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Research Article

Nanoclay-Incorporated Polycaprolactone Matrix via Electrospinning Techniques-Enriched Spectroscopic Responses

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Nanotechnology is one of the most common areas for current research and development in almost all technological fields. A significant factor is the synergistic benefit of nanoscale dimensions over larger scale alteration. Polymer nanoscience is the analysis and application of nanotechnology to polymer nanoparticle matrices, with nanoparticles described as those with at least one dimension of less than 100 nm. The use of polymer nanotechnology and nanocomposites in practical applications is a rapidly developing area. For making polymeric nanofibers from polymer melts and solutions, a spinning technique is used known as electrospinning. Electrospinning is an easy way to produce ultrafine fibers, which is nanosize. For its wide range of variety of spinning polymeric fibers, it is recommended, as well as producing fibers in nanosize accurately. The aim of this project is to use electrospinning to make nanoclay integrated polycaprolactone membranes. The effects of the nanoclay on morphology, thermal, and sorption behaviors of the electrospun membrane were further studied. The scope of this project work is that the electrospun nanocomposites are best studied for biomedical applications. Because of their influence over porosity, pore size, and fiber diameter, they make excellent scaffold materials.

1. Introduction

Every living being is made up of matter. Matter is made up of an infinite number of atoms once more. A simple molecular structure is formed when atoms cluster together to form molecules, which then interact with many other molecules [1]. Acting with matter on a scale of one-billionth of a meter, or 1 nm, is called nanotechnology. Nanotechnology modifies the matter at molecular and atomic levels. For modern research and wide range of scientific disciplines, nanotechnology is most used [2].

In various fields, like biochemistry, physical chemistry, surface microscopy, etc., all have been transformed by nanotechnology. Nanotubes, nanofibers, nanorods, nanowires, nanospheres, nanocrystals, and nanocomposites are only a few examples of nanoscale materials or structures that have piqued interest for a variety of high-tech applications [3–6]. A significant factor is the synergistic benefit of nanoscale dimensions over larger scale alteration [2]. Two or more materials with different chemical and physical properties and separate at a macroscopic scale are made to form composite materials. These materials are combined to form composite materials which have several properties. It has a fantastic and diverse variety of uses. Composites possess plenty of engineering advantages over that of the synthetic polymers and copolymers.

Polymer nanoscience is the research and application of nanoscience to polymer nanoparticle matrices, with nanoparticles having at least one dimension of less than 100 nm. In polymer nanotechnology, polymer nanocomposites play an important role. To increase the polymer's performance properties, nanoscopic inorganic materials, usually 10–100 Å in at least one dimension, are distributed in an organic polymer matrix. Nanocomposites are normally transparent due to the nanometer length scale, which minimizes light scattering. Polymer nanocomposites are a modern form of polymer that can be used instead of conventionally filled polymers. Filler dispersion nanocomposites have stronger properties than pure polymers because of their nanometer sizes [7].

For fabricating polymeric ultrafine fiber matrices, several methods are available, these include electrospinning temperature-induced separation, etc. Electrospinning, on the other hand, has proven to be one of the most effective method for making polymeric nanofibers from polymer melts and solutions. The diameter range of 3–10 nm is applicable to manufacture polymeric fibers with an increasing solution concentration using the same electrospinning experimental setup [8].

A simple electrospinning system typically includes three major components: a power supply with high voltage, a spinneret, and a disc for grounded collecting, which can be a metal plate or screen. In an external electric field, a suspended conical droplet is created where the electric field and surface tension are maintained at an equilibrium state. The droplet is created by spinneret when the charged polymer solution is fed into it [9].

Many variables influence fiber thickness and morphology. These include solution properties such as temperature and humidity as well as solution properties (density, elasticity, and surface tension) and the spinneret and collecting plate distance [4].

To produce control-sized fiber diameter distribution with error-free nanofibers, certain parameters should be followed [10]. These parameters are mostly based on the properties of the polymer solution, which include molecular weight and flow rate and atmospheric properties of the polymer solution can influence the electrospinning [11]. Through electrospinning processing technology in the biomedical field, the applications which include the morphology and diameter of the nanofibers can be regulated and modified through electrospun. Not only these but also 3D patterns and porosity can be modified. In a number of biomedical applications like scaffold preparation, coating materials, and several applications in the field of tissue engineering, electrospun fibers are used. Mostly multifunctional membranes are used in composite reinforcement and filtering the submicron particles media in the separation industry [12].

The ability to produce several varieties of drugs through electrospun fibers whether the drug may be solid or amorphous solution. Through these fibers, the resulting drug will be more efficient in drug release, high permeability (it has interconnecting porous structure), and can be the delivery vehicles that are some of the appropriate features of electrospun fibers in drug delivery. After surgery adhesion for preventing membranes, it can be used [13]. Therapeutic agents are delivered by electrospun fibers. Therapeutic agents using carriers made of polymeric nanofibers matrices have been delivered locally at particular application sites. Through this, the solubility of the drug and drug diffusion increases because the surface area is wide and porous structure is high in nanofiber-based systems [11]. Clay, a natural material with low loadings, may be used as a replacement for polymer reinforcers [7].

As a prosthetic or implant unit, electrospun nanofiber plays a crucial role. Polymeric nanofiber matrices have been successfully used as implants, either alone or in conjunction with other materials and structures [11]. Polyurethane, polyesters, polystyrene, and polypropylene are just a few of the latest polymer clay nanocomposites that have been created. Various approaches and clay loadings have been used to synthesize biocompatible polymers (polycaprolactone) [7].

Tissue engineering requires scaffolds that will not inhibit but rather enable stem cell to grow. The polymer chosen for this work is polycaprolactone (PCL) as it supports stem cell growth with its nontoxic and biodegradable nature [14]. It is a synthetic polymer that is used in food processing, tissue engineering, wound dressings, and drug delivery [15]. PCL is made by opening the ring of caprolactone in the presence of metal alkoxides. It is a good electrical conductor that is essential for electrospinning. The nanometer scale diameter products are produced by electrospinning [16–19]. The scaffolds can be made for any tissue required [20–26]. Flexibility, medium melting point (65°C), and low T_g (−61°C) are several of PCL's unique characteristics [27–32]. PCL is a biodegradable material and can be used in treatment process too [33–37]. The nanoclay was incorporated into PCL and was electrospunned. The changes in the morphology, thermal, and sorption behaviors of the membrane were further studied and briefly described in this paper.

2. Methodology

2.1. Feed Solution. Nanoclay (Cloisite 10A, Cloisite 10B) was taken at four different concentrations (1, 3, 5, and 9 wt%) in dichloromethane. The benefits of nanoclays include their widespread availability, ease of processing, high performance, and low cost. The different polymer solutions used in electrospinning are hexafluoroisopropanol, trifluoroethanol, dichloromethane, and chloroform. It was then kept overnight stirring for exfoliation to result. The term exfoliation refers, here, to remove the unwanted material of nanoclay and preparing the material with polymer solution for the process of electrospinning. To the well- stirred solution, PCL 10 wt% (PCL with a molecular weight of 80,000) was dissolved and again kept for overnight stirring. The resulting solution is taken as the feed solution for electrospinning. Electrospinning has been used to create nanofibers from various materials. Organic polymers in solution or in melt form are the most commonly used materials. Small molecules can also be electrospun directly into nanofibers if they self-assemble and generate enough chain entanglement. The viscosities of polymer solution have an impact on the electrospinning process. The electrospinning parameters include the applied electric field, needle-to-collector distance, flow rate, and needle diameter. The solvent, polymer concentration, viscosity, and solution conductivity are all solution parameters. The environmental parameters include relative humidity, temperature, and relative humidity.

2.2. Synthesis of Electrospun PCL Clay Nanocomposite Membrane. Electrospun PCL clay nanocomposite membranes were fabricated by the electrospinning process. The conditions used for electrospining of PCL clay nanocomposite membranes were maintained at 12 cm in the tip of the collector and voltage of 15 kDa (kilo Dalton) was applied at solution feed rate of 1 ml/hr. The main distinction between electrospinning and electrospun is the viscosity and viscoelasticity of the liquid involved, which affects the rate of reaction. The main advantages of the electrospinning technique are the ability to produce very thin fibers with large surface areas, the ease of functionalization for various purposes, superior mechanical properties, and ease of process.

2.3. Morphological Analysis of Nanocomposite Membrane. By scanning electron microscope, here, we analyze both the average fiber diameter of electrospun fibers and fiber morphology. To observe the surface morphology, JEOL JSM-6390 SEM instrument was used. To probe the crystal lattice structure of the nanocomposite, it is subjected to X-ray powder diffraction, which is a rapid analytical technique. For the sample, an X-ray is used, followed by X-ray diffractometry analyses of the clay dispersion. By Bruker AXS automated XRD model and D8 equipment X-ray, diffractograms were recorded with CuKα1 radiation ($\lambda = 1.54$ nm), 2θ range from 1° to 15°.

2.4. Thermal Analysis of Nanocomposite Membrane. During temperature changes at different rates, the weight loss of the sample may occur. To determine the balance, thermogravimetric analysis is used. On the balance, the pan is placed, and the sample is loaded on the pan. Now the sample is closed by a furnace and at a given rate and given environment, the temperature is changed.

Due to the varying in different rates of temperature, the constituents in the sample may burn off, so the weight percent of the constituents is recorded. Shimadzu TGA instrument was used to measure the TGA measurements. The heating rate of the sample ranges from 25 to 700°C at 10°C/min under nitrogen. At 410°C, the residue of the clay is removed before that the measurement of clay content is recorded. The concentration of the nanofiber synthesis is efficient and there is reduction of fiber diameter and bead formation.

2.5. Sorption Behavioral Study of Nanocomposite Membrane by Determination of Water Uptake and Water Retention. The electrospun membranes were kept in water for 24 hr to measure the water uptake. After 24 hr, the immersed samples were taken out from the water and weighed [38]. The water uptake of the membranes was calculated as before and after weight difference of the water uptake, by the following formula [39]:

$$\text{Water uptake} = \left[\frac{W_s - W_d}{W_d}\right] \times 100, \quad (1)$$

where W_s is the weight after water uptake and W_d is the weight of the dry membrane.

Water retention was calculated as defined in Equation (2):

$$\text{Water retention} = \left[\frac{(W_s - W_d)}{(W_e - W_d)}\right] \times 100, \quad (2)$$

where W_e is the equilibrium water content.

3. Results and Discussion

3.1. Morphological Analysis. Morphological analysis is the simple process of investigative possible resolutions to unquantifiable, complex problems connecting many factors.

3.1.1. Effect of Polymer Concentration. SEM is used to obtain information about the morphology of the nanofibers. The polymer concentration effect in the electrospun PCL nanofibers synthesis using dichloromethane as solvent is shown in Figure 1. As shown in Figure 1, with increase in polymer concentration, the nanofiber synthesis is efficient and there is reduction of fiber diameter and bead formation.

3.1.2. Effect of Nanoclay Content. Nanoclay was used as the nanofiller to enhance the properties of PCL. Nanoclays are layered with mineral silicate nanoparticles. Nanoclays are classified into several groups based on their chemical composition and nanoparticle morphology, including montmorillonite, bentonite, kaolinite, hectorite, and halloysite. Nanoclay, also known as layered silicates, is a widely used and researched nanoagent employed in the preparation of nanocomposites for packaging materials. Nanoclays are natural nanomaterials found in the clay content of soil, the most significant of which are montmorillonite and allophane. Montmorillonite is a hydrous crystalline phyllosilicate. In Figure 2, the influence of nanoclay on the morphology of the electrospun PCL membranes is shown. The fiber diameter is large and there is bead formation in the absence of nanoclay. As the concentration of nanoclay increases, the fiber diameter and the bead formation are greatly reduced.

3.1.3. Effect of Applied Voltage. The morphology of PCL nanofibers on the effect of applied voltage on is shown in Figure 3. At reduced voltage, 8 kV, there is reduced amount of fiber formation and an increased amount of bead formation. The nanofiber synthesis increases, and the bead formation decreases at high applied voltage, 15 kV. PCL solution of 10 wt%, nanoclay of 5 wt% with solvent dichloromethane, and solution feed rate of 0.5 ml/hr are the electrospinning parameters carried out.

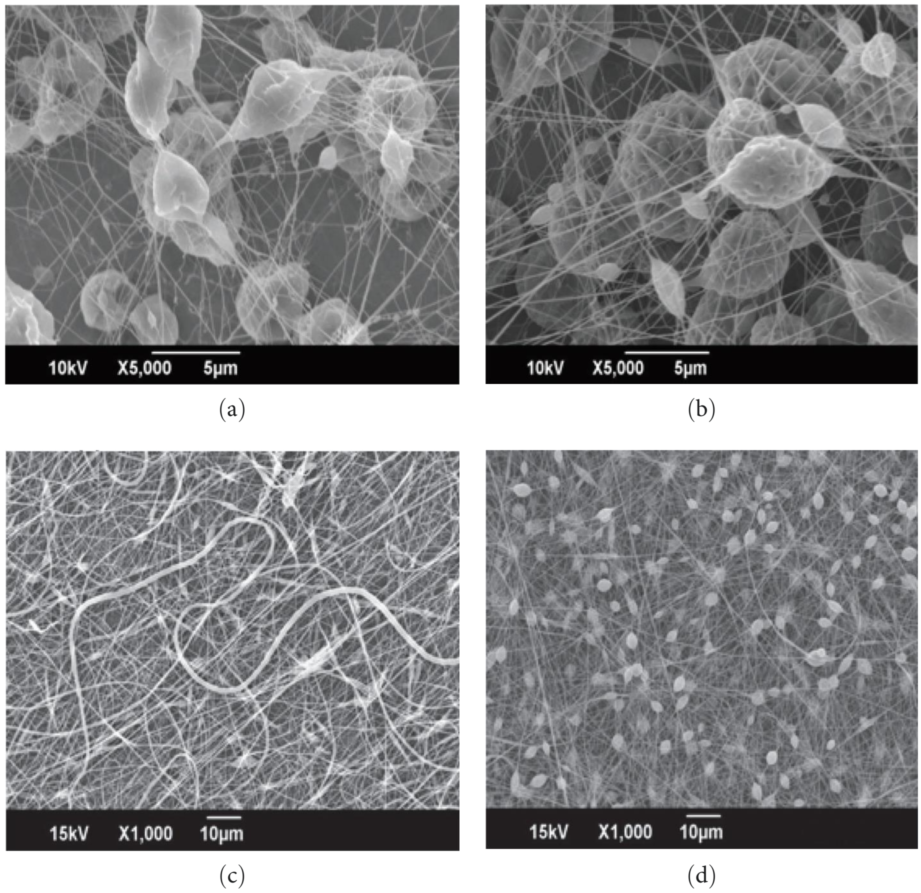

Figure 1: SEM micrographs of electrospun PCL nanofibers using DCM as solvent. (a) At 5,000x magnification of the first area of nanofiber; (b) at 5,000x magnification of the second area of nanofiber; (c) at 1,000x magnification of the first area of nanofiber; (d) at 1,000x magnification of the second area of nanofiber.

3.2. X-Ray Diffraction by Morphological Review. The fundamental principle of X-ray diffraction (XRD) is the constructive interference of monochromatic X-rays with a crystalline sample. A cathode ray tube generates these X-rays, which are then filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. XRD is a nondestructive technique for determining a material's crystallographic structure, chemical composition, and physical properties. It works by using the constructive interference of monochromatic X-rays with a crystalline sample. X-ray powder diffraction (XRD) is a rapid analytical technique that can provide information on unit cell dimensions and is primarily used for phase identification of crystalline materials. The analyzed material is finely ground and homogenized before determining the average bulk composition. As compared to pure clay, XRD offers quantitative details about the exfoliation and d-spacing of the clay layers in the polymer matrix. Cloisite 10A and Cloisite 15A XRD patterns are shown in Figure 4. It is evident from the figure that when nanoclay is incorporated into PCL, the d-spacing increases as result of intercalcation, as there is a shift in the 2θ value to lower angles.

3.3. Thermal Analysis by Thermal Gravimetric Analyzer. Thermal gravimetric analyzer weighs a sample as it is heated or cooled in a furnace. A TGA is made up of a sample pan supported by a precision balance. During the experiment that pan is heated or cooled in a furnace. Throughout the experiment, the mass of the sample is measured. Nanocomposite and polymer thermal stability is evaluated by using TGA. A TGA analysis is carried out by gradually raising the temperature of a sample in a furnace while its weight is measured on an analytical balance that remains outside of the furnace. If a thermal event results in the loss of a volatile component, mass loss is observed in TGA. The PCL clay nanocomposite membranes are more stable than pure polymers, their improvement in thermal stability because polymer matrices are incorporated of clay fillers. Figure 5 represents the TGA curves for pure PCL and electrospun PCL clay nanocomposite membrane. By heating them at 10°C/min, the pure polymer and the composite polymer of the TGA are obtained. The PCL clay thermal stability and virgin PCL are relatively similar. As compared to pure PCL, both intercalated and exfoliated nanocomposites have greater thermal stability. The onset temperature of degradation is the maximum for the nanocomposite with 1% clay. A plot of weight percentage vs. temperature obtained by measuring the mass of a sample while it is being heated gives the thermal gravimetric analysis graph. Instrumental factors include the furnace

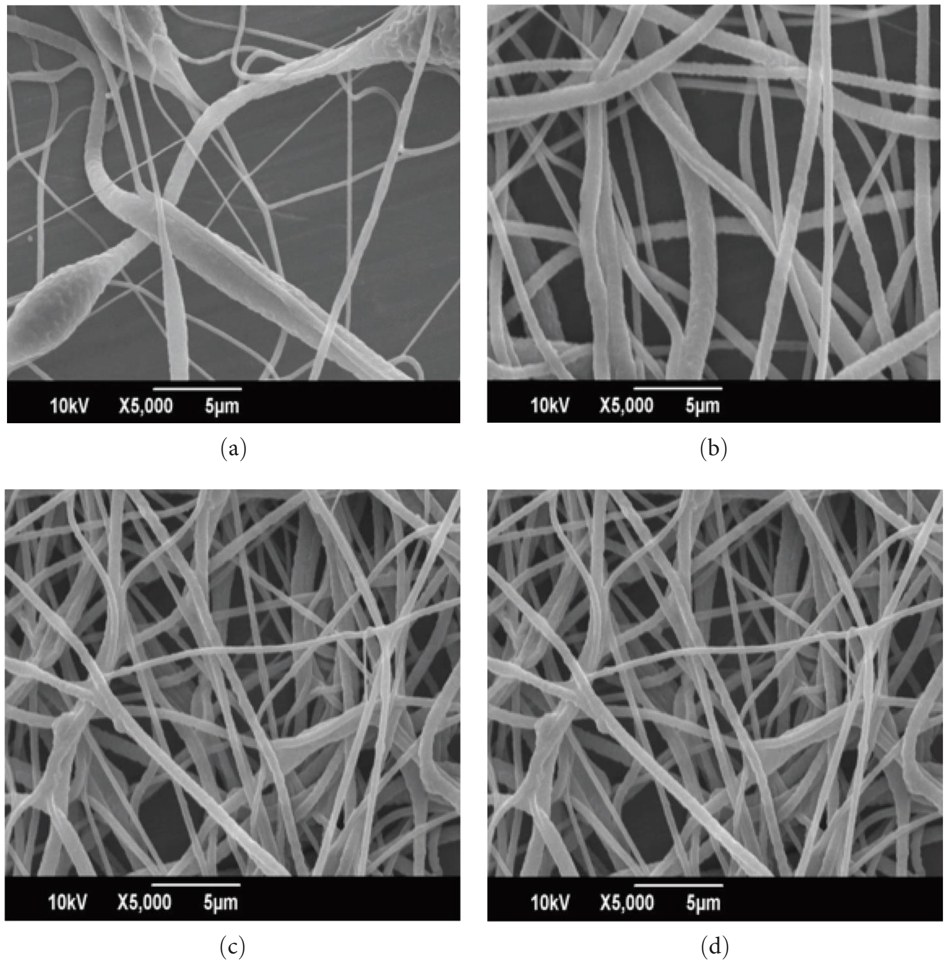

Figure 2: SEM images showing electrospun fibers of PCL containing (a) 0 wt% clay, (b) 1 wt% clay, (c) 3 wt% clay, and (d) 9 wt% clay.

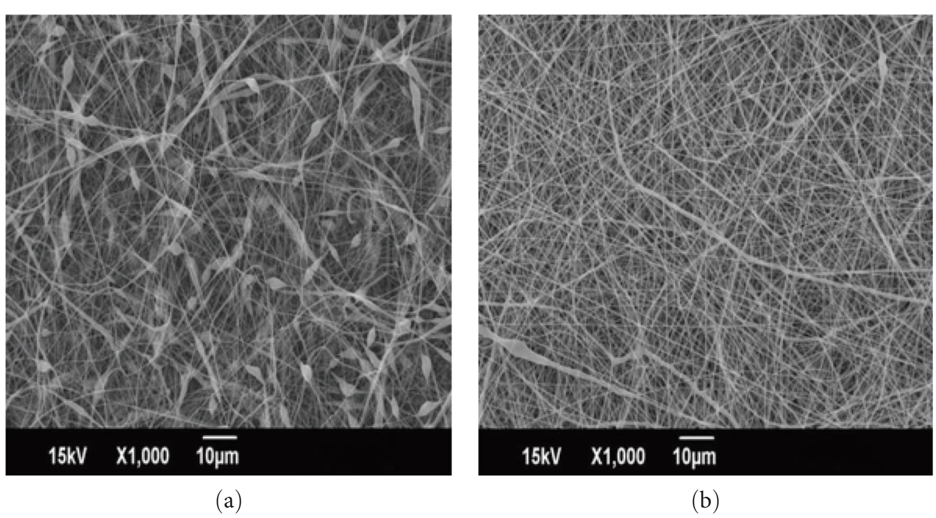

Figure 3: Electrospun PCL clay nanocomposite membrane at varying voltage (SEM image): (a) 8 kV; (b) 15 kV.

environment, gas flow rate; heating rate, geometry, and pan material affect the thermal gravimetric analysis. Typically, a heating rate of 3.5°C per minute is considered adequate for TGA reliability and reproducibility. TGA instruments can measure a variety of parameters, such as moisture loss, decarboxylation, pyrolysis, solvent loss, plasticizer loss, oxidation, and decomposition for biomass or other substances.

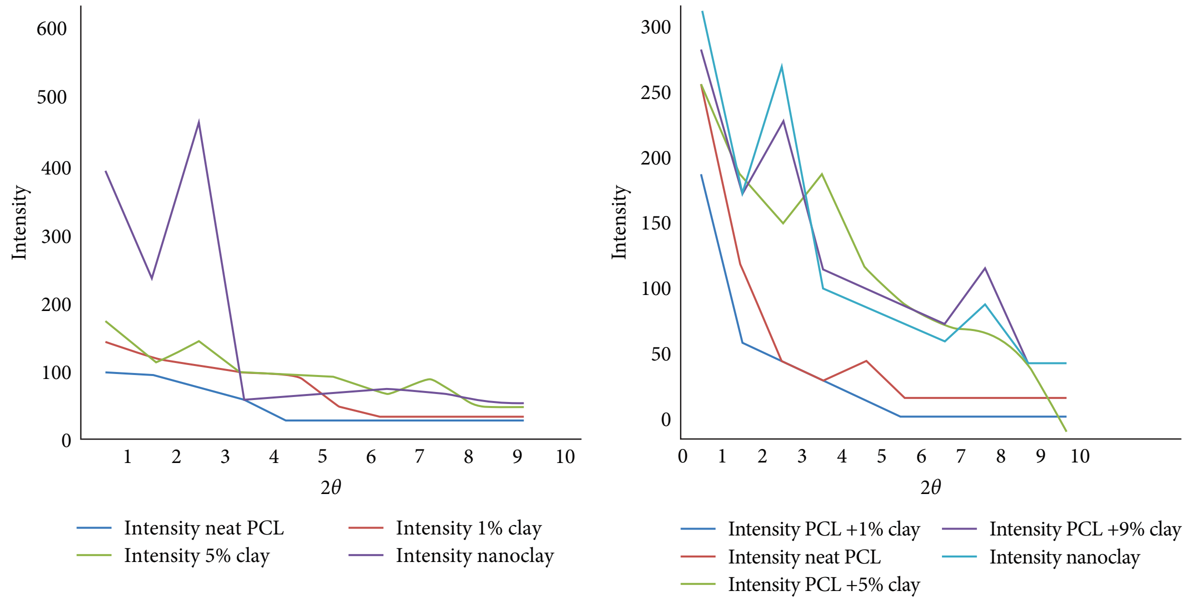

FIGURE 4: Images of XRD patterns: (a) Cloisite 10A; (b) Cloisite 5A.

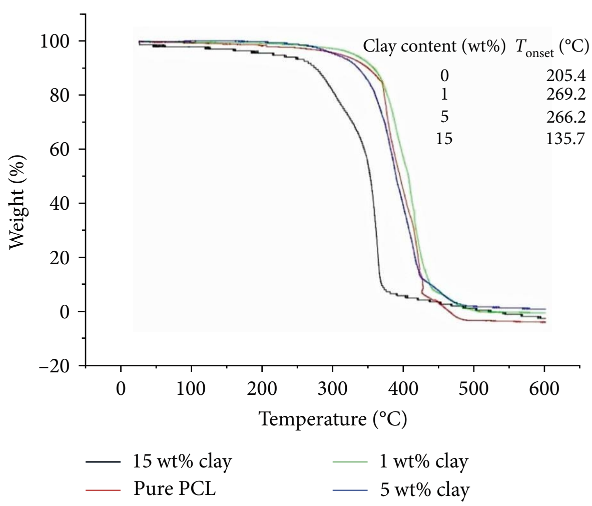

FIGURE 5: TGA curves for pure PCL and electrospun PCL clay nanocomposite membrane.

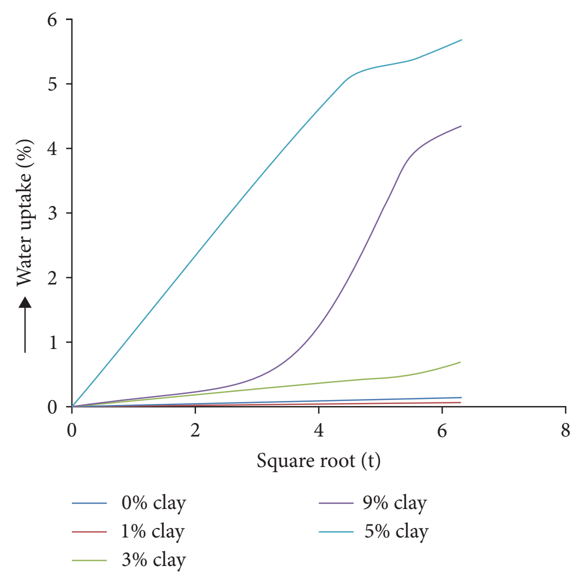

FIGURE 6: Water uptake of PCL Cloisite 15A nanocomposite.

3.4. Water Sorption Behavioral Study. The water uptake of the nanocomposites was found to be lower compared to the pristine polymer. Figures 6 and 7 indicate that the water absorption of the nanocomposite films is prepared by Cloisite 10A and Cloisite 15A. It may be seen that in both cases, there was a decrease in water absorption with the increment of clay content. For the penetrating molecule to move through the nanocomposites, the impermeable clay layers dictate a tortuous route. Two factors affect the nanocomposites water absorption: they are filler geometry and matrix molecular level interaction and filler. These nanosfilled samples produce decrease water uptake values with high tortuosity path, this is because silicates have platelet-like morphology.

When the water retention of the nanocomposites was studied, it was found that the water retention was higher for the 0% clay than that for the 9% of clay. There is fine distribution of the clay at lower loading and the clay begins to agglomerate at higher loading leading to poor water retention, as shown in Figure 8.

4. Conclusion

Instead of conventional filled polymers, polymer nanocomposites are used. It may be in the form of fibers, tubes, and crystals that are arranged together into several nanostructures for a

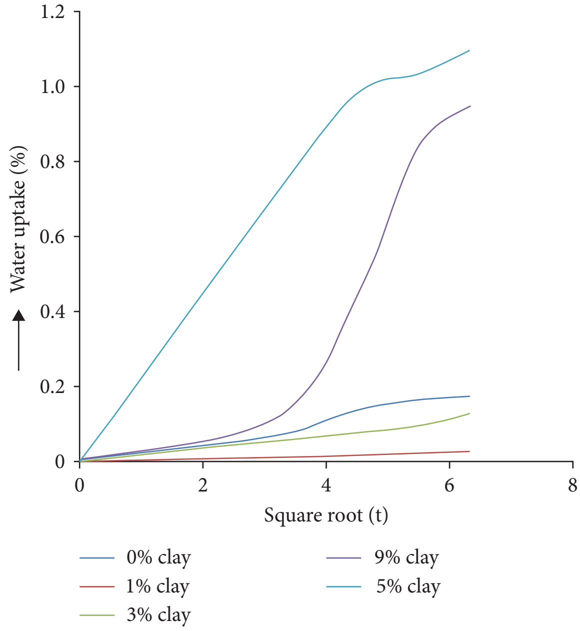

Figure 7: Water uptake of PCL Cloisite 10A nanocomposite.

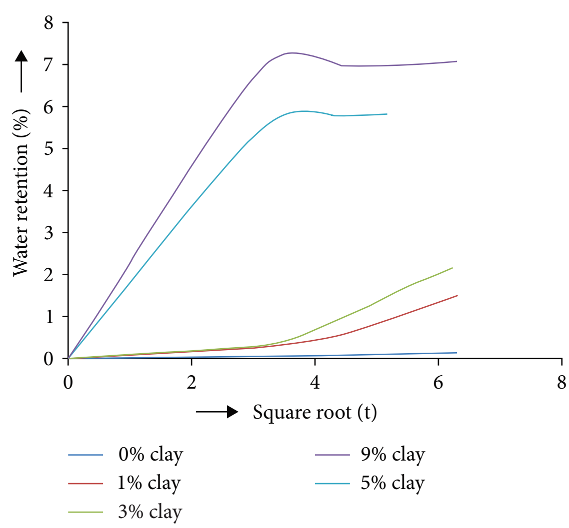

Figure 8: Water retention of PCL Cloisite 10A nanocomposite.

wide range of high-tech applications. Electrospinning has emerged as a popular nanotechnology in manufacturing nanofibers from a variety of materials. Nanofibers have a wide range of potential technological and commercial applications. Tissue engineering, drug delivery, seed-coating material, cancer diagnosis, lithium–air battery, optical sensors, air filtration, redox-flow batteries, and composite materials fields all make use of nanofibers. In this paper, the PCL clay nanocomposites were electrospuned at a voltage of 15 V, feed rate of 1 ml/min and 12 cm of tip-to-collector distance. This process is selected due to its simplicity, elegance, versatility, consistency, and by its own advantages. Compared to pure polymers, filler dispersion nanocomposites have increased applications because of their ultrafine meter sizes. The nanoclay filter, here, is used to improve the applications of pure polymers because it has manometer sizes. By introducing the nanoclay into the polymers, it increases the thermal stability, sorption, and morphology of the membrane. The nanocomposites obtained are best suited for scaffold production in the field of tissue engineering by improving the growth of the cell and organizing the tissues. These nanocomposites can able to manufacture nanosize fibers with special characteristics like high surface area and aspect ratio and have the ability to control the pore geometry. These special characteristics are helpful in cell growth (because of cell adhesion), expression of cell, and oxygen and nutrients transportation to the cells. If polymers of low molecular weight can be electrospun with low fiber diameter and the negligible bead formation, then it will be a remarkable achievement at the industrial level. These polymer clay nanocomposites possess diverse biomedical applications and are excellent materials for tissue engineering purposes.

Data Availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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