

Facile Synthesis of Poly (vinylalcohol)/Fibrous Cerium Phosphate Nanocomposite Membranes

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Abstract Nanosized fibrous cerium phosphates, $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$ (nCeP_f), was prepared and characterized. Poly (vinylalcohol)/fibrous cerium phosphate nanocomposite membranes of different weight percentages (2.5, 5, 10 and 20 wt %) were synthesized. and found to be transparent flexible thin films. They were characterized by chemical, XRD, TGA analysis, and transmission electron microscopy (TEM). TEM images of PVA/ nCeP_f nanocomposites show fibrous cerium phosphate in the nanometer scale, in the range of 12-15 nm, and was dispersed in the PVA matrix. The composite materials show to have mechanical and thermal stability properties superior to that of the original polymer. The exchange capacities of composite membranes were investigated and found to be equivalent to summation of ion exchange capacities of PVA and the inorganic filler (nCeP_f) wt % loading.

Keywords: poly (vinylalcohol), fibrous cerium phosphate, nanocomposite, membranes

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1. Introduction

Layered Tetravalent metal phosphates are very insoluble compounds with good thermal stabilities Their general formula are $\text{M}(\text{IV}) (\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ [1,2], (where M = Ti, Zr, Hf, Ge, Sn, Ce, n = 1-5).

Layered crystalline cerium phosphates have been studied for a long time as ion exchangers, their structures remains unknown until recently [2,3,4]. The reason is that, the composition, the structure and the degree of crystallinity of their precipitates results from reaction of solutions containing a Ce^{IV} salt is mixed with a solution of phosphoric acid of [$\text{PO}_4/\text{Ce}^{\text{IV}}$ ratio], strongly dependent on the experimental conditions such as rate and order of mixing of the solutions, stirring, temperature and digestion time. Fibrous cerium(IV)hydrogen phosphate is superior in handling qualities, chemically stable, and also has the property of large cation exchange capacity, on heating it is easily transformed into pyrophosphate CeP_2O_7 [4,5]. To date most of the work on fibrous cerium phosphate was carried out on its ion exchange [6,7,8] thermal behavior [4,5,9], intercalation [5,10] and electrical conductance properties [11].

Organic polymer-inorganic composites comprise an important class of synthetic engineering. The composite material may combine the advantage of each material, for instance, flexibility, processability of polymers and the selectivity and thermal stability of the inorganic filler [12,13,14,15,16]. Nanoscaled tetravalent metal phosphates and their organic nanocomposite membranes have gained great attention recently [14,15]. However, research in such area is still Terra incognita [12,13,14,16].

Poly (vinylalcohol) (PVA), is hydrophilic and biological degradable polymer with abundant hydroxyl groups [16]. Nano composites based on poly (vinylalcohol) (PVA), are gaining increase attention in various applications such as proton exchange, polymer electrolyte fuel cells [16,17], permeability membranes [18,19] drug delivery [20] and packaging materials [21,22] According to the open literature, the nanocomposite technique based on tetravalent metal phosphates is one of the most attractive, because of combination of polymer and a tetravalent metal phosphate result in obvious enhancements and thermal stability [12,13,14,16,17]. The interactions between PVA and the nano additives mainly through hydrogen bonding which allows efficient load transfer, are responsible for the marked increase in mechanical properties [23,24,25]. Most studies on PVA composites were with layered crystalline zirconium phosphate and titanium phosphate [12,13,14,16].

This paper describes the preparation and characterization of novel nanosized fibrous cerium phosphate, $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$ (nCeP_f), and its PVA nanocomposite membrane, where the (nCeP_f) weight % loading were (2.5, 5, 10, and 20 %).

2. Experimental

2.1. Chemicals

$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, H_3PO_4 (85 %), spectranal KBr (of BDH), PVA Mwt = 25125 g/mol (of Aldrich), used as such. Other reagents used were of analytical grade.

2.2. Instruments Used for Characterization

- X-Ray powder diffractometer Siemens D-500, using Ni-filtered CuK_α ($\lambda = 1.54056\text{\AA}$).

- Thermogravimetric analysis (TG/DTA) SII Extra 6000 Thermogram and TG/DTA Perkin-Elmer SII, was employed for the studies on thermal behavior of the resulting materials. The thermal analyses were carried out at temperature range 20 ~775°C in nitrogen atmosphere, the rate was 10°C/min.

- Fourier Transform IR spectrometer, model IFS 25 FT-IR, Bruker, was employed for characterization of fibrous cerium phosphate membrane at range from 4000- 450 cm^{-1} . The sample before characterization was mixed with KBr powder and dispersed into tablet.

- Scanning electron microscopy (SEM) Jeol SMJ Sm 5610 LV was employed for characterization of fibrous cerium phosphate membrane. For scanning electron all samples must be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. The sample usually coated with an ultrathin coating of electrically conducting material, deposited on the sample either by low-vacuum sputter coating or by high-vacuum evaporation. Conductive materials in current use for specimen coating include gold, gold/palladium alloy, platinum, osmium. In our sample sputtering gold coating were used, the parameters are 10.00kV, Mag 160 000, HFW 1.8u.

- Transmission Electron Microscopy (TEM) Zeiss TEM 10 CR was employed for characterization of PVA/fibrous cerium phosphate composite membranes, parameters of the image (size 216KB, dimension 1111x1507 pixels) Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. The specimen you want to look at must be of such a low density that it allows electrons to travel through the sample. our samples preparation for TEM analysis as follows:

1. Small piece of each specimen was put in hot water (80 Celsius) in small vial.
2. The vial was put in asonicator for dispersion for two minutes.
3. A drop of specimen was put on formvar supported grid and studied under TEM.

- pH Meter GWG 521, were used for estimation of the ion exchange capacities.

2.3. Preparation of Nanofibrous Cerium Phosphate, $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$ ($n\text{CeP}_f$)

150ml of 0.05M $\text{CeSO}_4 \cdot 4\text{H}_2\text{O}$ in 0.5M H_2SO_4 solution were added dropwise to 150ml of 6M H_3PO_4 at 80°C with stirring. After complete addition the resultant material left to digest at that temperature for 5h. To that one liter of hot distilled water, (~60°C), was added with stirring for 1hour. The resulting fibrous cerium phosphate was subjected to washing by reslurrying several times with distilled water up to pH 3.5, then filtered, washed with ethanol and dispersed in distilled water (2 liters), and kept in form of slurry aqueous solution.

2.4. Preparation of PVA/Nanofibrous Cerium Phosphate Composites

Poly (vinylalcohol) in 10 % concentration was prepared by dissolving 10g of PVA in 125 ml distilled water at 80°C with stirring for 1hour. kept at the same temperature until the total volume is equal to 100 ml. Different PVA/nanofibrous cerium phosphate composite membranes were prepared where ($n\text{CeP}_f$) weight % loading were (2.5,5,10, and 20 %).

Typically, to slurry aqueous solution of 0.1g nanofibrous cerium phosphate in 10 ml distilled water at 45°C, with stirring, for 15 minutes, 9 ml of PVA (10% in concentration) were added. The stirring was continued for 48 hrs at 45°C. The resulting mixture was poured into flat surface container, of desired thickness, and was allowed to dry in air. The fully dried transparent flexible thin film was peeled from the glass container and kept for characterization, and found to be PVA/ ($n\text{CeP}_f$) 10 wt% composite membrane. In similar manner different wt % of 2.5, 5, and 20% ($n\text{CeP}_f$) were used for the preparation of the rest of PVA composite membranes.

2.5. Exchange Capacity Determination

Exchange capacity of nanosized cerium phosphate was determined by addition of 25 ml of 0.10 M NaCl solution to 100 mg of the material, with stirring for one hour, then titrated with 0.10 M NaOH solution. Exchange capacities of composite membranes were determined by addition of 4ml of 0.05M NaOH to 0.05g of the composite thin film, left static for 48 hrs, then titrated with 0.05 M HCl. Similarly was done for pure PVA.

3. Results and Discussion

Nanofibrous cerium phosphate membrane, $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$ ($n\text{CeP}_f$), was prepared and characterized by chemical, XRD, TGA, FT-IR, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3.1. XRD

X-ray diffraction (XRD) was performed in the range 2θ 3° to 35° to investigate the structure of fibrous cerium phosphate membrane, $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$ ($n\text{CeP}_f$). XRD pattern of nanofibrous cerium phosphate membrane is shown in Figure 1, have reflection at 2θ 8.1° corresponding to d spacing 10.89Å. The interlayer distance d was calculated according to the equation: $d = \lambda / \sin 2\theta$ (where $\lambda = 1.54025$, $2\theta = 8.1^\circ$).

The XRD provide evidence for the formation of fibrous cerium phosphate [14,17].

3.2. TGA

Thermogram of fibrous cerium phosphate membrane is shown in Figure 2. The thermal decomposition occurs in continuous process. The thermal analysis curve represent mass losses equal to 19.09%. Three temperature regions can be considered over which the weight change occurs. The first weight loss occurs between temperature 20-120°C, corresponds to the loss of two water of hydration. The second weight loss occurs ~ 120-180°C, corresponds to loss of the remaining water of hydration, which is equal to 0.9 H_2O . At temperature range 180-

775°C condensation of POH groups occurs, that leads to the loss of structural water to give cerium pyrophosphate, CeP_2O_7 [14,16,17,26]. The stepwise losses of water of hydration up to 180°C, followed by initiation POH groups condensation were calculated by correlation of TG curve at a given temperature.

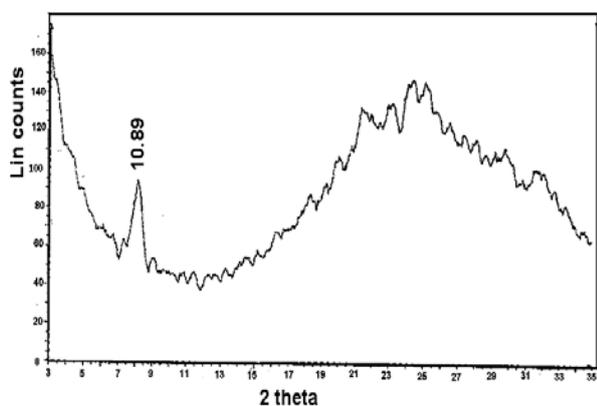


Figure 1. XRD of nanofibrous cerium phosphate

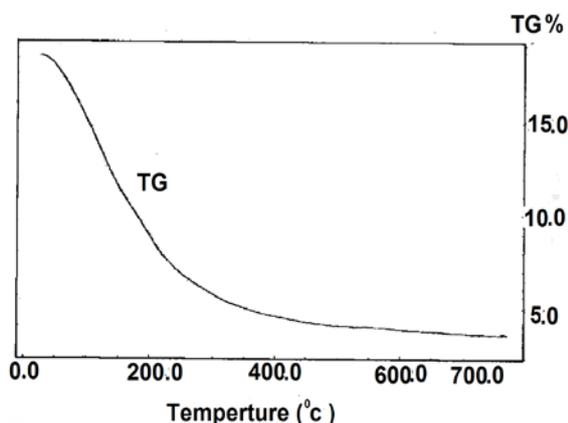


Figure 2. TGA of nanofibrous cerium phosphate

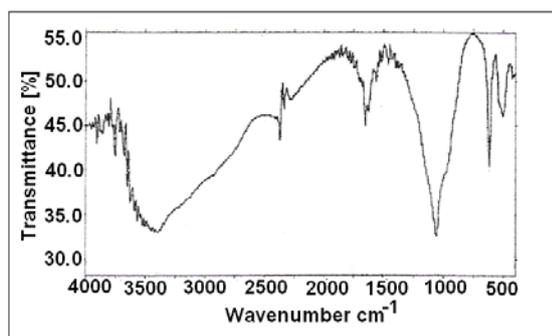


Figure 3. FT-IR spectra of nanofibrous cerium phosphate

3.3. FT-IR

Figure 3 shows FT-IR spectrum of fibrous $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$, with a trend similar to that of M(IV) phosphates [1,2,14,15,16]. It consists of broad band centered at 3350 cm^{-1} is due to OH groups symmetric stretching of H_2O , small sharp band at 1628 cm^{-1} is related to H-O-H bending, and sharp broad band centered at 1045 cm^{-1} is corresponds to phosphate groups vibration. The bands at the region $630\text{--}450\text{ cm}^{-1}$ are ascribe the presence of $\delta(\text{PO}_4)$. The FT-IR bands indicate presence of hydroxyl groups.

3.4. SEM

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample to produce information about the sample surface, topography and composition. By scanning the sample and detecting the secondary electrons, an image displaying the tilt of the surface is created. Morphology image of the nanosized fibrous cerium phosphate (nCeP_f) is shown in Figure 4. The photograph shows its average size is $\sim 20.5\text{ nm}$.

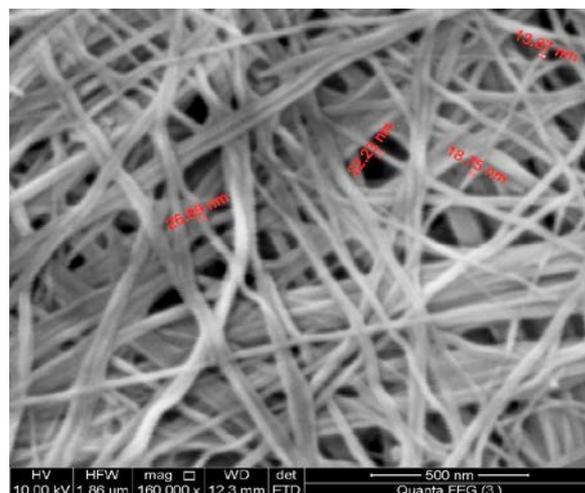


Figure 4. SEM morphology image of (nCeP_f)

3.5. Ino Exchange Capacity

The ion exchange capacity of $\text{Ce}(\text{HPO}_4)_2 \cdot 2.9\text{H}_2\text{O}$ found to be equal to 5.21 meq/g . The ion exchange capacities of PVA/ nCeP_f composite membranes found to be equal to sum of ion exchange of PVA and the inorganic filler.

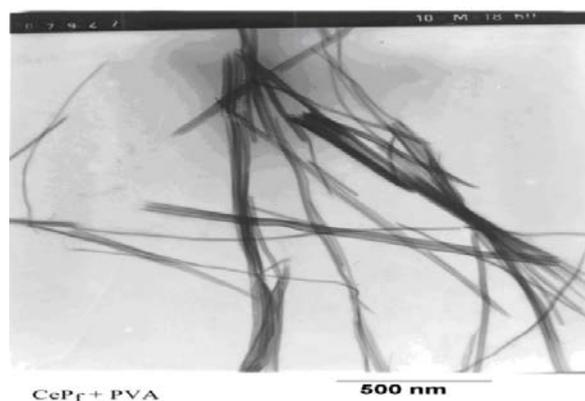


Figure 5. image (TEM) of PVA/ nCeP_f composite thin film, of 10wt% (nCeP_f)

3.6. TEM

Transmission electron microscopy was employed to investigate nano morphology and structure of fibrous cerium phosphate. Typical transmission electron microscopy image of the nanosized fibrous cerium phosphate (nCeP_f), dispersed in PVA matrix, is shown in Figure 5, which shows the morphology of fibrous cerium phosphate formed by fibrous with average size 15 nm , demonstrated that dispersibility of the nCeP_f is nanoscale in the PVA matrix.

3.7. PVA/nCeP_f Composite Membranes

Flexible transparent thin films homogeneous composites of PVA/ (nCeP_f) were prepared and characterized by, TEM and TGA.

3.7.1. XRD of Poly (Vinylalcohol)

X-ray diffraction (XRD) was performed in the range 2 θ 3° to 35° to investigate the structure of PVA. Figure 6 shows the X-ray diffraction pattern of the poly (vinylalcohol) with intense peak appearing near 2 θ = 19.75°, found to follow the same trend to the XRD of PVA reported in literature [12,14,16].

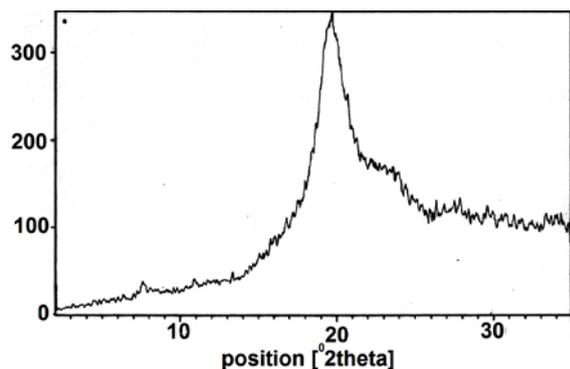


Figure 6. XRD pattern of PVA

3.7.2. TGA

The TGA measurements of (PVA) and PVA/ (nCeP_f) nanocomposites membranes with different (nCeP_f) contents are shown in Figure 7-Figure11, respectively.

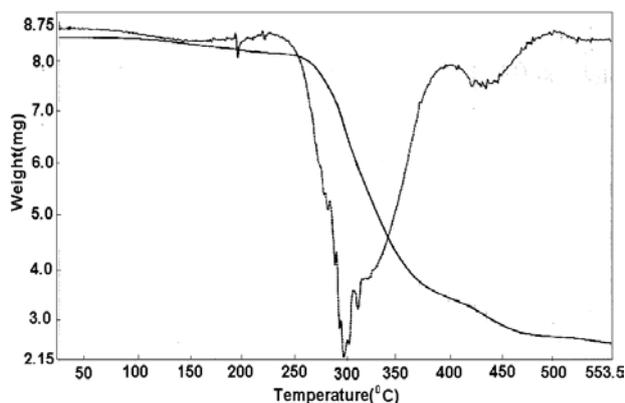


Figure 7. TG/DTA of PVA

The thermal decomposition of (PVA) is shown in Figure 7. Three temperature regions can be identified over which most of the weight change occurs. The first weight loss occurs between 75-115°C, corresponds to the loss of water of hydration. The second weight loss occurs ~ 300 – 360°C, corresponds to the side chain decomposition of (PVA). Third degradation between 410-600°C corresponds to decomposition of main chain [17] leaving about 42 % residue.

The thermal decomposition of all the composite materials found to follow the same trend. Thermal decomposition of the composites 2.5, 5, 10, and 20 wt% (nCeP_f) content are shown in Figure 8-Figure 11, which shows the decompositions occur at four temperature ranges, can be identified over which most of the weight changes occur.

Thermal decomposition of composite membrane of 2.5 wt% (nCeP_f), is given in Figure 8, shows the first weight loss occurs between 70-200°C, is concern to the loss of water molecules. The weight loss occurs between 200-330°C corresponds to the decomposition of side chain of (PVA), third and fourth degradation between 390 and 550°C corresponds to the decomposition of (PVA) main chain and condensation of P-OH groups of the inorganic material to pyrophosphate, CeP₂O₇. The residue results from thermal decomposition found to be equal to 1.84%.

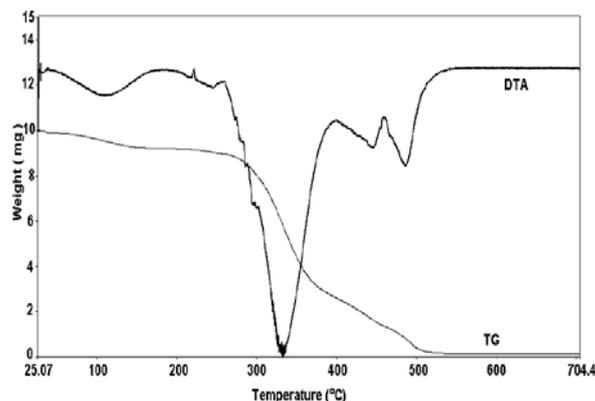


Figure 8. TG/DTA of PVA/ (nCeP_f) nanocomposite membrane(2.5 wt%)

Thermogram of composite membrane of 5 wt% (nCeP_f), is given in Figure 9, shows the first weight loss occurs between 70–180°, is relate to the loss of water molecules. The weight loss occurs between 200-390°C corresponds to the decomposition of side chain of (PVA), third and fourth degradation between 390°C and 600°C corresponds to the decomposition of (PVA) main chain and condensation of P-OH groups of the inorganic material to pyrophosphate, CeP₂O₇. The residue results from thermal decomposition found to be equal to 18.03%.

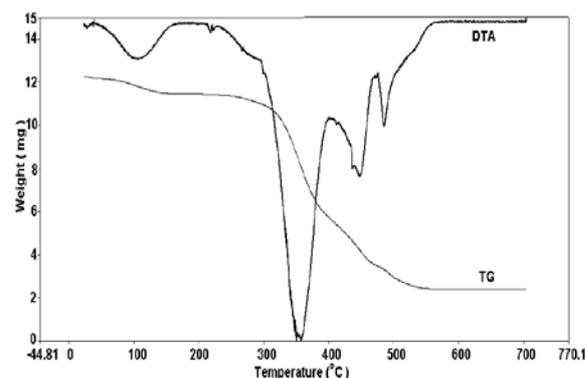


Figure 9. TG/DTA of PVA/ (nCeP) nanocomposite membrane(5 wt%).

Thermogram of composite membrane of 10 wt% (nCeP_f), given in Figure 10, shows the first weight loss occurs between 70-180°C, is concern to the loss of water molecules. The weight loss occurs between 180-350°C is corresponds to the decomposition of side chain of (PVA), third and fourth degradation between 380°C and 600°C corresponds to the decomposition of (PVA) main chain and condensation of P-OH groups of the inorganic material to pyrophosphate, CeP₂O₇. The residue results from thermal decomposition found to be equal to 17.96%.

For composite membrane of 20 wt% (nCeP_f), Its thermogram is shown in Figure11, the first stage decomposition occurs between 70–180°C, is concern to

the loss of water molecules. The weight loss occurs between 180-375°C corresponds to the decomposition of side chain of (PVA), third and fourth degradation between 375°C and 600°C corresponds to the decomposition of (PVA) main chain and condensation of P-OH groups of the inorganic material to pyrophosphate, CeP_2O_7 . The residue results from thermal decomposition found to be equal to 38.9%.

An improvement in the thermal stability, of the nanocomposites can be noticed. The presence of (nCeP) in PVA enhance thermal stability and mechanical properties of the composite membranes. All weight losses accompanied by endothermic peaks and leaving residues.

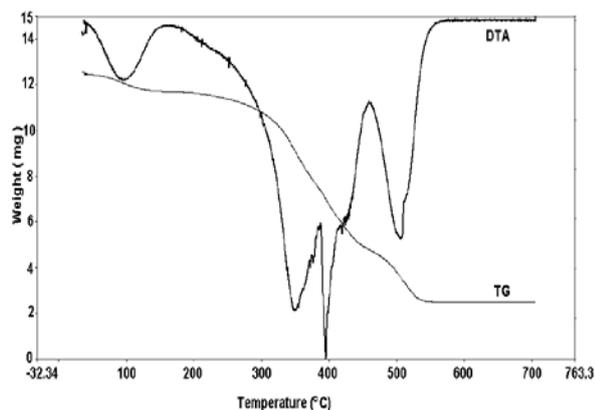


Figure 10. TG/DTA of PVA/ (nCeP) nanocomposite membrane(10 wt%)

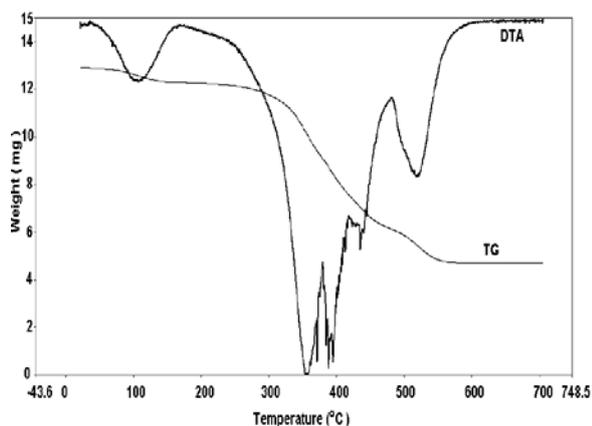


Figure 11. TG/DTA of PVA/ (nCeP) nanocomposite membrane(20 wt%)

4. Conclusions

Novel nanosized fibrous cerium phosphate, $Ce(HPO_4)_2 \cdot 2.9H_2O$ (nCeP), was prepared. A series of nanocomposite membranes were prepared from PVA and (nCeP), indicate that (nCeP) posses good miscibility in organic matrix which lead to the formation of homogeneous transparent flexible thin films. The thermal stability was improved. Consequently the presence of (nCeP) in PVA favored the increase of the thermal stability and mechanical properties, that may combine physical properties and characteristics of both organic and inorganic components within the single composite. Thermal stability is an important property which the nanocomposite morphology plays an important role. From the TGA analysis, it is obvious that PVA/nCeP_f composites degraded at higher temperature. These results

suggested that PVA chains were protected in the degradation process by nCeP_f. The resultant composites are promising for utilizations in fuel cells and as new sorbents.

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References

- [1] Clearfield, A., Inorganic Ion Exchange Materials, Boca Raton, CRC Press, FL, USA (1982).
- [2] Shakshooki . S.K, Naqvi .N, Kowaleczyk J.K, Khalil. S, Rais. M and Tarish. F, Effect of composition of ion exchange properties of amorphous zirconium- titanium phosphates, Reactive Polymer, 7 (1988) 221.
- [3] Salvado, M.A., Pertierra,P., Tropajo, C. and Garcia, G.R., Crystal structure of cerium(iv) bishydrogen phosphate derivative, J.Am.Chem.Soc, 129 (2007) 10970.
- [4] Alberti, G. and Costantino, U., Recent progress in the field of synthetic inorganic exchanger having a layered and fibrous structure, J. Chromatogr., 102 (1974) 5.
- [5] Romano,R. and Alves,O.S., Fibrous cerium(iv) phosphate host of weak and strong Lewis bases, 51, (2005) 211.
- [6] Hayashi,H., Ebina,T., Nagasi,T., Onodera.Y. And Iwasaki,T., Sorption of trivalent meta ion exchanger on fibrous cerium(iv) hydrogen phosphate, J. Chem. Soc. Japan, (1997) 558.
- [7] Metwally, S.S., El-Gammal, B., Ali, H.F. and Abo-EL-Enein, S.A., Removal and separation of some radionuclides by poly-acrylamide based Ce(iv) phosphate, Separation Sci. and Tech., 46 (2011) 11.
- [8] Parangi, T., Wani, P. and Chudasama, U., Synthesis, characterization and application of cerium phosphate, Desalination and Water Treatment, 38 (2012) 126.
- [9] Clearfield, A., Inorganic Ion Exchange Materials, Boca Raton, CRC Press, FL, USA (1988).
- [10] Arjona, A.M., Rodrigouez, A.G., Bueno, F.R, Sanchez, E.V. and Conejo, G.L., On the retention of n-butylamine by crystalline and fibrous Ce(iv) phosphate, J.Chem.Tech. Biotechnol, 42 (1988) 83.
- [11] Casciola, M., Costantino, U. and D'amico, S., ac Conductivity of cerium(iv) phosphate in hydrogen form, Solid State Ionics, 28 (1988) 617.
- [12] Yang, Y., Liu, C. and Wen, H., Preparation and properties of polyvinyl alcohol/exfoliated α -zirconium phosphate, Polym. Test, 28, (2009) 185.
- [13] Nagarale, R.K., Shin, W and Singh, P.K., Progress in ionic organic-inorganic composite membranes for fuel cell application, Polym. Chem., 1 (2010) 388.
- [14] S.K.Shakshooki, S.K,Eljmi, A.A.,Khalfulla, A.M. and Elfituri.S.S., Int. Conf. on Mater. Imperative, pp 49-70 (CD).Cairo, Egypt, 29/11-2/12, 2010.
- [15] Feng, Y., He, W., Zhang, X., Jia, X. and Zhao, H., The preparation of nanoparticle zirconium phosphate, Mater.Letters, 61 (2007) 3258.
- [16] Bao, C., Gua, Y., Song, L., Lu, H., Yuan, B., and Hu, Y., Facile synthesis of poly (vinyl alcohol) / α -titanium phosphate nanocomposite with markedly enhanced properties, Ind. Eng. Chem. Res., 50 (2010) 11109.
- [17] Yang, C. C., Chiu, S. J., Chien, W. C., Development of alkaline direct methanol fuel cells based on crosslinked PVA polymer membranes. J. Power Sources, 162 (2006) 21.
- [18] Helen, M., Viswanathan, B., Murthy, S. S., Poly (vinyl alcohol)-polyacrylamide blends with cesium salts of heteropolyacid as a polymer electrolyte for direct methanol fuel cell applications., J. Appl. Polym. Sci., 116 (2010) 3437.
- [19] Paralikara, S. A., Simonsen, J., Lombardi, J., Poly (vinyl alcohol) /cellulose nanocrystal barrier membranes. J. Membr. Sci., 320 (2008),248.

- [20] Sullad, A. G., Manjeshwar, L. S., Aminabhavi, T. M., Polymeric blend micro spheres for controlled release of theophylline. *J. Appl. Polym. Sci.*, 117 (2010) 1361.
- [21] Wang, X.L. and Wang, Y.Z., Synthesis and properties of thermophilic PVA-grafted lactic acid copolymer, *Ind.Eng.Chem.Res.*, 48 (2009) 788.
- [22] Spalids, A.A., Katsaros,F.K., Romanos, G.E., Kakizis, N.K., and Kanellopoulos,,N.K., preparation and characterization of novel PVA zoster flakes composites for packaging applications, *Composites Bi.Eng.*, 48 (2007) 398.
- [23] Soundrajah, H.J., Karumartre, B.S.B., and Rajapkse, R.M.G., Thermal properties of PVA montmorillonite nanocomposites, *J. Compos. Mater.*, 44 (2010) 303.
- [24] Liang, J.J., Huang,Y., Zhang,L., Wang,Y., Ma,Y.F., Guo, T.Y.and Chen.Y.C.,Molecular level dispersion of grapheme into polyvinylalcohol, *Adv.Funct. Mater.*, 19 (2009) 2297.
- [25] Sulvagione,H.J., Martinez, G., and Gmez, M.,A., Synthesis PVA/reduced graphite oxide with improved thermal and electrical properties, *J.Mater. Chem.*, 19 (2009) 5027.
- [26] Shakshooki, S.K., El-Akari, F.A., Al-fituri, S.M. and Elfituri, S.S., Fibrous cerium(iv) hydrogenphosphate membrane self supported benzimidazole polymerization agent, DOI:10.4026 Sci net., *Adv. Mater. Res.*, 856 (2014) 3-9.