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Surface characterization of Argon plasma treated electrospun P(HOLA-e-CL) clay nanocomposite

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In this work, the effects of Argon plasma surface modification have been studied on electrospun P(HOLA-e-CL) Clay Nanofiber Compositesin order to investigate the imposed limitation and possibilities to improve surface characteristics on fibrous assemblies. The evolution of induced changes in surface morphology and wettability by the plasma treatment has been characterized for increasing plasma exposure time using Scanning Electron Microscopy (SEM), FTIR and water contact angle measurements. Exfoliation and dispersion of DEALA MMT within P(HOLA-eCL) matrix was confirmed through Transmission Electron Microscopy (TEM).

Keywords: Contact angle, Argon Plasma, exfoliated clay (DEALA MMT), electrospunnanofiber composites

Introduction

Environmental and sustainability issues due to the disposal of plastics for the past decades have shifted research trends to investigating different types of biodegradable polymeric materials. Renewable biodegradable polymers such as polylcaprolactone a potential substitutes to traditional synthetic polymers. These biodegradable polymeric fibers have immense potential to be used as alternative for conventional materials in filtration and energy storage media, health and personal care textiles, thermal and sound insulations, geo-textiles, automotive textiles, tissue engineering scaffolds, water filtration and food packaging fillers (Bhardwaj, 2010) . In recent studies, researchers have an increasing interest in the fields of nanomaterials because of its excellent

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properties such as high surface area and small inter-fibrous pore size with high porosity. Therefore, these nanomaterials can be employed in a vast numbers of applications including filters, composite reinforcements, drug-delivery vehicles, and scaffolds for tissue cultures. One way to developenanomaterials was done by electrospinning.

Electrospinning is a versatile technique to fabricate biodegradable polymers into small thin fibers with the action of high electrostatic force to deposit randomly the continuous strand of a polymer liquid drawn through a spinneret on a grounded collector as a non-woven mat. Polycaprolactone (PCL), is a versatile synthetic polymer that has unique properties such as high flexibility, biocompatibility, slow biodegradability, non-toxicity and good mechanical properties (Van der Schueren, 2013).

Materials and methods

In recent studies, researchers have an increasing interest in the fields of nanomaterials because of its excellent properties such as high surface area and small inter-fibrous pore size with high porosity. Therefore, these nanomaterials can be employed in a vast numbers of applications including filters, composite reinforcements, drug-delivery vehicles, and scaffolds for tissue cultures. One way to developenanomaterials was done by electrospinning.

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Electrospinning is an interesting process for fabricating fibers with average diameters in the range of micrometers to nanometers (Tungprapa, 2007). The term “electrospinning” was derived from the word “electrostatic spinning” and it was first reported by Formhals who published a series of patents from 1934 to 1944, describing an experimental setup for the production of polymer filaments using an electrostatic force (Huang *et al.*, 2003a).

There are three essential components, a syringe, a fiber collector, and a high-voltage supplier. The syringe was used to contain a polymer solution and provide a capillary tube wherein the viscous drop was able to form. The fiber collector, usually a conductor metallic screen which can generate a magnetic field, is placed below in a defined distance below the syringe. The electric voltage usually 1 to 30 kV is applied across the syringe and the fiber collector to facilitate the charged jet to eject from the needle tip toward the surface of the fiber collector.

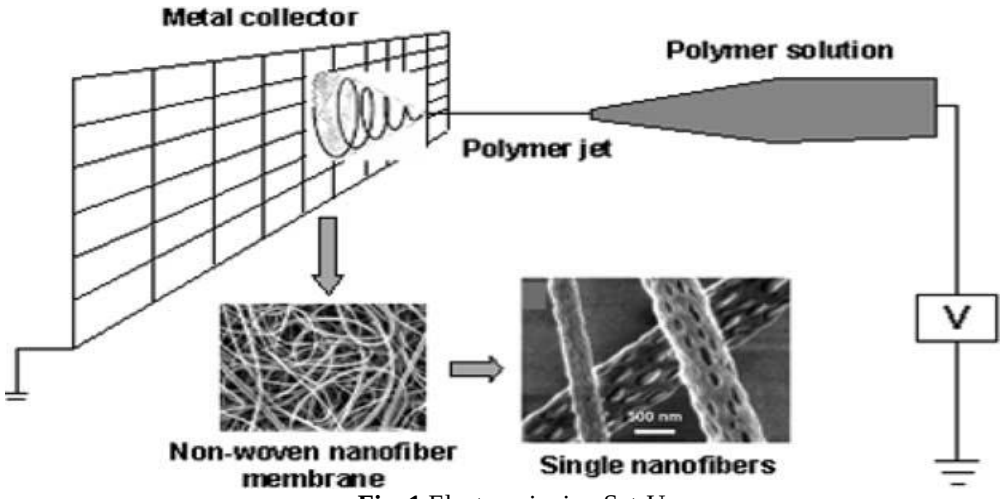


Fig. 1. Electrospinning Set-Up

Polymer nanofibers obtained by electrospinning are industrially and scientifically interesting due to their unique characteristics such as high surface-area to- mass or volume ratio, small inter-fibrous pore size with high porosity, vast possibilities for surface functionalization, etc.

These nanofibersare widely used in vast applications such as filters, composite reinforcements, drug-delivery vehicles, and scaffolds for tissue cultures (Huang *et al.*, 2003b). Several studies were conducted to produce nanofiber materials by electrospinning.

The Ring Opening polymerization of PCL-HOLA DEALA MMT and the electrospunfiber mats produced from the Institute of Chemistry, University of the Philippines, Diliman were exposed to Argon plasma. 25 mm by 30 mm fiber mats served as samples and were subjected to vacuum and plasma treatment using the Plasma Enhanced Chemical Vapor Deposition (PECVD). The actual photo and schematic diagram of the PECVD facility is shown in Figure 5. A detailed description of the system was discussed by (Malapit, 2001). The distance between the electrodes was maintained at 15mm.

The pressure inside the chamber was lowered until it reaches 3×10^{-3}torr. Argon plasma was then ignited at a constant gas flow rate of 100 sccm and working pressure of 0.4 torr but at different discharge currents (5mA, 10 mA,). Plasma exposure of the samples was set at 15 minutes and 25 minutes respectively.

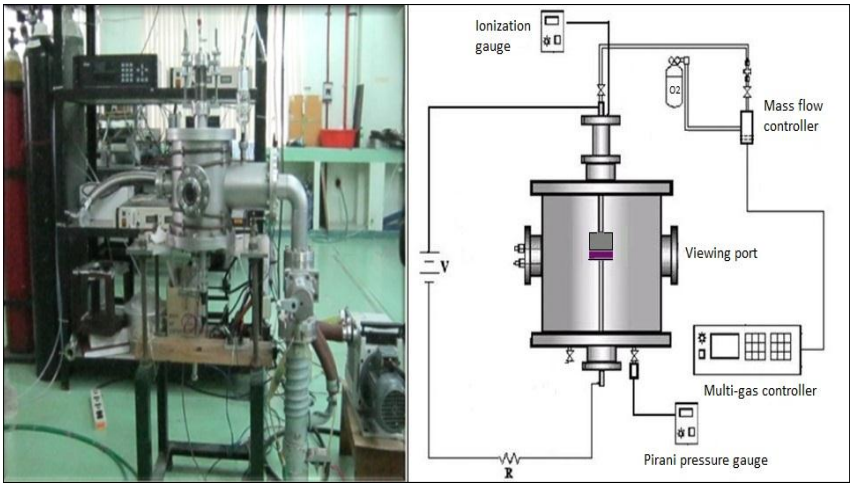


Fig. 2. Actual photograph (left) and schematic diagram (middle) of the Plasma Enhanced Chemical Vapor Deposition facility; PCL-PHOLA –DEALA MMT fiber mat sample (right)

Results and discussions

Characterizations of the electrospunnanofibers

The resulting nanocomposites were characterized to obtain chemical structure, thermal behavior, water absorbency and thermal behavior. Summary of instrumentation and analyses performed with their respective importance in the research and parameter used is shown in Table 1.

Table 1. List of instrumentations and analyses performed with their respective importance in the research and parameter used in the characterization

Instrumentations and analyses	Objective	Parameter
Wettability	To test the uptake of water in the nanofiber	Contact Angle Measurements
Fourier Transform Infrared Spectroscopy	To provide information about chemical characteristics of the nanofiber	ATR accessory 400-4000 cm^{-1}
Scanning Electron microscopy	To determine morphological characteristics of nanofiber	
Transmission Electron microscopy	To determine morphological characteristics of exfoliated nanofiber DEALA MMT	

Wettability: Contact Angle Measurements

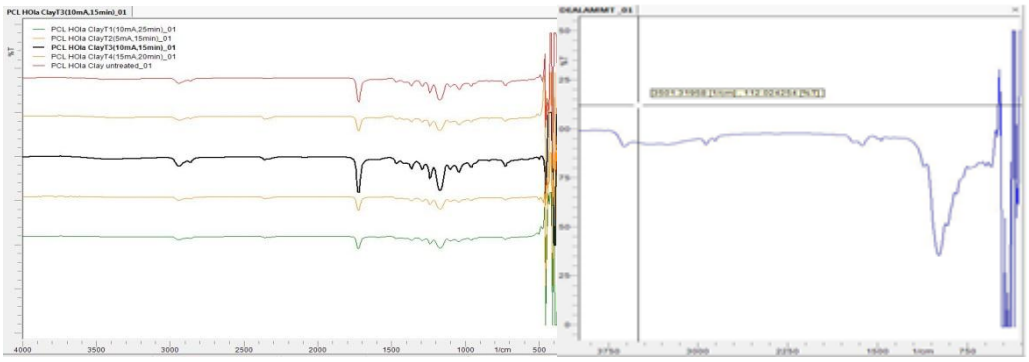
The wettability of the electrospunnanofibers can be measured through contact angle determination. Results are shown on Table 2.

Table2. Contact Angle of Electrospun PCL-PHOLA dealaMMTNanofiber at different discharge current (5mA,10mA) and set at different Plasma exposure time (min.)

Sample Treatment	Contact Angle (^{O})
Untreated	87.38
Argon 5mA,15min.	73.44
Argon 10mA.15 min.	73.15
Argon 10mA, 25 min	79.28

Among the electrospunnanofibers treated with argon plasma, the discharge current of 10mA at 25 minute plasma exposure showed the least hydrophilicity with a contact angle of 79.28^{O}. This implies that this specie exhibits least wettability relative to those exposed for 15 minutes at 5mA and 10mA counterparts. Exposure to Argon plasma enhanceshydrophility or low water absorbency of these materials which were seen to have applications for biomedical purposes (Mo, 2004; Laurienzo, 2010).

Fourier Transform InfraredSpectoscopy Analyses :



(a) (b)

Fig. 3. FTIR Spectra of (a) Argon Plasma Treated ElectrospunNanofiber and (b) DEALA MMT Clay

FTIR analysis was carried out to determine the chemical characteristics of nanofiber composites. IR spectra of PCL-HOLA DEALA MMT Nanofiber ,the peak 2950-3000 cm^{-1} was due to asymmetric CH2 while the peak at around 1700-1750 cm^{-1} corresponds to carbonyl stretching (C=O) while peak at The peak at 1200-1250 cm^{-1} can be attributed to asymmetric C-O-C stretching and 1150-1200 cm^{-1} can be attributed to symmetric C-O-C stretching.

The peaks observed were comparably the same with the IR spectra of PCL from the study of (Elzubair *et al*., 2006). In the study of Lerot and Low (1976) and Shewing *et al*. (1995) identified a band 1045-1052 cm^{-1} and assigned to a Si-O stretching vibration perpendicular to the surface of the clay platelet that is presence in the DEALA MMT , and 750-800 cm^{-1} correspond to Si-O deformation perpendicular to optical axis .

Table 3. Comparative Data of the peaks on the IR spectra of the P(CL-HOLA) DEALA MMT at different Argon Plasma Treatment

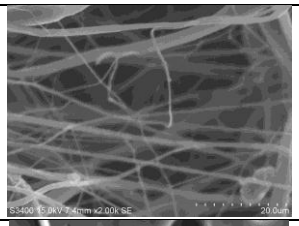
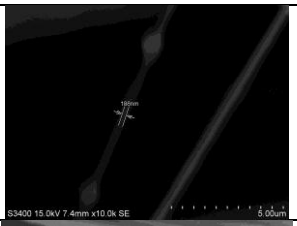
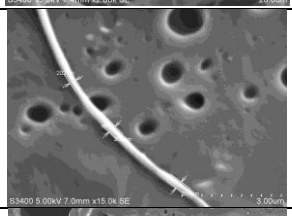
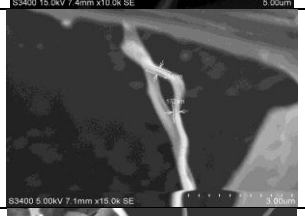
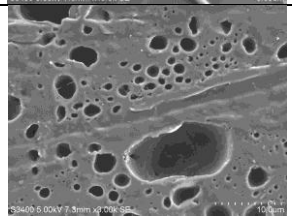
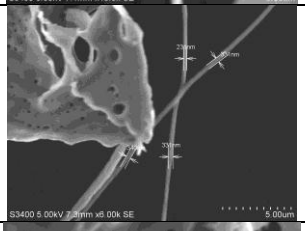
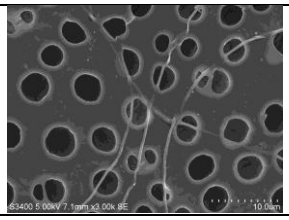
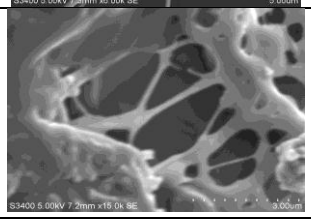
Band Position Wave Number (˙cm)	**Band Assignment**	**Clay (DEALA MMT)**	**PCL Nanofiber**	**P(CL-HOLA) DEALA MMT Argon Plasma Treated**
2950-3000	CH2 assymetric from PCL			CH2 stretching
1700-1750	C=O carbonyl group particularly esters	C=O carbonyl group particularly esters	C=O carbonyl group particularly esters	C=O carbonyl group particularly esters
1200-1250 cm^{-1}	C-O-C (asymmetric stretching PCL)		C-O-C (asymmetric stretching PCL)	C-O-C (asymmetric stretching PCL)
1150-1200 cm^{-1}	C-O-C (symmetric stretching from carboxylate group of PCL)		C-O-C (symmetric stretching from carboxylate group of PCL)	C-O-C (symmetric stretching from carboxylate group of PCL)
1045-1052	Si-O stretching	Si-O stretching		Si-O stretching
778-800	Si-O deformation perpendicular to optical axis	Si-O deformation perpendicular to optical axis		Si-O deformation perpendicular to optical axis

Scanning Electron Microscopy

SEM images in Table 4 showed that some pores are formed in the electrospunnanofibers. It also summarizes the effect of current discharge and exposure time to Argon Plasma to the average diameter size of the of the electrospunnanofibers. The morphology transition produces uniform and smooth porous fibers as the discharge current increases .

According to (Casper *et al.*, 2004) relative humidity affects the pores formation of the electrospunfibers during electrospinning. According to their study, the formation of the pores became evident when electrospinning in an atmosphere with more than 30% relative humidity.

Table 4. Morphology Profile and Average diameter size of Treated Argon Plasma ElectrospunNanofiber

Treatment	Average Diameter Size (nm)	Morphology Profile	Single Fiber Image
Untreated	188nm		
5mA, 15 min	193nm		
10mA,15 min	308nm		
10mA, 25 min	411nm		

Transmission Electron Microscopy Image of Exfoliated DEALA MMT(clay)

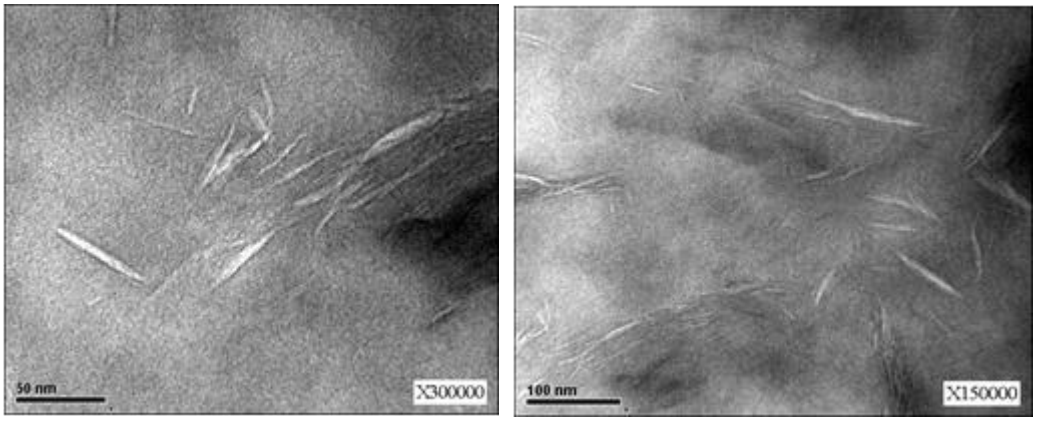


Fig.4a. Ave. Diameter Size = 0.875 nm **Fig.4b.**Ave. Diameter Size = 0.674nm

Fig. 4. TEM images of exfoliated PCL-HOLA deala MMT

As shown in Table 3, the Si-O deformation and the Si-O stretching vibrations perpendicular to the surface of the clay platelet found in the FTIR spectra of the electrospunnanofiber was supported by the TEM images Figure 4a and 4b showing the exfoliated deala MMT on the polymer matrix with 0.6740- nm @ x150K (Fig.4a) and 0.875 nm @ x 300K (Fig. 4b) average diameter distance of the clay.

Conclusion

Based from the results of this study, the following conclusions are made;

1. The DEALA MMT dispersion the electrospun P (HOLA-e-CL) was confirmed through Fourier Transform Infrared Spectroscopy. The exfoliated deala MMT was further detected through TEM.
2. The Argon Plasma treated Electrospun P (HOLA-e-CL) Clay Nanofiber composites were surface modified, thus increasing its diameter size as the discharged current and time exposure increases.
3. Surface modification done on the electrospunnanofiber composites produced uniform smooth porous fiber attaining transition changes on the morphology structure thereby enhancing the hydrophilicity of the materials at lower amount.

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