Egypt. J. Chem. **Vol. 66,** No. 6 pp. 75 - 83 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Synthesis and evaluation of friendly low cost flame retardant Material from local ores for the polymeric materials

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Abstract

The aims of this work are synthesis and evaluation of nano-particles Diatom as flame retardant material for fabricated 100% cotton and 50/50% cotton/PET[polyester]. The unmodified and that modified with Diatom samples were characterized by using Infrared (IR) absorption and the Scanning Electron Microscope (SEM). The Diatom nano-particles were introduced onto the fabricated cotton by different steps. The appearance of the absorption IR bands at the vibrationl bands at 1050-670 cm^{-1} are related to Si-O bond and at 590-447 cm^{-1} are related to SO_4^{-2} vibration unit indicate that Diatom nano-particles are introduced into the cellulosic units. The thermal stabilities of the untreated and that treated 100% cotton and 50/50% cotton/PET samples were performed. The Thermo-gravimetric (TG) curves show that there is no changes by modification with diatoms. The curves show that the treated sample exhibits the same weight loss, This means that these samples have the same thermal stabilities. The flammability of the samples were carried out by using Limiting Oxygen Index (LOI). The results of the examination show that the value of LOI have nearly the same value for the cotton samples, so that this part needs more studies.

Keyword: Evaluation- Diatoms-Flame Retardant-Polymeric materials-Natural ores

1. Introduction

World health organization (WHO) is issued several reports about the death, the injuries, the global plan for the protection and care of burns. These reports indicate that many thousands of people died annually and millions of dollars are lost due to the spread of the burns in the world (1,2).

The polymer materials were used successfully in different applications because they have excellent chemical, mechanical and electrical properties. The polymer materials have two main drawbacks, the first one is its flammability which represents an environmental pollution. other disadvantages is their low melting point which, create an atmosphere loaded with smoke and some toxic gases which by turn restricted the work of the firemen. For these reasons, the polymer materials must be modified to overcome these defects. This modification goes in two directions, improving the properties of the polymer materials and adding some flame retardant materials.

Fire retardant materials (FR) are compounds added to the fabricated materials to delay the spread of flame through the burned medium.

The most common flame retardant materials are the halogenated or phosphorus compounds. These compounds commonly produce some toxic gases. The fire retardant materials may be classified into organic, inorganic and organic-inorganic materials, each of these classes has some advantages and some disadvantages. The inorganic flame retardant materials are the more acceptable compounds because they are hydrated in nature and produce water vapour at low temperatures and produce some oxides such as MgO, SiO_2 and Al_2O_3 which work as flame retardant at high temperatures. Furthermore. They could absorb the evolved toxic gases such as CO, CO_2, SO_2 and other toxic gases(3-10) . As examples the inorganic flame retardant materials are, Silicate, borate, phosphates, metal hydroxides. Many improvements were done in order to develop research work

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Receive Date: 10 July 2022, Revise Date: 09 September 2022, Accept Date: 18 September 2022
DOI: 10.21608/EJCHEM.2022.149925.6492

concerning FR materials: increasing the surface area of the fire retardant materials by preparing them in nano- particles to enhance their spread into the burned medium.

Some friendly-environmental fire retardants were prepared, such as:-Fire retardant materials based on carbons, including activated carbon, carbon nano-tubes, graphine oxide, carbon black, multiwall nanotubes, expanded graphite, multi-layer graphene and graphene. Also, the using of the same ores such as clays because they are hydrated structure and composed of silicate and alominate.

The main objective of this work is synthesis of friendly and low cost flame retardant materials. This flame retardant materials will be prepared from some available materials such as diatoms ore. This ore consists mainly of silicate and other oxides. At high temprature, these oxide produce silicate glassy layers isolated the flame from the burned surface.

II-Materials and Methods

II.1-Materials

Natural diatom sample was collected from Kom Oshim, east of Fayium state, Egypt. ,6M H_2SO_4, 3glycidyloxypropyltrimethoxysilane (GPTMS, 99%) and 2-propanol (99%) were provided from Aldrich. 1-Methlylimidazole were supplied from BASF. hydrochloric acid (HCl) grade in lab. 120 g/ cm^2 of 100% fabricated cotton and 160 g/ cm^2 of 50/50% cotton/polyester were used. The fabricated samples were kindly supplied by Misr Spinning and Weaving Co., Mehalla El Kobra, Egypt. **II.2-Methods**

Two methods of modification for diatoms were used, the first method of modification of diatom is thermal-acid treatment, that the natural diatom (S base) was calcined at 900 (S2), 1000(S3), and 1100(S4)^oC in air atmospheric furnace for 5 h. Then these samples was exposed to an acid treatment. The acid treatment was carried out with 6 M H_2SO_4 at room temperature for 24h and at about 100^oC for24 h with reflux conditions. 10 g was mixed with 50 mL of the acid solutions and stirred during the time. Consequently, the suspensions were centrifuged and the solids were washed with deionized water until the washed water to pH = 7 and then dried at 100^oC for 12 h. The second method of modification is acid - thermal treatment, samples were obtained by using the natural diatom was exposed to 6 M H_2SO_4at about 100^oC for 24 h and then calcined at 900 (S5), 1000(S6), and 1100(S7)^o C for 5h.

II.3- Treatment of the fabricated fibers

Before introducing the modified diatoms onto cotton the fiber passes through the following steps

II.3.1. Hydrolysis of GPTMS

3-Glycidyloxypropyltrimethoxysilane (GPTMS,10 ml) was added to 2-propanol (180 ml) and HCl (1.22 ml, 0.01 M) with stirring at r.t. for 1 h. The resulting hydrolyzed mixture was used in the modification of fabric under study.

III.3.2. Fabric treatment

Samples of fabric (20 cm x20 cm) Cotton/PET and 100% cotton were immersed in the finishing bath containing 50 ml) hydrolyzed GPTMS and different concentration between (0.05, 0.08,0.1g) of modified diatom suspended in 50 ml distilled water with magnetic stirring for 30 min. then using sonication in order to it good suspension , 1-Methylimidazole (few drops). The fabric samples were squeezed to 100% wet pick-up, followed by drying at 100 ^oC for 3 min. then cured at different temperatures (120, 140 , 160^o C) for 3 min. All samples were washed thoroughly with tap water to get rid of the unreacted materials then dried at room temperature overnight.(11)

II.4-Instruments:-

The chemical analysis of the diatom sample was mesured by(XRF SPECTRO ZEPOSE 1 German)

The XRD curves were accomplished in reflection mode by X-ray diffractometer (MiniFlex-600, Rigaku Corporation, Japan) with a scanning 2θ angle ranging from 10-70^o at a scanning speed of 10^o/min. To determine the surface functional groups of the samples; FT-IR (Nicolet iS50, Thermo Fisher Scientific Ltd., USA) spectrum was recorded at the wavenumber range of 4000-500 cm^{-1}. A high speed gas sorption analyzer (NOVA 2000 series, Chromatic, UK) was used to determine the nitrogen adsorption-desorption isotherms. To estimate the specific surface areas, pores volume, average pore diameters and pore-size distribution the Brunauer–Emmett–Teller (BET) method was employed. The thermo-gravimetric analyses (TGA) of the prepared samples were carried out using (Shimadu TGA-50 H) under N_2 flow over rate 30 ml/min at 10°/min. The crystal morphology and microstructure analysis of the prepared samples scanning electron microscopy (FESEM, Model FEI, QUANTA FEG 250). Samples were sputtered with a thin film of gold to ensure a high quality image. Their particle sizedistributions were measured by laser light-scattering-based particle sizer (MalvernMastersizer S Ver 2.15) with wet method using water as a medium to disperse the samples. Complete analysis of the diatom was carried out by using

energy dispersive X-ray fluorescence(EDXRF) model XRF SPECTRO ZEPOSE 1 German)

The samples of fabricated cotton incorporated with diatomes were characterized by using the same techniques which described elsewhere in the previous II.4.

II.5- Evaluation of the flame retardant :

The flame retardant properties of the treated and untreated fabricated samples were performed by using LOI apparatus ISO 4589-2ASTM D 2863. Elevated Temperature Oxygen Index ISO 4589-3, UK Naval

Engineering standard NES 714 which measure the percentage of oxygen that has to be present the support burning of the sample

III-Results and Discussion

III.1- The chemical analysis of the diatom sample (S base), Table 1

shows that diatoms consists mainly of silica (SiO_2= 83.6) with relatively small percentage of other oxides such as Al_2O_3, Fe_2O_3, CaO,

Table 1: chemical analysis of natural diatom

Oxide	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O	CaO	MgO	Loss/others
Percentage	83.6	4.24	1.07	—	—	—	6.17	—	4.86

III.2- X-ray diffraction analyses

XRD of natural diatom (S base) and Calcined samples [at 900ºC (S1), at 1000ºC(S2) and at 1100ºC (S3)] followed by sulfuric acid treatment are shown in Figure (1). The XRD pattern of the natural diatom included three different phases related to quartz [JCPDS (005-0490)], Kaolinite [JCPDS (089-6538)] and calcite [JCPDS (88-1808)]. The XRD patterns of Calcined samples at different temperatures followed by sulfuric acid exhibit different phases as anhydrous calcium sulfate [JCPDS (006-0226)], Aluminum hydrogen sulfate hydrate [JCPDS (022-0005)] beside to quartz. This means that the calcination converted the calcite to calcium oxide and sulfuric acid treatment converted calcium oxide to Calcium sulfate and the kaolinite to aluminum hydrogen sulfate hydrate.

X-ray diffraction analyses of treated samples by sulfuric acid followed by calcination at 900ºC (S4), 1000ºC(S5) and 1100ºC (S6) are shown in Figure (2). The XRD patterns of treated samples by sulfuric acid followed by calcination at different temperatures exhibit similar phases, except the phase of aluminum sulfate hydrate (Alunogen)[JCPDS (026-1010)] instead of aluminum hydrogen sulfate hydrate . The appearance of aluminum sulfate hydrate may be due to alteration product of kaolinite by acid treatment and the calcination. The presence of hydrated form of aluminum sulfate in despite of the calcination process at high temperatures may due to the water vapour which can be easily released from the structure and is responsible for the slightly variable composition of alunogen when the compound is in contact with air of ambient humidity (12)

III.3-Thermal analysis

The thermogravimetric analyses (TGA) of the natural diatom (S base) and Calcined samples [at 900ºC (S1),1000ºC(S2) and 1100ºC (S3)] followed by sulfuric acid treatment are shown in Figure (3). All the TGA curves showed three weight loss steps where the range of first weight loss step lies from 50ºC to 150ºC and may assigned to the loss of absorbed water on the surface of natural diatom and treated samples. the second weight loss step started at 150ºC and ended at 250ºC may be due to the liberation of water molecules inside structures of diatom and treated samples. For natural diatom, the third weight loss step started from 650ºC to 750ºC was due to the decomposition of calcite into the Calcium oxide and CO_2 and thermal degradation of kaolinite (13,14). For treated samples, the third weight loss step occurred at the same range (650ºC to 750ºC) was assigned to conversion of aluminum hydrogen sulfate to aluminum sulfate (15). The weight loss % for each step was illustrated at table (2).

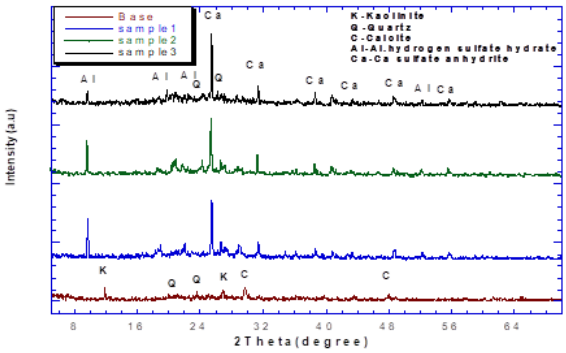


Fig.1: XRD of natural diatom (S base) and Calcined diatom [at 900ºC (S1), 1000ºC(S2) and 1100ºC (S3)] followed by sulfuric acid treatment.

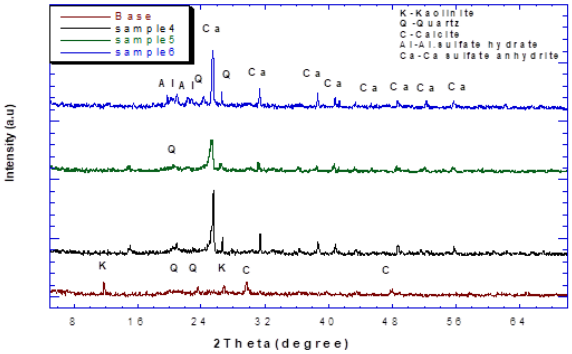


Fig.2: XRD of natural diatom (S base) and treated samples by sulfuric acid followed by calcination at 900ºC (S4), at1000ºC(S5) and 1100ºC (S6).

Table 2: The weight loss % values of natural diatom (S base) and Calcined diatom followed by sulfuric acid treatment at 900ºC (S1) 1000ºC(S2) and 1100ºC (S3)

Sample	At first step	At Second step	At third step	Total weight loss
S base	24%	12%	23%	59%
S 1	20%	9.7%	19%	48.7%
S 2	11.6%	10.10%	18.7%	40.4%
S 3	30%	15.3%	19.2%	64.5%

The thermogravimetric analyses (TGA) of the natural diatoms (S base) and treated diatom by sulfuric acid followed by calcination at 900ºC (S4), 1000ºC(S5) and 1100ºC (S6) are shown in Figure (4). For the treated samples (5 and 6) three weight loss steps were

appeared. The first one occurred at 50ºC- 200ºC was assigned to the loss of water absorbed on the surface of treated samples whereas the Second step occurred at 570 ºC -770 ºC may be due to the liberation of crystallized water molecules of Alunogen ($Al_2(SO_4)_3.17H_2O$). the third step was appeared at 780 ºC - 980 ºC for sample (5) and at 750 ºC -920 ºC for sample (6) was due to the decomposition of $Al_2(SO_4)_3$ into Al_2O_3 and SO_3 (REF-S-5). For the treated sample (4), the first and second weight loss steps only occurred. . The weight loss % for each step was illustrated at table (3).

III.4-Morphology and microstructure

The morphology of natural diatom (S base) and Calcined diatoms followed by sulfuric acid treatment at 900ºC (S1) 1000ºC(S2) and 1100ºC (S3) are shown in figure (5). The microscopic examination of the natural diatom demonstrates different morphological shapes of diatom frustules like cylinder and platy. These diatom frustules were associated with fragments as calcite fractions and Kaolinite that blocked the pores of diatom frustules. After thermo-chemical treatment, the structure of diatom frustules was characterized by the occurrence of numerous fine microscopic pores and cavities (16).

Table 3: The weight loss % values of natural diatom (S base) and treated diatom by sulfuric acid followed by calcination at 900ºC (S4),1000ºC(S5) and 1100ºC (S6).

Sample	At first step	At Second step	At third step	Total weight loss
S base	24%	12%	23%	59%
Sample 4	7.7%	26.8%	-----	34.5%
Sample 5	4.5%	21%	21%	46.5%
Sample 6	4.3%	20%	14%	38.5%

The morphology of the treated diatoms were shown in Fig 6. The chemo-thermal treatment negatively affected on the diatom frustules structure but improved the crystallinity of the other product phases that previously mentioned at XRD discussion.

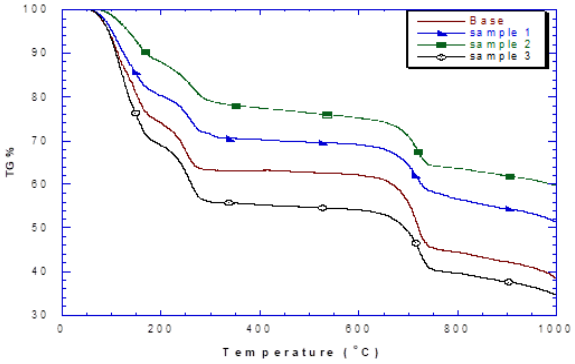


Fig.3: TG Analysis of natural diatom(S base) and Calcined diatoms followed by sulfuric acid treatment at 900ºC (S1) 1000ºC(S2) and 1100ºC (S3).

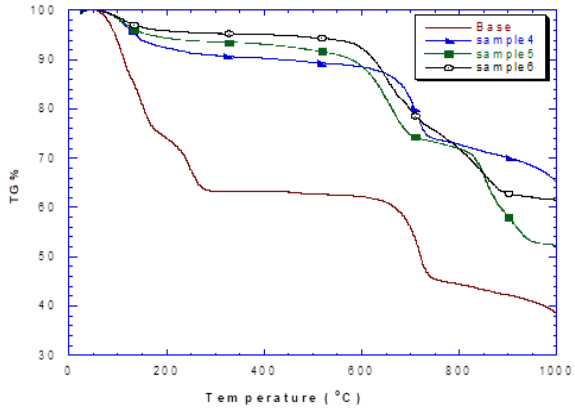
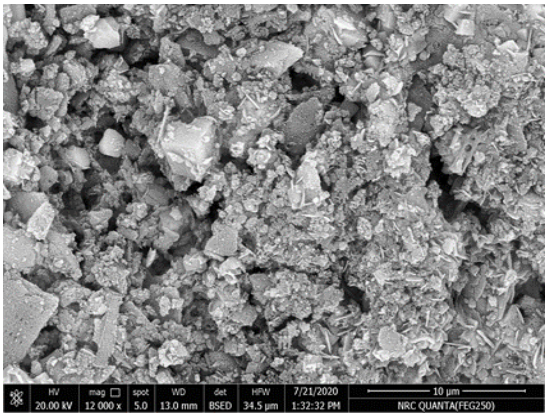
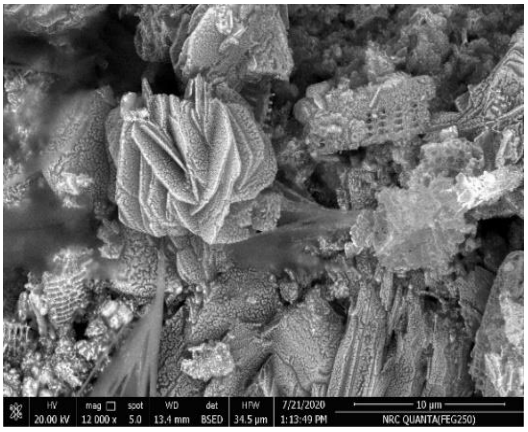


Fig.4: TG Analysis of natural diatom(S base) and treated diatoms by sulfuric acid followed by calcination at 900ºC (S4),1000ºC (S5) and 1100ºC (S6).

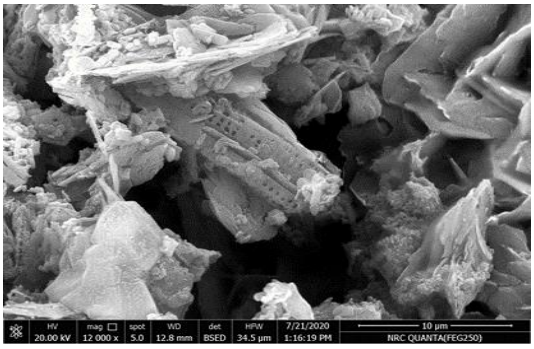


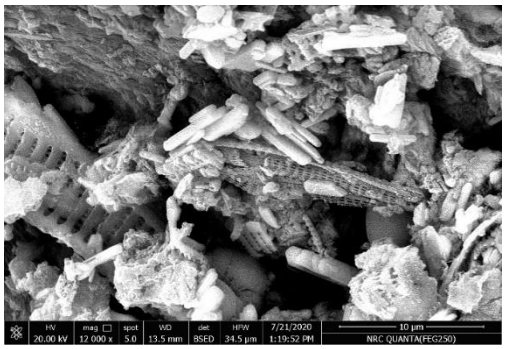
Base

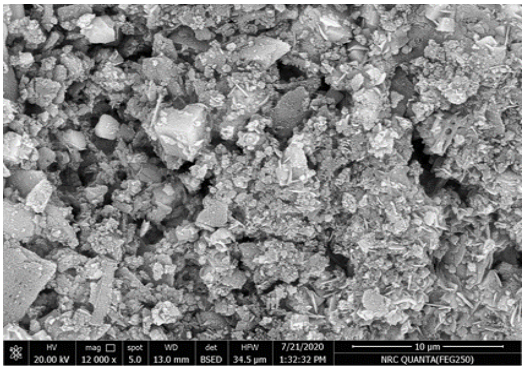


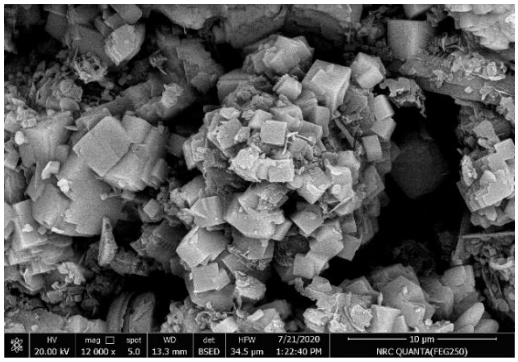
Sample (1)

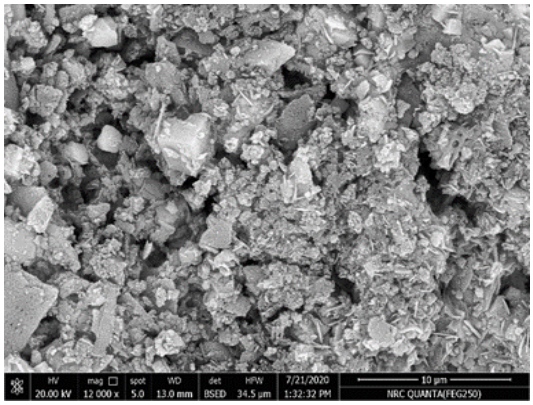
Fig.5: SEM images of natural diatom (S base) and Calcined diatom [at 900ºC (S1), 1000ºC(S2) and 1100ºC (S3)] followed by sulfuric acid treatment.


Sample (2)


Sample (3)


Base


Sample (4)


Sample (5)

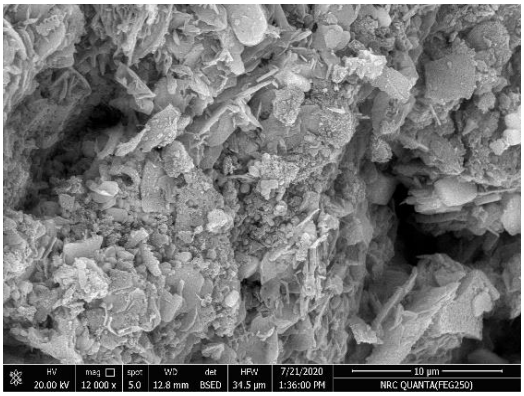

Sample (6)

Fig.6: SEM images of natural diatom (S base) and treated samples by sulfuric acid followed by calcination at 900ºC (S4), at1000ºC(S5) and 1100ºC (S6).

III.5-Surface area measurements

The BET specific surface area of the natural diatom and all treated samples are listed in table (4). The surface area shows little improved by thermal- acid treatment while The surface area was greatly improved by acid-thermal treatment.

Table 4 shows the porous characteristics of the obtained samples. Results clearly indicate that samples S1 to S4 are non-porous materials however S zero and S1 contain low amount of some mesopores while S2 and S3 account small amount of micropores as detected by NLDFT. After modification acid -thermal treatment the porous textures are strongly increased indicating that the formation of porous materials of S4, S5 and S6 as a result of treatment effect. S4 exhibited the highest total surface area and total pore volume. Mean pore diameter (R_P, nm) values are varied according to their type and modification effect.

Depending on thermal analysis and surface area measurements, sample (4) is the most stable material has the height surface area and pore volume distribution. So it can be applied as a fire retardant additive.

V- Characterization of untreated and treated samples

To explain the incorporation of diatoms onto the cotton or cotton /polyester fibers, the samples were exposed to different examination

Table 4: Porous characteristics of the obtained samples.

Samples	S_{BET}, m^2/g	V_P, cm^3/g	R_P, nm	Mesopore size by NLDFT
S zero	0.25	0.0064	105	15.9
S1	0.49	0.0019	15.7	7.25
S2	4.31	0.0065	5.99	1.29
S3	2.08	0.0039	7.59	0.730
S4	19.2	0.036	7.47	6.75
S5	16.2	0.032	7.96	8.99
S6	16.2	0.032	8.05	0.730

V.1-IR of of the prepared fabricated samples

Fig.(7) shows FTIR of diatom, 100% cotton fabric and treated by diatom (a), 50/50% cotton/PET fabric and treated by diatom (b). All spectra show vibrational band at 3950-3000cm^{-1}corresponding to asymmetric stretching of OH and (17). For diatom and 100% cotton fabric samples, vibrational band at 1650-1640 cm^{-1} corresponding to vibrational bending mode of OH was appeared (17). For 100% cotton treated with diatom samples (fig. - a), strong band was occurred at 2890 cm^{-1} corresponding to asymmetric stretching of OH (11). The vibrational band at 1020 cm^{-1} is correlated to C–O stretch but the bands 1410 and 1360 cm^{-1} are related to C–H scissoring and C–H bending vibration, respectively. Another band was appeared at 1100 cm^{-1} which is related to C–O–H bending of a secondary alcohol (18).for diatom, the vibrationl bands at 1050-670 cm^{-1} are related to Si-O bond (19) and at 590-447 cm^{-1} are related to SO_4^{-2} vibration (20). For 100% cotton and 50/50% cotton/PET treated ,additional band at around 1700 cm^{-1} was observed corresponding to C=O of ester group due to overlapping of the carbonyl bond of ester and the modifying agent.

V.2-Thermal gravimetric analysis (TGA) of the prepared fabricated samples

In our research, it is clear that the prepared nano-particles of diatom after treated chemically (sulphuric acid) are thermally stable and may be suggest as flame retardant materials. In present study, the thermal stability of the fabricated cotton and that treated with diatom will be measured. The (figure 8) represents the TG curves has carried number 1,2 for untreated and treated 50/50% cotton /PET and other two numbers 3,4 for untreated and treated 100 % cotton respectively.

It is clear that the thermo gravimetric profile behaves the same trends of the thermal weight loss. The TG curves show that the untreated 100% cotton fabric and that treated with diatom are nearly the same. These indicate that the weight loss for the untreated 100% cotton fabric and other treated are nearly the same. While, the untreated and treated 50/50% cotton /PET samples have the same weight loss.

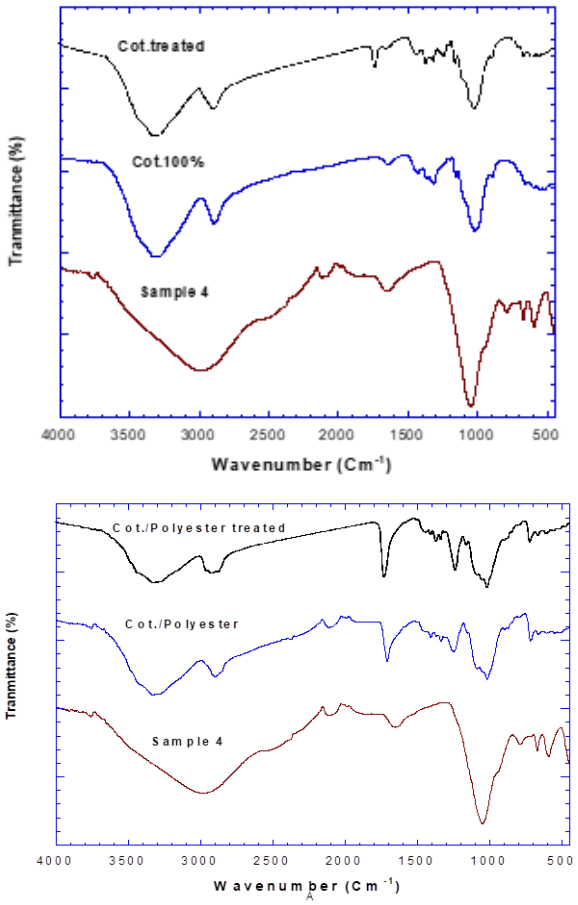


Fig.7- FTIR of diatom, a)100% cotton fabric and treated by diatom , b) 50/50% cotton/PET fabric and treated by diatom

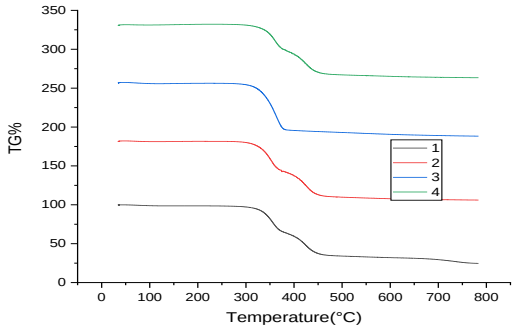
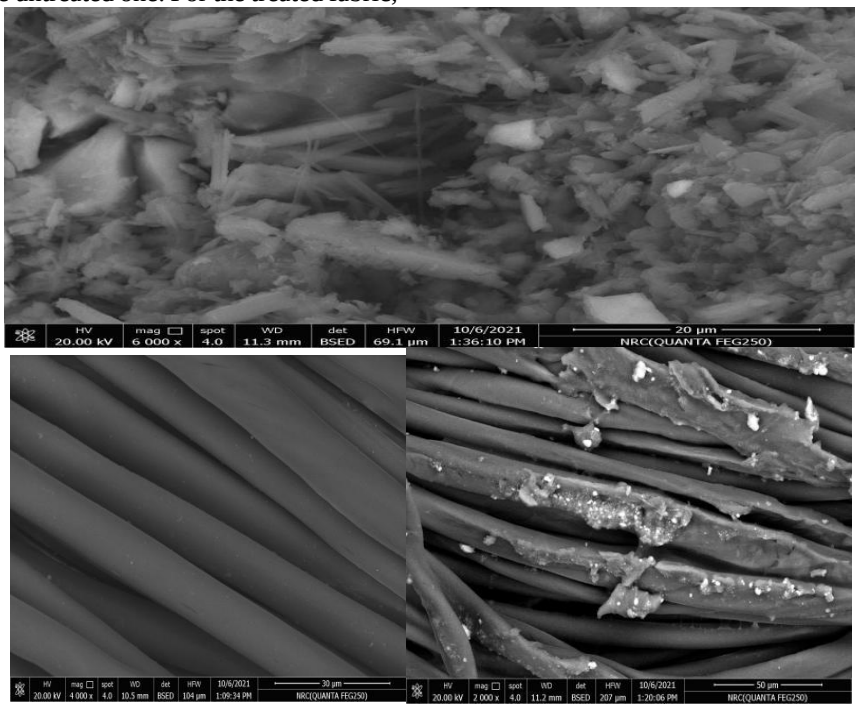


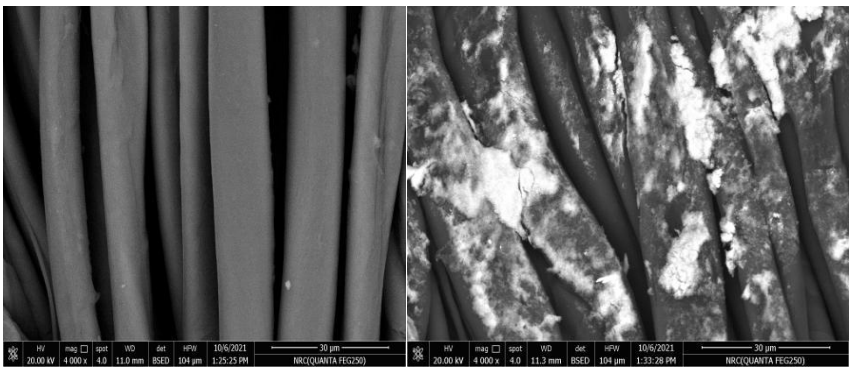
Fig.8-Thermal gravimetric analysis (TGA) of the prepared fabricated samples

V.3-The morphology of the prepared fabricated samples

It is clearly seen from Fig.(9) that the surface of all control textiles fabric shows straight fibers arranged in parallel directions with smooth image and no observed layers formed on the fibers surface. After fabric treatment, the surface has showed deposited layer composed of GPTMS/diatom on the surface of fabrics with variation in the quantity according to the kind of fabric. The appearance of modified fabric was different from the untreated one. For the treated fabric; non-homogenous layer of coating on the surface with increasing the roughness of the surfaces indicating successful treatment procedure applied in this study. In comparison of untreated and treated pure cotton fabric; the former one appear as smooth arrays of fibers, while the later one became rough with appearance of coating layers and some aggregation of diatom and GPTMS. For CO/PET the treated fabric is also rough and there are some aggregations of coating chemicals.



(a) untreated (50/50% cotton/PET) (b) the treated(50/50% /PET)by Diatom



c) untreated 100% cotton d) treated 100% cotton fabric

Fig.9-The morphology of the prepared fabricated samples

V.4-limiting oxygen index (LOI)

To evaluate the effects of diatoms on the flamability of the fiber samples were performed by LOI and the obtained results were recorded in Tables (5,6,7). As we know that the atmospheric air contains about 20% oxygen. If the LOI less than 20%, the material is flammable while if it is higher than 20%, it is less flammable. According to the value of LOI, the ability of the material to flame is classified less than <20% is highly flame, more than >20% is low flame

The measurements of the LOI of both the base and the incorporated with diatoms samples shows that all the samples have LOI less than 20%, this mean that the addition of diatoms don't effects on the flammability of the fibers. Further more, the LOI values were measured under 120/140 and 160 curing tempura.

Also, no effects were observed with the curing. This finding needs further treatment and studies (21)

Table 5-Effect concentration of diatom on the limiting oxygen index (LOI)

Type of fabrics	Conc. Of Diatom g/100 ml	limiting oxygen index (LOI)
Control 100% cotton fabric	0 0.05 0.08 0.1	flammable
Control 50/50% cotton/PET	0 0.05 0.08 0.1	flammable

Finishing formulation: wet pick-up 80%: dry at 100 ºC for 3min. then curried at 140 ºC/90sec., crosslinking agent is GPTMS.

Table 6-Effect of different cross linking agent on limiting oxygen index (LOI)

Type of fabrics	Conc. Of Diatom g/100 ml	Different cross linking agent	limiting oxygen index (LOI)
Control 100% cotton fabric	0.15g 0.15g 0.15g 0.15g	-without -GPTMS -Binder based on polyacrylate -DMDHEU	Flammable Flammable Flammable Flammable
Control 50/50% cotton/PET	0.15g 0.15g 0.15g 0.15g	-without -GPTMS -Binder based on polyacrylate -DMDHEU	Flammable Flammable Flammable Flammable

Finishing formulation: Conc. of Diatom is (0.15g/100 ml), wet pick-up 80%: dry at 100 ºC for 3min. then curried at 140 ºC/90sec.,

Table 7-Effect of curing temperature on limiting oxygen index (LOI)

Type of fabrics	Curing temperature º C	limiting oxygen index (LOI)
Control 100% cotton fabric	0 120 140 160	Flammable Flammable Flammable Flammable
Control 50/50% cotton/PET	0 120 140 160	Flammable Flammable Flammable Flammable

Finishing formulation: Conc. of Diatom is (0.15g/100 ml) wet pick-up 80%: dry at 100 ºC for 3min., crosslinking agent is GPTMS (10ml hydrolyzed in 100ml)

VII- Conclusion

The improvement of the diatoms properties were carried out by two methods. The characterization of the modified samples show that the diatoms sample treated with sulphoric acid and calcined at 900 have a good properties to be use as flame retardant material , The diatoms unites were incorporated through the cotton or cotton / polyester fibers as indicated by the IR and the morphology techniques

The incorporate samples were evaluated as flame retardant by measuring the LOI unfortunately, the values of the LOI still meanly constant. This finding indicates that the diatom units were not incorporated to the fibers successfully and not suitable to be use as flame retardant for fibers as it is , so it needs another methods of modification and incorporation of diatoms to be able to be use as flame retardant material

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