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The new generation from biomembrane with green technologies for wastewater treatment

Ahmed M. El-hadi *^,1, 2^ and Hatem R. Alamri[3]

[1] Umm Al-Qura University, Faculty of Applied Science, Department of Physics, Al-Abidiyya, P.O. Box, 13174, Makkah 21955, Saudi Arabia

[2] Higher Institute of Engineering and Technology, Department of Basic Science, El Arish, North Sinai 9004, Egypt

3 Physics Department, Jamoum University College, Umm Al-Qura University, Makkah 21955, Saudi Arabia

* Correspondence: amabdelatti@uqu.edu.sa;

Tel.: +669541042942

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Abstract: Water pollution in developing countries affects the public health of humans and the environment. It is therefore essential to develop environmentally friendly biopolymer, sustainable and low-cost membranes. Biopolymer nanofiber membranes are made by an electrospinning process of polylactic acid (PLLA) with additives. The main objective of this study is to manufacture biodegradable nanofiber membranes for use in filtering the suspended elements in wastewater at the level of drinkable or in agricultural fields. It is known that PLLA is brittle and therefore it is difficult to apply in industry. To solve this problem and enhance its flexibility. Flexible biopolymer polypropylene carbonate (PPC) and plasticizer are the addition in PLLA to reduce its glass transition and enhance its crystallization by adding Poly(3-hydroxy butyrate) PHB. In this work, 20 wt% of PPC was added to PLLA matrix to improve its elasticity and elongation at break. DSC shows that the addition of PPC, PHB, and TEC did affect the thermal properties like T_g, T_{cc} and T_m of the PLLA blends. The position of the T_g, T_{cc}, and T_m is shifting, the consequence the chain mobility is increased, therefore the crystallinity is enhanced. Electrospun fibers of PLLA/PPC/PHB/TEC were successfully manufactured. Tensile tester showed the increase in elongation at break of PLLA blend films, the elongation at break increases by 285 times. It observed with the increasing the elongation at break, a decrease in stress strength. After improving the mechanical properties with the higher elongation at break values, this blend is optimal for filtrations process.

Keywords: PLLA nanofibers membranes; electrospinning, PPC; PHB; plasticizer; biopolymer blends; water purification.

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1. Introduction

There is now a rising demand for biopolymers, which are manufactured from renewable source materials and are biodegradable and do not cause any problems for the environment [1]. Poly(L-lactide) (PLLA) has great consideration because it is biodegradable, non-toxic to the environment and the human body [2]. PLLA has a brittleness with the very low elasticity which limits its application as a general-purpose plastic. It is known that the brittle of PLLA due to slow crystallization rate, due to the formation of a large spherulite with cracks [3] and higher glass transition (Tg is equal 60 ^{o}C), making its practical applications in the industry limited. Therefore, many efforts have been made to improve the crystallization process of PLLA by adding PHB as the bio macromolecules [1, 4]. Physical polymer blends [5 - 9] are one of the most economical methods to develop new polymers with improved physical properties for industrial applications. Because the miscibility of polymer blends is one of the major effects on properties of blends, therefore the focus of miscibility from polymer blends has increased much attention [10]. It is one of the most effective and promising methods to increase the crystallization rate for PLLA, as well as adding the plasticizers [1, 11] to reduce the Tg. PLLA has been selected for biomedical application because of its full biodegradability ability, its degradation products are non-toxic, bio-compatibility. PPC is too biodegradable and excellent mechanical properties like high flexibility, high elongation at break and toughness [12]. Among the most promising polymers are PLLA and PPC. A combination of PLLA, PPC, PHB, and plasticizer at different ratios as biopolymer blends for obtaining suitable properties to use in tissue engineering, food packaging applications [4] and filtration process. It is possible to produce textiles made of nanofibers for several application, especially in the field of filtering technology with very thin diameter [13-16]. The research project is based on the development of nanofibers membrane from PLLA, PPC, PHB, and TEC that are complete biodegradable. Mechanical properties of these PLLA blends are the important criterion to determine its applications in industry special in bio-filter for water treatment. The mechanical behavior of pure PLLA and its blend was calculated in order to examine the effect of additives in PLLA blend. Plasticizers act like diluents when mixed with the polymer. Plasticizers have a low molecular weight, which leads to an increase the free volume between molecules chains. As a result, the glass transition temperature is lower, increased the elongation at break and reduction in tensile strength [17].

Water is one of the most natural important human resources due to the large people growth in developing countries, which causes changes in the lifestyle. The request for drinking water and all purposes in the house as well as harvest large amount of wastewater from home or factories. This caused a big problem in the pollution of water resources when it is cast into rivers, seas or in the groundwater causing the serious health problem in most developing countries for humans and animals. One of the most important of these challenges raised by that people grow, therefore the government must be provided fresh water for all these people. The consequence, the need for innovative new technology to improve the treatment of drinking water

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purification and sewage treatment. A membrane technology of nano-fiber which help in improving the efficiency of the elimination contaminations in the water [18-20].

One of the most important methods to produce nanofibers of various sizes and shapes of biopolymers is electrospinning because of its fibers with different diameters and large surface area to its volume ratio which makes it capable of industrial applications such as solar cells, fuel cells and biosensors as well as medical purposes such as drug delivery, tissue engineering, and surgical suture. Electrospinning [13,14] is an easy, fast and cost-effective process for producing fibers from 3 µm to 500 nm. In the electrospinning process, a drop of the polymer solution is placed at the end of a needle by a syringe pump with small flow rate. The voltage is then applied to the polymer solution, making electrical charges on the tip of the needle to overcomes the surface tension and is pulled by the high voltage, then at the end are collected on the ground collector to the manufactured membrane. By this process, the size of the pores of the membrane is very small less than 1 nm to output the larger particles than the water molecules.

The aim of study investigates the effect of additives PHB, PPC and plasticizer with different weight percentages on toughness, flexibility and the biodegradation of PLLA. The main purpose of this project is to manufacture PLLA nanofibers membrane for purification the water and removal of all contaminants from wastewater by a strong motor to flow water in the membrane, so it must be the mechanical properties of the nanofibers membrane good. The blends were characterized by differential scanning calorimetry (DSC), thermogravimetric (TGA), scanning electron microscopy (SEM) and tensile testing and. The PLLA films were mechanically tested to obtain its elongation at break and stress strength.

2. Experimental

2.2 Materials and blend preparation

PLLA with molecular weight Mw = 2.2 3 x 10^5 g/mol and PPC with average Mw = 0.5 × 10^5 by GPC, PHB with Mw = 2.3 3 x10^5 g/mol, and TEC were provided by Sigma-Aldrich Chemicals Ltd.

The solutions for casting blends were prepared by dissolving all component in dicholoromethane (DCM), then poured in petri dish, after evaporation the solvent, the obtained films were dried in oven at 60 °C for 24h. The samples of PLLA/ PPC/ PHB / TEC blends were prepared with different weight ratios as follows in table 1.

The blends prepared in table 1.

		PLLA	PPC	PHB	TEC
1	blend 1	55	20	10	15
2	blend 2	50	20	10	20
3	blend 3	45	20	10	25
4	blend 4	40	20	10	30

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2.3 Methods

2.3.1 Differential scanning calorimetry (DSC)

Thermal analysis was carried out from -50°C to 200°C at heating and cooling rates of 10°C min^{-1} using a differential scanning calorimeter (Shimadzu-DSC 50, Japan). Samples of weight 400 ± 100 µg were sealed in aluminum sample pans and were kept under a dry nitrogen atmosphere. The analysis of the DSC curves was carried out for the second heating run data to determine the glass transition temperature (T_g), the melting temperature (T_m), and the melt crystallization temperature (T_c).

2.3.2 Mechanical analysis

The mechanical properties of PLLA blends film were tested using a Shimadzu universal testing machine equipped with a 10 kN load cell and interfaced with a computer. All samples like dog bone specimens were cut in a dumb-bell shape (Dumb Bell Ltd SDL-100 Japan) with dimension (length 80 mm, width 6 mm and thickness 0.1 mm. Tensile tests were performed at room temperature, at a crosshead speed of 5 mm·min^{-1} agreement with ASTM D882, Five specimens of each formulation were tested and the average values are described. From the relation between stress σ (in Pa) and elongation ε (in %), $\varepsilon = (L_0 - L)/L$, L_0 = original length, L = length after elongation. At the end, the fracture surface of the electrospun samples was investigated by SEM.

2.3.3 Thermogravimetric Analysis (TGA)

Thermogravimetric for the pure PLLA and its blends were tested by using a TGA (Q500) instrument. Samples weight between 10 mg to 20 mg were heated under an air flow (90 mL/min) from room temperature to 600 ^{o}C with the heating rate of 20 ^{o}C/min.

2.3.4 Electrospinning Equipment

PLLA blends solved in different chemical solvents with different concentrations and located in a plastic syringe (10 mL) that attached to a needle with an inner diameter (ID) of 1.3 mm. Electrospinning was done at room temperature with a high-voltage power supply from USA (model NO. ES60P-20W, Gamma High Voltage Research, Orlando, FL, USA). All fibers were pure PLLA and their blends collected on the aluminum foil. A syringe-pump (No. BS-9000-USA, Braintree Scientific, Braintree, MA, USA) was used to feed the polymer solutions into the needle tip. The electrospun fibers were collected on a grounded collecting plate. When the electrical voltage increases, the fiber diameter is reduced due to the increased elongation of the jets by the electric field. It also causes an increase in the flow mass of the polymer.

2.3.5 Scanning Electron Microscopy (SEM)

The surface morphology of the PLLA blends nanofibers was observed using a scanning electron microscope (JSM-6360LA, JEOL Co., Boston, MA, USA) at an accelerating voltage of 3 kV. The samples were sputter-coated with gold for 120 s to a thickness of 2–3 nm using a sputter coater (EMITECH K550X, Kent, UK). Images of

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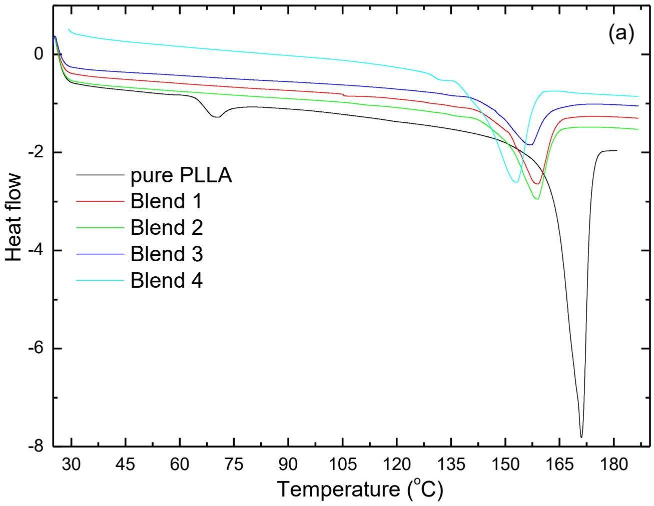
several sample fibers were obtained using SEM to measure the fiber diameter. The samples are coated with gold.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC) analysis

The miscibility of PLLA/PPC/PHB with plasticizers blends was measured by DSC from the first run, the cooling run from melting and second run from cooling at a heating rate of 10 ^{o}C min^{-1}. DSC curves verified for pure PLLA, their blends are shown in Fig. 1. Pure PLLA demonstrations a glass transition temperature T_g at around 61 ^{o}C [17] and melting peak (T_m) at 188 ^{o}C. Pure PPC shows a T_g at around 30 ^{o}C [4]. At the first heating, T_g is obviously shown for pure PLLA, which indicates that it is amorphous, but the T_g of the blends appears unclear due to high of crystallite form by addition of PHB to PLLA matrix. Through the first heating, the rearrangement of the macromolecules becomes crystallized, therefore sharp melting peak was presented, It can be observed that the T_g decreases with increasing plasticizers content for blend 1 at 27 ^{o}C, blend 2 at 27 ^{o}C, blend 3 at 21 ^{o}C and blend 4 at 7 ^{o}C. It is known that the T_g of polymer blends is the standard for determining the miscibility. The cold crystallization temperature is found at 100 ^{o}C of for blend 1, and shifts to 102 ^{o}C of for blend 2, at 92 ^{o}C of for blend 3, at 78 ^{o}C for blend 4. The melting temperatures of blends were calculated at 160 ^{o}C for blend 1, 160 ^{o}C for blend 2, 158 ^{o}C for blend 3 and 153 ^{o}C for blend 4, respectively. Addition of PHB and TEC has the influence on the position of the T_g, T_{cc}, and T_m. The decrease of T_g, T_{cc}, T_m lead to the increase of chain mobility, therefore the crystallinity is enhanced by the demonstration in Table 2. this depends on both PHB and plasticizer with the different ratio. The pure PLLA and its blends showed no crystallization during the quenching (cooling run with 20 ^{o}C min.$^{-1}$) from melting, consequently, they were completely amorphous due to rapid cooling to show only the T_g. Cold crystallization temperature Tcc has appeared only at second heating. PLLA and PPC with plasticizer exhibit a single T_g behavior during a cooling run and second run. It is observed shifting in the T_g, T_{cc}, and T_m, this means that there is some physical crosslinking between PLLA, PHB, and TEB.



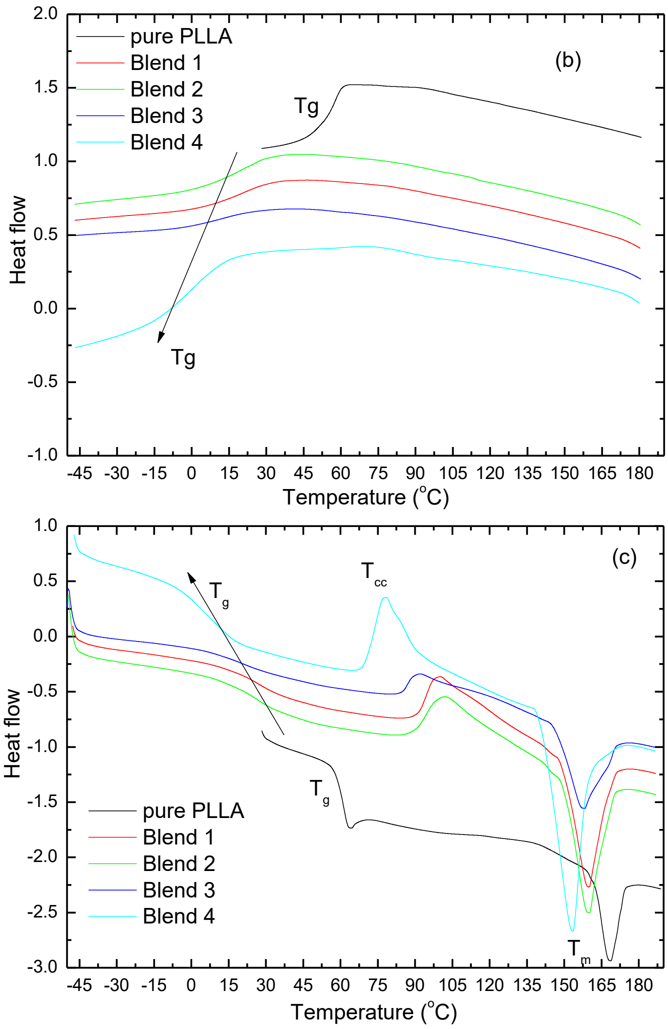


Figure 1. DSC of pure PLLA and its blends 1,2, 3 and 4; (a) the first heating run; (b) the cooling from melting and (c) the second heating run.

The crystallinity (X%) of PLLA and its blends was evaluated using Equation (1):

$$X = \Delta H*100 / (\Delta H_m^0 (1- \frac{\%\, wt\, filler}{100})) \qquad (1)$$

where ΔH_{cc} is the enthalpy of cold crystallization for the sample) or $\Delta H = \Delta H_m - \Delta H_{cc}$ (for second heating curves, as ΔH_m is the enthalpy of melting of the sample), ΔH_m^0 is the enthalpy of melting at 100% crystalline polymer matrix (93.0 J/g for PLLA [21] and % wt filler is the total weight percentage of PHB and TEC. After extracting the weight percentage of PHB and TEC these values correspond to the crystallinity of blends.

Table 2: Thermal properties of pure PLLA and its blends at different concentrations

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	Pure PLLA	blend 1	blend 2	blend 3	blend 4
T_g (°C)	61	27	27	21	7
T_{CC} (°C)	135	100	102	92	78
T_m (°C)	168	160	160	158	153
ΔH_m (J/g)	7.1	29	24	25	22
ΔH_c (J/g)	--------	14	11	7	9
X (%)	8	23	20	30	25

where ΔH_m, ΔH_{cc} and X (%) are the enthalpy of melting, enthalpy of cold crystallization and weight fraction of PLLA respectively.

3.2. Mechanical properties

It was measured the mechanical properties of the PLLA blends by the study of stress versus strain. Pure PLLA shows a brittle fracture and very low elongation at break 6 % and a high tensile strength 19 MPa, which is in agreement with the results [2,17, 22]. The stress-strain curves for PLLA blends are shown in Fig. 2 and the tensile strength (σ) and elongation at break (ε) are plotted in Fig. 2. It can be seen that as the weight percentage of additives in the blends are increased, the tensile strength decrease, i.e. tensile strength decreases from 11 MPa for blend 1 to 5 MPa for blend 4, The effect of additives content on the fraction of elongation at break of PLLA blend is shown in Fig. 2. The elongation of PLLA blends is improved with the addition of PPC, TEC, and PHB. The elongation at break in PLLA blends is increased from 158 % for blend 1 to 282 % blend 4. The tensile stress decreased from 19 to 5 MPa by increasing the plasticizer beside PPC and PHB with the ratio from 45 % to 60%. The decrease in the tensile stress of blends. This is due to the low stress of PPC. The combination of PPC with other additives in the PLLA blend improved the strain at break as compared to pure PLLA. It was observed that the elongation at break of film blend 4 was higher than the other blends 1, 2 and 3. The decrease in elongation at break of blend 1, as compared to blend 4, is related to the decrease the T_g, besides the shape of particle size of PPC. It was also found that the Tg of the PLLA decreased with increasing TEC percentage. A small amount of PPC (20%) has been added to improve the mechanical properties and larger quantity lead to immiscible blend [4]; i.e. when the content of PPC more than 30%, the blends became immiscible. Tensile test results indicate a significant improvement in the elasticity and ductility of PLLA blends, which are well associated with the decrease in T_g observed in DSC curves. The enhancement in the mechanical properties of PLLA blend film was attributed to the presence of PPC in the blend. the mechanical property showed that the entanglement of PPC chains can improve the mechanical properties of the blend film and electrospun fiber membranes by reducing the brittleness of pure PLLA.

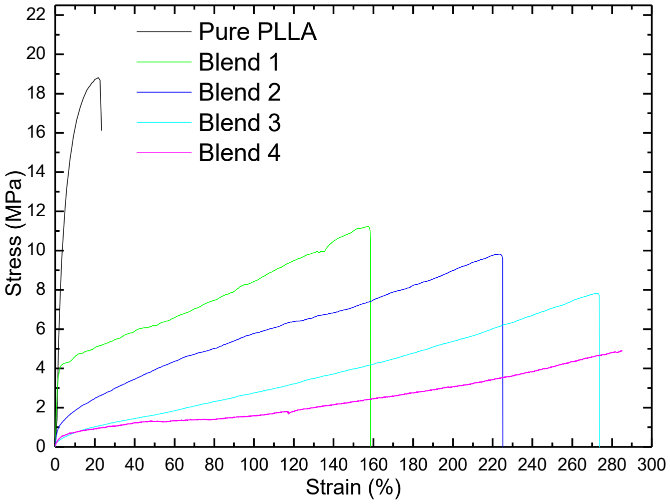


Figure 2. Mechanical testing of stress-strain for PLLA and its blends films at room temperature with speed 5 mm/min.

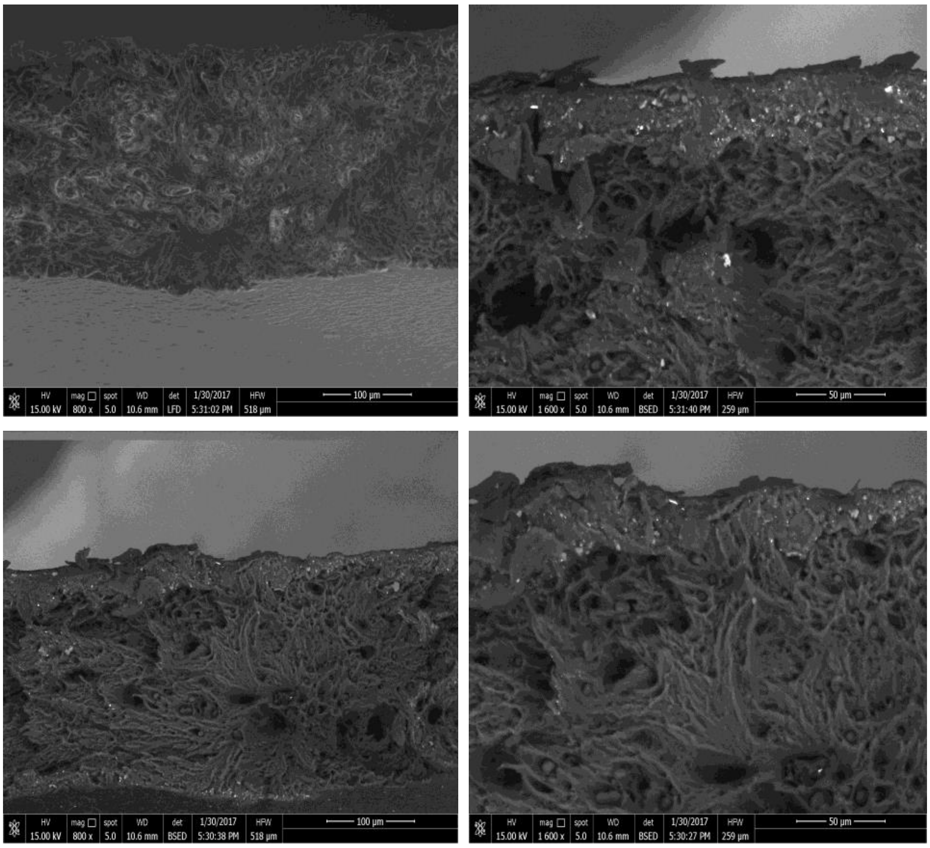
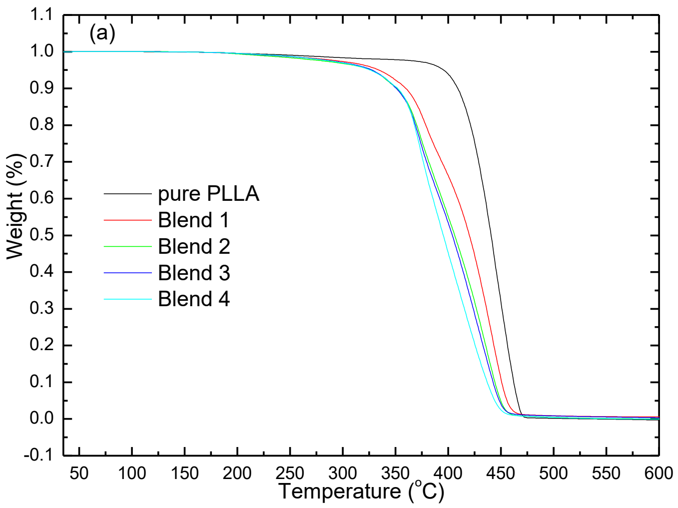


Figure 3. SEM picture of the fracture surface of blends 1 and 3 after tensile testing; (a, b) blend 1; (c, and d) blend 3

The fracture surface of PLLA blends of are given by SEM micrographs in Fig. 3. It observed that the fracture surface of PLLA blends had plastics deformation in the stress direction. It is known that a brittle fracture surface for PLLA during the mechanical test [17]. However, the PLLA blends showed different behaviors under tensile testing. The PPC particles act as stress factors on the elastic property in the PLLA matrix. Many particles with holes are observed on the fractured surface, and these voids are magnified along the stress direction, as shown in fig. 3. The fracture surface after the cold drawing process is rough and smooth, where many particles are observed in the holes and are clear with large plastic deformation. To conclude, the compatibility between the dispersed PPC phase in PLLA matrix in the blending process is necessary for toughness. SEM images of fractures of blends 1 and 3 can be seen in figure 3. It is found that The domain size of PPC between 1 to 5 µm, This means that PLLA and PPC are partially miscible. No larger domains are found in the PLLA matrix. Adding PPC, PHB and TEC did major changes in the elongation at break of PLLA.

3.3. Thermogravimetric analysis (TGA)

TGA play a very important role to determine the thermal stability of polymeric materials. It is a process in which material is decomposed by heating, which causes the breaking of bonds between the molecule. The thermal stability of PLLA, PPC, plasticizer, and their blends was investigated using thermogravimetric analysis (TGA). Pure PLLA was stable without major weight loss up to 415 °C, while its blends of PLLA showed a continuous decrease in weight loss 368 °C. Thermal properties of pure PLLA and its blend were investigated by thermogravimetry analysis (TGA). The TGA and DTGA thermogravimetric curves give information about the degradation of the polymeric materials. Fig. 4 (a) and (b) shows TGA and DTGA results, respectively of pure PLLA and its blends with PPC and plasticizers. From TGA curves in Fig. 4 (a), there are two major stage of breakdown the chain in blends. In region 350 ^{o}C as the first weight loss corresponding to breakdown of the chain PPC. The second weight loss in region 412 ^{o}C corresponding to decomposition of PLLA. As shown in Fig. 5 (b), pure PLLA has one decomposition peak at approximately 415 ^{o}C. After adding plasticizer and PPC, The decomposition temperature of the blends is the slight change when compared to pure PLLA, but its peak intensity decreases with increasing plasticizer content and PPC. The addition of plasticizer, PHB and PPC leads to a small decrease in the thermal stability of the PLLA blends. This degradation peak at 370 ^{o}C corresponds to the degradation of the PPC, PHB and plasticizers which has a lower thermal stability than pure PLLA.



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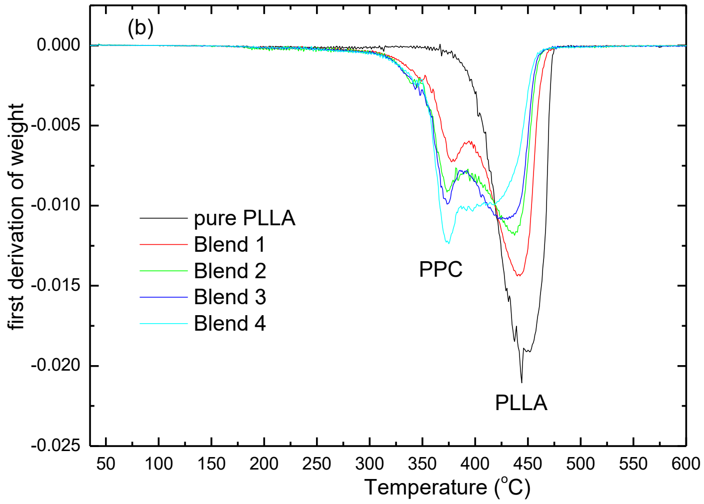

Figure 4. Thermogravimetric analysis of pure PLLA and its blends (a) thermogravimetric curves and (b) derivative thermogravimetric curves.

3.4. Fiber Morphology by Scanning Electron Microscopy (SEM)

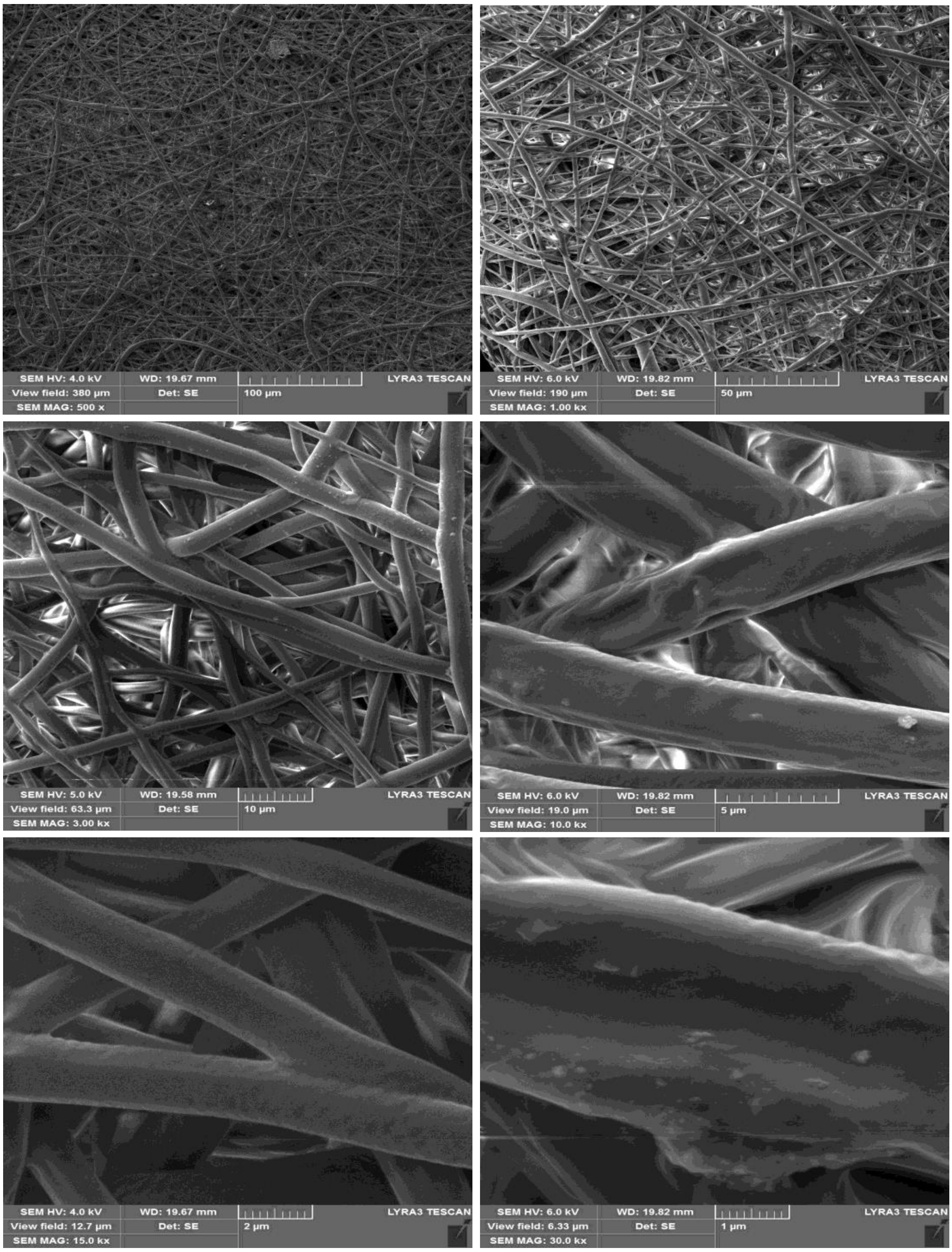

Figure 5. SEM micrographs of electrospun mats of blend 3 at different magnifications

Electrospinning is obtained when a great voltage is applied to a polymer with solvent. A polymer solution has placed a syringe connected to the positive electrode and the syringe pump is moved to push the solution. The collector is connected with the negative pole of the ground. The application of the large electric field to pull the solution from needle to very small jet and elongated, and then the solvent is evaporated, which leads to the formation of nanofibres. Figure 5. shows the morphologies of PLLA/PPC/plasticizers electrospun fibers. the obtained fibers have, uniformly, smooth and cylindrical morphology with a diameter between 1, 2 um and 500 nm and without beads.

3.5. Biodegradability test in wastewater

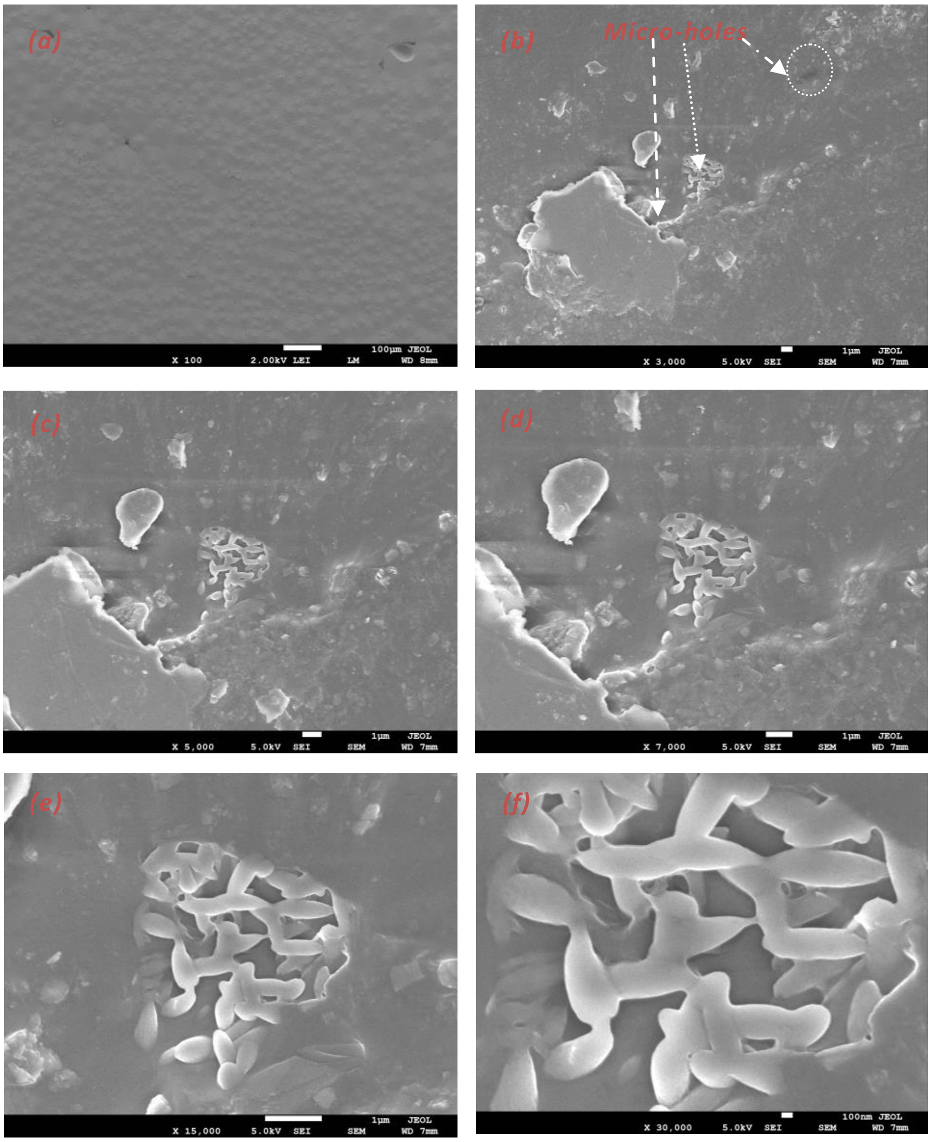

Figure 6 Scanning electron micrograph of surface images of blend 3 film; (a) before the degradation ; (b-f) after immersion in wastewater for 8 weeks with the different scale.

The changes in the PLLA blend film surfaces were analyzed by SEM before and after biodegradation. It is known that plastic materials can be decomposed by various mechanisms: mechanical, thermal, UV-photo and biological degradation. During the degradation of polymers the physical properties and the chemical properties are changed, this is due to environmental factors, such as light, heat, humidity and biological activity. SEM observation of the film of blend 3 before the degradation with a smooth surface and flat surface in figure 6 a. Bioplastics degradation is caused by bacteria or fungus, where bacteria eat bio-plastics as a source of carbon, and then an area that appears to grow inside. The sample after immersed in wastewater for 2

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months, the surface of the sample was found degraded in some areas. The surfaces are observed with pores and different sizes in micron. The degradation at the surface begins after 2 months in wastewater. The degraded surfaces are observed, and some pores with different sizes have been found. There are some micro holes from the elimination of the amorphous regions from blend 3 than crystalline regions.

3.6. Filtration Test

One of the advantages of membrane mat from nanofibers is the ability to filter the soil, dirt, clays, particles, and microbes from wastewater. The fiber diameter, pore diameter, and filtration efficiency were measured. In figure 7 show that the dust particles collected on the surface of the membrane. Large particles of clays are deposited on the pores of the fibers, leading to closed the fiber pores. It show that the soil and clays with different size are larger than the pore sizes in membrane mat and remain primarily on the surface of the membrane mat.it show too before treatment unclear water and after treatment clear water These nanofibers were manufactured from the PLLA blends as biomembranes and tested as water filtration in order to encourage the industry in future to use these membranes for many application than the fiber from petrochemical. The efficiency of removal of suspended elements in wastewater was measured in terms of membrane weight before and after filtration, and the weight of the dust was calculated after drying. Figure 7 showed the morphology of PLLA nanofibers before and after filtration. For the PLLA membrane before filtration, we could estimate the diameter size of the nanofibers are about 3 um-500 nm, the nanofiber PLLA membrane with dimension 40 mm x 35 mm x 0.3 mm and the pore size is very small. After filtration, the sample filter was covered by various dust particle, color, some trace organic pollutants. we could observe that the PLLA membrane was still strong enough and the surfaces of the nanofiber were attached to particles. The clay particles of waste, fine sand and slight soil held by porous and attached to the nanofibers.

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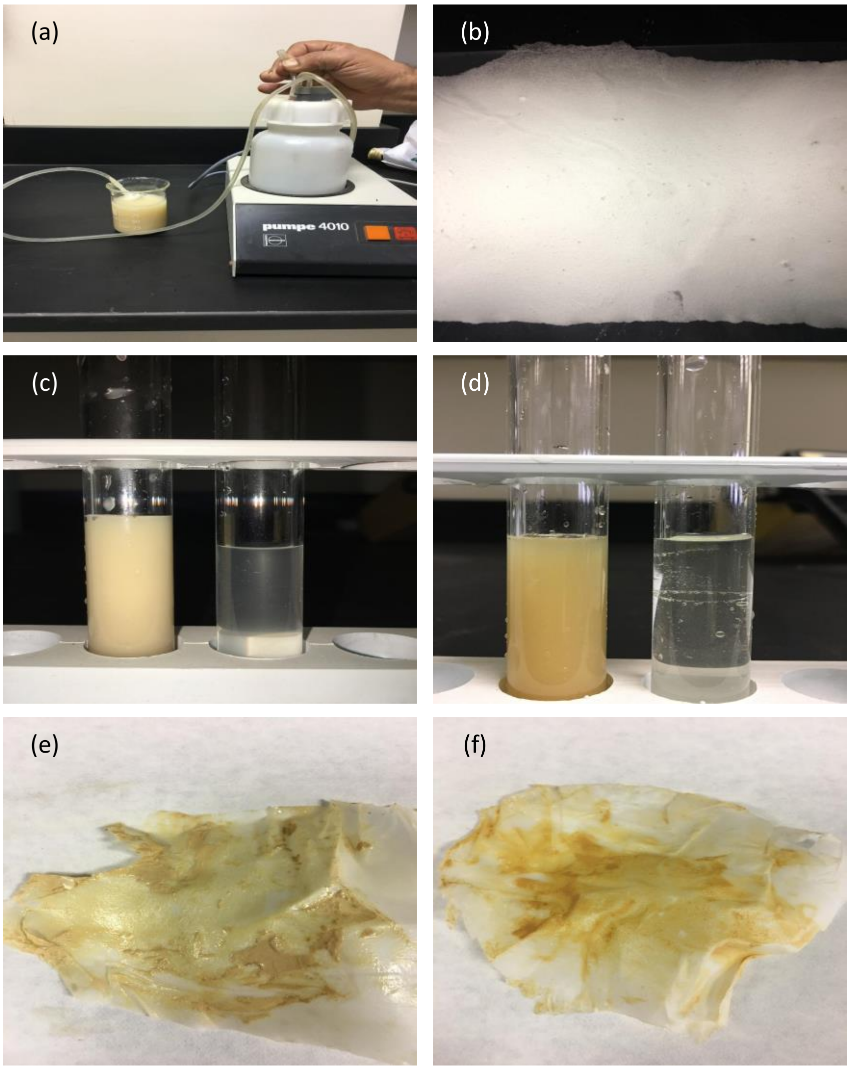

Figure 7. Wastewater treatment processes,(a) pump with unprocessed wastewater; (b) the surface of membrane before filtration process; (c) direct filtration by nanofibers membrane from wastewater with very small clays in the saudi soil; (d) direct filtration by nanofibers membrane from wastewater with sand from Saudi earth; (e) particles at the surface of membrane after filtration process from clays and; (f) particles at the surface of membrane after filtration process from very small sand.

SEM images showing sludge and dust are collected on the surface of the PLLA electrospun fibers filter directly after filtration test in figure 8 and 9 (a, b, c, d, e, and f). This membrane has been tested by using a pump and flask with wastewater samples. When examining the sample blend 3 of the filter after the filtration process and study the surface of the filter by SEM from the front and back and the cross-section of the membrane. We observed that all particles and sand may be collected on the surface, a small portion in the existing half layer and a very small part of the particles present on the surface of the back membrane and is almost clean compared to the front. It is interesting to note that most sand and clays are attached with fibers. The results showed that when the wastewater was filtered through the membranes, the clean water was achieved. This can be a low-cost filtration select for the wastewater treatment for using in agriculture field. The PLLA nanofibers membrane were successfully manufactured by the electrospinning method and the resulting membranes are very strong during filtration testing using wastewater to determine the effective filtration of PLLA membrane. Water pollution in developing countries affects the public health of humans and the environment. It is therefore essential to develop environmentally friendly biopolymer, sustainable and low-cost membranes.

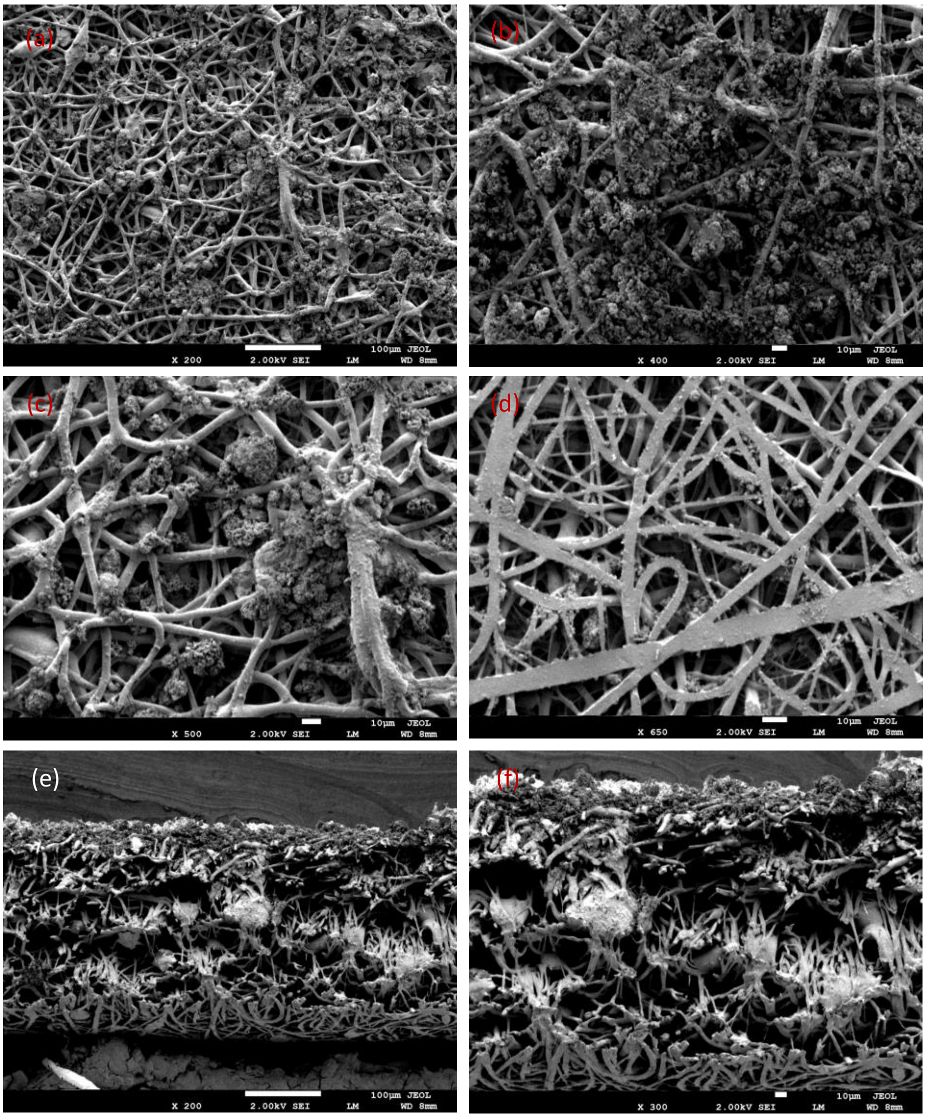

Figure 8. SEM images of nano and microparticles of clays from Saudi soil at the surface of the membrane after filtration process; (a, b and c) Top the membrane layer with cylindrical fiber; (d) The bottom membrane layer with flat fiber; (e and f) Cross-section of the membrane with the different scale.

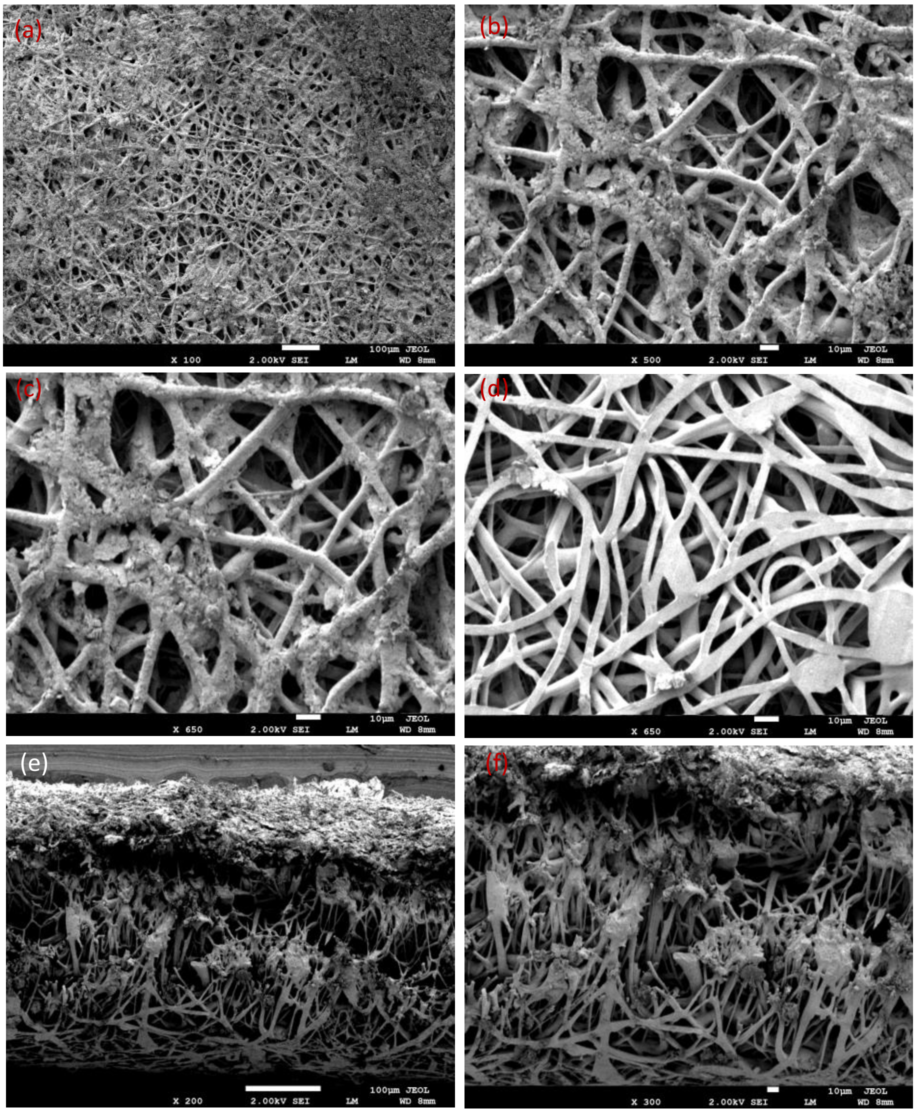

Figure 9. SEM images of nano and microparticles of fine sand from saudi earth at the surface of the membrane after filtration process; (a, b and c) Top membrane layer with cylindrical fiber; (d) Bottom membrane layer with flat fiber; (e and f) Cross-section of the membrane with the different scale.

4. Conclusions

Older filters from glass fiber and charcoal can be replaced by filters from bioplastics membrane. These filters are better than conventional filters to remove organic and bacterial compounds in sewage and are very promising in the future to reduce man-made pollution in developing countries. The main objective of this study is to manufacture nanofibrous PLLA membranes using electrospinning technique after improving its physical properties.

The experimental outcomes are as follows:

1. The effect of plasticizer (TEC) on mechanical properties leads to an improve the elongation at break, therefore reducing the tensile strength of the films. The elongation at break in PLLA blends is from 158 to 285 %. The fine structure with many PPC particles combined in PLLA matrix improved mechanical properties with very large stretching deformation in the blends in

comparison with pure PLLA. Addition of plasticizer (TEC) has the influence on the change of the Tg, Tcc, and Tm, this leads to the increase the chain mobility.

2. PLLA films and membranes were successfully manufactured using electrospinning technology. The obtained fibers have uniformly smooth morphology with a diameter of nanofibers web is about 500 nm - 3 µm and very small pore, the fiber structure without beads. The electrospun nanofibers membranes can be filtered the nano and micro size elements suspension in wastewater. One can be obtained high-purity water from wastewater sources by using an electrospun membrane for drink water and agriculture demands.
3. The biodegradability test of the PLLA blends was investigated using SEM in wastewater, The degradation at the surface begins after 2 months in comparison with pure PLLA. The degraded surfaces are observed, and some pores with different sizes have been found.
4. Membrane separation is one of the most systems to remove the contaminants from water. Using this method the liquid waste can be disposed from the industry or home in a sustainable and economical, Therefore the Nanofibers is the new solution to confirm clean water and preserve a sustainable environment in the future.

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Author Contributions: Ahmd El-hadi planned the experiments, analyzed the data and wrote the paper; Hatium Alamri performed the experiments..

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