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Preparation of a novel composites based polyester nonwovens with high mechanical resistance and wash fastness properties

Ahmed Abed [a, b, c], Nabil Bouazizi [a*], Stéphane Giraud [a], Ahmida El Achari [a], Christine Campagne [a] , Olivier Thoumire[d], Reddad El Moznine [b], Omar Cherkaoui [c], Julien Vieillard[e] , Abdelkrim Azzouz[e]

[a] ENSAIT, GEMTEX – Laboratoire de Génie et Matériaux Textiles, F-59000 Lille, France
[b] *Laboratory LPMC, Faculty of Science El Jadida, Chouaib Doukkali University, El Jadida, Morocco.*
[c] *Laboratory REMTEX, ESITH, Route d'El Jadida, km 8, BP 7731 – Oulfa, Casablanca, Morocco*
[d] *Normandie Univ., UNIROUEN, CNRS, PBS (UMR 6270), 55 rue Saint Germain, 27000 Evreux, France*
[e] *Normandie Univ., UNIROUEN, INSA Rouen, CNRS, COBRA (UMR 6014), 55 rue Saint Germain, 27000 Evreux, France*

*CORRESPONDING AUTHOR. Dr. Bouazizi Nabil, E-mail addresses: bouazizi.nabil@hotmail.fr

Abstract

In this work, polyester fiber were functionalized by oxides (Ox) like titanium dioxide (TiO_2), zinc oxide (ZnO) and silicon oxide (SiO_2), using polyvinylidene fluoride (PVDF) as binder to obtain the PET-PVDF-Ox samples. Chitosan polymer (CT) was coated on last samples to ensure the good surface compatibility, resulting in the PET-PVDF-Ox-CT composite. The obtained products were thermally pressed and fully characterized. The chemical coatings, physical and thermal properties were investigated. It was found that coated PET nonwoven is highly hydrophobic materials with good diffusion resistance. Incorporation of TiO_2, ZnO and SiO_2 resulted in the formation of strong cross-linked CT network, producing improved dripping resistance of PET nonwoven. In addition, the modification steps allows to highly increasing the mechanical resistance. This was explained by the good surface compatibly and the interfacial bonding occurred in the matrix. Moreover, soil release tests confirmed the high durability against washing for PET-PVDF-Ox-CT composites. Thus,

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regarding to the above results, the current work developed a facile process for the fabrication of new composite based nonwovens with good durability and high mechanical resistance.

Keywords: Polyester Fiber; Chitosan; PVDF; Oxides; Mechanical resistance; Durability

1. Introduction

Textiles have increased significantly their specific and high performance applications. One of the main fields of application for these materials is the construction industry. Textile surface produced by nonwoven technology provides a way to impart new and diverse properties like self-decontamination, hydrophilicity, hydrophobicity, retaining comfort and mechanical strength [1]. The nonwovens fabrics are fibrous structures with randomly oriented fibers, presenting important properties and characteristics to be used in different kind of applications. Hence, the increasing interest for the personal health and comfort has created the necessity to improve the mechanical properties of nonwovens. Nonwovens surface modification was considered an interesting way to enhance the properties. Therefore, value addition to PET nonwovens by functionalization produced considerable industrial attention, attributed to their potential use in physical, thermal, biological and medical protection. The outstanding mechanical character of composites is a result of the load transfer from polymer matrix to filler materials that are of higher stiffness and failure strength [2]. Thus, composite with a good tensile modulus, that target ideal mechanical strength are strongly requested [3]. It was found that the composites reinforced with chemical treatments such as the incorporation of metallic nanoparticle, the grafting of organics moieties can increase the tensile modulus. However, the chemical modifications for many works were not sufficient to produce composites with stable structure, due to the local buckling behaviors occurring during the preparation. In addition, the composites are not sustainable with heterogeneous contents with low thermal stability. There, the functionalization and fabrication of composite materials are quite required to resolve the above problems.

Up to now, the oxides (Ox), such as metallic oxide [2] and their included hydroxyl groups showed that nonwovens can produce water vapor at high temperatures through decomposition reactions [3, 4]. On the other hand, the incorporation of Ox was used as elements for mechanical resistance, which can also increase the stress tensile [5]. Materials oxides have received considerable attention in several environmental applications, as it have many interesting properties that combined the mechanical, electrical, optical and biological properties [6]. Among them, zinc oxide (ZnO), titanium dioxide (TiO_2) and silicon dioxide (SiO_2) are widely studied in many aspects and were the most efficient candidates due to their important application mechanical resistance, transparent electronics, varistors, surface acoustic wave devices, piezoelectric transducers and solar cells [7]. The modification with organic substance makes great contribution to the dispersion of fillers and its strengthened barrier effect properties.

Intensive researches have been focused on developing advanced nanocomposites with improved surface properties by using oxides [8]. In this regard, many oxide types were activated and modified by the addition of some active agent such as amine derivate for enhancing mechanical, electrical and sensing properties or polyvinylidene fluoride (PVDF) [9]. Due to the excellent mechanical, chemical and ecofriendly properties, polyvinylidene fluoride were widely used in various advanced applications like mechanical resistance. Nanocomposites based PVDF and oxide provided high thermal stability, mechanical properties, and impact resistance [10]. This was explained by the presence of PVDF which incorporate Ox, but also by the possible crosslink with the material [11]. In this aim, researchers have employed some natural polymers as chitosan which show many advantages over artificial materials [12, 13]. Recently, the chitosan was established as a good candidate in total biodegradability, non-toxicity and fiber formation properties [14-16]. Indeed, the chitosan can improve the mechanical properties when optimizing particle distribution and

surface compatibility [16]. To the best of our knowledge, studies relating a combination chitosan and PVDF additives have not been reported.

On the basis of the above ideas, polyester nonwovens (PET) were employed for the fixation of Ox like TiO_2, ZnO and SiO_2, with the presence of poly (vinylidene fluoride) (PVDF) as binder. Then, chitosan (CT) was employed as natural polymer to reinforce the immobilization of PVDF-Ox into nonwovens fibers. The obtained materials PET-PVDF-Ox-CT were used as sustainable materials to increase the, mechanical resistance, and wash fastness properties improvements. Different modified nonwoven were systematically characterized by field emission scanning electron microscopy (SEM), optical microscopy, Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), and water contact angle. The surface compatibility and the changes of mechanical, properties were investigated on the basis of the materials structure, stability and the reusability.

2. Experiments

2.1. Materials

Poly (vinylidene fluoride) (PVDF), inorganic nanoparticles ZnO and TiO_2 were purchased from Sigma-Aldrich. SiO_2 nanoparticles were synthetized by sol gel synthesis and the protocol is described in supporting file. Acetone and N, N-dimethylformamide (DMF), ethanol, sodium triphosphate (PPT), distilled water, ammonia hydroxide (NH_4OH, NH_3 basis), sodium hydroxide (NaOH) and tetraethoxysilane (TEOS) were obtained and used as obtained. Polyester nonwovens (PET) with 0.9µm fiber diameter were obtained from CETI (**supporting information**).

2.2. Preparation and design of composite based nonwovens

Scheme. 1 illustrates the preparation and design route employed for nonwoven composite. The process mainly consisted of the following steps:

Firstly, in order to remove impurities and spinning oil present on the surface, the polyester (PET) nonwoven was treated according our previously published work [16]. Briefly, PET was

activated by air atmospheric plasma to introduce both –OH and –COOH groups at the fiber surface (**supporting information**). Secondly, three solutions were prepared, containing different oxides (i.e. TiO_2, ZnO or SiO_2) and PVDF as reagents with a weight ratio (3:5) and mixture of acetone and DMF (45:5 v/v) as solvent. The resulting solution was stirred for 2 h at 50 °C. After that, at room temperature, PET nonwovens were impregnated into the dispersed solution for 2 hours. The coated nonwovens were taken out from the solution and dried in at 50 °C for 24 h to clean and remove residual solvent in the resulting PET-PVDF-TiO_2, PET-PVDF-SiO_2, and PET-PVDF-ZnO composites. Thirdly, each composite (i.e. PET-PVDF-Ox) was prone to the chemical grafting of chitosan (CT) by padding with an aqueous solution of 3 g/L chitosan polymer in presence of sodium triphosphate (PPT). The fabric was then dried (110 °C, 3 min) and cured (170 °C, 30 s) using a hot air dryer (Werner Mathis AG, Switzerland). Finally the obtained products denoted PET-PVDF-Ox-CT was hot-pressed before further characterization and tests.

…….. (Scheme.1) ……..

2.3. Characterizations

The treated and original PET nonwovens were fully characterized in this work. Fourier transform IR spectroscopy was carried out using a Tensor 27 (Bruker) spectrometer with a ZnSe ATR crystal. The samples were analyzed by FTIR directly without any further preparation, and background spectra were recorded on air. For field emission scanning electron microscopy (SEM) using a JEOL JEM-ARM200F HR setting with a field emission gun and probe aberration corrector, materials were previously metallized by a gold layer at 18 mA for 360 s with a Biorad E5200 device, and EDX images to evaluate the chemical contrast. Thermal analysis was performed by thermo gravimetric analysis (TG-DTA, A6300R). The water contact angle measurements were carried out by using Digidrop device from GBX. This

instrument uses a goniometric method to calculate the contact angle between water and a solid surface.

2.4. Wash fastness and durability tests

Washing process was performed by using the AATCC standardization for home laundry test [27] and can be summarized briefly as follows: 2 g of Na_2CO_3 and 1 g of commercial detergent were both dissolved in one liter (1L) washing solution. Droplets of sunflower oil are deposited on unmodified and modified nonwovens PET, PET-PVDF-TiO_2-CT, PET-PVDF-SiO_2-CT and PET-PVDF-ZnO-CT, then all samples were completely immersed in the washing solution using 1:50 material to liquor ratio at 40°C for 60 min, under continuous stirring. After that, nonwoven composites were removed from solution, and then rinsed with tap water until neutralization. Finally, the samples were dried in oven at 70°C and this process was repeated 3 times.

2.5. Mechanical measurements

Before the measurements of mechanicals properties, all materials were subjected to a hot press for 5 minutes at 120 ° C between two metal metals. The mechanical properties were of great importance to evaluate the strength of the as-prepared composite. For this, mechanical tests of all samples were carried out using MTS (2/M) testing system. According to the test procedure ISO 9073-3, each composite was cut in 20x5 cm^2 (L, l) size and then the measurements of tensile strength were obtained.

3. Results and Discussions

3.1. Role of thermal pressure

The thermal pressure employed for the prepared composite PET-PVDF-Ox-CT in this work was an interesting step for both the construction and the tailoring of the surface compatibility of the finished materials. During the thermal pressure, the particles of Ox were connected the one to the other and compacted, due to the increases in the strong crosslink at

the particle-particle contact. The thermal pressure causes the breaking of the TiO_2, SiO_2 and ZnO, layers on the PET fibers surfaces, resulting in direct metal to fiber contacts. In this situation, the process improves the crosslink between Ox particles and the other additives. Therefore, it leads to produce materials with a high density in Ox particles. Afterward, with this pressure the Ox particles are uniformly distributed along the PET nonwovens. Consequently, an enhancement in the surface compatibility/density of the composite was obtained, which will be an advance on the improvements of the mechanical behavior.

3.2. Morphological properties

The surface morphology of untreated and treated PET nonwoven was determined by SEM analysis, and the results are shown in **Fig. 1**. The original PET nonwoven exhibits a random network of overlapped fibers and multiple connected pores with a fairly smooth surface. From the PVDF coating process, the microstructure presented a continuous film structure with a thickness layer about few microns. Visible changes were observed after the fixation of PVDF/Ox, indicating that PET surface was totally covered by the PVDF/Ox particles. Regarding to the good dispersion of Ox onto PET fibers, it was supposed that a strong interfacial interactions between PET, PVDF and Ox are involved. By comparing the treated PET (i.e. PET-PVDF-ZnO, PET-PVDF-SiO_2 and PET-PVDF-TiO_2), SEM images of PET-PVDF-TiO_2 showed an uniform distribution with high particles density at the fiber surface, resulted in a much smoother surface structure and the formation of bulkier aggregates of much smaller particles. This fact can be explained in terms of strong interaction between PET:PVDF-Ox, particularly for PET-PVDF-TiO_2, which promotes structure morphology with tailored surface.

…….. (Figure.1) ……..

On the other hand, optical microscopy confirmed this phenomenon by the preponderance of uniform aggregates film at the fiber surface (**Fig. S1**). Therefore, it appeared that both

PDFV-Ox and CT successfully covered the PET fiber, in agreement with FTIR analysis, contact angle and TGA analysis (discussed in the following parts).

Wettability and diffusion resistance are of great importance to evaluate nonwovens for environmental application. The contact angle and capillarity of the fiber surface were investigated and the results are reported in **Fig.2**. As seen, the water contact angle of original PET, PET-PVDF-SiO_2-CT, PET-PVDF-ZnO-CT and PET-PVDF-TiO_2-CT are 1.97, 110.20, 120.41, and 111.20, respectively. This result indicated that modified PET nonwoven was more hydrophobic than pristine PET. Herein, nonwovens with good hydrophobicity would be beneficial not only for the improvement of mechanical and fire retardancy properties, but also the durability. Deeper insights in the changes of the apparent contact angles with time were investigated, and the results are summarized in **table. 1**. According to the obtained results, it was fund that PET-PVDF is very hydrophobic materials, as compared to the other samples. Even, during 1 hour, the water cannot penetrate in PET-PVDF-Ox-CT samples, due to the high hydrophobicity of PVDF and the lotus effect. In our case, some unsaturated atoms like F, Ti, Si and Zn can decreased this hyper hydrophobicity, as supported by the measurements on the contact angle. Herein, the role of chitosan was to ensure the crosslink between unsaturated atoms and hydroxyl groups from chitosan. Thus the hydrophobicity was slightly increased by the CT grafting. This was confirmed by the droplet volume and the contact angle values, which were unchanged in time. By contrast, Ox is hydrophilic materials and hence the water could penetrate on the surface in less than 3 s (**table S3**).

…….. (Figure.2) ……..

…….. (Table.1) ……..

3.3. Structural properties

Figure 3 and **figure S5** showed the XRD patterns of pure PET, PET-PVDF-SiO_2-CT, PET-PVDF-TiO_2-CT and PET-PVDF-ZnO-CT composites. These patterns were recorded to

analyze the structure and crystalline phase of prepared oxides. The broad diffraction band observed 18˚ and 25˚ was attributed to the amorphous nature of the Ox. According to the JCPDS no 29-0085 and literature, the XRD diffraction of PET-PVDF-SiO_2-CT exhibits a broad peak centered at 2θ = 22˚. This peak is associated to the SiO_2 particles, which shows the successful addition of amorphous SiO_2 in the PET fibers [17]. For the PET-PVDF-TiO_2-CT pattern, the broader peaks observed at 36.8˚ and 60.9˚ were due to the formation of TiO_2. Wile, the main peak observed at 2θ = 44˚ in the PET-PVDF-ZnO-CT pattern confirmed the presence of ZnO nanoparticles, according to JCPDS card no 04 0850 [50]. In addition, **figure 4** confirms the successful preparation of PET-PVDF-Ox-CT composites by EDX-XRF analysis, where elemental F, N, Si, Ti and Zn can be observed in the sample composition. The elemental F and N can be observed in all spectrum of PET-PVDF-Ox-CT, suggesting the presence of PVDF and CT in the materials. Elements of carbon and oxygen can also be observed in all EDX spectrums which demonstrated the presence of various functional groups in the composites structure.

…….. (Figure.3) ……..

…….. (Figure.4) ……..

3.4. Infrared analysis

Infrared studies were carried out to ascertain the purity and nature of the functional groups that exhibited on prepared composites. The FTIR spectra of original and modified PET nonwovens are shown in (**Fig. 5** and **Fig. S2**). The structure of original nonwoven displayed some bands in the region 1720-650 cm^{-1}, attributed to the stretching vibration of CH_2, C=O, and aromatic C=C. The peak observed at 3100 was attributed to the stretching vibration C-H present in the polyester fibers. The broad absorption peaks at around 3437 and 1456 cm^{-1} are attributed to stretching vibrations of OH groups corresponding to the adsorbed water molecules on the samples surface. After PVDF fixation, the bands obtained at 869 cm^{-1} were

attributed to the vibrations of υCF_2 for amorphous PVDF [19]. The chemical fixations of Ox were confirmed by the presences of new supplementary peaks at low wavenumber. The band observed at 515 cm^{-1} is attributed to the Zn–O stretching vibration, indicating the characteristic band of pure ZnO [19]. In addition, the deposition of SiO_2 particles were confirmed by the enlargement of the band at 1100 cm^{-1} assigned to the stretching vibration of O–Si–O. Indeed, the impregnation of TiO_2 particles was confirmed by the band at 700 cm^{-1} assigned to the stretching vibration of Ti-O [20]. Chitosan grafting induced a shift of the υCF_2 peaks from 869 cm^{-1} to 875 cm^{-1} which might be due to the restriction on the vibration by the interaction occurred between TiO_2, CT and CF_2 groups [21]. The peak obtained at 1625 cm^{-1} was assigned to the NH_2 group bend scissoring, indicating that chitosan were successfully coated the modified PET fibers [22]. In addition, the band appeared at 1420 cm^{-1} and 1156 cm^{-1} were attributed to the OH bending of primary alcoholic group and to C-N stretch in chitosan, respectively. From the FT-IR results, it can be summarized that CT, PVDF and Ox are correctly attached to PET. We estimated that the grafting occurs through the interaction of amine groups ($–NH_2$) and hydroxyl groups (–OH) through hydrogen bonding, which was in good agreement with hypothesis presented in the literature [23, 24].

Interestingly, the grafting of PVDF showed a characteristic peak appeared at 1108 cm^{-1} and assigned to the stretching vibration of the C-O-C band of PVDF. This peak was disappeared for both PET-PVDF-TiO_2 and PET-PVDF-TiO_2-PPT-CT modified nonwovens. This is due to effective chemical grafting of PVDF, which involved specific interaction between C-F_2 in PVDF and TiO_2/CT. Deeper insights in the IR spectra of PET-PVDF-TiO_2 and PET-PVDF-TiO_2-CT revealed a markedly decreases in the peaks intensity which provides significant evidence of the additional functional groups from the additives. The latter should confirm the good compatibility between PVDF and TiO_2-CT.

…….. (Figure.5) ……..

3.5. Thermogravimetric analysis

Thermogravimetric analysis was performed to provide onset temperature and analyze the thermal properties of the untreated PET and treated nonwovens composites. Under nitrogen atmosphere, all samples were heated from room temperature to 800 °C at 20 °C/min and the results are showed in **figure. 6** and **figure. S3-4**. As first overview, the sample presents one single step for decomposition. The composite starts to decompose at 180–200 °C, which was in good agreement with previous reports [25-27]. The primary mass loss at the range of 100-200 °C is assigned to the evaporation of adsorbed water and the later decomposition is ascribed to the depolymerization of both PVDF and CT as organic molecules. The weight loss registered for PET-PVDF-OM at the range of 300-400 °C, indicating the effect of Ox on the thermal properties (**Table S4**). Here, the initial decomposition temperature of PET, PET-PVDF-ZnO, PET-PVDF-TiO_2 and PET-PVDF-SiO_2 are 333°C, 335°C, 491°C and 480 °C, respectively. The high temperature at maximum weight loss rate can also be found for these hybrids and the solid residues PET-PVDF-ZnO, PET-PVDF-TiO_2 and PET-PVDF-SiO_2 at 600 °C are 66.3%, 65.8% and 84.5%, respectively, showing again their good thermal stability, particularly for PET-PVDF-TiO_2 which was another confirmation of the good dispersion of TiO_2 particles.

…….. (Figure.6) ……..

3.5. Mechanical properties

As discussed above, the thermal behaviors and hydrophilicity are studied, and it is important to investigate the mechanical behavior of the composites. The results of the stress–strain are shown in **Figure. 7**. It is clear that all functional composites displayed an enhancement on the tensile strengths. The highest tensile strengths are obtained for the composite PET-PVDF-Ox-CT, whereas the lowest values are registered for unmodified PET. Here, the tensile strengths depend manly on the functionalization process, which cause some favorable influence on the

mechanical properties. The tensile strength of the PET-PVDF-Ox-CT is close to 10.20 MPa, which is adequate for nonwovens application. The tensile strength was increased from 2.30, 8.93, 9.81 to 10.19 for PET, PET-PVDF-SiO_2-CT, PET-PVD-ZnO-CT and PET-PVDF-TiO_2-CT, respectively. By comparing the results obtained for different OM, the modification with TiO_2 particles represented the higher tensile strength, as compared to the ZnO and SiO_2. This evidences the good dispersion and fixation of TiO_2 particles into fiber surface, which regenerate an improvement on the mechanical behaviors. Results are confirmed by the hydrophobicity and SEM analysis. Thus, it was found that addition of PVDF, Ox and CT enhanced highly the mechanical properties of the resulting composite. According to the data obtained from the mechanical test, the increase in the hardness can certainly be attributed to the surface compatibility and the presence of the reinforcement nanoparticles (**Table. 2**). In other words, the nano-size of both reinforcing particles and PVDF/CT increased the interfacial contact between the particles and the fiber, leading to hardness elevation. As seen, the as-synthesized PET-PVDF-Ox-CT composite sample displayed 70% higher strength than the pristine sample. Interestingly, Young's modulus a PET-PVDF-TiO_2-CT composites demonstrates the higher resistance (154.19 MPa). It was found that addition of PVDF/TiO_2/CT, Young's modulus increased, suggesting the reinforcing effects of TiO_2 were stronger than those of ZnO and SiO_2, due to the large distribution of particle into fiber surface. In all of the cases, the incorporation of PVDF/Ox/CT resulted in an increase of the storage modulus for all composites. However, PET-PVDF-TiO_2-CT showed the higher elastic stress (10.19 MPa) than the other counterparts, confirming again the significant performance of PVDF, TiO_2 and CT for PET functionalization.

Since the presence of PVDF on the surface of PET-PVDF-Ox-CT increases significantly the hydrophobicity, the formation of intermolecular bonding between PET and Ox-CT can facilitate the stress transfer, producing increases on the mechanical stress. These facts reflect

the role of PDVF, which was attributed to the interfacial adhesion of coupling agent that could transform the inorganic surface from hydrophilic to hydrophobic nature. Thus, PET-PVDF-Ox-CT composite provides a great improvement of mechanical properties.

…….. (Figure.7) ……..

…….. (Table.2) ……..

3.6. Role of PVDF and oxides on the mechanical properties

Direct impregnation of Ox on PET sample results in limited improvement of the Young Modulus. So, we estimated that besides on the above results, the Ox and CT as additives have a key role in the improvements of the mechanical properties. Here, chitosan played and interesting role not only for the mechanical properties reinforcement, but also to ensure and maintained the Ox at the surface fiber during the employments. In addition, the surface compatibility between all components was also responsible for the significantly enhanced mechanical properties. Regarding to the values registered for PET-PVDF-TiO_2-CT, the mechanical properties should be closely dependent on the interaction between polymer matrix CT/PVDF and TiO_2, which evidences the compatibility and link between the components. Hence, the air voids (AV) have a negative effect on the mechanical properties. In presence of PVDF, we observed a large difference between PET-PVDF-SiO_2-CT, PET-PVDF-ZnO-CT and PET-PVDF-TiO_2-CT is due to the changes on the amount of AV presented for each sample [28]. In addition, lots of microvoids were created on the outer surface during the fabrication process, whereas there are visible changes in the cross-section. Herein, the heating pressure was of great importance, which drastically decreases the AV. Thus, the differences between all composites are explained in term of the Ox density present on the fiber surface. Consequently, PET-PVDF-TiO_2-CT presents the lower amount of AV, as high density of TiO_2 particles were immobilized, as compared to the other counterpart ZnO and SiO_2 **(Scheme.2).** Additionally, the differences in AV confirmed the strong interaction between

PVDF and Ox at the fiber interface, which generates the formation of air voids. Therefore, the improvement on the mechanical properties can be attributed the good surface compatibility PVDF/TiO_2/CT elements, which reduce the AV formation during the fabrication, particularly for PET-PVDF-TiO_2-CT.

…….. (Scheme.2) ……..

3.8. Effect of oxides on mechanical properties and proposed mechanism

TiO_2, ZnO and SiO_2 oxides were used in this study to clearly identify the effect of metal on mechanical properties (**Tables.3**). Results demonstrate that all oxides increased mechanical properties. Particularly, TiO_2 appeared to be more effectively, as compared to the other Ox. This allows that Ti metal present a strong oxidation promoter while the parent metal had a good compatibility with the other additives like PVDF and CT. Thus, it is worth mentioning that composites containing TiO_2 are still interesting than or closes to that for ZnO and SiO_2, in mechanical properties [29].

This indicates the high amount of TiO_2 loaded on PET fiber, which can be attributed to the texture parameters such as the surface area. This must involve strong interactions of the terminal OH groups from PET with titanium particles at the expense of PVDF-TiO_2. Thereby, this was a clear evidence of the key role of Ox fixation, especially for$VTiO_2$ in composite stabilization. Consequently, the stabilization resulting by the addition of OM induced visible increases on the thermal and mechanical properties. However, the surprisingly higher thermal stability noticed for PET-PVDF-TiO_2-CT must be due to a more pronounced chemisorption of heat inside TiO_2 protected by organic moiety (PVDF/CT). To clearly demonstrate the role of the metal, additional attempts were performed and supported by soil release test. Except for silica, the stains are disappeared for TiO_2 and ZnO. As seen, the stains are completely released for the TiO_2 metal oxide, confirming again the high capacity of titanium atoms to

promote not only the strong interactions with the surface nonwoven but also the good compatibility of the resulting composite.

As discussed above, PET-PVDF-TiO_2 -CT presents a significant improvement on the result obtained on the mechanical properties of PET-PVDF-TiO_2-CT demonstrates a significant increase in tensile strength and yield strength. Contributions of these improvements were explained by the reinforcement induced from the addition of OM particles. This is due to grain dispersion eventually leading to the occurrence of potential load transfer. Herein the possible strengthening mechanisms related to the improvement on the mechanical properties was attributed to the high dispersion and dislocation strengthening, as evidenced by the decreases in AV and the thermal stability of PET-PVDF-TiO_2-CT composites [30, 31].

…….(Table.3)……..

3.7. Sustainable and wash fastness property

Since detachment of the additive elements from the PET nonwovens would reduce the mechanical, a good wash resistant property is one of the key criteria for our PET-PVDF-Ox-CT composites to be sustainable materials for practical applications. **Figure.8** showed the washing tests during three cycles. As seen, in washing process, no loss on the PET-PVDF-Ox-CT contents during the washing environment was observed. This demonstrates that Ox was strongly attached to PET even in washing bath. Moreover, the retained and trapped Ox inside the PVDF is satisfying for further washings to achieve durability may be up to three more cycles. In addition, PET-PVDF-TiO_2 and PET-PVDF-ZnO-CT were tested after wash resistance, and the results show that no visible changes can be observed. This can be explained not only by the strong covalent bonds between the Ox, PVDF and CT, but also the good compatibility between these elements during the preparation of composite. Interestingly, with severe washing in the detergent solution, the Ox retained on composites, presumably due

to growth of Ox inside the construction and pores of nonwovens fiber, during the fixation and heating process. This was confirmed by SEM-EDX and FTIR analysis, indicating the presence of Ti and Zn metals after four washing cycles of PET-PVDF-ZnO-CT and PET-PVDF-TiO_2-CT.

…….. (Figure.8) ……..

4. Conclusions

In this work, the influence of inorganic (TiO_2, ZnO, SiO_2) and organic (CT) moieties on the structure and mechanical properties of PET-PVDF/Ox/CT composite fiber was determined. SEM images revealed that oxides particles were well dispersed at the fiber surface. FT-IR analysis confirmed the good deposition of CT into PET-PVDF/Ox. DSC tests revealed the improvements on the thermal stability. It was found that tensile strength and strain of PET nonwovens were enhanced by PVDF/Ox/CT incorporation. The fixation of PVDF/Ox/CT into PET fibers strongly enhanced the tensile strength and thermal stability of obtained materials. The good durability of the prepared composite was confirmed by wash fastens test, indicating solid functional nonwovens against washing. The developed treatment method can be used in textile industry to produce functional nonwovens with high mechanical resistance. The study provides a reference for production and structure optimization and contributes to the design of modern fisheries equipment and engineering.

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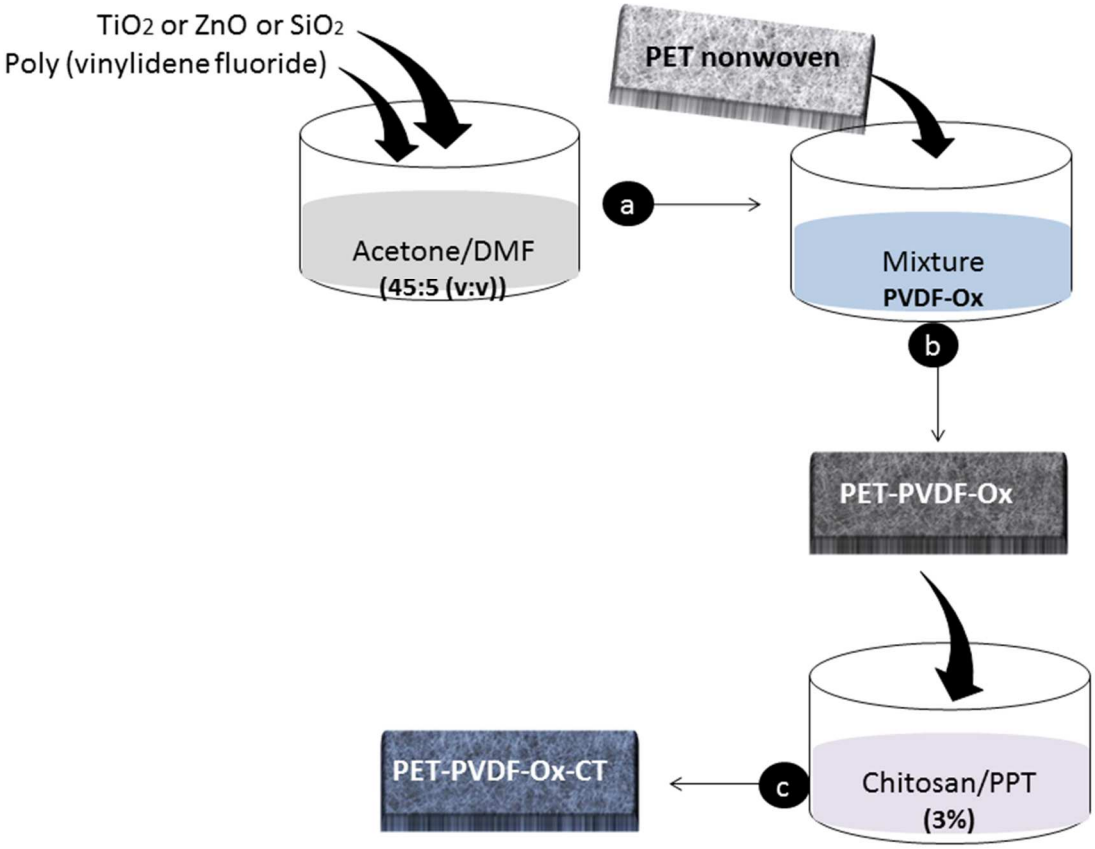
List of Figures

List of tables

Scheme.1


TiO2 or ZnO or SiO2
Poly (vinylidene fluoride)
PET nonwoven
Acetone/DMF
(45:5 (v:v))
a
Mixture
PVDF-Ox
b
PET-PVDF-Ox
Chitosan/PPT
(3%)
c
PET-PVDF-Ox-CT

Scheme.2

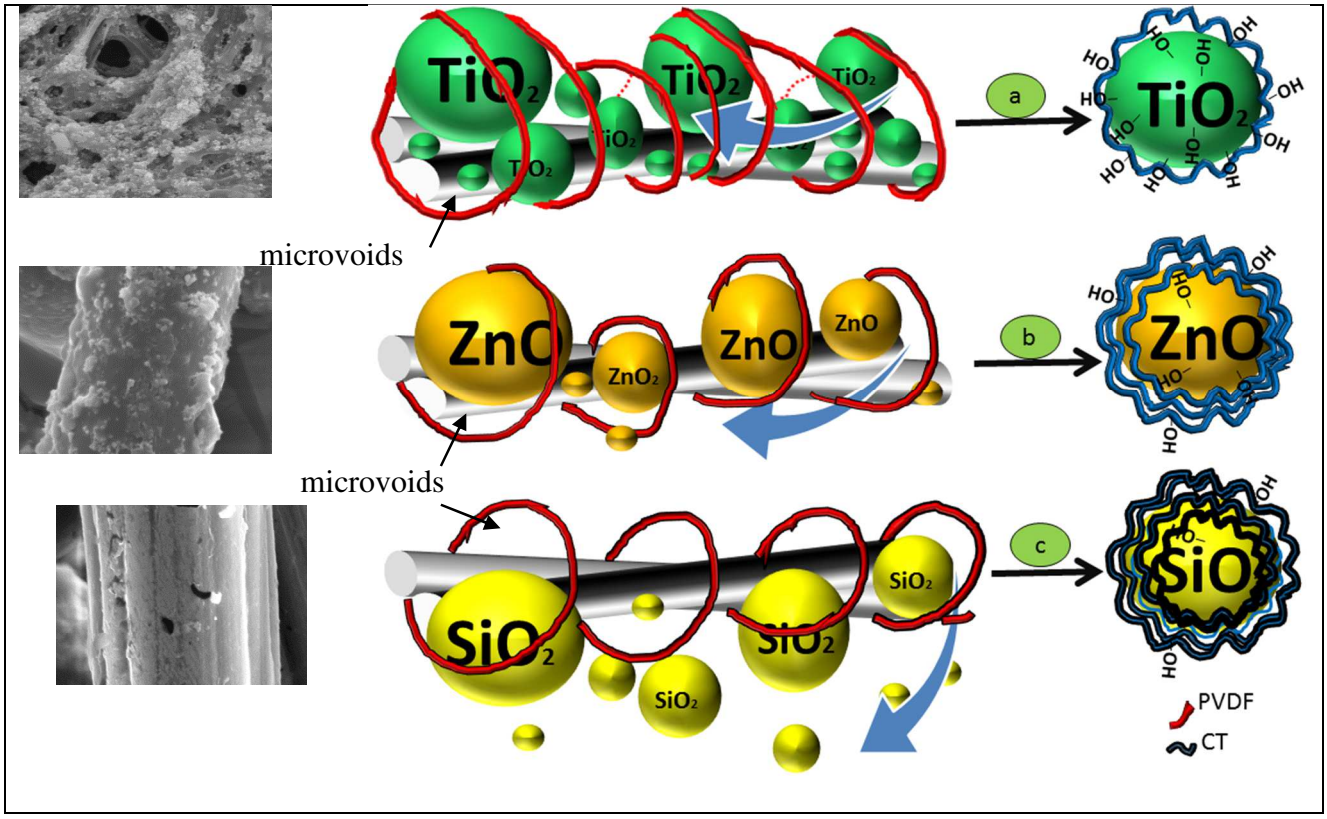


Figure.1

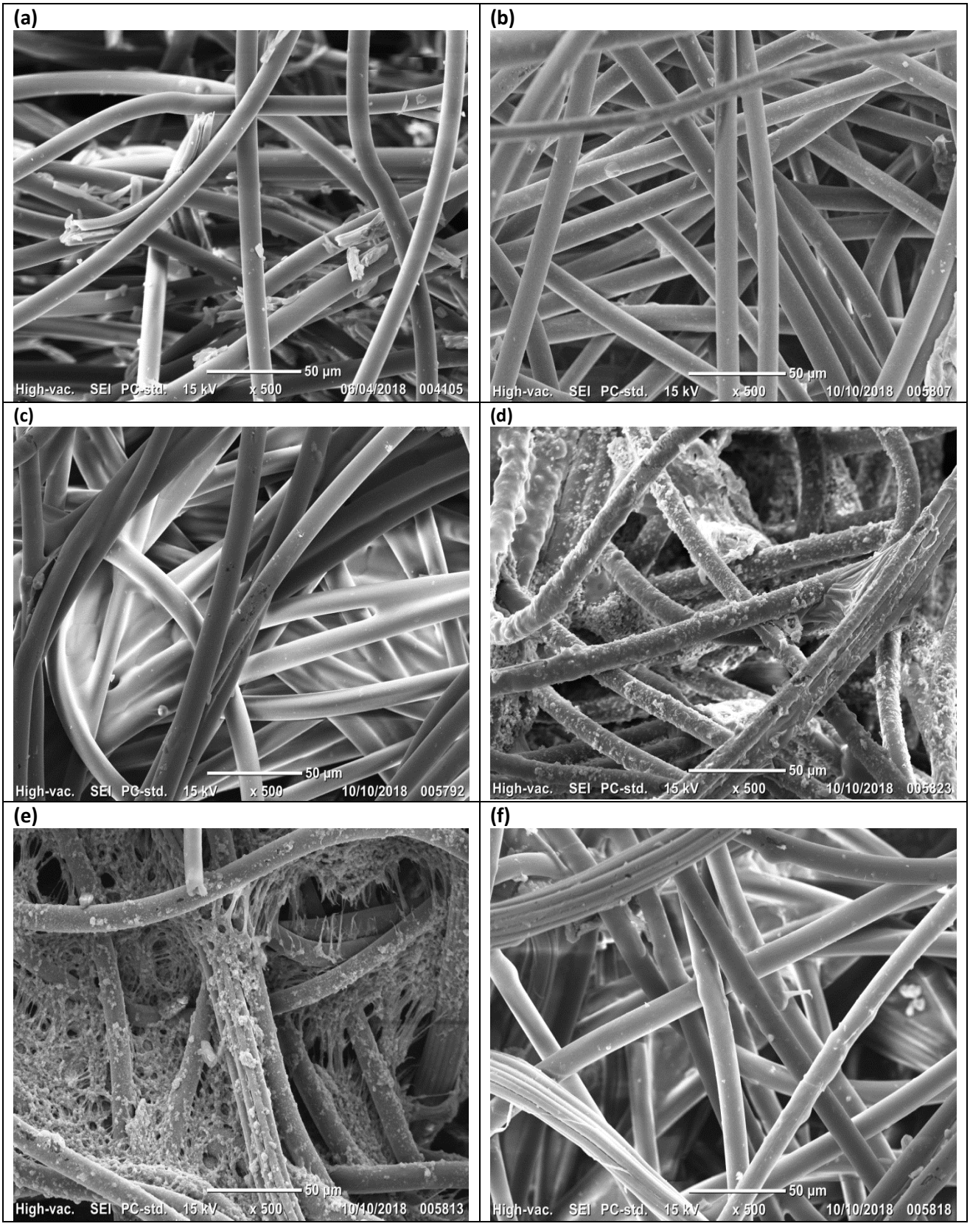

(a)
50 µm
High-vac. SEI PC-std. 15 kV x 500 06/04/2018 004105
(b)
50 µm
High-vac. SEI PC-std. 15 kV x 500 10/10/2018 005807
(c)
50 µm
High-vac. SEI PC-std. 15 kV x 500 10/10/2018 005792
(d)
50 µm
High-vac. SEI PC-std. 15 kV x 500 10/10/2018 005823
(e)
50 µm
High-vac. SEI PC-std. 15 kV x 500 10/10/2018 005813
(f)
50 µm
High-vac. SEI PC-std. 15 kV x 500 10/10/2018 005818

Figure.2

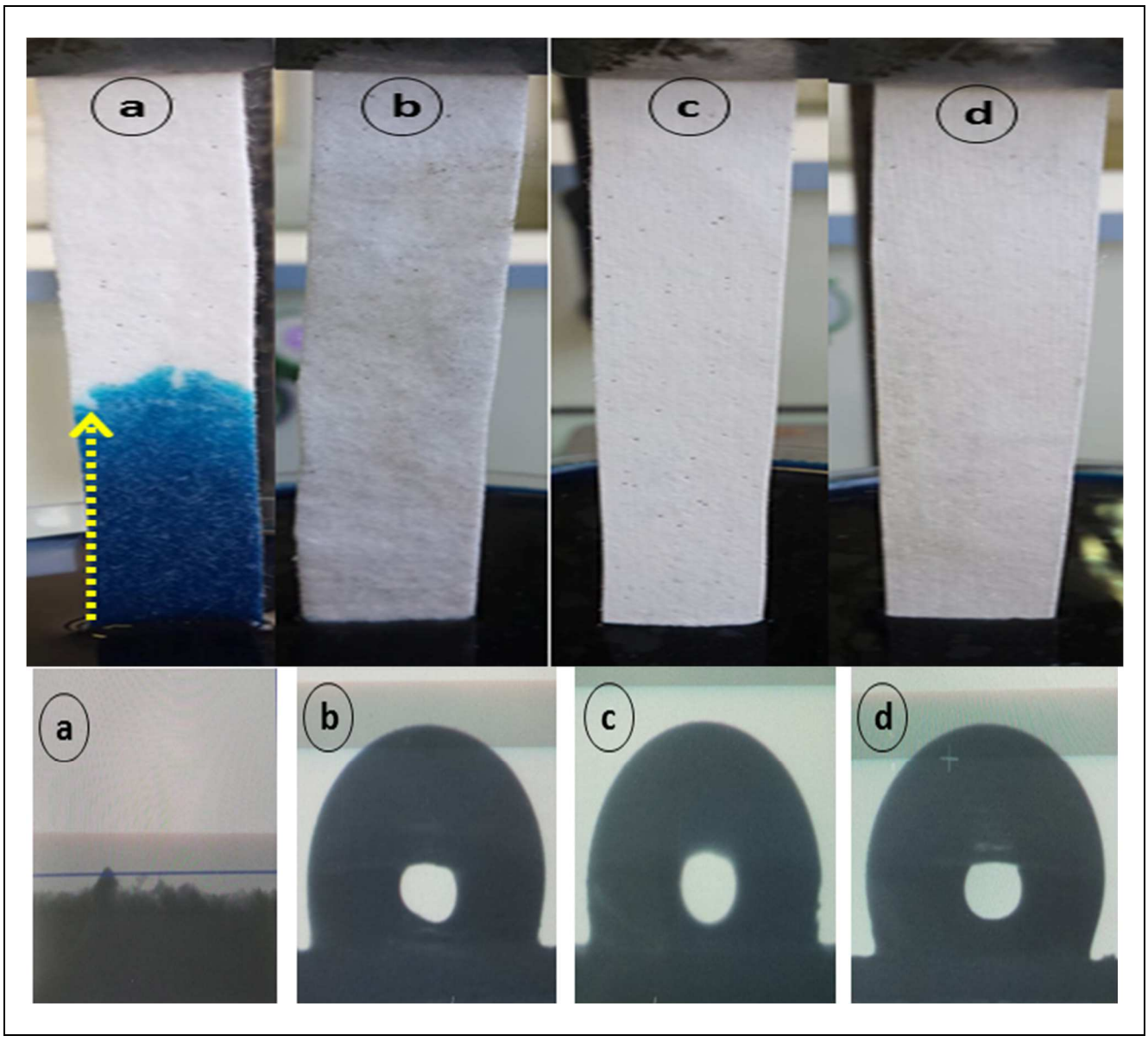


Figure.3

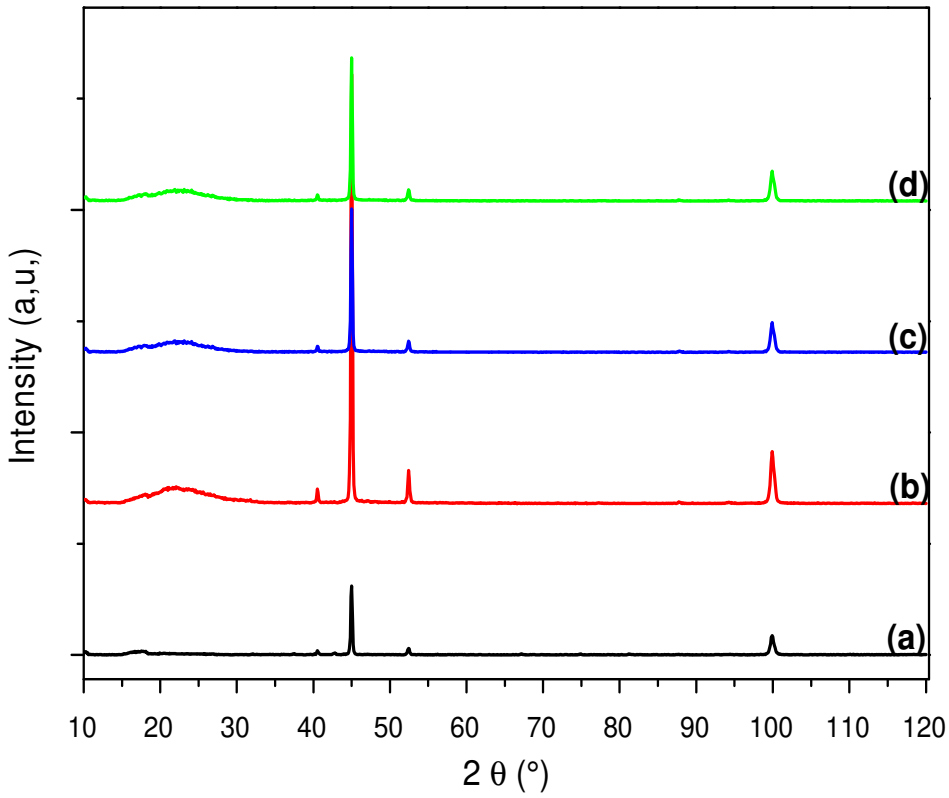
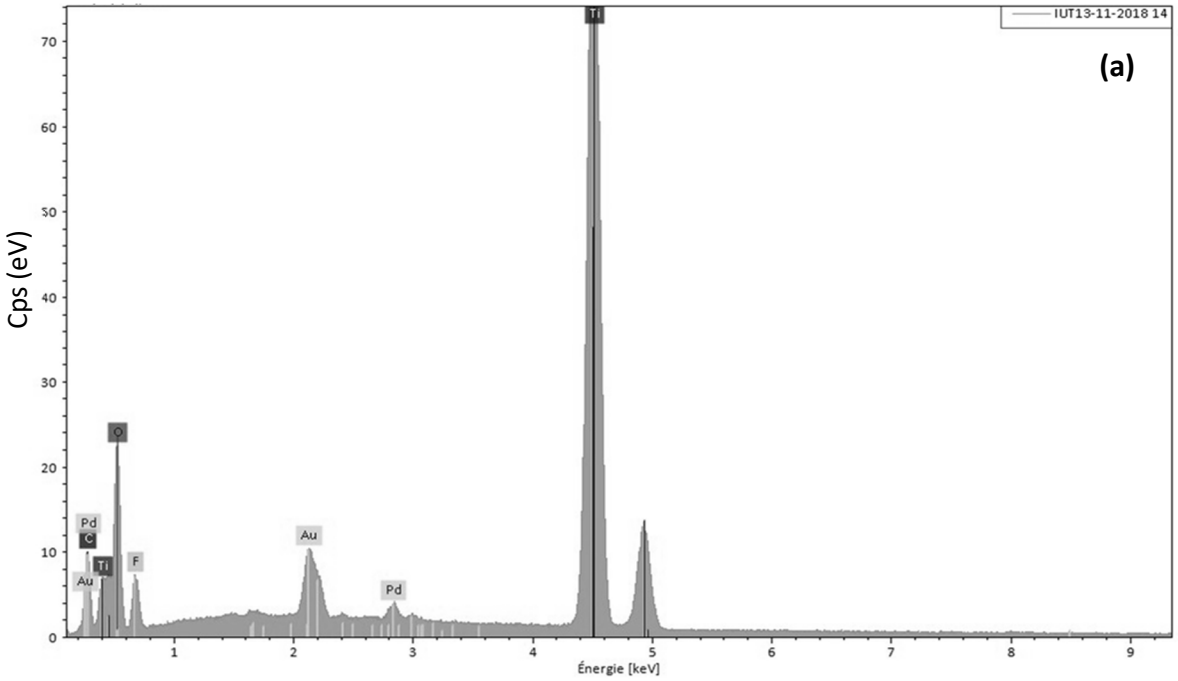
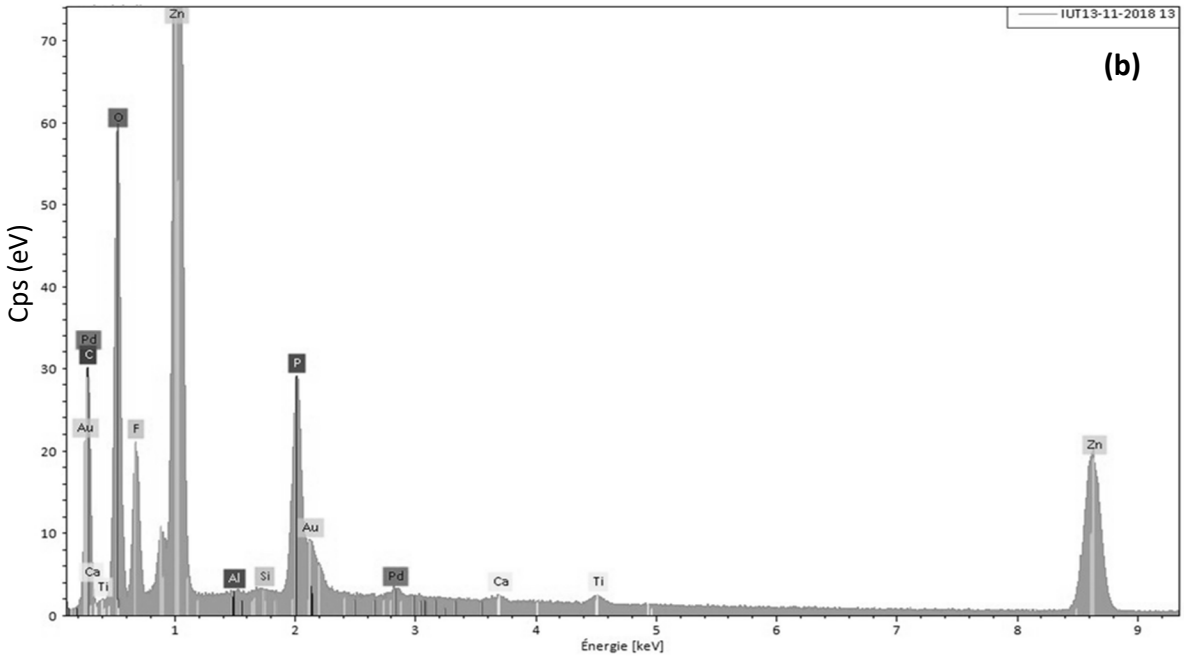


Figure.4


IUT13-11-2018 14
(a)
Cps (eV)
Énergie [keV]
Ti
O
Pd
C
Au
Ti
F
Au
Pd


IUT13-11-2018 13
(b)
Cps (eV)
Énergie [keV]
Zn
O
Pd
C
Au
F
P
Au
Zn
Ca
Ti
Al
Si
Pd
Ca
Ti

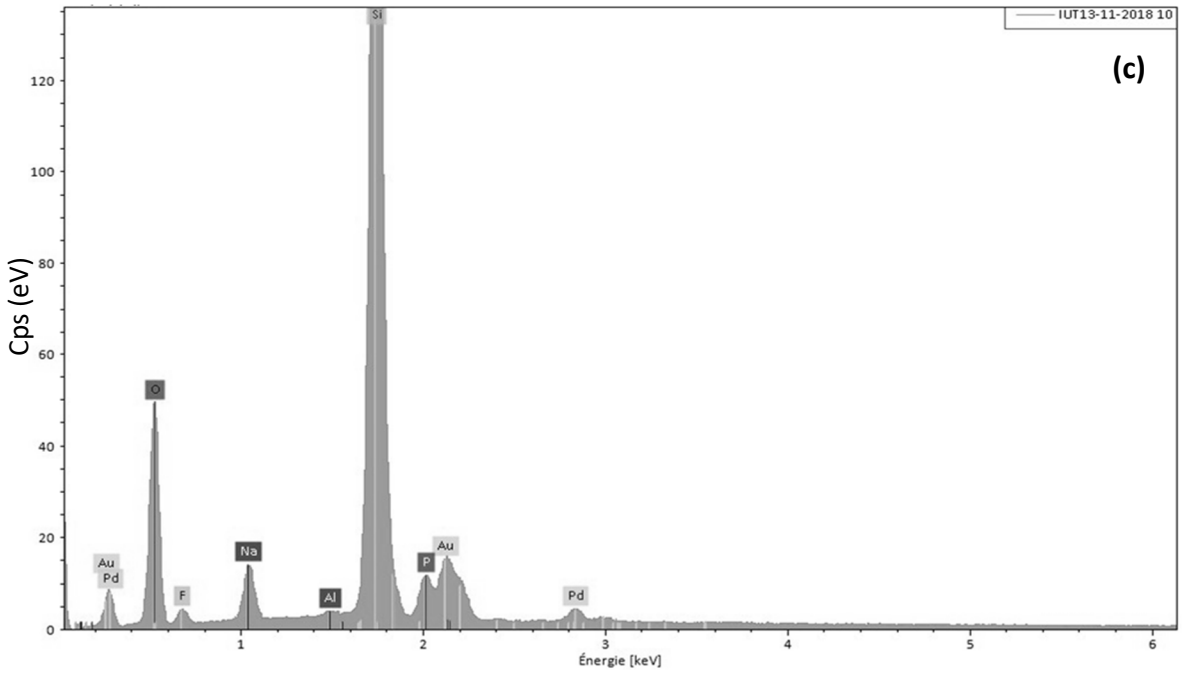

IUT13-11-2018 10
(c)
Cps (eV)
Énergie [keV]
Si
O
Na
Al
P
Au
Pd
F

Figure.5

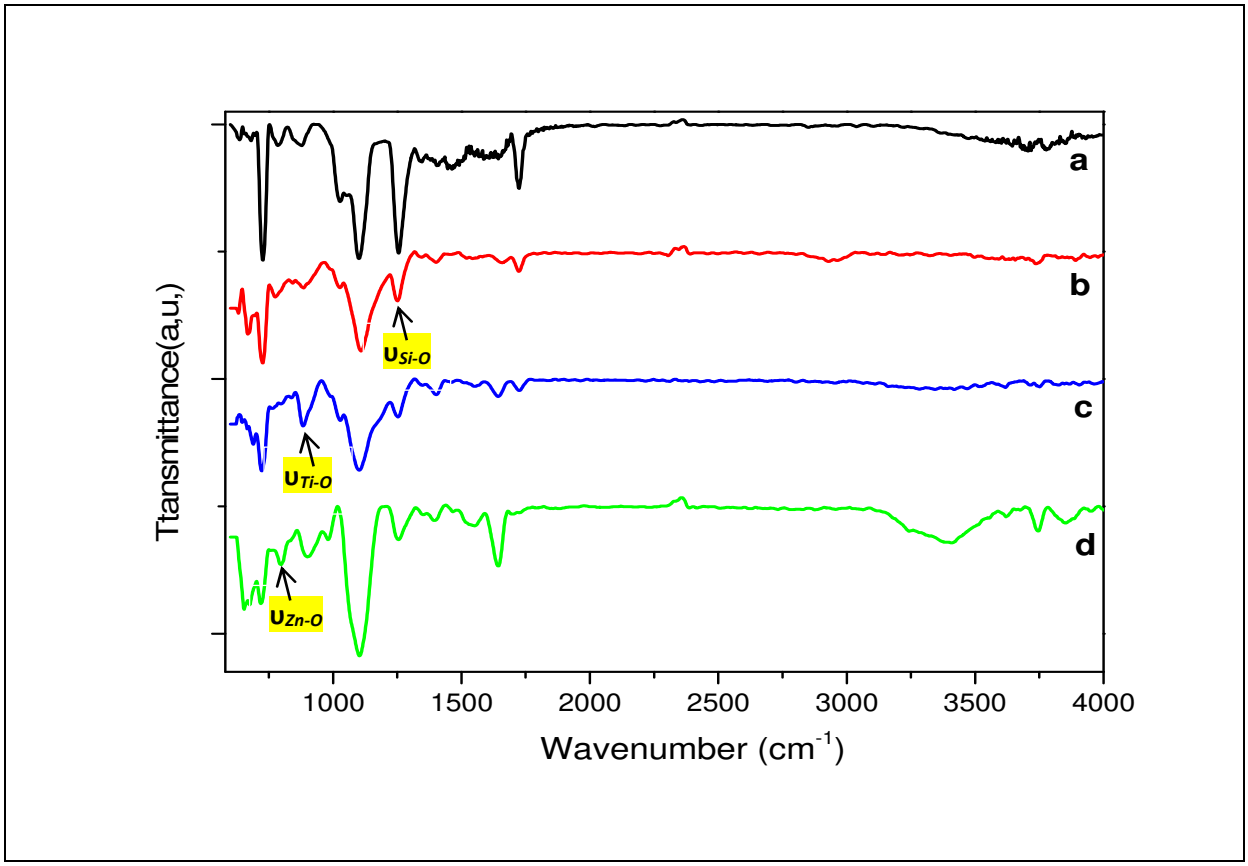

Ttansmittance(a,u,)
a
b
c
d
U_{Si-O}
U_{Ti-O}
U_{Zn-O}
1000
1500
2000
2500
3000
3500
4000
Wavenumber (cm^{-1})

Figure.6

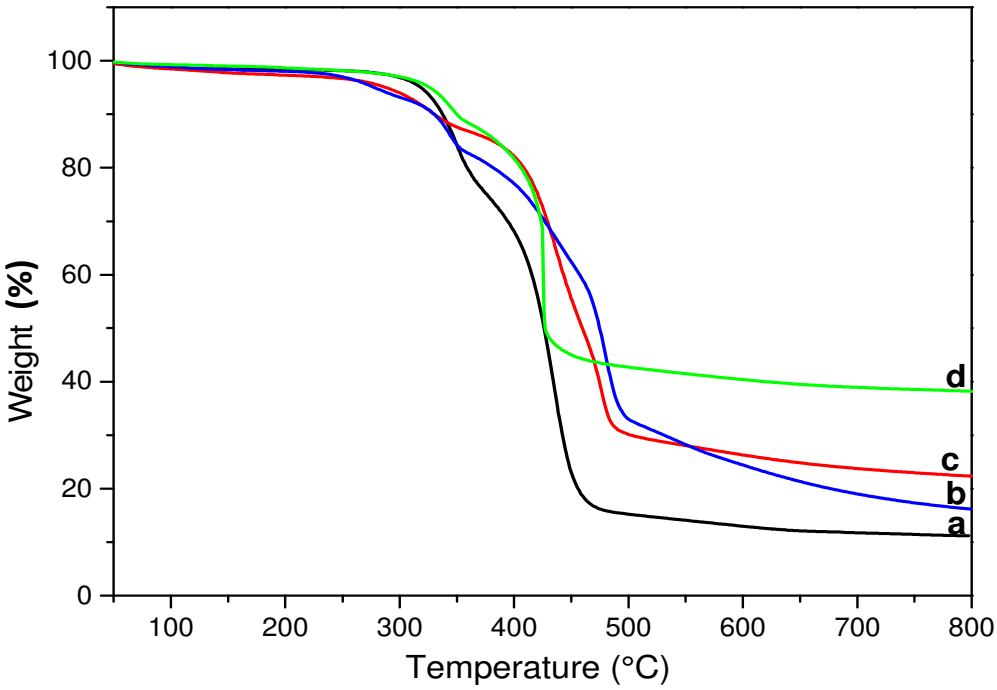

Weight (%)
Temperature (°C)
100
80
60
40
20
0
100
200
300
400
500
600
700
800
a
b
c
d

Figure.7

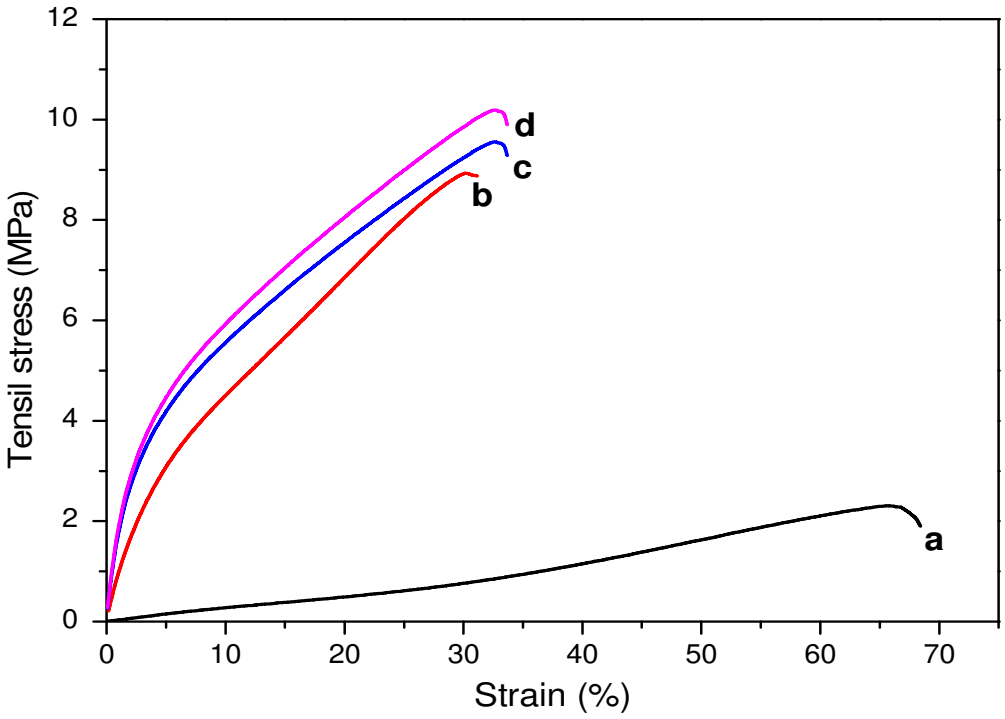


Figure.8

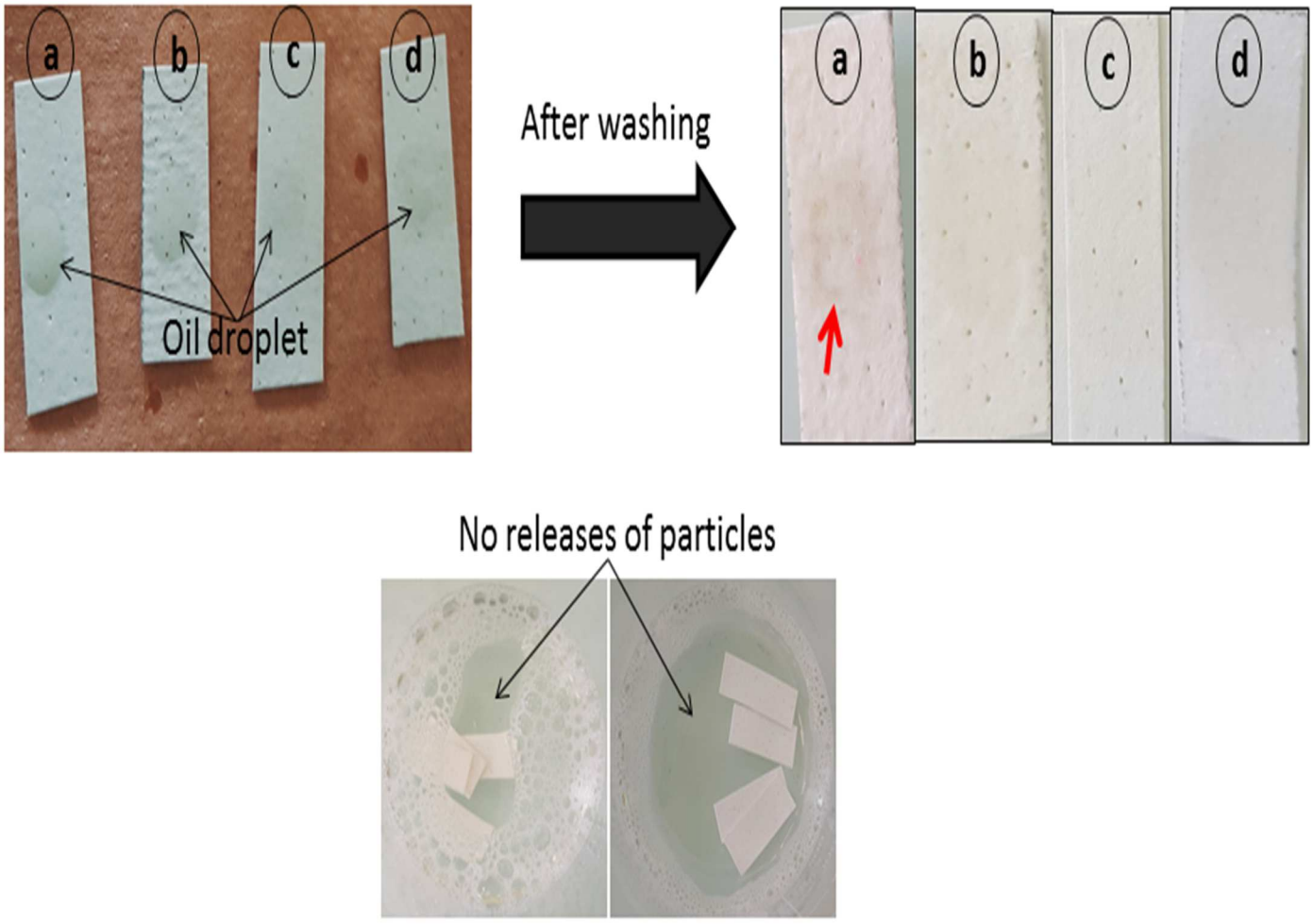

a
b
c
d
Oil droplet
After washing
a
b
c
d
No releases of particles

Table.1

Samples	Contact angle Θ (°)			
	1 min	5 min	30 min	60 min
PET	2	0	0	0
PET-PVDF-SiO_2-CT	110	110	108	103
PET-PVDF-ZnO -CT	120	115	114	114
PET-PVDF-TiO_2-CT	111	109	105	101

Table.2

Samples	σ* (MPa)	E* (MPa)
PET	2.30	0.50
PET- PVDF- SiO_2-CT	8.93	73.00
PET- PVDF-ZnO-CT	9.81	127.00
PET- PVDF-TiO_2-CT	10.19	154.00

* σ and E where determined according to ISO 9073-3 norms.

Table. 3

Samples	**σ(MPa)**	**E (MPa)**
PET	2.30	0.50
PET-PVDF	8.70	54.00
PET-CT	3.90	9.00
PET- SiO_2	4.47	8.00
PET-PVDF-SiO_2	9.66	18.00
PET-TiO_2	11.40	27.00
PET-PVDF-TiO_2	9.88	32.00
PET-ZnO	8.64	20.00
PET-PVDF-ZnO	9.44	24.00

Graphical abstract