Polyamide Nanofibers Reinforced Titanium Nanoparticles Composites for hydrophobic surfaces

K D Salman1,*, Z M Razlan2

1Department of Electro-mechanics Engineering, University of Technology, Baghdad-Iraq
2School of Mechatronic Engineering, Universiti Malaysia Perlis, Pauh Putra Campus, 02600 Arau, Perlis, Malaysia

*Corresponding author: drkhansaa_ds@yahoo.com

Abstract. In this study, samples of polyamide (6) (PA 6) nanofibers armed with TiO2 nanoparticles were prepared using an electrospinning method for the preparation of nanocomposite fibres. The nanofibers were prepared under 0.15% weight, 25 kV applied voltage, 15 cm electrospinning distance, 0.48 mm tip diameter and 0.3 ml/hr injection rate to obtain nanofibers with a diameter of about 100 nm and then reinforced with (50 nm diameter) Titanium Nanoparticles. The properties and morphology of the surface were studied using the atomic force microscopy (AFM) scanner. The polyamide structure was also examined by the Fourier transform infrared radiation (FTIR) infrared device, and the contact angle was measured with water using a contact angle analyzer. The results showed that the diameter of the fibres ranged between 80-100 nm and contain some beads. The infrared test also showed that the intensity of the peaks decreases after the transformation of polyamide into nanofibric. The resulting surface has the hydrophobic properties, especially after the addition of Titanium nanoparticles.

1. Introduction
The ultra-hydrophobic material restores the water at a very high contact angle, allowing the surfaces to remain dry. These materials lead to many benefits such as ease of manufacturing, low cost, scalability, a small quantity of large area coats, eliminating existing water corrosion. [1], this is the aim of this research. A number of methods have been used to disperse ultra-super hydrophobic surfaces, such as electrochemical deposition [2], electrophoresis [3], chemical etching [4], layer after self-assembly of layer [5], chemical vapor deposition [6]. Nanotechnology has entered into this field, in order to improve the hydrophobic surfaces, scientists deliberately to form micro and nano surface protrusions, that will increase the water droplets by hand (or even any other means), so as to protect the optimal surface, He walked in the term science material "lotus effect" refers to the hydrophobic surfaces [7]. There are many previous studies on the hydrophobic coatings such as Qian F. et. al (2013), who found the TiO2/ high density poly ethylene (HDPE) nanocomposite have super hydrophobic properties without any chemical exposure, while it transfers for hydrophilic surface after exposure to UV-RAD. [8]. Also, Srinivasan A. et. al (2013) studied the fabricate Graphene-loaded TiO2 thin films on glass substrates by the spin-coating technique. They conclude the resulting fabric has inexpensive, transparent, conductive, super hydrophilic, and highly photo-catalytically active properties. [9].

2. Experimental Part
2.1. Materials
Polyamide-6 as white, transparent from Alibaba Company (China) to preparation nanofibers by electrospinning technique was used. Formic acid from Sigma-Aldrich as a solvent was used. C-Titanium (TiO2) nanoparticles with (50 nm) diameter from Sigma-Aldrich offers Aldrich-791342, used as a reinforcement material.
2.2. *Electrospinning set up*

The electrospinning solution held in a syringe connected to the syringe pump to regulate fluid flow, while the positive high voltage power supply is connected to the metallic needle, and the negative energy supply is connected to the ground metal collector, as in Figure 1.

![Figure 1. Set Up of Electrospinning](image)

2.3. *Fabrication of Super-Hydrophobic/ Super Hydrophilic Textile*

20 ml of polyamide 6 (PA 6)/formic acid pumped by electrospinning system for (15 hr), and collected on aluminum foil (20 cm * 20 cm\(^2\)), then it cut according to a required test as in table (1).

| Samples | Dimension, cm\(^2\) | Test |
|---------|---------------------|------|
| 1       | 1                   | AFM  |
| 2       | 1                   | Contact angle |
| 3       | 17.5                | FTIR |

**Table 1. The dimensions of Samples According to Tests**

3. *Results and discussion:*

3.1. *FTIR analysis*

Figure 2 (a) shows the infrared analysis of the polyamide, and Figure 2 (b) shows a FTIR analysis of polyamide nanofibres. Note that there are new links created after the transformation of polyamide from microstructure to nanostructures. Also observed from this nanoparticle structure of polyamide polycrystalline has more crystallization than the macroscopic structure, increasing the amorphous structure leads to increased crystalline peak amplitude and density. As nanostructures are highly crystallized, so the nanoparticle sample shows a weaker peak. This was confirmed by Zimba et al. [10], which observed these peaks more clearly in the amorphous PA structure of nanocrystalline structures.
3.2. Contact angle

Figure (4) show the relationship between the contact angle of (3a. foil aluminum, 3b. foil aluminum coated by PA nanofibers, and 3c. foil aluminum coated by PA nanofibers reinforced with TiO$_2$ nanoparticles). We show from this shape the contact angle of foil aluminum is smaller than 90º, this leads to hydrophilic behavior as in Figure (3a), also the contact angle changes with time dramatically. Figure (3b) shows the hydrophilic behavior of PA nanofibers, this is because the PA surface able to create a bond with water and the contact angle is smaller than 90º. Figure (3c) shows the hydrophobic behavior of (PA + TiO$_2$) nanofibers this is because the TiO$_2$ adding leads to hydrophobic behavior of surfaces because it leads to increasing of the roughness of surfaces. Also noticed that, the contact angle decrease with remaining time on the surfaces, with (PA + TiO$_2$) surface it decrease slowly because this surface is more roughness than other samples with (aluminum foil, & PANF), this is because the these surfaces have less roughness [11].

Figure 3a. Contact angle of aluminum foil with time
Figure 3b. Contact of (0.15w/v) PA6 surfaces nanofibers with time

Figure 3c. Contact angle of (PA 6 + TiO$_2$) surfaces nanofibers with time
Figure 4. Show the relationship between the contact angle and remaining time of water droplet to 3a.
Aluminum foil, 3b. PA nanofibers and 3c. (PA+TiO$_2$) nanofibers coating

3.3. AFM results
Figure (5 a,b) shows the AFM results of the morphology of 5a. PA 6 nanofibers surfaces and 5b. (PA 6 +TiO$_2$) surface.

Notice the PA 6 nanofibers surface has roughness less than (PA 6 +TiO$_2$) surface this is because the TiO$_2$ nanoparticles adding leads to increasing of the roughness of the surface and this leads to increasing of the hydrophobic behavior of surface.

Figure 5. AFM of surface, a. PA 6 nanofibers and b. PA+TiO$_2$ nanocomposite nanofibers
4. Conclusions
In this paper, we conclude that:
1. The polyamide 6 nanofibers have hydrophilic behavior with contact angle about (68.98°).
2. The adding of TiO$_2$ nanoparticles leads to increasing of the contact angle of result nanocomposites nanofibers (PA6 + TiO$_2$ nanoparticles) and hydrophobic behavior of the surface.
3. This leads to using of this nanocomposites membrane surface in prevention, packaging, protection, and limiting of pollution applications.

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