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New textiles of biocidal activity by introduce insecticide in cotton-poly (GMA) copolymer containing β-Cd

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ABSTRACT

The present work deals with the preparation of innovative cotton textiles which act against blood sucking insects such as mosquitoes. Thus experiments were designed to incorporation of efficient insecticide (Permethrin, bioallethrin) in the macro-molecular structure of modified cotton fabrics. Chemical modification of cotton was realized by grafting with glycidyl methacrylate alone or in combination with β-cyclodextrin by irradiation using fasting electron beam. Retreatment of the so obtained modified cotton was also made to increase the amount of CDs, and in turn, their cavities within the molecular structure of the modified cottons. Finished fabrics were though evaluated using chemical analysis; physical testing, bioassay tests and IR as well as SEM. Results obtained conclude that the amount of insecticide in the finished fabrics increases by increasing of the fixed amount of cyclodextrins which incorporate through their cavities the insecticide. The bioassay test shows that finished cotton fabrics display fast acting against mosquitoes.

1. Introduction

For thousands of years, insects and their relatives coexist with the man. The animal kingdom contains approximately 850 thousand of insects along with about one million different species. Of these, about 10 thousands species are actually destructive and the remaining species are either beneficial or harmless (Elliot, 1995). Destructive insect species, for example, blood sucking insects can torment humans and animals and can transmit disease. They are all parasites of humans or other host animals and are abundant at certain times of the year. Blood sucking insects can be grouped as mosquitoes, flies, lice, and true bugs (Ann Walker & William, 2000; Melcon, Lazzari, & Manrique, 2005). Mosquitoes are found all over the world, except in Antarctica. There are more than 2700 millions species of mosquitoes in the world. *Anophelus*, *Culex* and *Aedes* are most commonly genera responsible for bites in human (Mark & Fradin, 1999). Only female mosquitoes bite. Male mosquitoes feed primarily on flower nectar, whereas female mosquitoes require a blood meal to produce eggs (Mark & Fradin, 1999). Mosquitoes are a vector agent that carries disease-causing and parasites from person to person without catching the disease themselves. Female mosquitoes suck blood from people and other animals as part of their eating and breeding habits. When a mosquito bites, it also injects saliva and anti-coagulants into the blood which may also contain disease-causing viruses or other parasites. Mosquitoes can lead to death through causing many types diseases that are caused by bacteria, parasites or viruses. These diseases include malaria, yellow fever, encephalitis and dengue fever.

Insecticides are agents of chemical or biological origin that have been developed to control insects. Control may result from killing the insects or otherwise preventing it from engaging in behaviors deemed destructive. Insecticides may be natural or man-made and are applied to target pests in a myriad of formulations and delivery systems (sprays, baits, slow-release diffusion, etc.) (Ware & Whitacre, 2004). To date, six pyrethroid insecticides (alphacypermethrin, eyfluthrin, deltathrin, etofenprox, landed-cychalothrin and Permethrin) have been recommended by the World Health Organization (WHO) in the framework of the WHO Pesticide Evaluation Scheme (WHO PES) for the treatment of mosquito nets (Hebeish, Mosustafa, Hamdy, EL-Sawy, & Abdel-Mohdy, 2008; Hougard, Duchon, Zaim, & Guillet, 2002; Sukumar, Harshan, & Boobar, 1991)

The present work aims at production and characterization of high performance chemically modified cotton fabrics that act against mosquitoes. Experiments were therefore designed to establish new methodology for effective incorporation of insecticides: namely, Permethrin and bioallethrin in the molecular structure

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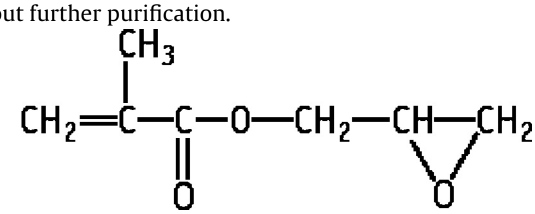
of cotton fabrics. Chemical modifications of cotton were effected through irradiation grafting using fast electron beam. Retreatment of the obtained modified cotton was also made to increase the amount of insecticide. The work was extended to studying factors affecting the treatment and insect repelling assessment.

2. Materials and methods

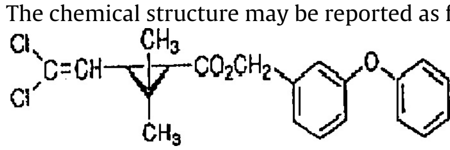
2.1. Materials

Duck cotton fabrics (400 g/m^2, 21 × 61 cm) were obtained from Misr Spinning and Weaving Co., Mehalla El-Kobra, Egypt. The fabrics were used after purification by boiling for 2 h in an aqueous solution of 1% sodium carbonate, then thoroughly washed with water and dried at ambient temperature.

Glycidyl methacrylate (GMA) has the following structure. It was purchased from Fluka Chemika GmbH, Germany, and was used without further purification.



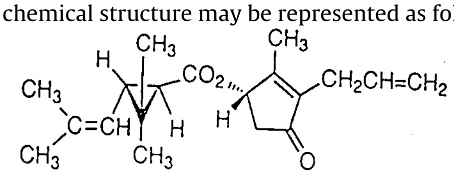
Permethrin and Bioallethrin were kindly supplied by El-Nasr Company for Intermediate Chemicals, Cairo, Egypt. Permethrin does not repel insects, but instead works as a contact insecticide, causing nervous system toxicity leading to death or knockdown of the insect. The chemical structure may be reported as follows:



The structure of Permethrin was established on the basis of its spectral data studies. The IR spectrum of Permethrin, which has been carried out using our experience at NRC-laboratories as a part of the present investigation, shows strong absorption bands at:

3040 (C—H, aromatic); 2956 (C—H, aliphatic); 1731 (C=O ester); 1585, 1488 (C=C) and at 692 cm^{-1} (Cl—C=C—).

Bioallethrin is non-residual products with rapid knockdown action. Its chemical structure may be represented as follows:



The structure of Bioallethrin was established on the basis of its spectral data studies. The IR spectrum of Bioallethrin, which has been carried out using our experience at NRC-laboratories as a part of the present investigation, showed bands at: 3460 (OH); 3065 (C—H vinylic); 2959 (C—H, methyl); 1740 (C=O ester); 1588 (C=C conjugated); 1485 (COO symmetric stretching); 1450 (C—H cyclo Alkane); 1375 (C—O ether); 1242 (C—O Alcohol); and 1162 Cm $^{-1}$ (C—O—C anti symmetric).

2.2. Fabric treatment

2.2.1. Graft of cotton fabric with GMA/β-CD

Radiation grafting method was used to graft glycidyl methacrylate (GMA) and β-cyclodextrin (β-CD) onto cotton fabrics. Irradiation of samples was carried out using the electron beam accelerators (Energy 1.5 Mev, Power 3.75 Kw, Beam current 2.5 mA and Scan width variable up to 90 cm) at National Center of Radiation Research and Technology (NCRRT), Cairo, Egypt. The required dose was obtained by adjusting the electron beam energy parameters and conveyor speed.

The cotton fabrics were impregnated in a finish bath containing either GMA monomer, or GMA monomer and β-CD, or GMA monomers and Permethrin for 1 h, then passed through squeeze rolls of laboratory paddar to give a wets pick up of ca 100% based on the original weight of the fabric. The fabric samples were then irradiated with linear electron beam. The treated samples were then washed with proper solvent to remove non-reacted matter and finally dried under normal laboratory conditions. The graft yield was determined gravimetrically. After grafting of cotton fabrics with GMA and β-CD, a simple procedure was adopter to ensure that the CD cavities were not blocked by GMA during the graft polymerization process (Goel & Neme, 1995).

2.2.2. Reaction of cyclodextrin with cotton cellulose fabrics grafted with GMA

Retreatment process. Cotton fabrics grafted with GMA or GMA/β-CD were reacted with β-CD. The fabrics were placed in a solution containing 2% β-CD, 1 M NaCL, and 1% NaOH (Vismara, Melone, Gasaldi, Cosentino, & Torri, 2009) The solution was stirred at 80 °C for the desired time. The grafted fabric was washed with distillated water, then dried and weighed.

2.2.3. Inclusion of insecticidal complexes into cotton copolymers containing GMA and β-CD moieties

Once the β-CD compound was grafted, additional insect repelling agents were incorporated inside the inclusion compound. One gram of the cotton-g-GMA/β-CD fabric was immersed in a 25 ml mixture (90% distilled water and 10% ethanol) containing 2% of a guest molecule (Permethrin). The fabric was soaked for 24 h in this solution at room temperature to form the inclusion complexes. Samples were then washed several times with cold distilled water and ethanol. The rinsed fabric was air-dried (Vismara et al., 2009).

2.3. Evaluation of treated fabrics

2.3.1. Determination of graft yield

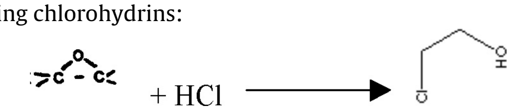
Graft yield was determined from the gain in weight of cotton fabric due to graft polymerization after removing the ungrafted polymer with the proper solvent. After grafting, the fabric was thoroughly washed with distilled water and ethanol then dried at 50 °C.

The weight of the dried sample (W_2) was compared with the original weight (W_1) and the percentage graft yield was calculated as follows:

$$\%\text{Graft yield} = \frac{W_3 - W_1}{W_1} \times 100$$

2.3.2. Determination of remaining epoxide

α-Epoxide is a group of cyclic ethers in which the oxygen atom forms a three-membered ring with two adjacent carbon atoms. Because of the strained three-membered ring, α-epoxies are the most reactive of the oxides and are far more reactive than ordinary ethers. Thus, they react with hydrogen chloride to form the corresponding chlorohydrins:



This reaction forms the basis of the method used in this work for the determination of α-epoxy groups. It is termed the acidimetric method (Vogel, 1975).

Table 1
Effect of radiation dose, GMA concentration and insecticide content on the add-on %, epoxide content and insecticide content of cotton fabrics grafted with GMA in presence of insecticide.

Factors		Add-on (%)		Epoxide content (%)		Insecticide content (mg/m^2)	
		Permethrin	Bioallethrin	Permethrin	Bioallethrin	Permethrin	Bioallethrin
Radiation dose ($\times$ 10 KGy)	1	10.5	21.6	0.5807	0.8499	101.0	121
	2	20	30.3	0.8937	0.6154	121	481.2
	3	12.6	32.3	0.7953	0.4606	74.2	238.8
	5	14	25.2	0.2667	0.6789	54.2	443
GMA conc. (% ows)	30	25.2	25.4	0.4192	0.1207	57	491
	40	29.2	18	0.4126	0.3724	52.8	317.5
	50	14.7	22.1	0.5650	0.3313	65.6	377
	60	13.2	25.6	0.6295	0.5765	49.8	359
Insecticide conc. (%)	1	12.4	16	0.6154	0.9603	47.4	298
	2	13	21.3	0.7139	0.4334	92.9	403.3
	3	14.5	22	0.6295	0.2905	150.2	752.5
	5	14.5	27.8	0.0410	0.0537	169.4	846.4

Reaction condition: [GMA], 50% ows; [Insecticide], 2% dose, 3 $\times$ 10 KGy.

2.3.3. Quantitative analysis of insecticides in treated fabrics

A variety of methods are available for the determination of insecticides in washed and unwashed fabrics (Burakhta & Khasainova, 2001; Hengle, Mower, & Shibamoto, 1997). Most of the methods developed so far for the analysis of commercially available insecticides formulations are either gas chromatographic or liquid chromatographic methods. Ultraviolet–visible spectrophotometer has also been used for this purpose.

In the present study, a fast, selective and sensitive method of insecticide analysis in treated cotton fabrics using gas chromatography (GC) with electron capture was employed for quantification of the insecticides. Samples were taken from different locations on the material and cut into pieces (0.5 $\times$ 0.5 cm). All pieces were combined and mixed thoroughly. Fifty milliliters of n-hexane were added to an aliquot (5 g) of each sample. For extraction, the samples were treated in an ultrasonic bath.

Analysis of hexane Permethrin extracts was conducted with a Hewlett-Packard Model 5890 A GC, equipped with column HP-1 (25 m $\times$ 0.2 mm $\times$ 0.2 μm film thickness) and flame ionization detector (FID). The injector and detector were operated at 250 and 280 °C, respectively. The oven temperature was programmed from 200 °C to 250 °C at 5 °C/min and held for 1 min. The GC analysis was carried out at Mycotoxin Lab., National Research Center.

Analysis of hexane bioallethrin extracts was conducted with a GC-17 A, column AT-50, and flame ionization detector (FID). The injection and detector temperatures were operated at 250 and 300 °C, respectively. The oven temperature was programmed from 200 °C to 250 °C at 10 °C/min (10 min). The GC analysis was carried out at Chromatography Lab., Micro Analysis Center, Faculty of Science, Cairo University.

2.3.4. Mosquito bioassay test

Treated fabrics containing insecticides were used for bio-assays test. Repellent effect, knockdown effect and mortality, resulting from tarsal contact with treated materials were measured using standard World Health Organization (WHO) test (Ansari, Kapoor, & Sharama, 1998; Kapoor & Anari, 2003). Each piece of treated sample was tested using about 15 adult mosquitoes. The number of repellent and knockdown mosquitoes was recorded at fixed intervals (every 10 min, depending on repellent and knockdown rates) for 60 min. The mosquito mortality was observed after 1–24 h. These tests were conducted in parallel with cotton fabrics grafted with GMA only (blank) and untreated (control) samples.

2.4. Washing

Treated cotton fabrics were washed in an aqueous solution containing 2 g/l sodium carbonate and 5 g/l liquid soap (Egyptol: non ionic detergent, from Starch and Yeast Co. Alex., Egypt) at 60 °C for 15 min for one wash. Ability of the treated fabric to retain the insecticide after washing is expressed as percent retention as follows:

$$\text{Retention efficiency\%} = \frac{\text{activity after washing}}{\text{activity before washing}} \times 100$$

or

$$\text{Retention efficiency \%} = \frac{\text{amount of insecticide after washing}}{\text{amount of insecticide before washing}}$$

2.4.1. Infrared spectroscopy

The infrared analysis of the treated cotton fabrics were carried out in Infrared Laboratory, Central Services Laboratory, National Research Center, by using JASCo Japan, FT/IR 6100, Fourier Transform Infrared Spectrophotometer.

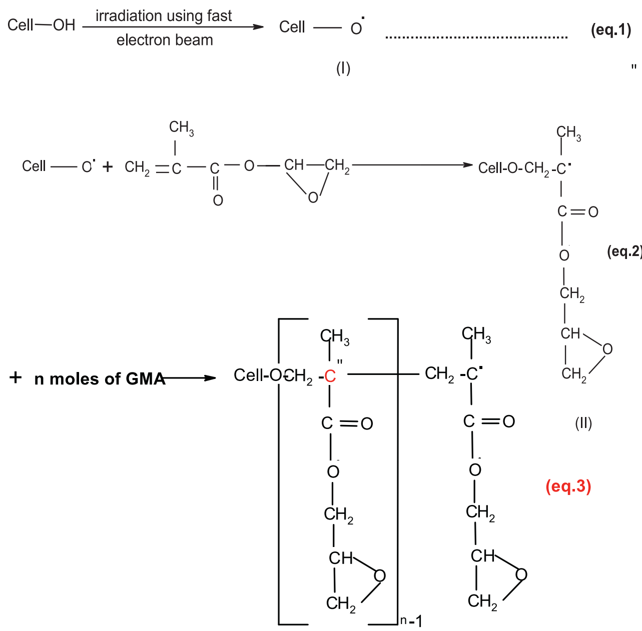
2.4.2. Scanning electron microscopy (SEM)

SEM analysis of the treated fabrics was performed using a JEOL (JXA-840 A); Electron Probe Micro-Analyzer, Edward (England), 150 A. Sputter Coater; from Scanning Electron Microscope Division; Central Services Laboratory, National Research Center. Samples were coated with gold according to the method described in the operation manual provided by the manufacturer.

3. Results and discussion

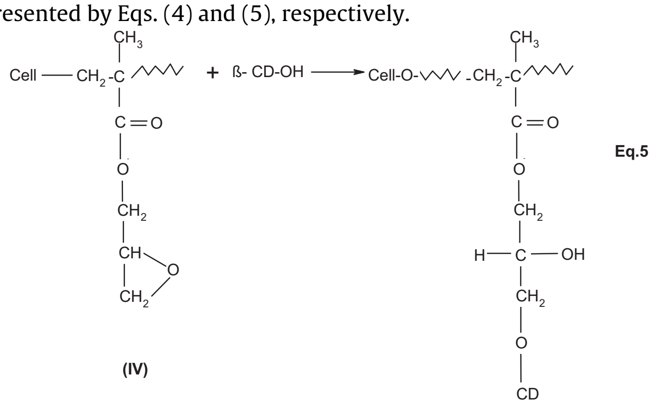
3.1. Tentative mechanisms

GMA is a dual functionality vinyl monomer. It acquired epoxy groups which has the ability to undergo consecutive modification. Acrylic and epoxy function ability render GMA capable to react with a wide variety of functionalized molecules. Reactions involved in grafting GMA onto cotton cellulose (Cell-OH) may be drawn as follows:



Eqs. (1) and (2) represent the initiation stage of grafting whereas Eq. (3) represents the propagation stage.

When β-CD is present during grafting onto cotton cellulose, the β-CD would be attached chemically to the cellulose through grafting via ring opening of the Epoxide groups. Creation of free radicals on both the cellulose and β-CD would also provide a possibility for chemical attachment through combination of cellulose macro radical with β-CD radicals. These two means of attachment are represented by Eqs. (4) and (5), respectively.



$$\text{Cell-O}^{\cdot} + \text{CDO}^{\cdot} \longrightarrow \text{Cell-O-O-CD} \quad \textbf{(eq.5)}$$

Where β-CDOH stands for β-CD and CDO for β-CD free radical.

3.2. Grafting of cotton fabric with GMA

The present investigation includes a study on grafting of GMA in presence of either Permethrin or bioallethrin as insecticides onto cotton fabric. The results of this study are set out in Table 1. As is evident, this table address the effect of radiation dose, GMA concentration and insecticide concentration on the graft add-on and the contents of both Epoxide and insecticide.

Table 1 discloses the effect of radiation dose on the add-on %, Epoxide content and insecticide content. Results of Table 1 show that the percentage add-on increases by increasing the radiation dose within the range studied (from 1×10 KGy to 5×10 KGy) in case of Permethrin. On the other hand, the values of add-on % in case of bioallethrin-though assume similar trend within a radiation dose range of 1×10 KGy–3×10 KGy, the add-on displays lower value at a radiation dose of 5×10 KGy. This indicates that the nature of the insecticide not only determines the extent of the add-on but also the trend obtained by correlating the add-on with the radiation dose.

The general tendency of the Epoxide content and insecticide content is to decrease by increasing the radiation dose within the range studied (Table 1). This suggests (a) that the Epoxide groups undergo ring opening not only by insecticides but by other matter containing labile hydrogen in the graft polymerization system and (b) that the insecticide undergoes structural changes under the influence of high radiation dose thereby offset its interactions with the poly (GMA)-Cotton graft copolymers.

Table 1 also depicts the effect of GMA concentration on the percentages add-on, Epoxide content and insecticide content. The results reveal that with both insecticides, the add-on % values are comparable within GMA concentration range of 30–60% ows. Different situation is encountered with the Epoxide content and the insecticide content. While the Epoxide content trends to increase by increasing GMA concentration, the insecticide content tends to decrease. This suggests that the inclusion of the insecticide specially via ring opening of the Epoxide groups of the graft is not favored at high GMA concentrations. The latter are always associated with huge amount of homopolymer that is formed on the charge of grafting.

Table 1 discloses the effect of insecticide concentration on the percentages add-on, Epoxide content and insecticide content. Results show that increasing the Permethrin concentration from 1 to 5% ows exert no significant effect on the add-on of the poly (GMA)-cotton graft copolymer. Meanwhile the Epoxide content is greatly reduced when Permethrin at a concentration of 5% ows was used. In contrast, the Permethrin content increases significantly by increasing the Permethrin concentration from 1 to 5% ows. This indicates that inclusion of Permethrin in the copolymer occurs via physicochemical deposition of Permethrin particles beside reaction of Permethrin with the copolymer via ring opening of the Epoxide groups of the graft.

Table 1 makes it evident that increasing the concentration of bioallethrin causes increment in the percentages add-on and bioallethrin content but the Epoxide content decreases. Inclusion of bioallethrin in the copolymer, unlike Permethrin, seems to take place essentially via ring opening of the Epoxide groups thereby decreasing the Epoxide content of the copolymer. This again reflect, the effect of nature of the insecticide on the magnitude of its own content within the cotton fabric, on the magnitude of the add-on and on the magnitude of the Epoxide content of the copolymer.

3.3. Grafting of cotton fabrics with GMA and β-CD

Table 2 shows the effect of radiation dose on the graft yield (add-on %), Epoxide content and the bonded amount of β-CD (fixed β-CD %). Results reveal that the add-on % increases noticeably by increasing the radiation dose to 3×10 KGy. Therefore, the add-on tends to decrease. Percentage of Epoxide content and fixed β-CD attains also the highest values at a reaction dose of 3×10 KGy. This is rather logical because the number of grafted chains and chain lengths produced in such mutual grafting is a function of total radiation dose and the dose rate (Wood, 1990). With this in mind, current results indicate that radiation was targeted to the favor of grafting when the radiation dose was up to 3×10 KGy. Above this latter value, possible adverse effect of radiation and dual function ability of GMA may occur thereby decreasing its graft ability. It is also likely that abundance of free radicals on the backbone of the cotton cellulose at higher radiation dose allows modification of the cellulose, particularly via cross linking, and in so doing decreases the susceptibility of

Table 2
Effect of radiation dose, GMA concentration, β-CD concentration on add-on %, epoxide content and fixed β-CD when cotton fabrics were grafted with GMA and β-CD.

Factors		Add-on (%)	Epoxide content (%)	Fixed β-CD %
Radiation dose (× 10 KGy)	1	21.8	0.3074	3.72
	2	21.3	0.6612	4.01
	3	27.6	0.7044	4.37
	5	25.2	0.1470	4.18
GMA conc. (% ows)	30	17.4	0.2885	2.15
	40	28.1	0.8205	3.80
	50	30.4	0.7726	4.05
	60	34	0.2533	4
β-CD conc. (%)	1	20.7	1.2192	2.60
	2	20.4	0.5755	3.91
	3	27	0.6022	3.91
	5	27.9	0.8471	3.71

Reaction condition: dose, 3 × 10 KGy; [GMA], 50% ows; [β-CD], 5% ows.

cotton cellulose to grafting. However, the lower molecular weights of the graft upon using higher radiation dose cannot be ruled out.

Table 2 shows the effect of GMA concentration on the add-on %, Epoxide content and the fixed β-CD, when grafting was carried out at fixed radiation dose and fixed β-CD concentration. Results reveal that the add-on % increases with the increase of GMA concentration. Higher grafting yields are expected at higher monomer concentration (Hebeish, Waley, Abdel-Mohdy, & Aly, 1997). The significant increment in the percent of polymer add-on by increasing monomer concentration could be attributed to the greater availability of monomer molecules in the vicinity of the cellulose at a higher monomer concentration. Table 2 shows that the Epoxide content increases significantly by increasing the GMA concentration from 30% to 40%. Further increase in GMA concentration to 50%ows decreases the Epoxide content and this decrease become, very striking upon increasing GMA concentration to 60% ows. The increase in Epoxide content by the increasing GMA concentration is in conformation with the results of the percentage add-on. On the other hand, the striking decrease in the Epoxide content at higher GMA concentration, i.e. 60%, could be interpreted in terms of ring opening. Ring opening of the Epoxide group could be effected through reaction with β-CD as evidenced by the increase in fixed β-CD by increasing GMA concentration. It is also possible that ring opening occurs through reaction with the hydroxyl groups of cotton cellulose. Ring opening by reaction of Epoxide groups with water or any other matter-containing labile hydrogen under the conditions used may additionally take place.

Table 2 shows the effect of β-CD concentration on the add-on %, Epoxide content and fixed β-CD on the cotton fabrics. It is observed that increasing the β-CD concentration from 1 to 4% ows acts much in favor of percentages add-on and fixed β-CD. The opposite holds good for the percentages Epoxide content. This is rather a manifestation of ring opening of the Epoxide group through reaction with β-CD molecule, which are greatly available in the micro environment of the Epoxide groups at higher β-CD concentrations.

Based on the foregoing, it is concluded that radiation dose 3 × 10 KGy, GMA concentration 50% ows and β-CD concentration 5% ows constitute the optimal for loading cotton fabric with GMA and β-CD moieties.

3.4. Retreatment process

Trails were carried out to enhance the amount of CDs on the cotton fabric in order to increase the amount of complexes guest substances (insecticides). Increasing the amount of CDs is effected by a retreatment process where CDs are allowed to act upon cotton fabrics grafted with GMA in presence of CDs.

Two samples were selected from each of the previously treated cotton fabrics (Cell-g-GMA and Cell-g-GMA/β-CD). These samples were treated with β-CD as shown in Table 3 in order to growing the amount of cyclodextrins on the grafted cotton fabrics. Our work was further extended to incorporate Permethrin as insecticide agent into the grafted and retreated grafted samples.

It is clear from the obtained results (Table 3) that, by retreatment process, the amount of β-CD increases from zero to 3.8% for Cell-g-GMA, and increases from 3.91% to 9.8% for Cell-g-GMA/β-CD sample. At the same time, the Epoxide content for Cell-g-GMA decreases from 0.9537% to 0.3640%, and for Cell-g-GMA/β-CD sample the Epoxide content decreases from 0.6791% to 0.4751%. The decrease in the Epoxide content after the retreatment process is unequivocally due to ring opening of the Epoxide groups by β-CD.

As expected, the incorporated Permethrin increases by the retreatment process of the grafted cotton fabrics with β-CD. This could be ascribed to the increase of fixed amount of CDs which are inevitably accompanied by the increase in cavities. The latter are available for incorporation of the insecticides. It is clear from the above results that the retreatment process decreases, the Epoxide content meanwhile increases, the fixed CDs and, therefore the incorporated insecticide.

- Cell-g-GMA: cotton fabric grafted with GMA.
- Cell-g-GMA/β-CD: cotton fabric grafted with GMA and β-CD.
- Retreatment conditions: grafted samples were soaked in aqueous solution of 2% β-CD, 1 M NaCL, 1%NaOH at 80 °C for 1 h.
- Incorporation conditions: fabric was soaked for 24 h in solution (90% water, 10% ethanol) containing 1% permethrin.

3.5. Insect repelling assessment

3.5.1. Mosquito bioassay test results

Following the grafting and insecticidal treatment studies, testing was further performed to determine the insect repelling capabilities of the treated fabrics. Besides untreated cotton samples (control) and blank samples (Cell-g-GMA and Cell-g-GMA/β-CD) were also tested.

Figs. 1–3 show the toxic activity testing of the treated fabrics. The test indicates that all treated samples exhibit toxic activity. The effect of incorporated insecticides on the toxic effect of cotton fabric treated therewith against mosquitoes is expressed as: repellency percent, knockdown percent and mortality percent.

Generally, it is noticed during the experiments that the mosquitoes in the control testing got on the fabric and stayed on for extended periods of time. For treated samples, the mosquitoes that went on the fabric did not stay for long time periods. After few minutes, the mosquitoes that approached the treated samples were repelled and went away from them, i.e., these samples showed the best repellency, as compared to control and blank samples.

The bioassay results reveal that the incorporated insecticide into the grafted fabrics acts in three ways: firstly it has strong excited repellency action, secondly it has moderate knockdown action, and thirdly it has a striking killing action. Also, the results show the repellency values, knockdown values, and mortality values of treated fabrics incorporated with insecticide are higher than that of control and blank sample.

By and large, results of cotton fabrics grafted with GMA and Permethrin or bioallethrin (Fig. 1a,b) reveal that the repellent action, knockdown action and killing action against mosquitoes increase by increasing the amount of Permethrin in the treated fabric, also increase by increasing the exposure time. These treated samples showed lower initial knockdown activity and killing action against mosquitoes. This may be due to the bonding of insecticide with the fabric. As a rennet only part of the total amount of insecticide would

Table 3
Effect of retreatment of grafted samples with β-CD on the major characteristics of the grafted cotton products.

Fabric samples	Graft yield (%)	Properties of grafted samples			Properties of retreated grafted samples		
		Epoxide content % (ows)	Fixed β-CD % (ows)	Incorporated permethrin (mg/m^2)	Epoxide content %	Fixed β-CD %	Incorporated permethrin (mg/m^2)
Cell-g-GMA	27.6	0.9537	0.0	35.2	0.3640	3.8	81.3
Cell-g-GMA/β-CD	26.40	0.6791	3.91	58.72	0.4751	9.8	93.40

Reaction condition:
Cell-g-GMA: cotton fabric grafted with GMA.
Cell-g-GMA/β-CD: cotton fabric grafted with GMA and β-CD.
Retreatment conditions: grafted samples were soaked in aqueous solution of 2% β-CD 1 M NaCl, 1%NaOH at 80 °C for 1 h.
Incorporation conditions: fabric was soaked for 24 h in solution (90% water, 10% ethanol) containing 1% permethrin.

be bioavailable directly on the fiber's surface which may be chiefly responsible for reduced biocidal activity.

Fig. 2 shows the comparative toxicity of different insecticide-treated and untreated fabrics. The test was carried out for: (a) untreated fabric (control sample), (b) cotton fabrics grafted with GMA or GMA and β-CD (blank sample); (c) cotton fabrics grafted with GMA and Permethrin, (d) cotton fabric grafted with GMA and β-CD incorporated with Permethrin, and (e) cotton fabric grafted with GMA and β-CD retreated with CDs and incorporated with Permethrin. This study was carried out for the measurement of the repellency, knockdown and mortality action.

It is clear from the results that, with untreated and blank samples more than 80% of mosquitoes are able to survive and pass the test period. It is also seen that noticeable, small different are observed in repellency percent, knockdown percent and mortality percent for cotton fabrics grafted with β-CD. But there are a significant

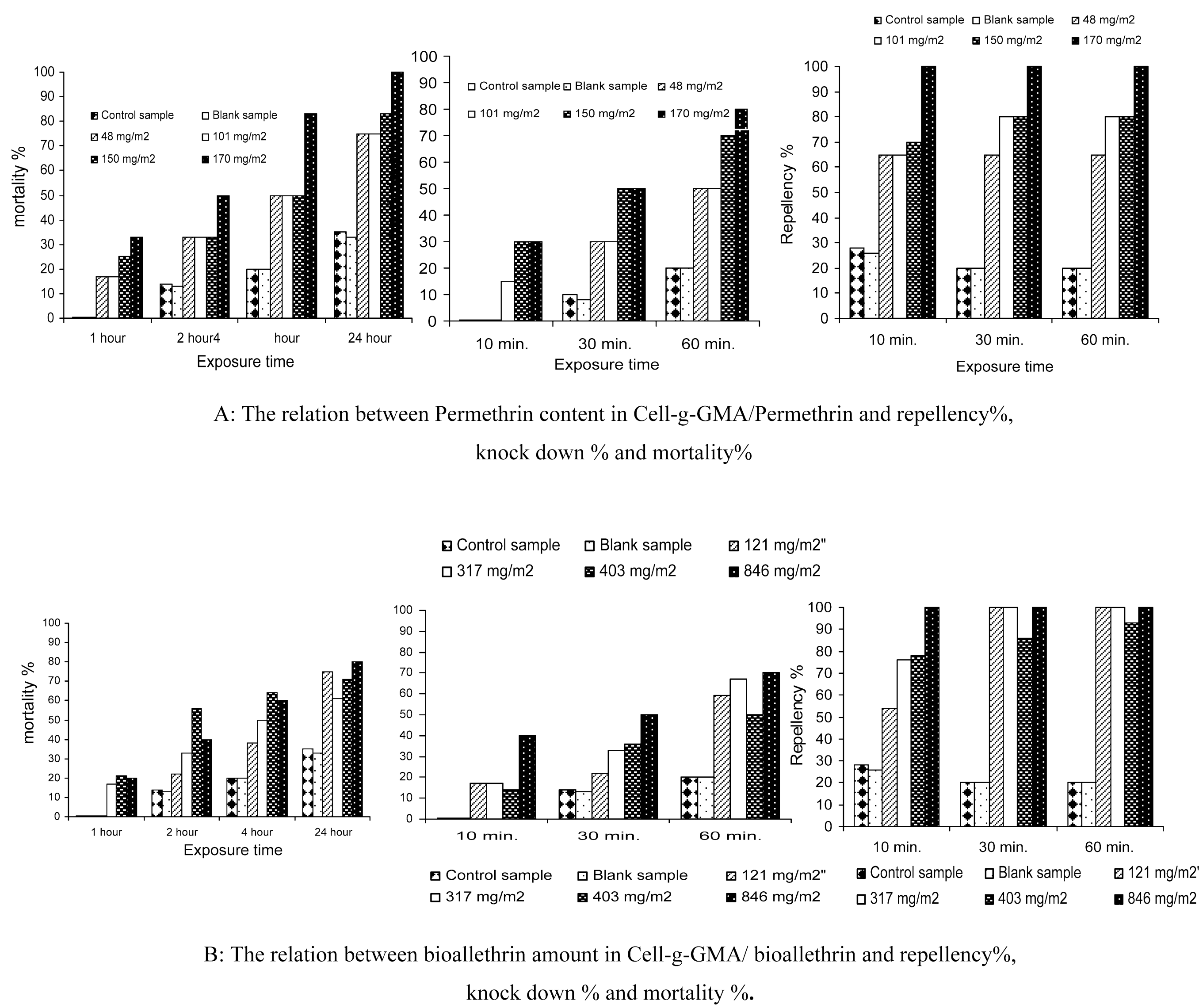


Fig. 1. The relation between permethrin content and bioallethrin amount in Cell-g-GMA/permethrin/bioallethrin and repellency %, knock down % and mortality %.

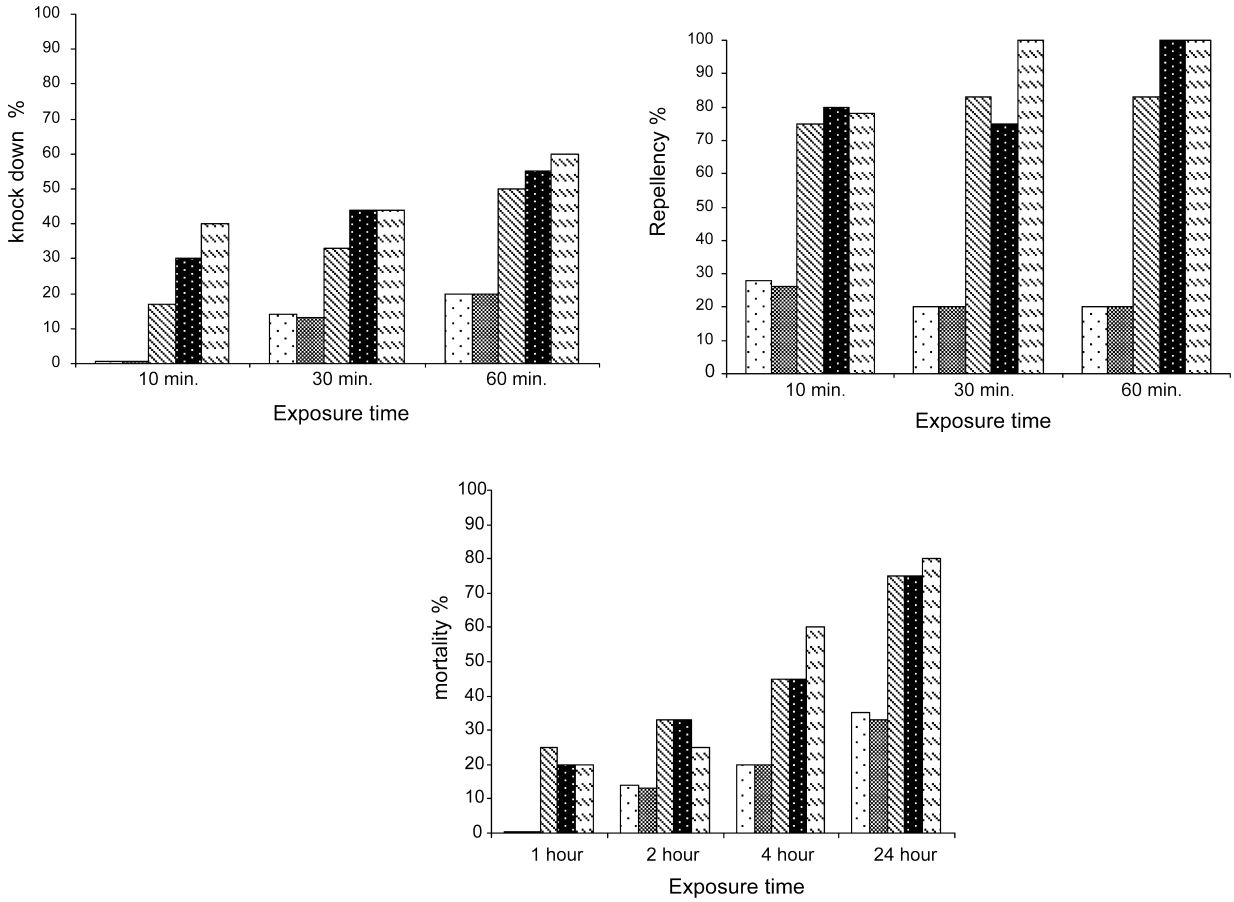


Fig. 2. Relation between treated fabric type and the repellency %, knock down % and mortality % against mosquitoes
Control sample
Blank sample
Cell-g-GMA/permethrin
Incorporated permethrin into Cell-g-GMA/CD retreated w ith B-CD
Incorporated permethrin into Cell-g-GMA/CD retreated w ith B-CD.

difference in repellency, knockdown and mortality percent between the grafted samples and the retreated samples.

This may be due to the increasing of cavities by retreatment process which, in turn, increases the incorporated amount of insecticide. Also the values of repellency, knockdown and mortality increase by increasing the exposure time.

3.5.2. Effect of washing on treated fabrics

Following the incorporation of Permethrin into treated samples for insect repellent finishing, samples were washed according to AATCC Test Method 61. Insecticide bioassay test results of treated fabrics after washing are shown in Fig. 3. Obviously, insecticide-treated fabrics display insecticidal activity after washing.

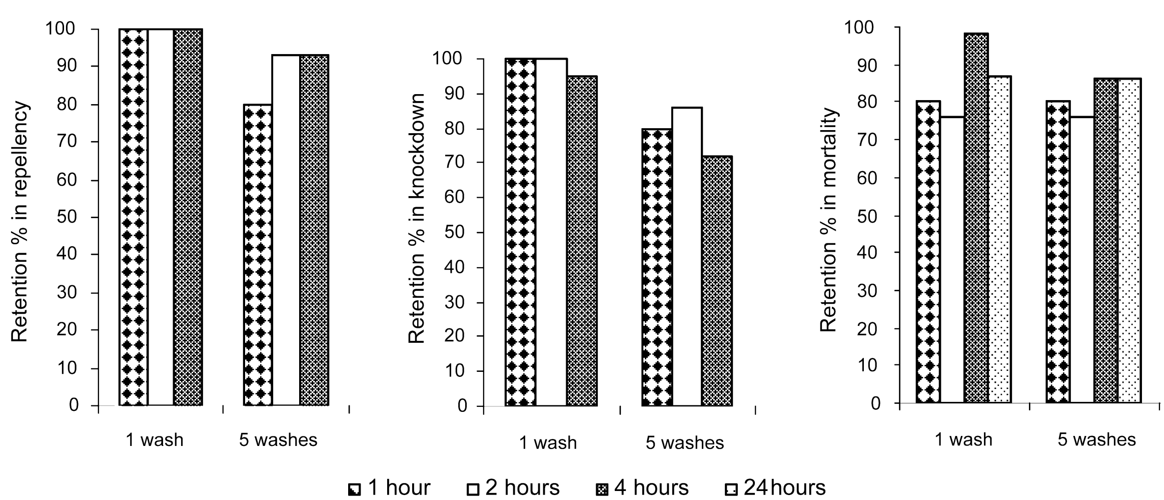


Fig. 3. Effect of Washing of Cell-g-GMA/β-CD incorporated with permethrin on toxic activity retention at different intervals of time.

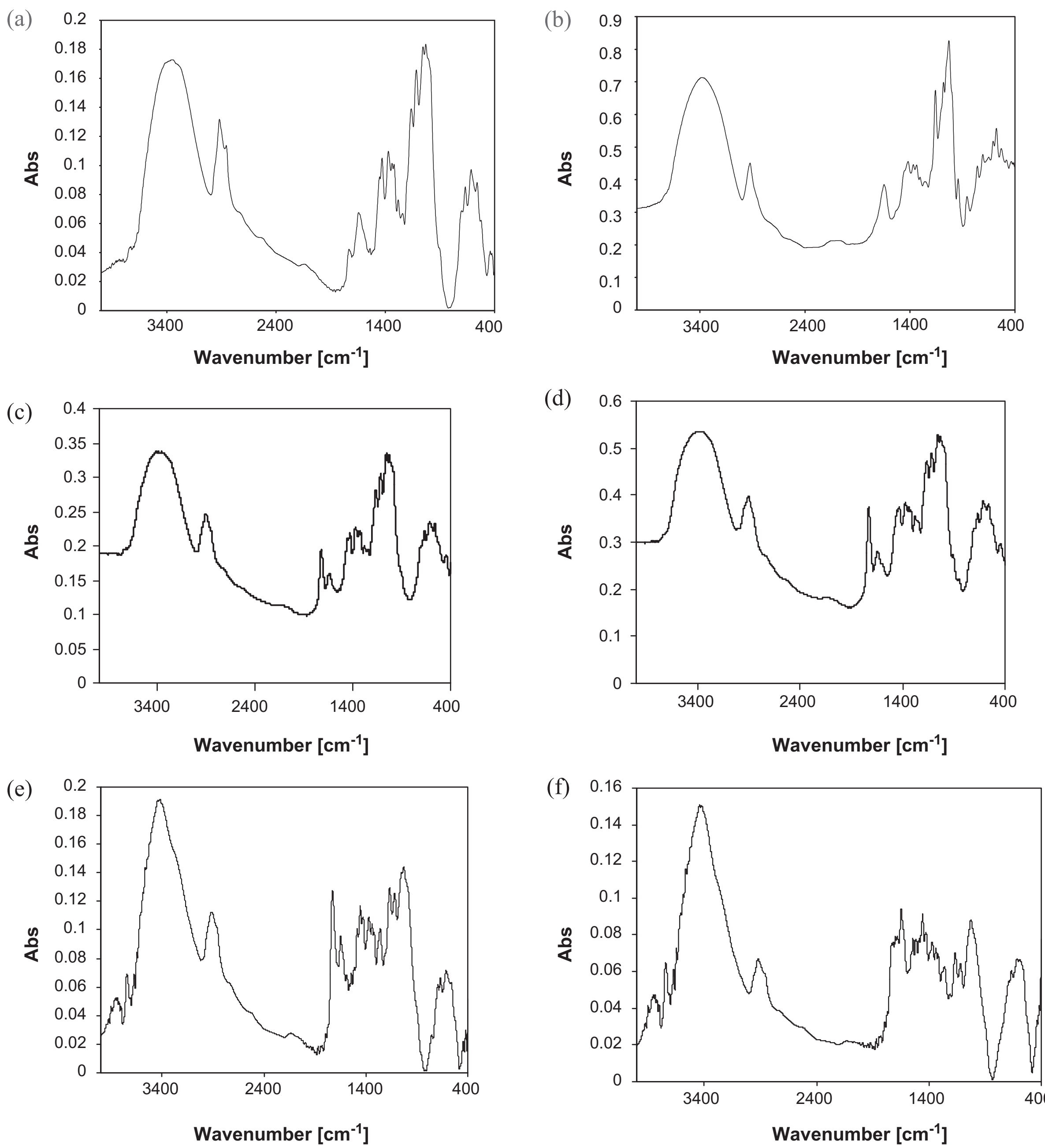


Fig. 4. IR spectrum of: (a) untreated cotton; (b) β-CD; (c) Cell-g-GMA; (d) Cell-g-GMA/β-CD; (e) incorporated permethrin in cellulose graft with GMA; (f) incorporated permethrin in cellulose graft with GMA Cell-g-GMA and β-CD.

Fig. 3 shows bioassay test results, expressed as repellency percent, knockdown percent and mortality percent of treated cotton fabrics before and after washing.

Fig. 3 shows a comparative study of washing effect on the insecticidal activity of treated fabrics against mosquitoes. Compared with untreated sample (control), treated fabrics are still more effective against mosquitoes after washing in terms of repellency, knockdown and mortality effect. From Fig. 3, it is revealed that the insecticidal activity is slightly reduced by washing. The retention percent in insecticidal activity is more than 80% depending on the time of exposure and number of washes.

The measured initial insecticide amounts obtained after treatment of fabrics as well as the remaining amounts after washing, for Cell-g-GMA/β-CD incorporated with Permethrin as insecticide agent. The chemical analysis shows lower residual dosage of insecticides by washing. It is clear that there are losses of Permethrin in treated fabrics, where the retention percent reaches about 87% and 57% after one wash and 5 washes, respectively. For treated samples, it is clear that the high amount of insecticide (Permethrin) remaining after washing is due to incorporation of insecticide in the cavities of cyclodextrins bonded on the fabrics.

3.6. Infrared spectroscopy

The cellulose sample grafted with GMA was prepared by treating cellulose with glycidyl methacrylate. The main functional groups attributed to cellulose and GMA are apparent in the spectrum (Fig. 4c). These include the absorption bands at 3414 (OH), 2906 (CH, aliphatic), 1725 (C=O, ester), 1164 (C—O, stretching) and at 1114 Cm^{-1} (C—O—C, Epoxide). The absorption band present at

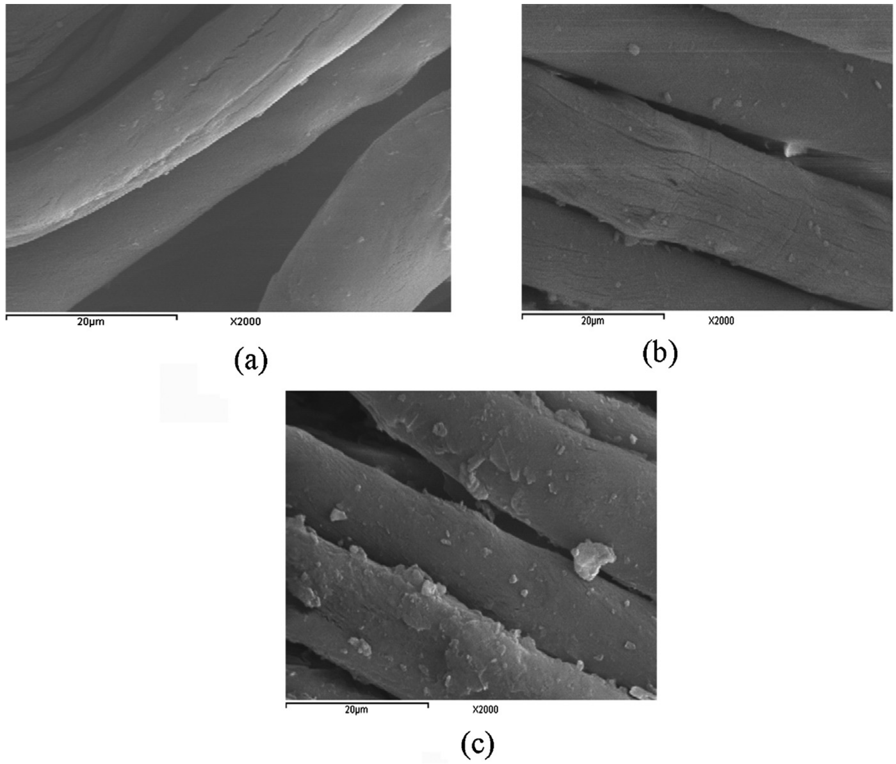


Fig. 5. Scanning electron micrographs of: (a) untreated cotton fabric; (b) Cell-g-GMA; (c) Cell-g-GMA/β-CD.

1641 cm^{-1} cannot be attributed to the CH=C group absorption in GMA group absorption in GMA since it is also recorded in the spectrum of cellulose itself. This indicates that this group is implicated in the grafting process.

The cellulose sample grafted with GMA was further treated with β-CD, or the cellulose sample grafted with mixed GMA and β-CD, to give Cell-g-GMA/β-CD. The IR-spectrum of β-CD (Fig. 4b) reveals the presence of strong absorption bands at 3385 (OH) and 2932 cm^{-1} (CH). The same bands absorb in the IR-spectrum of cellulose at 3344 and 2917 cm^{-1}, respectively. However, the IR-spectra of cellulose and β-CD are not super imposable in the finger print (1500–650 cm^{-1}) region. Moreover, the IR-spectra of the cellulose grafted samples Cell-g-GMA and Cell-g-GMA/β-CD are also not super imposable in the finger print region. This indicates that additional grafting of sample Cell-g-GMA has been completed with β-CD, most probably via cleavage of the Epoxide ring in Cell-g-GMA by one of the hydroxyl groups found in the molecule of β-CD. The main features of the IR-spectrum of Cell-g-GMA/β-CD are the presence of strong absorption bands at 3353 (OH), 2904 (CH) and 1728 cm^{-1} (C=O, ester) which ensure presence of the gycidyl methacrylate moiety in the sample (Fig. 4d).

Incorporation of Permethrin into the cellulose sample grafted with GMA is represented by the IR-spectrum in (Fig. 4e). The IR-spectrum of Permethrin show strong absorption bands at: 3040 (C—H, aromatic); 2956 (C—H, aliphatic); 1731 (C=O ester); 1585, 1488 (C=C) and at 692 cm^{-1} (CL—C=C—). Careful comparison of the IR-spectra of samples Cell-g-GMA and incorporated Permethrin into Cell-g-GMA confirm that they are super imposable in the finger print (1500–650 cm^{-1}) region. Moreover, the pattern of functional group-absorptions in the IR-spectrum of Permethrin is totally different from those of samples. Therefore, it is safe to conclude that there is no sign for incorporation of Permethrin in the cellulose sample grafted with GMA.

Incorporation of Permethrin into the cellulose sample grafted with GMA and β-CD is represented by the IR-spectrum in (Fig. 4f). Careful comparison of the IR-spectra of samples Cell-g-GMA/β-CD and incorporated Permethrin into Cell-g-GMA/β-CD particularly in the finger print region (1500–650 cm^{-1}) indicates that they are super imposable. Moreover, the pattern of functional group-absorptions in the IR-spectrum of Permethrin is totally different from those of samples. This indicates that sample incorporated Permethrin into Cell-g-GMA/β-CD is devoid of Permethrin.

3.7. Scanning electron microscopy (SEM)

SEM was conducted to view the extent of grafting on the cotton fabrics. Fig. 5(a) shows the SEM micrograph of a sample of untreated cotton, where the surface is smooth and free from any additions. Fig. 5 (b) shows a sample of cotton grafted with GMA, in which it is clear that the surface has layer of addition and particulates on fibers. Fig. 5(c) illustrate an SEM micrograph of a sample grafted with GMA and β-CD, in which surface morphology is different from that of GMA only, some flakes of β-CD are apparent on the surface. The particulate and speckled matter on the cotton fibers in the resulting micrographs confirm the grafting of GMA and additional β-cyclodextrin compounds.

4. Conclusions

- During grafting GMA together with β-CD onto cotton cellulose, the β-CD would be attached chemically to cellulose through ring opening of the Epoxide groups. Creation of free radicals on both cellulose and β-CD under the influence of high energy irradiation would also provide a possibility of the attachment through chemical combination of cellulose macroradical with β-CD radicals.
- Retreatment of cotton graft with GMA alone or together with β-CD, with β-CD, decreases the Epoxide content meanwhile increases the CDs and therefore incorporated insecticide.
- Retreatment increases the β-CD cavities and, in turn, the incorporated amount of insecticide. The toxic activity properties are

proportionally related to the amount of incorporated insecticide in the fabric which, in turn, depends on the cyclodextrin cavities of fixed CDs on the fabric.

- The toxic activity of the finished fabrics, expressed as repellent action, knockdown action and killing action against mosquitoes increase by increasing the amount of insecticide in the finished fabrics as well as by prolonging the exposure time.

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