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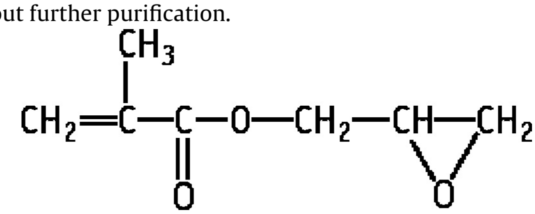
of cotton fabrics. Chemical modifications of cotton were effected through irradiation grafting using fast electron beam. Retreatment of the obtained modified cotton was also made to increase the amount of insecticide. The work was extended to studying factors affecting the treatment and insect repelling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

2. Materials and methods

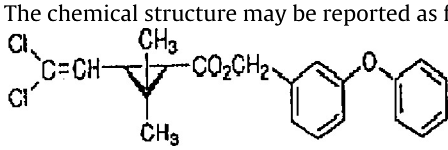
2.1. Materials

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.



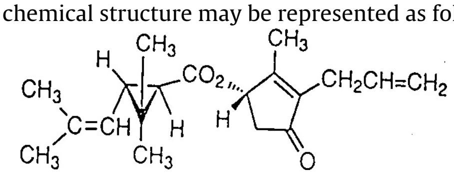
Permethrin and Bioallethrin were kindly supplied by El-Nasr Company for Intermediate Chemicals, Cairo, Egypt. Permethrin does not repel insects, but instead works as a contact insecticide, causing nervous system toxicity leading to death or knockdown of the insect. The chemical structure may be reported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

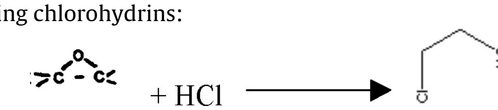
Graft yield was determined from the gain in weight of cotton fabric due to graft polymerization after removing the ungrafted polymer with the proper solvent. After grafting, the fabric was thoroughly washed with distilled water and ethanol then dried at 50 °C.

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).