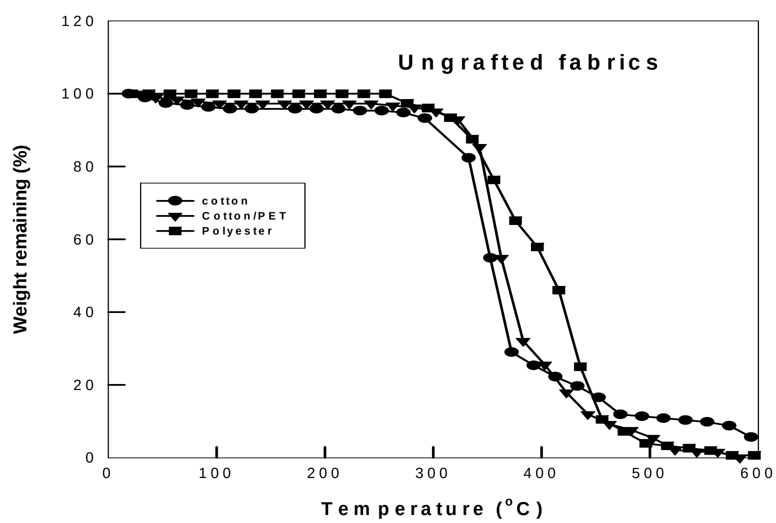


Figure 4: Initial TGA thermograms of different ungrafted fabrics

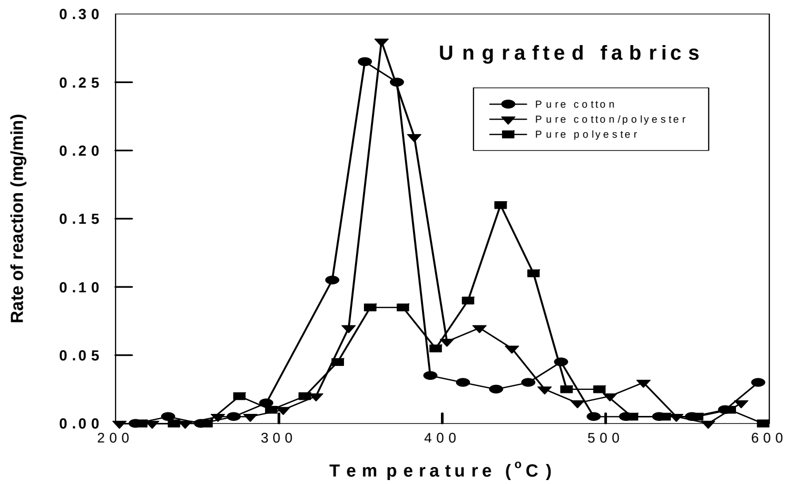


Figure 5: Rate of reaction curves of different ungrafted fabrics

Thermal Stability of Metal Complexes of Grafted Fabrics

The thermal stability of cotton, cotton/PET blend and PET was not greatly affected after grafting and complexation with Co (II), Ni (II) and Cu (II) metal ions. The percentage weight loss at different decomposition temperatures and the maximum values of the rate of reaction which illustrated in **Table1** of the different complexes of fabrics indicates that the thermal stability of the different cobalt metal complexes of fabrics can be arranged based on weight loss as follow: PET > cotton/PET blend > cotton.

Table 1. The maximum values of the rate of reaction of different grafted fabrics complexed with Co (II), Ni (II) and Cu (II) metal ions.

	Maximum value of rate of reaction		
Type of fabrics	**Cotton**	**Cotton/PET blend**	**Polyester**
Ungrafted fabric	352	362	435
Fabric/cobalt complex	327	344	435
Fabric/nickel complex	354	351	418
Fabric/copper complex	333	352	428

Based on the results on Figures 10-17, it can be conclude that the thermal stability of cotton, cotton/PET blend and PET graft copolymer fabrics and complexed with Co (II), Ni (II) and Cu (II) metal ions can be arranged as follow:
Grafted fabrics complexed with Cu (II) > grafted fabrics complexed with Ni (II) > grafted fabrics complexed with Co (II).

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