

Surface Modification of Silica–PAN Composite Nanofibers Induced by CO₂-Pulsed Laser

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ABSTRACT: In this study, the modification induced by CO₂-pulsed laser on the surface morphology of silica–polyacrylonitrile composite nanofibers has been investigated. Applied surface modification method is based on different infrared adsorption of materials. Two types of composite nanofibers containing silica nanoparticles with various diameters are irradiated with CO₂-pulsed laser of 1084 wavenumber (cm⁻¹). Surface morphology of

irradiated composite nanofibers was analyzed using field emission scanning electron microscope (FE-SEM). FE-SEM scans show characteristic modification on the surface of nanofibers with controlled distribution and dimension. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: E9–E15, 2012

Key words: laser treatment; composite nanofibers; surface modification; CO₂-pulsed laser

INTRODUCTION

The advantages of polymer materials such as high strength, good mold ability, and flexibility could be combined with the great properties of inorganic materials such as high strength, heat strength, heat stability, and chemical resistance through producing composite materials.^{1–3} The wide range applications of nanofibers such as filters, catalysis, tissue engineering, wound dressing, scaffold, and sensors could be extended with enhancing their mechanical, electrical, optical, thermal, and magnetic properties by incorporating inorganic nanoparticles in their structures.^{4–6} Due to the improved mechanical, electrochemical, and heat stability properties of silica-filled composite nanofibers, they have attracted much interest in recent years.^{7,8} Few studies have been performed to modify and increase the surface area and roughness of silica-composite nanofibers. Nanoporous inorganic (silica) nanofibers have been fabricated by electrospinning the blend solutions of poly vinyl alcohol (PVA) and colloidal silica nanoparticles, followed by selective removal of the PVA component.⁹ In another study, porous polyacrylonitrile nanofibers have been prepared by selective removal of silica nanoparticles from PAN/silica composite nanofibers using hydrofluoric acid.¹⁰ By increasing the surface area of silica containing composite nanofibers, their application in mesoscopic

research, nanodevices, optoelectronic devices, and chromatographic supports with high adsorption capacities could be improved.¹¹

Among different methods for surface modification of polymers, laser-assisted treatment offers advantages over chemical and physical methods.^{12,13} In the last decade, this method has rapidly grown and attracted considerable interest among scientists.^{14,15} Among different polymeric material, the surface of fibrous materials could be effectively modified using laser-assisted treatment methods. Polyethylene terephthalate fibers were irradiated by UV excimer lasers with different draw ratios, the interaction producing ripple/roll-like structure and changes in physical and chemical properties, resulting in better dyeability and adhesion to coating.¹⁶ The optimal-working parameter of pulsed laser to remove the surface soiling of fibrous material was proposed in research by Strlic.¹⁷

The main aim in this research is changing the smooth fibers with dense cross-section that are generally obtained via electrospinning into the fibers with rough and porous surface structure. As the most of chemical-treatment methods for surface modification of polymers makes some environmental concerns and pollution problems, there is an essential need to develop a new physical treatment method, so in this research CO₂-pulsed laser radiation is used to modify the morphological structure of nanofibers. A variety of applications could be favored with increasing the surface roughness, porosity, and surface area of nanofibers,¹⁸ in tissue engineering topographical structure of various nanostructures plays a crucial role in cell attachment and biocompatibility of artificial biomedical materials.¹⁹ Increasing the surface roughness improves

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TABLE I
Specification of Silica Nanoparticles

SiO ₂ nanoparticles			
1	Average particle size	10 (nm)	80 (nm)
2	Content of silicon oxide	99%	99.9%
3	Specific surface area	>600 (m ² /g)	>800(m ² /g)
4	Shape	Nearly spherical	

mechanical interlocking of fibers to the matrix in the composite materials.²⁰ Wetting properties of nanofibrous web could be very much influenced by geometrical structure and surface roughness, an existing rough surface can effectively improve the hydrophobicity of surface.²¹

EXPERIMENTAL MATERIALS AND METHODS

Polyacrylonitrile (PAN) was kindly supplied by Polyacryl. The weight-average molecular weight (*M_w*) being 100,000. *N,N*-dimethylformamide (DMF) acid was provided by Merck. Silica (SiO₂) nanoparticles were purchased from Nabond. The specification of silica nanoparticles that are used in this study is shown in Table I.

To obtain a homogenous dispersion of silica nanoparticles in the PAN solution in DMF, at first a controlled amount of silica nanoparticles (20% to PAN) with an average particle diameter of 10 and 80 nm were dispersed into DMF by probe ultrasonic stirrer (UP2005) for 30 min. Then, PAN was added to that solution (13.5%). Afterward, the resulted-solution was magnetically stirred for 8 h and became ready for electrospinning.

In this study, the electrospinning process was performed at room temperature, electrospinning solution was placed in a 1 mL syringe (solution reservoir) with a stainless-steel needle (external diameter 0.7 mm). A high voltage of 20 kV is applied between the tip and the collector drum. Electrospinning solution is pumped at a constant rate of 0.25 mL/h using a digitally controlled syringe pump (Top 3500). The distance between the tip and the collecting drum is 15 cm. A drum with diameter of 8 cm and length of 30 cm, connected to a variable-speed motor, was used to collect the uniform nanofibrous web. The speed of the drum was carefully chosen at 1.2 rpm (m/s) to prevent fiber breakage during the collection. The residual solvent associated with nanofiber mat was removed by keeping the mat in the atmosphere for at least 2 days at 20°C. The Fourier transform infrared (FT-IR) spectra of the samples were recorded on a Nexus FTIR Spectrometer 670 from 4000 to 400 cm⁻¹ with a 2-cm⁻¹ resolution. The surface morphology of composite nanofibers was observed by a field emission scanning electron microscope (FE-SEM; HIT S-4160 at 15 kV).

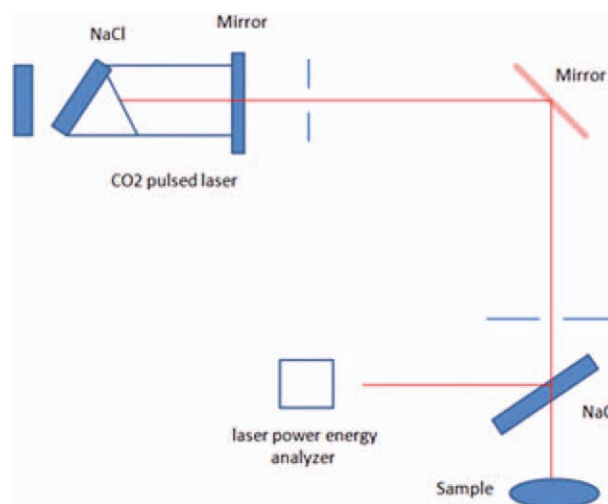


Figure 1 The experimental set up for laser irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Laser treatment is performed using a CO₂-pulsed laser (Lumonics 103-2) with a pulse duration or full width at half maximum (FWHM) of the applied CO₂ laser is about 80 ns in standard room conditions. The pulse width, pulse duration, or FWHM of the applied CO₂ laser is about 80 ns, and its tail is about 3–4 μs. The wavelength of CO₂-pulsed laser is measured by a CO₂-laser spectrum analyzer (Opt.Instrument 16-A Nexus) and is set at 9225 nm. Due to strong absorbance of the laser energy by the air, laser energy is controlled by varying the distance between the sample and the laser, and its values are measured by a laser power energy analyzer (Coherent LMP-10). Irradiation was performed on a circular region of 1.7 cm diameter only in one side of the fabric. To detect the location of laser beam, a piece of paper could be used; the burn pattern on the paper appears the location of the laser spot. The experimental set up for laser irradiation is shown in Figure 1.

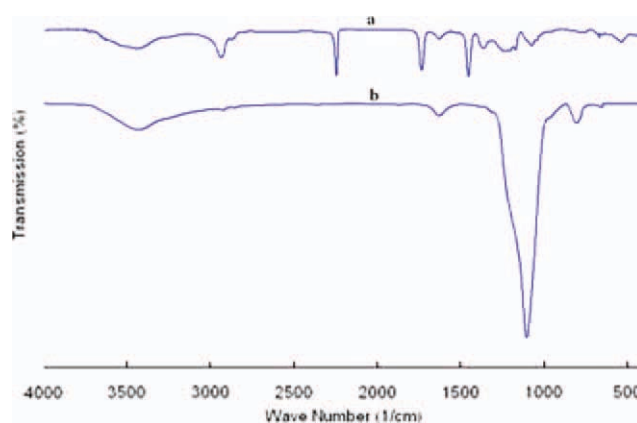


Figure 2 Infrared spectrum of (a) PAN (b) silica nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

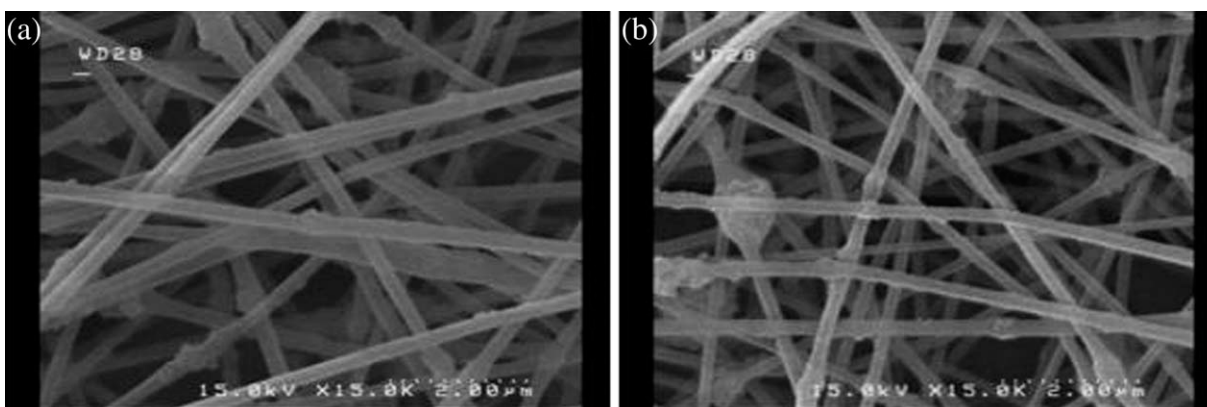


Figure 3 FE-SEM scans of silica-PAN composite nanofibers filled with silica nanoparticles of diameter (a) 10 nm (b) 80 nm.

In this study, laser beams emitted from CO₂ laser in TEM₀₀ mode have an intensity distribution across the beam, which is in the form of a Gaussian-intensity profile. With increasing the propagation distance (distance between the sample and laser), diffraction causes the light wave to spread as they propagate, so in this research to produce a circular-irradiation spots with uniform intensity on the sample surface, a long-distance between the laser irradiation source and the sample (5 m) is selected, two masks containing small array of circular region are placed in the center of the beam (Fig. 1), allowing a small and relatively uniform section of the beam to be used for sample irradiation. We expect that the laser spot has a linear distribution and be relatively homogenous on the samples surface.

RESULT AND DISCUSSION

FT-IR spectra

FT-IR spectra of silica nanoparticles, PAN, and the resulted silica-PAN composite nanofibers are shown in

Figure 2. In this study, surface treatment of nanofibers is based on different infrared absorption of materials. In a composite nanofiber, nanoparticles absorb the infrared light and their bonds are broken; however, the polymer transmits the light and remains without any changes. Considering the IR spectra of silica nanoparticles show a characteristic peak with relatively high intensity around 1100 cm⁻¹, which is the characteristic peak of SiO₂ asymmetric stretching vibration.²² As shown in Figure 2, at a wave number of 1100 cm⁻¹, PAN transmission is much greater than silica but regarding limitation in laser wave length adjustment, the laser wave number is selected at 1084 cm⁻¹.

Surface morphology of nanofibers

FE-SEM scans of untreated silica-PAN composite nanofibers containing silica nanoparticles at an average diameter of 10 and 80 nm are shown in Figure 3. Incorporating silica nanoparticles in the nanofiber structures has a great effect on the fibers morphology characteristics such as fiber diameter, surface

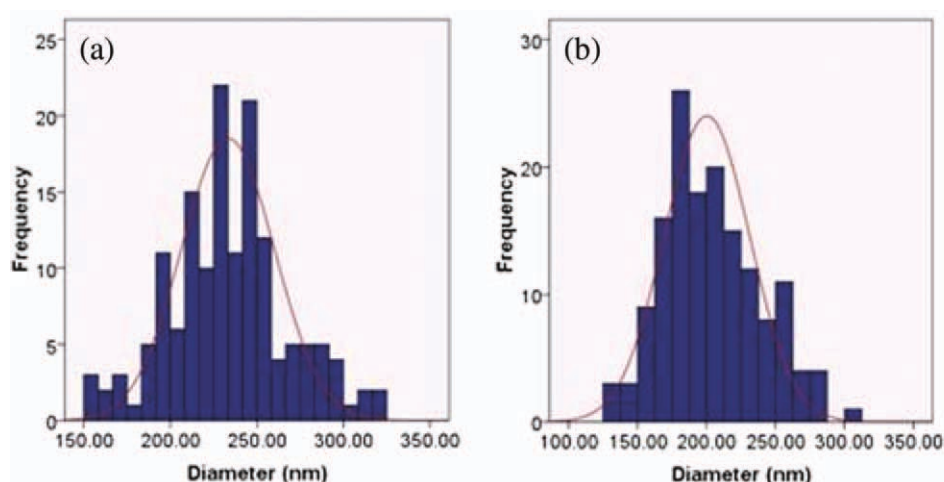


Figure 4 Diameter distribution of composite nanofibers filled with different silica nanoparticle diameter (a) 10 nm (b) 80 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

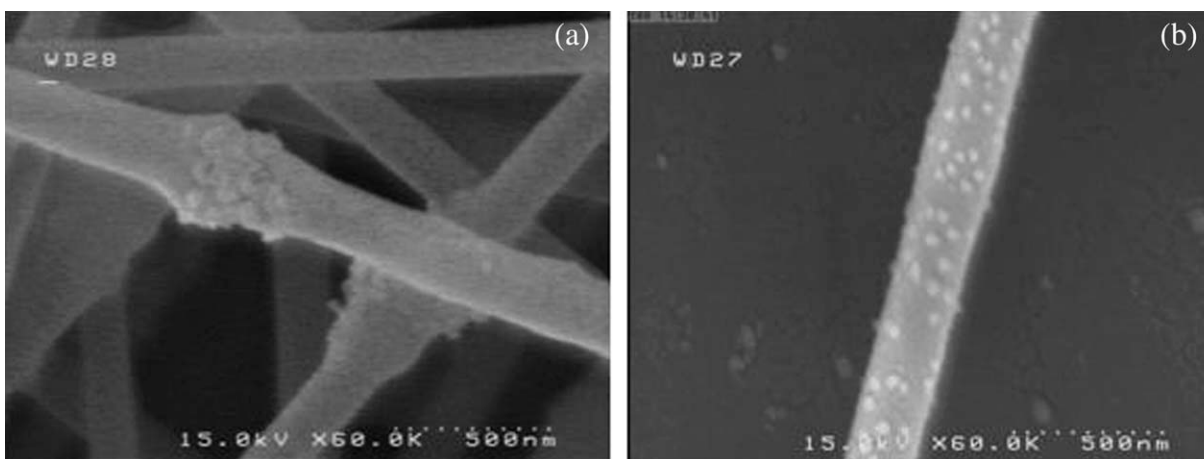


Figure 5 FE-SEM scans of composite nanofibers containing silica nanoparticles of 80 nm diameter (a) untreated nanofiber (b) irradiated nanofiber.

roughness, and fiber orientation.²³ As it is shown in Figure 3, surface roughness increases by increasing the silica diameter. With regard to these scans, it is observed that dispersion of silica nanoparticles of 80 nm diameter in PAN is less homogenous compared with silica nanoparticles with a 10-nm diameter. An average diameter of 10 nm silica-filled composite nanofibers is 235 nm with coefficient of variance of 14%; however, an average diameter of 80 nm silica-filled composite nanofibers is 205 nm with coefficient of variance of 17%. It shows that composite nanofibers with smaller silica particle sizes have a larger diameter and narrow fiber diameter distribution compared with the composite nanofibers filled with larger silica particles. The diameter distribution of composite nanofibers filled with different silica nanoparticle diameter is shown in Figure 4.

Laser treatment

The laser treatment was carried out in air using a CO₂-pulsed laser, having capable of emitting a radiation at 9.225 micron, with an 80-ns pulse duration. Laser influence (energy/unit area) is selected at 100 mJ/cm². This influence is required to break the silica bonds of nanoparticles in the unit area of resulted nanofibrous web and is determined using eq. (1). In this equation: q is the mass flow rate of the spinning solution, t is the electrospinning duration, c is the concentration of spinning solution, p is the ratio of silica nanoparticles weight to PAN polymer weight, e is the bonding energy of Si–O, n is the number of Si–O bonds in the molecule, A is the surface area of the collector, and M is the molar mass of the molecule.

$$F\left(\frac{j}{\text{cm}^2}\right) = \frac{q(\text{mL/h}) \times t(\text{h}) \times c(\text{g/mL}) \times p \times e(\text{J/mol}) \times n}{A(\text{cm}^2) \times M(\text{g/mol})} \quad (1)$$

According to preliminary tests, the samples are irradiated with 20 pulses of laser with 100 mJ/cm² influence, and the laser wave number is set at 1084 cm⁻¹.

The peak power density is the peak power divided by the cross-section of the laser beam. The peak power of a laser pulse is the maximum occurring optical power. Due to the short-pulse durations, which are possible with CO₂-laser pulses, peak powers can become high even for moderately energetic pulses. The peak power density depends upon the size of the laser beam at some focus. In this study, the peak power is 395 kW/cm².

A circular region with diameter of 17 mm was ablated from the surface of the nanofiber mat and exposed to the laser irradiation.

Surface modification

Surface modification of nanofibers is characterized using a FE-SEM after irradiation with 20 pulses of 100 mJ/cm². In this study, a selective laser-etching method is applied to modify the nanofibers surface structures and increase their surface area. In

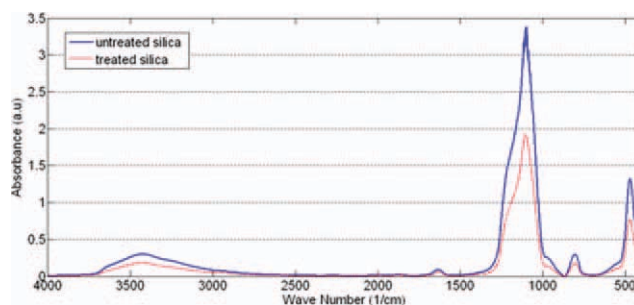


Figure 6 FT-IR spectra of treated and untreated silica nanoparticles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

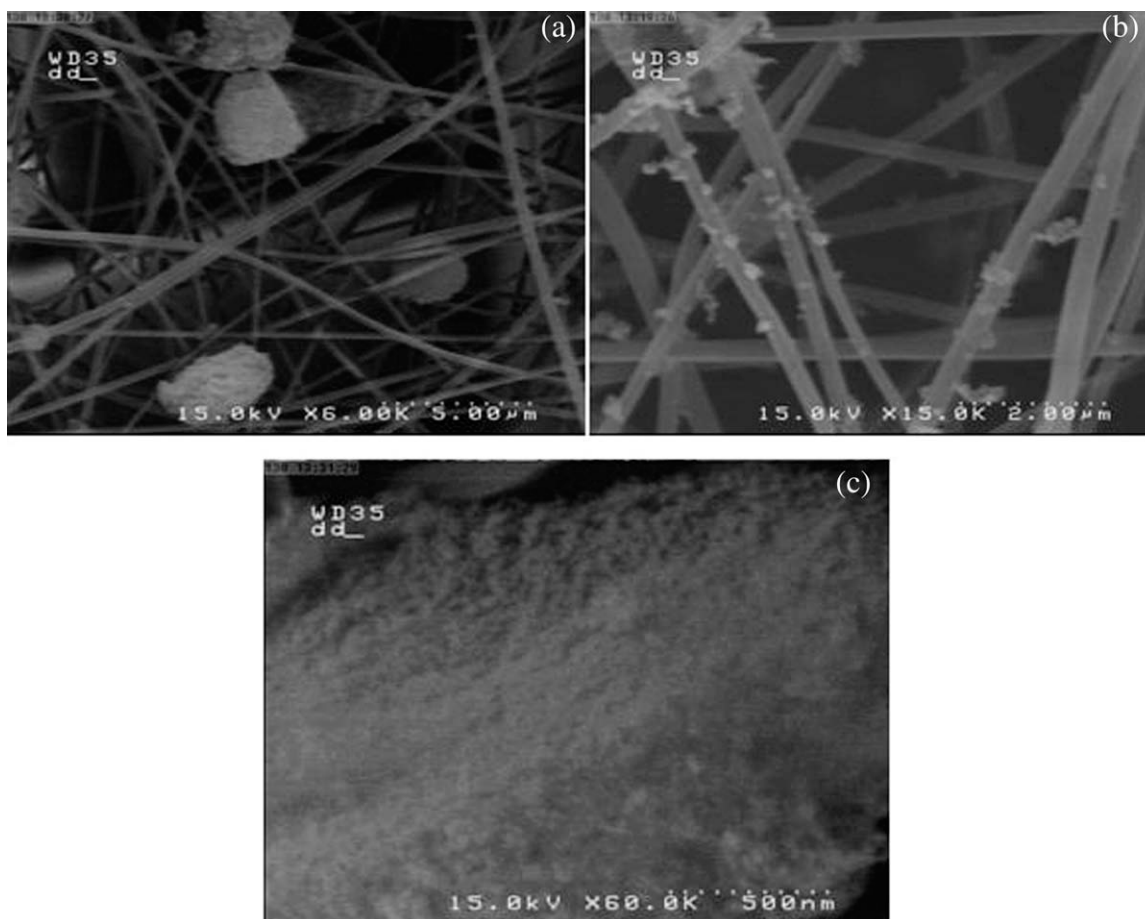


Figure 7 FE-SEM scans of (a) unirradiated-coated nanofibers (b) irradiated-coated nanofiber (c) irradiated-silica nanoparticle surface.

this method, etching occurs in selective points, these points being silica nanoparticles that have greater absorbance when compared with polyacrylonitrile. By absorbing the radiation pulse, chemical bonds excite the energy level above the dissociation energy and Si–O bonds are decomposed. By breaking these

bonds, a large number of small, volatile fragments are produced and since the numerous fragments need a large free volume, an enormous pressure builds up in the small volume within the polymer at the site of irradiation, and they are ejected explosively. This event is shown in Figure 5.

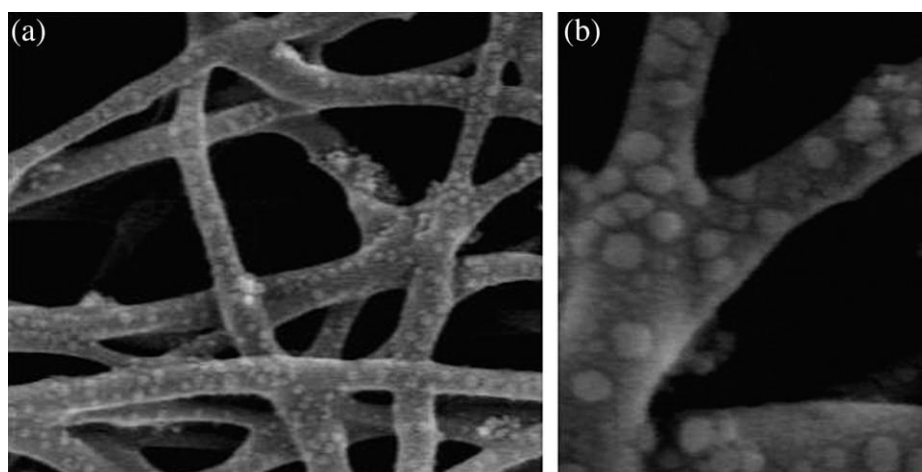


Figure 8 FE-SEM scan of nanofiber treated with 20 pulses of $100 \text{ mJ}/\text{cm}^2$ laser influence for 80 nm silica-filled composite nanofibers (a) $\times 15,000$ (b) $\times 60,000$.

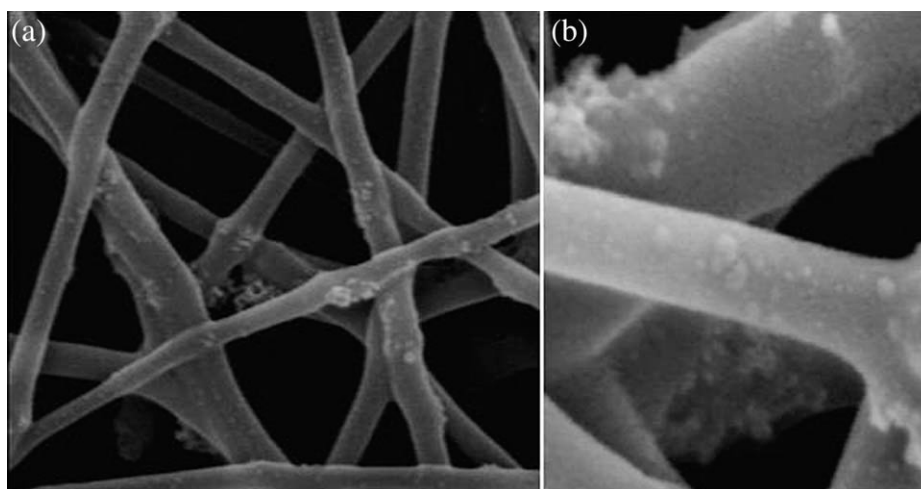


Figure 9 FE-SEM scan of nanofiber treated with 20 pulses of 100 mJ/cm^2 laser influence for 10 nm silica-filled composite nanofibers (a) $\times 15,000$, (b) $\times 60,000$.

Absorption of infrared light by nanoparticles causes the silica bonds to break, which is because of the greater absorbance of silica in the laser irradiation wavelength, this is also confirmed by the last researches about irradiating material containing silica by CO_2 -pulsed laser, in the work was performed by Mukhamedgalieva, crystalline natural silicate was irradiated by CO_2 -pulsed laser and selective dissociation of Si–O bonds were observed.²⁴ In another study, drops of crystalline silicone melt out on the glass like SiO_x samples with irradiating samples by CO_2 laser. As CO_2 -laser wavelength falls within the band of infrared absorption of the samples, breaking of Si–O bonds initiated by CO_2 -laser radiation, which leads to the release of elementary silicon.²⁵ To investigate the effect of CO_2 -laser irradiation on chemical structure of silica nanoparticles, FT-IR spectroscopy of silica nanoparticles of diameter of 80 nm irradiated with 20 pulses of 100 mJ/cm^2 and untreated silica nanoparticles are analyzed, as shown in Figure 6 the intensity of characteristic absorption peak of Si–O for irradiated silica decreases compared to untreated silica nanoparticles, which is due to the breaking silica bonds with absorbing laser energy.

To understand more details about this event in a new experiment, PAN nanofibers are coated with silica nanoparticles of 80 nm diameter and irradiated with the same condition as composite nanofibers. FE-SEM scans of resulting nanofibers show that all PAN nanofibers remain unchanged although absorbing the infrared light by silica nanoparticles cause the breaking of all Si–O bonds and production of a large number of small fragments that need a large volume and are ejected explosively. In Figure 7, FE-SEM scans of coated nanofibers before and after irradiation are shown. As shown in Figure 6(C), irradiating with laser cause to form porous structure for silica nanoparticles.

Considering the surface of irradiated silica nanoparticles, it can be observed that with this method the surface area of nanofibers increases greatly but when silica nanoparticles are inside the polymeric nanofibers, they just absorb a part of IR radiation and by breaking the silica bonds their size increases, so their porous surface structure will come out of the surface of nanofibers and the PAN nanofibers will have controlled porous structure. The resulting modified structure for composite nanofibers filled with silica nanoparticles of 10 and 80 nm diameters are shown in Figures 8 and 9. These scans show that the roughness of the modified composite nanofibers containing silica nanoparticles of 80 nm diameter is more than the composite nanofibers filled with the silica nanoparticles of 10 nm diameter. When silica nanoparticles are irradiated with laser, absorbing IR light cause to break the silica bonds, this event produces a large amount of small fragments, when the diameter of nanoparticles is 80 nm, by breaking their bonds their volume increase more than the

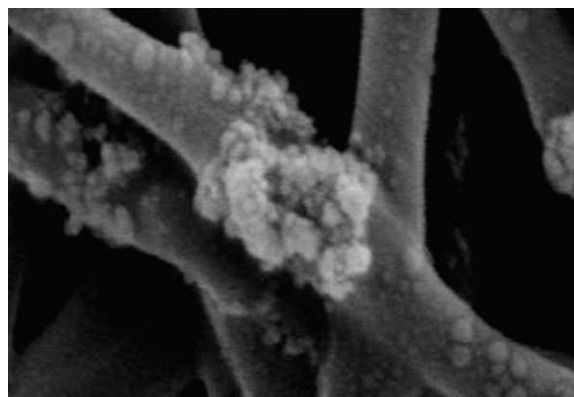


Figure 10 FE-SEM scans of nanofiber treated with 20 pulses of 100 mJ/cm^2 laser influence ($\times 60,000$).

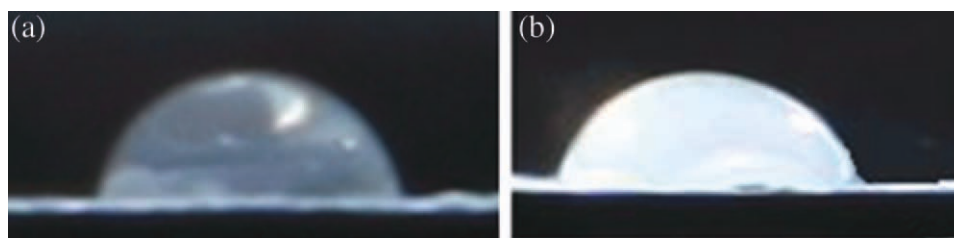


Figure 11 Water contact angle measurement of (a) treated (b) untreated nanofibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

volume of silica nanoparticles of 10 nm diameter, in addition, the diameter of nanofibers containing silica nanoparticles of 80 nm diameter is less than composite nanofibers containing silica nanoparticles of 10 nm diameter, so when silica nanoparticles of 80 nm diameter absorb the IR light and their volume increase, their porous structure will come out of the fibers surface more than silica nanofibers of 10 nm diameter, it makes the surface with more roughness for nanofibers containing silica nanoparticles of 80 nm diameter comparing with nanofibers containing silica nanoparticles of 10 nm diameter.

Some defects will be appeared in the modified surface structure of nanofibers, if silica nanoparticles do not have homogenous dispersion in PAN. In a few parts of the nanofibers where silica nanoparticles were aggregated, the energy of irradiated photons was absorbed by all of them, and a different structure was formed as shown in Figure 10.

To investigate change in the surface morphology of the nanofibers, the water contact angle of treated and untreated composite nanofibers containing silica nanoparticles of 10 nm diameter are measured. Figure 11(a,b) shows that water contact angles for treated and untreated nanofibrous web are 62° and 54° . So with modifying the surface morphology of nanofibers with laser irradiation method, the hydrophobic properties of the nanofibers increase.

CONCLUSION

The surface of silica-PAN composite nanofibers has been successfully modified by laser treatment. This laser treatment is based on different absorption of infrared materials. Absorption of infrared light by nanoparticles causes the silica bonds to break, while PAN transmits that light. Absorbing the infrared light by silica nanoparticles in the composite nanofibers breaks the silica bonds and produces numerous small fragments, which needs large free volume, and has an enormous pressure at the irradiation sites. As a result these fragments could eject explosively, and the porous structure will come out of the surface area of nanofibers.

The modified structure has characteristic morphology; the silica nanoparticles shape and size determines the shape and dimension of the modified sites. To have homogenous modified surface structure, homogenous dispersion of silica nanoparticles in PAN has a great importance.

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