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DETERMINATION AND CHARACTERIZATION OF TRICLOSAN ON POLYETHYLENE TEREPHTHALATE FIBERS

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ABSTRACT: In this study, in order to investigate the presence of the triclosan on the polyethylene terephthalate (PET) fibers after finishing treatments, both triclosan and its derivate solutions were prepared and the presence of triclosan was found at retention time of 12.04-12.18 min. by GC-MS. SEM results showed that fiber surface became very smooth and bright after coating and the vibrational bands in the region of 722 and 570 cm^{-1} implied the presence of triclosan on fiber surface by FTIR studies.

Key words: Triclosan, polyethylene terephthalate, SEM, FTIR, characterization

POLİETİLEN TEREFTALAT LİFLERİNDEKİ TRİKLOSANIN BELİRLENMESİ VE KARAKTERİZASYONU

ÖZET: Bu çalışmada, bitim işlemi sonrasında polietilen tereftalat liflerinde triklosan varlığını incelemek için saf triklosan ve ticari bir triklosan çözeltisi kullanılmıştır. GC-MS yardımıyla 12,04-12,18 dakika zamanlarında triklosan varlığı bulunmuştur. SEM sonuçları, uygulamadan sonra lif yüzeyinin daha düzgün ve daha parlak olduğunu ve FTIR çalışmalarındaki 722 ve 570 cm^{-1} bölgelerindeki titreşim bantları ise, lif yüzeyinde triklosanın varlığını göstermektedir.

Anahtar kelimeler: Triklosan, polietilen tereftalat, SEM, FTIR, karakterizasyon

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1. INTRODUCTION

Polychloro phenoxy phenols (polychlorinated phenoxy phenols, PCPPs) are a group of organic polyhalogenated compounds such as triclosan and predioxins. The chemical structures of the PCPP's isomers are presented in Figure 1 [1-4].

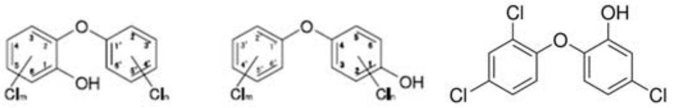

Figure 1. The chemical structures of the PCPP's and triclosan

Triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol) is a chlorinated aromatic compound which has functional groups representative of both ethers and phenols. It has a broad spectrum antibacterial and antifungal activity that's why it is used in many consumer and professional healthcare products including soaps, lotions and creams, toothpastes, deodorants, and also incorporated into polymers and textiles fabrics at concentrations that range from 0.1 to 1%. Triclosan's hydrolytic and light stability is very high, but it is lipophilic and almost insoluble in water (0.004%), but soluble in ethanol, diethyl ether, and stronger basic solutions such as 1 M sodium hydroxide. The use of triclosan in medical applications is limited because of its poor aqueous solubility of less than 0.001 mg/ml. Thus, the formulation of triclosan in different products is difficult and these products have less antimicrobial activity than expected on the basis of their properties [5-9].

The aim of this study is to investigate the presence of triclosan on PET fibers. It is presented more detailed findings on the characteristics of triclosan and its trace on PET fibers. SEM results showed that fiber surface became very smooth and bright after coating and the vibrational bands in the region of 722 and 570 cm^{-1} implied the presence of triclosan on fiber surface.

2. EXPERIMENTAL

2.1. Materials

We used 100% PET fabric (39x28 courses/wales and 60g/m^2) due to their increasing presence in the production of medical, healthcare and hygiene materials. Triclosan (5-choloro-2-(2,4-dicholorophenoxy)phenol, purity, 97%) was purchased from Sigma-Aldrich Chemicals and triclosan derivative was supplied by Rudolf Chemie.

2.2. Treatments

Triclosan was applied to PET fabric by laboratory type padder through conventional pad-dry process. The fabrics were padded through squeeze rollers made by Mathis with two dips and two nips, at a setting 0.5 bar to give a wet pick-up of between 30-35% on weight of fabric. Treatment conditions were as follows: 60 g/l of antibacterial chemicals, drying at 150 C for 5 min in Mathis oven.

2.3. Measurements

2.3.1. GC/MS

The chemicals were determined using Agilent 6890N GC with 5975C MSD equipped with Agilent Tech 7683B Injector automatic liquid sampler and Agilent DB-5 GC column (30 m length, 0.25 mm ID, 0.25 µm film thickness). Helium was used as the carrier gas, with a column flow rate of 1.0 ml/min in constant-flow mode. Injections (10µL volume) were made in the splitless mode (splitless time 1 min) and injector temperature was 280^{0}C. The GC interface and the ion source temperatures were set at 325^{0}C. The GC oven temperature was kept at 80^{0}C for 1min, followed by the first ramp at 20^{0}C /min to 120^{0}C, second ramp at 10^{0}C/min to 325^{0}C, and holding for 10 min. The mass spectrometer was operated in the electron impact ionisation mode (70 eV). MS spectra were recorded in the range from 100 to 550m/z units.

2.3.2. SEM

The surface morphologies of the swatches were observed with a JEOL JSM 7000 field emission scanning electron microscope (Tokyo, Japan). The standard procedure was followed, in which samples were coated with gold for 150 s before a scanning electron microscopy examination.

2.3.3.FTIR

The molecular structure of the untreated and treated swatches was analyzed by the attenuated total reflection Fourier transforms infrared spectroscopy (ATR-FTIR) and spectra were obtained using a Nicolet 6700 FTIR spectrometer. The swatches were scanned at frequencies from 400 to 4000 cm^{-1}, the number of scan times was 32, and the resolution was set at 2 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. GC Mass Studies

The studied compound structures were determined by comparing the GC-MS peaks of the compounds with those of the standard solutions. Pure triclosan and its commercial derivative were dissolved in 1 ml of methyl alcohol in the different concentrations and these mixtures were shaken in a test-tube for 2 min. The mass spectra of triclosan and its derivate were shown in Figure 2, typical GC-MS chromatograms were indicated in Figure 3 and GC-MS values were given in Table 1. The range of the retention time for the samples was between 12.00-12.18 min. The only one sharp peak was obtained 12.02, 12.14, and 12.18 min. as the main peak of triclosan. Considering triclosan derivative, it was found that there were four peaks that represented by different compounds in the solution at different retention time. The chromatographic peak at 12.04 min. was detected as the main peak of triclosan. The calibration graph was obtained by plotting the concentration ratio against the peak area ratio (peak integration). The good linearity was obtained in the calibration graphs of different concentrations.

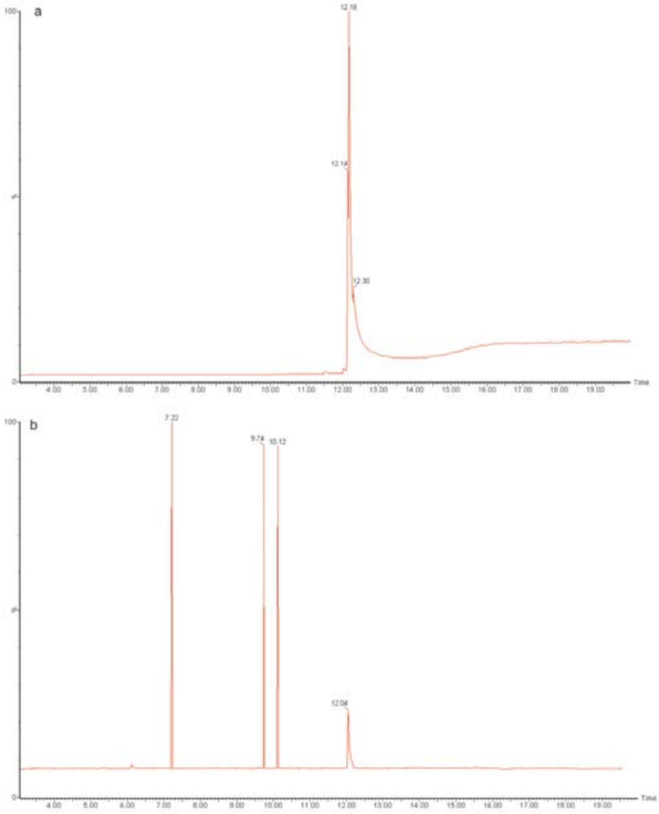

Figure 2. Chromatogram of triclosan (a) and triclosan derivative (b)

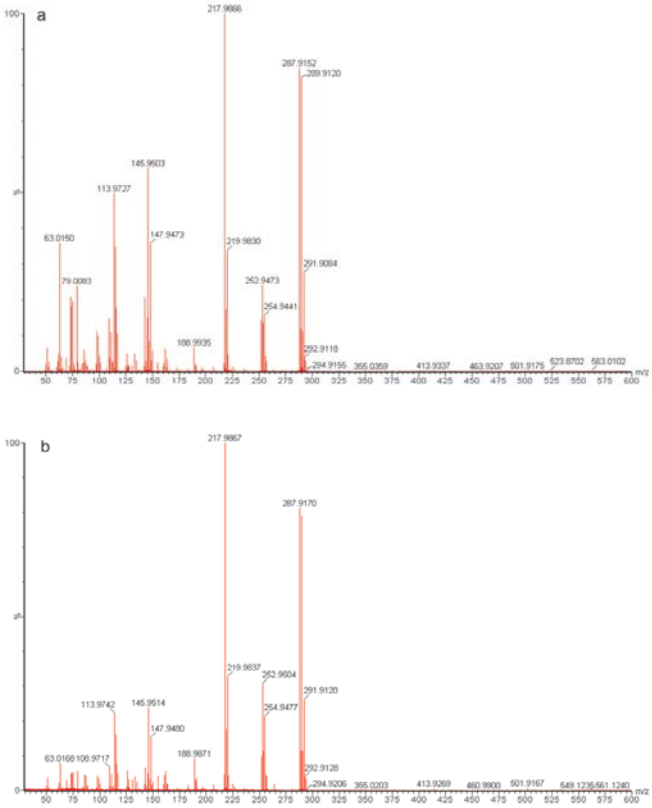

Figure 3. Spectrum of triclosan (a) and triclosan derivative (b)

Table 1. GC-MS values of triclosan and its derivative

Compound	Retention time (min)	Molecular ion (m/z)	Relative intensity	Proposed structure
Triclosan	12.02	287.9487	288 / 35.0	86.4% triclosan
	12.14	287.9485	290 / 43.8	95.3% triclosan
	12.18	287.9152	288 / 84.6	97.0% triclosan
Triclosan derivate	12.04	287.9170	288 / 83.8	90.0% triclosan

3.2. SEM analysis

Surface morphology of PET was analyzed by SEM and surface images are shown in Fig.4. The untreated fiber in Fig.4(a) had relatively smooth surface, which had poor ability to hold water but the some impurities can be seen on the fiber surface. Compared with the untreated sample, surface in Fig.4(b) was slightly covered by triclosan after finishing. It also provided evidence of treatment occurring only on the surface of fiber.

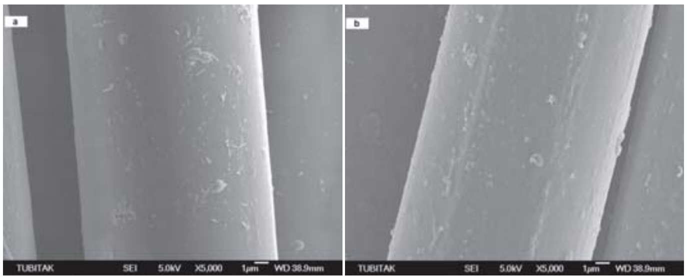

Figure 4. SEM micrographs photographs of untreated PET (a) and treated with triclosan (b)

3.3. FTIR analysis

The ATR-FTIR spectra were used to determine the chemical changes caused by antibacterial treatments, and results are shown in Fig.5. It is well known that the existence of an aromatic rings in a structure is normally readily determined from the C-H and C=C-C ring-related vibrations. The C-H stretching occurs above 3000 cm^{-1} and is typically exhibited as a multiplicity of weak-to-moderate bands in Fig.5(a). The other most important set of bands are the aromatic ring vibrations centered around 1600 and 1500 cm^{-1}, which usually appear as a pair of band structures. The untreated PET have the following main absorption bands at 3424 cm^{-1} (C=O, carbonyl overtone), 2967 and 2906 cm^{-1} (two strong glycol C-H stretching), 1712 cm^{-1} (C=O stretching), 1577 (ring C-C stretching), 1504 cm^{-1} (ring C-H in-plane bending, ring C-C stretching), 1469 cm^{-1} (CH_2 bending, O-C-H bending), 1407 cm^{-1} (ring C-H in-plane bending, ring C-C stretching), 1338 cm^{-1} (CH_2 wagging, O-C-H bending), 1239 cm^{-1} (C(=O)-O stretching, ring ester C-C stretching , C=O in-plane bending), 1091 cm^{-1} (glycol C-O stretching), 1015 cm^{-1} (ring C-C-C bending, ring C-C stretching, ring C-H in-plane bending), 967 cm^{-1} (O-CH_2 stretching, C(=O)-O stretching, chain folding), 870 cm^{-1} (ring C-H out-of-plane bending, ring ester C-C out-of-plane bending, C=O out-of-plane bending, ring torsion), 845 cm^{-1} (ring C-C stretching, C=O in plane bending, C-H_2 rocking), 791 cm^{-1} (ring C-H out-of-plane bending, C=O rocking and CCO bending), 722 cm^{-1} (C=O out-of-plane bending, ring torsion, ring C-H out-of-plane bending) [10-11].

For triclosan, the strong absorption of halogenated hydrocarbons arises from the stretching vibrations of the carbon-halogen bond and the most prominent and informative bands in the spectra of aromatic compounds occur in the low-frequency range between 900 and 670 cm^{-1}. After triclosan application, such new bands were detected between 3000 and 2800 cm^{-1} for aromatic C-H stretching bands and 1800-1600 cm^{-1} for weak combination and overtone bands in Fig.5(b). These strong absorption bands result from the out-of-plane bending of the ring C-H bonds. In-plane bending bands appeared in the 1300-1000 cm^{-1} region. Skeletal vibrations, involving C-C stretching within the ring, are absorbed in the 1610-1585 and 1500-1400 cm^{-1} regions. When several chlorine atoms are attached to one carbon atom, the band is usually more intense and at the high-frequency end of the assigned limits. The C-CI absorption bands were observed at frequencies range of 722-570 cm^{-1} and strong CH_2 wagging bands were observed for the CH_2CI group in the 1300-1150 cm^{-1} region. We attribute such new bands to coating triclosan on surface of PET, which is consistent with the SEM pictures [10-13].

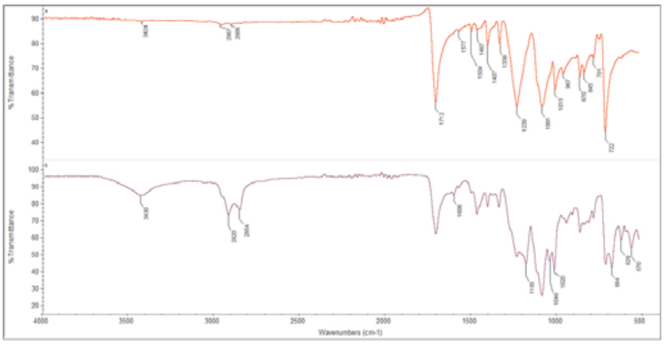

Figure 5. FTIR spectra of untreated PET (a) and treated with triclosan (b)

4. CONCLUSIONS

Triclosan has a broad spectrum antimicrobial activity but it is lipophilic and the use of triclosan for textile industry is also limited because of its poor aqueous solubility. The aim of this study is to investigate the presence of triclosan on PET fibers. SEM results showed that fiber surface was coated by triclosan after treatment and the new vibrational bands implied the presence of triclosan on fiber surface.

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