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Preparation and characterization of electrospun pullulan/montmorillonite nanofiber mats in aqueous solution

Mohammad Rezaul Karim [a,b,*], Hyun Woo Lee [a], Ran Kim [a], Byung Chul Ji [a], Jin Won Cho [a], Tae Won Son [c], Weontae Oh [d], Jeong Hyun Yeum [a,*]

[a] Department of Advanced Organic Materials (Natural Fiber) Science & Engineering, Kyungpook National University, Daegu 702-701, South Korea
[b] Center of Excellence for Research in Engineering Materials, College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia
[c] School of Textiles, Yeungnam University, Kyongsan 712-749, South Korea
[d] Department of Nanoengineering, Dong-eui University, Busan 614-714, South Korea

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ABSTRACT

Pullulan (PULL)/montmorillonite clay (MMT) nanofiber blend mats with various weight ratios have been fabricated by the electrospinning technique in aqueous solution. The PULL/MMT nanofiber mats are characterized by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) and mechanical measurements. The study shows that the introduction of MMT results in improvement in tensile strength, and thermal stability of the PULL matrix. XRD patterns and TEM micrographs suggest the coexistence of intercalated MMT layers over the studied MMT contents. XRD analyses also reveal an increase of the crystallinity of the blend nanofiber mats with addition of MMT fillers. Moreover, FT-IR divulges that there might be possible interaction occurred between the MMT clay and PULL matrix.

1. Introduction

Polymer/MMT clay hybrid nanocomposites have attracted great interest due to MMT filled polymer composites often exhibit remarkable improvement in material properties with only a low percentage of MMT fillers added. One of the major findings that have stimulated the interest in MMT filled nanocomposites is the work by Okada and coworkers (1990). They reported that with only a small amount of layered silicate (MMT) added into nylon-6, pronounced improvements in thermal and mechanical properties can be obtained. Subsequently, Vaia and his group (Vaia, Ishii, & Giannelis, 1993) reported that it is possible to melt-mix polymers with layered silicates, without the use of organic solvents. Today, efforts are being conducted globally; using almost all types of polymer matrices to produce MMT based nanocomposites. The main advantages of these nanocomposites are improved thermal and mechanical properties, reduced flammability and better barrier properties comparing to unfilled polymer. The composite studies focus on the method of their preparation, structure characterization, mechanical and thermal properties as well as processing.

Pullulan is an extracellular microbial polysaccharide produced by the fungus-like yeast, *Aureobasidium pullulans* (Kachhawa, Bhattacharjee, & Singhal, 2003; Yuen, 1974). It is a neutral glucan (like amylose, dextran, cellulose), with a chemical structure somewhat depending on carbon source, producing microorganism, fermentation conditions. The basic structure is a linear α-glucan one, made from three glucose units linked α-(1,4) in maltotriose units which are linked in a α-(1,6) way. The three glucose units in maltotriose are connected by an α-(1,4) glycosidic bond, whereas consecutive maltotriose units are connected to each other by an α-(1,6) glycosidic bond. The regular alternation of (1 → 4) and (1 → 6) bonds results in two distinctive properties of structural flexibility and enhanced solubility (Leathers, 1993). The unique linkage pattern also endows pullulan with distinctive physical traits along with adhesive properties and its capacity to form fibers, compression moldings and strong, oxygen impermeable films. The α-(1,6) linkages that interconnect the repeated maltotriose units along the chain are responsible for the flexible conformation and the ensued amorphous character of this polysaccharide in the solid state (Gidley, Cooke, & Ward-Smith, 1993). Pullulan's solubility can be controlled or provided with reactive groups by chemical derivatization. Due to its excellent properties, pullulan is used as a low-calorie ingredient in foods, gelling agent, coating and packaging material for food and drugs, binder for fertilizers and as an oxidation-prevention agent for tablets. Other applications include contact lenses manufacturing, biodegradable foil, plywood, water

* Corresponding authors. Fax: +82 53 950 6744.
E-mail addresses: mrkarim@knu.ac.kr (M.R. Karim), jhyeum@knu.ac.kr (J.H. Yeum).

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solubility enhancer and for enhanced oil recovery (Israilides et al., 1998; Leathers, 2003; Schuster, Wrenzig, & Mersmann, 1993). It is water soluble, insoluble in organic solvents and non-hygroscopic in nature. Its aqueous solutions are stable and show a relatively low viscosity as compared to other polysaccharides. It decomposes at 250–280 °C. It is moldable and spinnable, being a good adhesive and binder. It is also non-toxic, edible and biodegradable.

Electrospinning is a very simple and effective approach to produce nanofibers, including aligned nanofibers and crossbar structures with the diameters ranging from micrometers to few nanometers scale, which may have be found attractive for various applications in biomedical engineering, filtration, protective clothing, catalysis reaction and sensors (Li & Xia, 2004; Reneker & Chun, 1996). In a typical electrospinning process, a high voltage is applied to create electrically charged jets of polymer solutions. The jets dry and form nanofibers, which are collected on a target as non-woven mat. The principle of the electrospinning method is quite simple; the electrostatic field stretches the polymer solution into fibers at the same time as the solvent evaporates. However, the process is difficult to control and several variables have an influence on the properties of the end product. Furthermore, the quality of the fibers is typically inconsistent, for example, the fiber deposition may be uneven or the distribution of fiber diameter may be large. Research on PULL/MMT nanofiber mats by electrospinning technique has not been a focus in enormously. To the best of our knowledge, no reports are available on the morphology and crystalline structure of PULL/MMT nanofiber mats by electrospinning technique.

In this study, we have demonstrated for the first time, ultrafine PULL/MMT nanofiber mats can be fabricated by using the electrospinning technique. The PULL/MMT nanofiber mats are investigated using FE-SEM, TEM, FT-IR, XRD, DSC, TGA, mechanical measurements and the related characterizations are also discussed.

2. Experimental

2.1. Materials

Pullulan was a food grade preparation (PF-20 grade) from Hayashibara Biochemical Laboratories Inc. (Okayama, Japan) and Montmorillonite (MMT) was purchased from Kunimine Industries Co., Ltd., Japan. Doubly distilled water was used as a solvent to prepare all solutions.

2.2. Preparation of PULL/MMT blend solutions

The PULL solutions (10, 15, 20, 25 and 30 wt.%) were prepared in doubly distilled water at room temperature under magnetic stirring for 2–3 h. MMT powder was dissolved also in the doubly distilled water under magnetic stirring for 1 h at room temperature. The PULL/MMT blend solutions were prepared by mixing of bulk PULL (20 wt.%) and different amounts of MMT (1, 3, 5 and

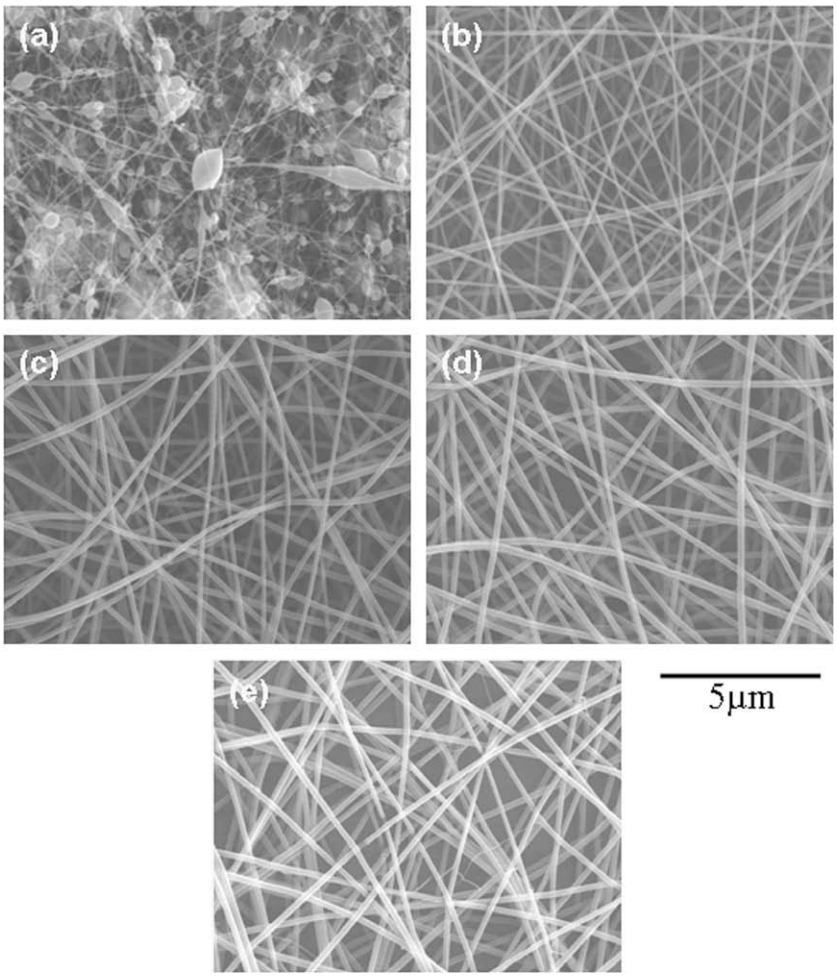

Fig. 1. FE-SEM images of pullulan nanofiber mats prepared with using different pullulan solution concentrations of (a) 10 wt.%, (b) 15 wt.%, (c) 20 wt.%, (d) 25 wt.% and (e) 30 wt.% (applied voltage = 15 kV and TCD = 15 cm).

10 wt.%) in aqueous solutions at room temperature with gently stirred for another 2 h.

2.3. Electrospinning of PULL/MMT nanofiber mats

During electrospinning, a high voltage power (CHUNGPA EMT Co., Ltd., Seoul, Korea; model CPS-60K02VIT) was applied to the PULL/MMT solution contained in a syringe via an alligator clip attached to the syringe needle. The solution was delivered to the blunt needle tip via syringe pump to control the solution flow rate. Fibers were collected on an electrically grounded aluminum foil placed vertically to the needle tip.

2.4. Characterizations

The morphology and properties characterization of electrospun bulk PULL and blend PULL/MMT fibers was observed with a field-emission scanning electron microscope (JEOL, model JSM-6380) after gold coating, a transmission electron microscopy (TEM) (HITACHI, model H-7600) with an accelerating voltage of 100 kV, a Fourier transform infrared (FT-IR) (Bruker IFS 120HR), and an X-ray diffraction (XRD) (Philips model X'Pert APD). The thermal behavior of PULL and PULL/MMT fibers was studied with a DSC (model Q-10) and TGA techniques (model Q-50) from TA instruments, USA.

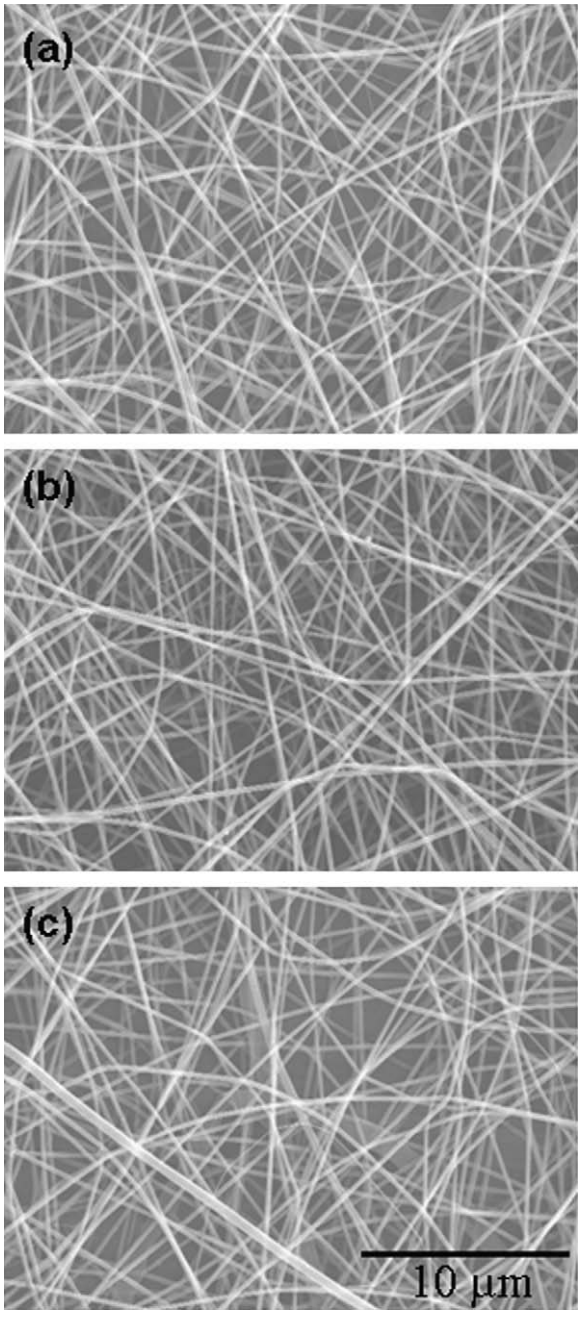

Fig. 2. FE-SEM images of pullulan nanofiber mats prepared with using different applied voltage of (a) 10 cm, (b) 15 cm and (c) 20 cm (polymer solution concentration = 20 wt.% and applied voltage = 15 kV).

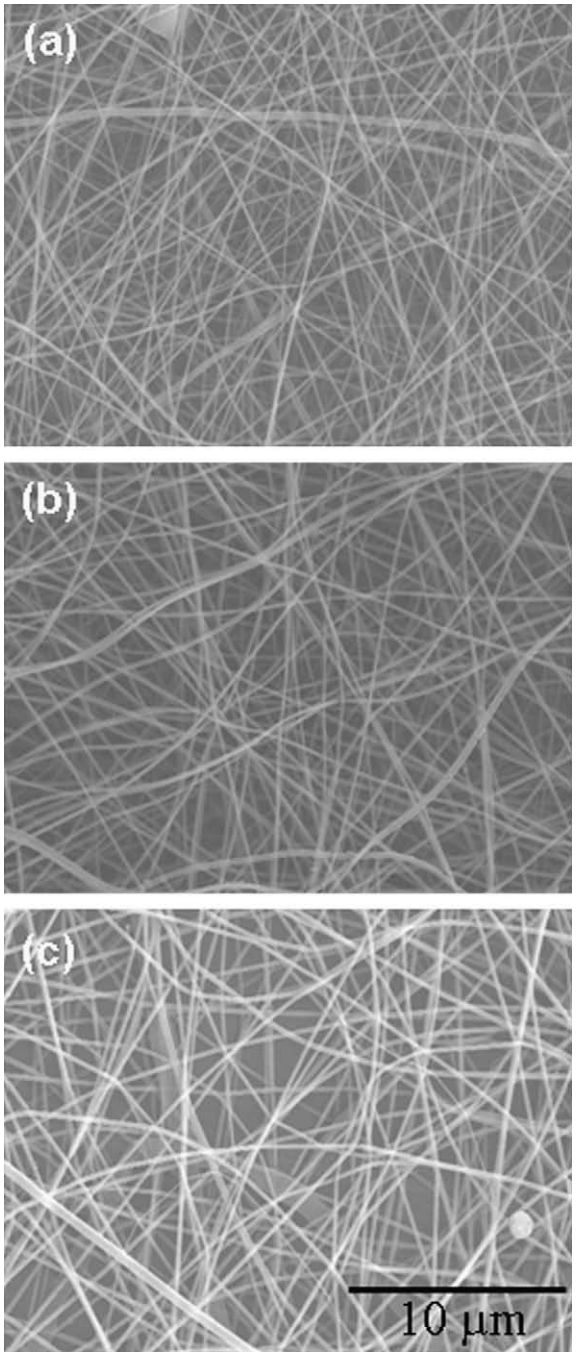

Fig. 3. FE-SEM images of pullulan nanofiber mats prepared with using different applied voltage of (a) 10 kV, (b) 15 kV and (c) 20 kV (polymer solution concentration = 20 wt.% and TCD = 15 cm).

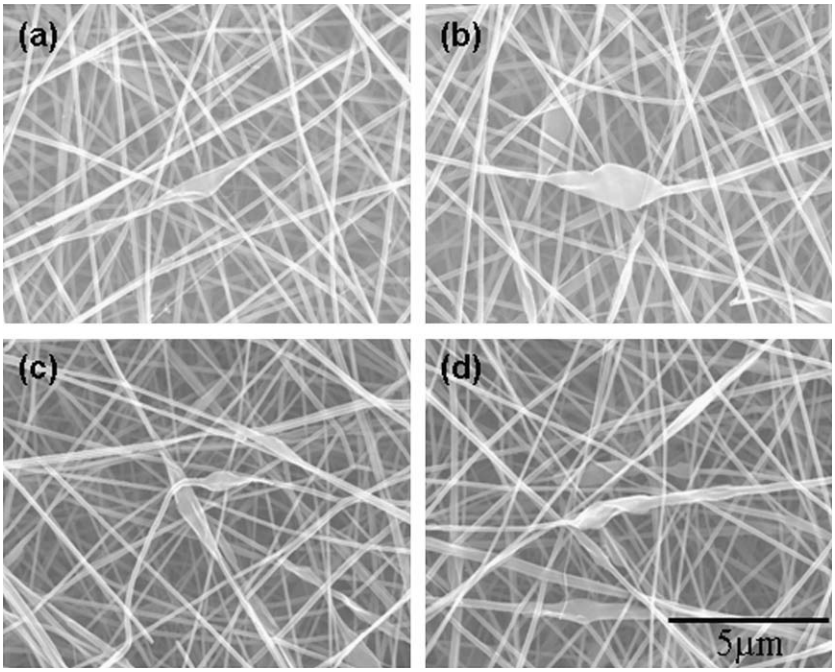

Fig. 4. FE-SEM images of PULL/MMT nanofiber mats prepared with different MMT contents of (a) 1 wt.%, (b) 3 wt.%, (c) 5 wt.% and (d) 10 wt.% (polymer solution concentration = 20 wt.%, applied voltage = 15 kV and TCD = 15 cm).

A mechanical property (tensile strength) was determined by the ZWICK Z005 (ZWICK materials testing machine, Germany).

3. Results and discussion

3.1. Morphology of PULL/MMT nanofiber mats

Because both polymer and filler used in this study have hydrophilic character, the modification of MMT for component mixing is not necessary. As described in the literature (Chiellini, Corti, D'Antone, & Solaro, 2003), the solution dispersion method of PULL/clay nanocomposite preparation is often used and successful. Such method combined with vigorous stirring is also used in this work to prepare solutions for electrospinning method. Morphology of electrospun nanofiber can be affected by the electrospinning instrument parameters including electric voltage, tip-collector distance (TCD) and solution parameter such as polymer concentration, feed mass ratio and surface tension. To obtain the suitable electrospinning conditions for thinner and uniform PULL/MMT fibers, it is conducted a series of experiments on various conditions for optimizing the solution concentrations.

3.1.1. Pullulan solution concentration

Changing the polymer concentration could alter the fiber diameter and morphology very effectively, as shown in Fig. 1. In a fixed applied voltage (15 kV) and tip to collector distance (15 cm), it is used 10, 15, 20, 25 and 30 wt.% of PULL solution concentration. It is found that at a 20% PULL concentration is ideal condition to obtain thinner and uniform PULL fibers (Fig. 1c). It has been obtained a nanometer range of ultrafine electrospun nanofiber mats (100–500 nm) in aqueous solutions as shown in Fig. 1c.

3.1.2. Applied voltage

A series of experiments are carried out when applied voltage is varied from 10 to 20 kV at an optimum PULL solution concentration of 20 wt.% with the tip to target distance of 15 cm as shown in Fig. 2. The morphological structure can be slightly altered by changing the applied voltage. At low voltage (10 kV), ultrafine fibers is not obtained rather few beads and fibers are seen (Fig. 2b). At high voltage (20 kV), it is found non-uniform PULL ribbon-like fibers with larger diameter (Fig. 2c). The best result of uniform PULL fibers are obtained by the applied voltage of 15 kV with the diameter range of 100–500 nm as shown in Fig. 2b.

3.1.3. Tip to target distance

Tip to target distances have also a significant effect on the electrospun PULL fibers as shown in Fig. 3. Three different tip-to-collector distances (e.g., 10, 15 and 20 cm) are studied and found that at a 15 cm tip to collector distance is the ideal one to synthesize the PULL/MMT fibers (Fig. 3b).

3.1.4. MMT contents

MMT contents do not effects enormously on the morphology of electrospun PULL fibers. Fig. 4 shows the nanofibers including various quantities of MMT. The diameter of fibers and the formation of beads are strongly influenced by the viscoelasticity of the solution (Fong, Chun, & Reneker, 1999). The diameter of PULL/MMT nanofibers is unaffected as well as fibers homogeneity remains identical with increasing of MMT contents from 1 to 10 wt.% (Fig. 4a–d). From Fig. 5a, TEM image supports that the coexistence of MMT clay (dark layers) and PULL matrix (light dark area) for PULL/MMT electrospun fiber mats with 5 wt.% MMT.

3.2. Tensile strength

Fig. 5b shows the tensile strength of PULL/MMT nanofibers with different MMT contents. It is found at low (1 and 3 wt.%) and high (10 wt.%) MMT contents, the tensile strength is lower than 5 wt.% of MMT in the nanofiber mats. The maximum tensile strength is found at about 13.1 MPa for 5 wt.% MMT content. This result appears to be related to the lack of interfacial interaction between the clay and the matrix polymers; thus, many defects and agglomerations occur in areas of the interface (Chang, Jang, Ihn, Lee, & Sur, 2003).

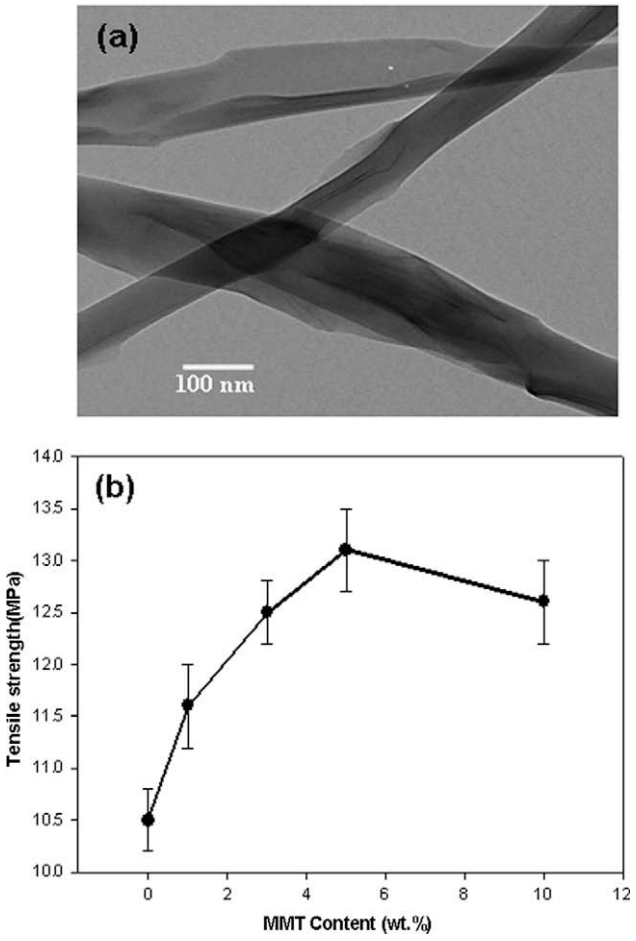

Fig. 5. (a) TEM image of electrospun PULL/MMT nanofiber mats (MMT content = 5 wt.%, TCD = 15 cm, applied voltage = 15 kV and polymer solution concentration = 20 wt.%), and (b) tensile strength of electrospun PULL/MMT nanofiber mats with various MMT contents (TCD = 15 cm, applied voltage = 15 kV, and pullulan solution concentration = 20 wt.%).

3.3. XRD data

The spacing between clay platelets, or gallery spacing, is an indicator of the extent of intercalation/exfoliation of clay platelets within a polymer matrix and can be observed by using X-ray diffraction. Generally intense reflection in the range of 3–9° (2θ) indicates an ordered intercalated nanocomposite. In exfoliated nanocomposites, on the other hand, where single silicate layers (1 nm thick) are homogeneously dispersed in the polymer matrix, and XRD patterns with no distinct diffraction peak in the range of 3–9° (2θ) could be observed (Barber, Calhoun, & Moore, 2005; Zhu et al., 2007). Fig. 6a shows the XRD patterns of as received PULL and MMT, and electropsun PULL/MMT nanofiber mats with 5 wt.% of MMT contents. Here, the XRD patterns show an intense diffraction peak in 3–9° for electrospun PULL/MMT nanofiber mats, indicating the possibility of having intercalated silicate the layers of clay dispersed in PULL matrix. There is a broad peak appearing near 19.4°, corresponding to a *d*-spacing of 4.52 °C for bulk PULL (Biliaderis, Lazaridou, & Arvanitoyannis, 1999).

3.4. FT-IR spectra

FT-IR spectra give additional information about the structure of nanofiber mats studied. In Fig. 6b, examples of spectra of as received PULL powder and electrospun PULL/MMT (1, 3, 5 and

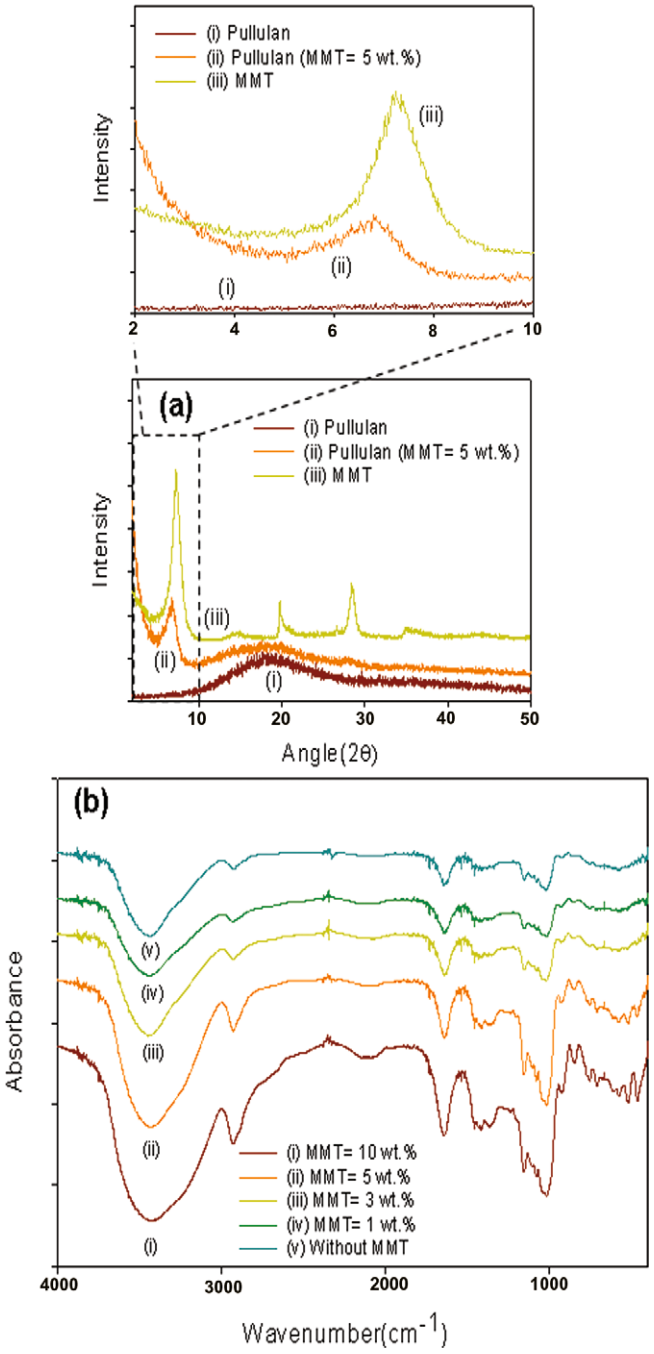

Fig. 6. (a) XRD data of as received PULL and MMT, and electrospun PULL/MMT nanofiber mats (TCD = 15 cm, applied voltage = 15 kV, and polymer solution concentration = 20 wt.%), and (b) FT-IR data of eletrospun PULL/MMT nanofiber mats with various PULL/MMT mass ratios (TCD = 15 cm, applied voltage = 15 kV, and polymer solution concentration = 20 wt.%).

10 wt.% of MMT) nanofiber mats at 400–4000 cm^{-1} range are shown. Pure PULL exhibits identical bands as shown in Fig. 6b (v). In the specific area (1500–650 cm^{-1}) which is characteristic for the pullulan molecule as a whole, the spectra for commercial pullulan as well as those for PULL/MMT electrospun fiber mat samples exhibited similar features (Fig. 6b (i–v)). Such results confirm the identical chemical structure of the samples. Strong absorption in 850 cm^{-1} is characteristic of the α-glucopiranosid units. Absorption in 755 cm^{-1} indicates the presence of α-(1,4) glucosidic bonds, and spectra in 932 cm^{-1} proves the presence of α-(1,6) glucosidic bonds. Besides, in the areas for reference and evaluated samples the frequencies are analogous (Seo et al., 2004). Bands at 2850–

3000 cm^{-1} are due to stretching vibrations of CH and CH_2 groups and bands attribute to CH/CH_2 deformation vibrations are present at 1300–1500 cm^{-1} range. Also very intensive, broad hydroxyl band occurs at 3000–3600 cm^{-1} and accompanying C—O stretching exists at 1000–1260 cm^{-1}. The absorption band corresponding to hydroxyl groups of pullulan and MMT (3420 cm^{-1}) is reduced relative to the band of CH stretching vibrations (2930 cm^{-1}) as the interfacial interaction proceeds. Low intensive carbonyl band, is detected at 1724 cm^{-1} in PULL spectrum and gradually reduced after adding the MMT fillers. All these bands are also present in PULL composites with MMT (Fig. 6b (i–iv)). The small shifts of absorption maximum and alteration of band shape are results of changes in the nearest surrounding of functional groups. These observations are illustrated in Fig. 6b for bands in region 1000–1750 cm^{-1}. Thus, the FT-IR spectroscopy supplies also evidences of possible interactions between PULL matrix and MMT clay, which are suggested above.

3.5. Crystalline, melting and thermal properties

The PULL/MMT nanofibers melting and crystalline point is investigated by DSC on various MMT contents. Fig. 7 shows the DSC thermogram of electrospun PULL/MMT fibers with different mass of MMT contents at a polymer concentration of 20 wt.%. Pure PULL polymer shows a large thermogram peak of melting transition (T_m) at ~99 °C. This peak is shifted to 101.4, 102.2, 104.1 and 106.2 °C with the addition of 1, 3, 5 and 10 wt.% of MMT, respectively. The DSC for the nanofibers shows clearly the melting transitions of the PULL, in which there are significant effects of the MMT contents. It is suppressed due to the polymer confinement in accordance with previous work (Strawhecker & Manias, 2000). It seems that the inorganic layer affect all polymer morphology also, even though the MMT content is still low with respect to the PULL matrix (Alla, El-Din, & El-Naggar, 2006).

Thermal stability of electrospun PULL/MMT nanofibers is measured using TGA in nitrogen atmosphere. Fig. 8 shows TGA thermograms of different decomposition temperature with MMT content of 1, 3, 5 and 10 wt.%. The most below curve of the TGA data (Fig. 8a) represents the bulk PULL, i.e., as received PULL powder with no MMT contents and the most upper curve (Fig. 8e) is for mass ratio of 10 wt.% of MMT, i.e., the highest mass ratio of MMT content is used in our work. Fig. 8b–d are displaying three middle

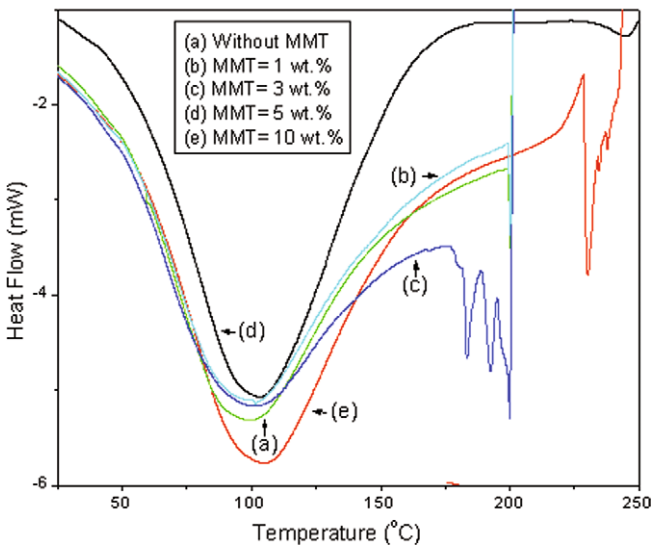

Fig. 7. DSC data of electrospun PULL/MMT nanofiber mats with various PULL/MMT mass ratios (TCD = 15 cm, applied voltage = 15 kV, and polymer solution concentration = 20 wt.%).

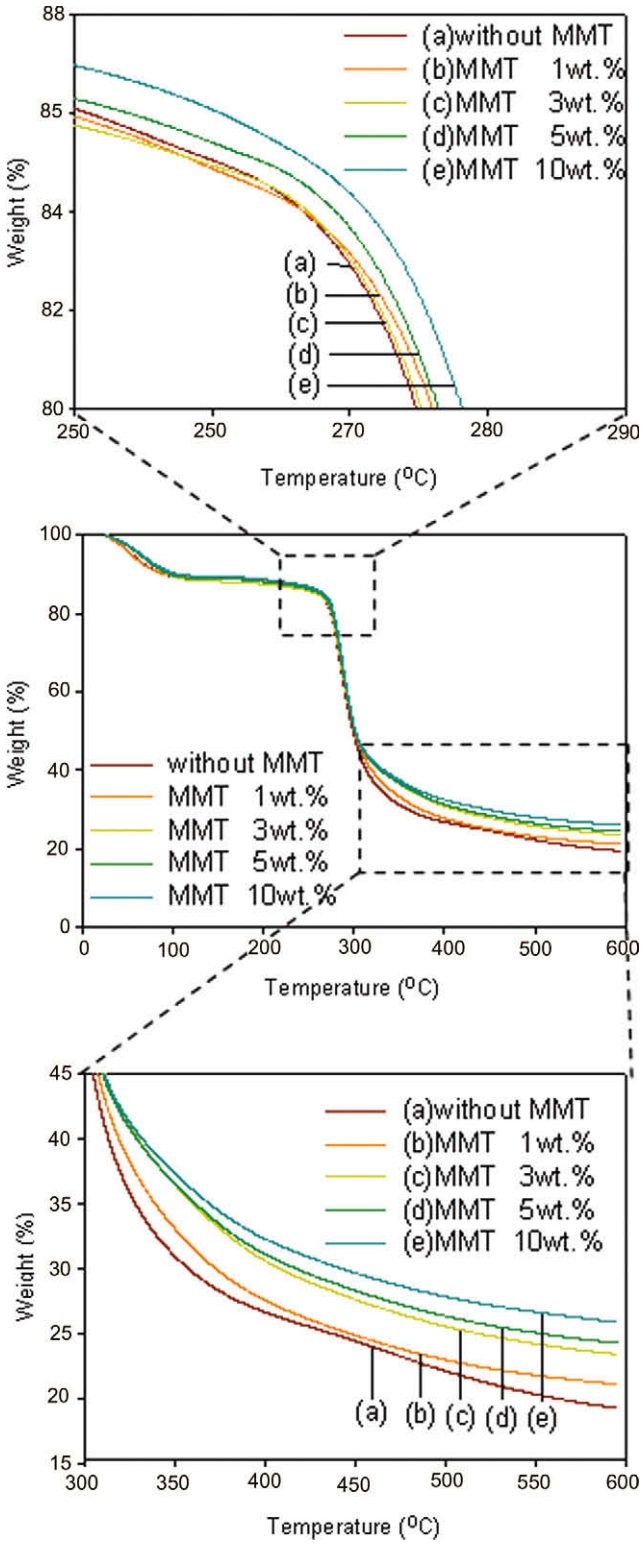

Fig. 8. TGA data of electrospun PULL/MMT nanofiber mats with various PULL/MMT mass ratios (TCD = 15 cm, applied voltage = 15 kV, and polymer solution concentration = 20 wt.%).

mass ratios of MMT contents at the same trend of thermal stability like the Fig. 8a and e. Within up to 265 °C, there is increased in thermal stability from the pure PULL nanofibers to PULL/MMT (1–10 wt.%) nanofibers. The higher thermal stability of high MMT content rate might be attributed to its higher chain compactness due to the interaction between the PULL and the clay materials.

4. Conclusions

PULL/MMT clay nanofiber mats could be fabricated by the electrospinning method in aqueous solutions. The polymer concentration, applied voltages and tip-to-collector distances are the main important factors influencing the electrospinnability of the bulk PULL solutions as well as the morphology of the electrospun nanofiber mats. Uniform PULL/MMT fibers with an average diameter of nanometer-scale (50–500 nm) could be prepared from the 20 wt.% of PULL containing different amount of MMT contents (1–10 wt.%). The study shows that the introduction of MMT results in improvement in tensile strength, and thermal stability of the PULL matrix. XRD patterns and TEM micrographs suggest the coexistence of intercalated MMT layers over the studied MMT contents. The DSC thermogram shows clearly that the PULL polymer with these levels of MMT has influenced on the melting transitions as well as crystallinity. Also, FT-IR reveals that there might be possible interaction occurred between the MMT clay and pullulan matrix.

Acknowledgement

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