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Controlled preparation and chemical actuation of polyacrylonitrile microfibers

Preparación controlada y actuación química de microfibras de poliacrilonitrilo

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ABSTRACT

Pure polyacrylonitrile fibers with diameter size at micrometric scale were obtained and collected radially using an immersion-jet wet spinning system. High purity polyacrylonitrile powder was used as precursor polymer. This method is a fast and easy approach to fabricate micrometric PAN fibers. Fiber diameter can be easily controlled by adjusting the size of the spinneret. Uniform, smooth and continuous PAN microfibers were suitable modified by thermal stabilization and alkaline hydrolysis to obtain pH-sensitive fibers. The effect of diameter size fiber on the chemical actuation behavior was investigated in terms of length change characteristics under the influence of pH solutions. The microfibers showed expanding/contracting behavior and force generation stimulated by changes in pH from 1-14. By means of scanning electron microscopy, the formation of PAN fibers with diameters on the micrometer scale of 91-287 μm could be corroborated. FT-IR spectroscopy revealed that the nitrile ($\text{C}\equiv\text{N}$) groups of PAN were converted to carboxylic groups (COOH), which are necessary to provide the deformation of the PAN gel microfibers.

Keywords: Microfabrication; Microfiber; Polyacrylonitrile; Chemical Actuation

RESUMEN

Se obtuvieron fibras puras de poliacrilonitrilo con un diámetro a escala micrométrica y se colectaron radialmente mediante un sistema de hilatura húmeda por inmersión. Como polímero precursor se utilizó polvo de poliacrilonitrilo de alta pureza. Este método es rápido y sencillo para fabricar fibras de PAN micrométricas. El diámetro de la fibra puede controlarse fácilmente ajustando el tamaño de la hilera. Las microfibras de PAN uniformes, lisas y continuas se modificaron adecuadamente mediante estabilización térmica e hidrólisis alcalina para obtener fibras sensibles al pH. Se investigó el efecto del tamaño del diámetro de la fibra en el comportamiento de actuación química en términos de

características de cambio de longitud bajo la influencia del pH de las soluciones. Las microfibras mostraron un comportamiento de expansión/contracción y generación de fuerza estimulado por cambios en el pH de 1-14. Mediante microscopía electrónica de barrido se pudo corroborar la formación de fibras PAN con diámetros en escala micrométrica de 91-287 μm . La espectroscopia FT-IR reveló que los grupos nitrilo ($\text{C}\equiv\text{N}$) del PAN se convirtieron en grupos carboxílicos (COOH), los cuales son necesarios para proporcionar la deformación de las microfibras gelificadas de PAN.

Palabras clave: Microfabricación; Microfibra; Poliacrilonitrilo; Actuación química

INTRODUCTION

Recently, much attention has been paid to polyacrylonitrile (PAN) fibers due to their unique properties such as thermal and mechanical stability, good solvent resistance, high degree of molecular orientation, as a precursor for producing carbon fibers by carbonization procedure, chemo-mechanical and electro-chemical performance characteristics (Papkov *et al.*, 2012; Rahaman *et al.*, 2007; Wang *et al.*, 1994; Zhao *et al.*, 2016; Frank *et al.*, 2012; Shiga and Kurauchi, 1990; Doi *et al.*, 1992; Kalashnik *et al.*, 2010; Gu *et al.*, 2005) and subsequent technological applications as textile, reinforcement fibers, linear actuator and artificial muscles (Shi *et al.*, 2014; Feng *et al.*, 2011; Choe and Kim, 2006; Liu *et al.*, 2015; Shi *et al.*, 2016; Wu *et al.*, 2016). The properties and hence the applicability of these fibers not only depends on their diameter, but also on their chemical purity. Although there are many studies that have demonstrated the special properties and applications of PAN fibers, these have been limited to those commercially available. The commercial PAN fibers have slightly different chemical composition than pure PAN fibers, they are co-polymerized with a small amount of other polymers (such as acrylamide, methyl acrylate, vinyl acetate, methyl methacrylate, and ionic and acidic comonomers like sodium methallyl sulfonate, sodium 2-methyl-2-acrylamido propane

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sulfonate, sodium *p*-styrene sulfonate, sodium *p*-sulfophenyl methallyl ether, and itaconic acid) for enhancing the solubility, spinnability, hydrophilicity, drawability, thermo-oxidative stabilization and performance characteristic (Samatham *et al.*, 2006; Sedghi *et al.*, 2008; Lee *et al.*, 2007). However, there is little or no disclosed information about commercially available fibers, making it difficult to study their special properties depending on the chemical composition characteristics. Pure PAN fibers have been little explored so far due to their poor properties and difficulty in handling (Liu *et al.*, 2006) and embrace new challenges for research and technological applications.

Pure PAN fibers have been prepared by an electrospinning technique with diameters in the nano meter scale (Yördem *et al.*, 2008; Sidorina and Druzhinina, 2016), but the limitation of fiber dimensions, the non-uniformity due to fast solvent evaporation and the randomness of the spinning process remain challenging tasks. Wet spinning or dry-jet-wet spinning are alternative methods to prepare PAN fibers, where the spinnerets-extruded PAN is brought into a coagulation bath to precipitate the polymer (Mahmod *et al.*, 2011; Sreekumar *et al.*, 2004). If these techniques are extended to directly fabricate pure PAN fibers in micrometric scale, results in an easy and practical way with predetermined properties, it will greatly simplify the procedure for fabricating long micro-structure and therefore provide new opportunities for other applications such as artificial muscles development.

In this paper, we demonstrate that pure PAN fibers with controlled diameter on the micrometer scale could be conveniently prepared in an easy and versatile way by a single-step approach, using an immersion-jet wet spinning system. We further investigate the effect of diameter on the actuation behavior of pH-sensitive PAN microfibers to evaluate the feasibility of the use as a bio-mimetic linear actuator.

MATERIAL AND METHODS

Materials

In order to ensure the purity of PAN fibers, high purity polyacrylonitrile powder (PAN, average $M_w = 150,000$, purity > 99.5 %), sodium hydroxide (NaOH, reagent grade ≥ 98 %), hydrochloric acid (HCl) and dimethylformamide (DMF, anhydrous 99.8 %) were used, purchased from the Sigma-Aldrich Corporation (St. Louis, MO, USA). HPLC-grade water was used at all times to wash the laboratory equipment used in samples preparation.

Immersion-jet wet spinning system

The immersion-jet wet spinning system implemented to prepare pure PAN microfibers consisted of a syringe pump (KD Scientific KDS-100, Holliston, MA, USA), a syringe equipped with a spinneret (single-hole stainless steel tip, hypodermic needle), a glass plate with a coagulation bath (with a length of 10 cm), and a winding drum (3 cm diameter) attached to an electric motor. In the spinning process, the viscous PAN solution was loaded into a plastic syringe attached to a syringe pump, placed in a parallel mount to maintain constant

flow feed inside the coagulation bath. Precursor solution was pumped through spinneret into a water coagulation bath so that the exchange between the polymeric solvent and water takes place until the polymer completely coagulates. The resulting fibers were continuously wound on a winding drum. Figure 1 shows schematically the spinning arrangement used. All the immersion-jet wet spinning parameters were fixed during the spinning process. To evaluate the effect of chemical actuation properties, PAN fibers with different diameters were prepared. Single-hole stainless steel tips (right insert in Figure 1) with different inner diameters 108, 127, 260, 311 and 337 μm (hypodermic needles 33 G, 26 G, 25 G, 24 G and 23 G, were used as spinneret to obtain solid fibers with different diameters at a micrometric scale, denoted as M1, M2, M3, M4 and M5, respectively.

Preparation of PAN fibers

Firstly, the PAN powder was pre-dried at 60 °C for 24 h, then 2.5 g were dissolved in 26.4 mL DMF with stirring at 600 rpm and temperatures in the range of 40 - 50 °C for 24 h. The white dispersed mixture turned into a transparent light-yellow solution after heating with a dynamic viscosity of 1.5167 Pa·s, kinematic viscosity of 1548.6 mm²/s and density of 0.9794 g/mL (Lee *et al.*, 2007). The precursor PAN-DMF (10 %, w/v) solution was used for spinning all fibers. After the polymer solution was loaded into a 3 mL plastic syringe attached to a syringe pump and subsequently released into a coagulation bath at a fixed extrusion velocity of 0.25 mL/min. After coagulation at about 10 cm in the bath the fibers were continuously collected at the same initial feed speed in radial form using a winding drum. These were best experimental conditions to obtain continuous fibers without the presence of rosary or serpentine type defects. The coagulation temperature was always maintained at 4 °C to improve the mechanical properties of the fibers due to less quantity of micro-pores inside the fibers (Bahrami *et al.*, 2002). After spinning, the polymeric fibers were washed thoroughly in

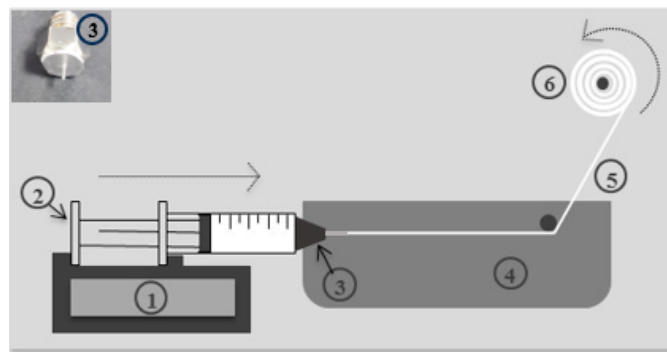


Figure 1. A schematic illustration of the immersion-jet wet spinning system setup used to directly spin PAN fibers: ① syringe pump, ② plastic syringe, ③ spinneret, ④ glass plate with coagulation bath, ⑤ spun fiber, and ⑥ winding drum.

Figura 1. Ilustración esquemática de la configuración del sistema de hilatura húmeda por chorro de inmersión utilizado para hilar directamente fibras de PAN: ① bomba de jeringa, ② jeringa de plástico, ③ hilera, ④ placa de vidrio con baño de coagulación, ⑤ fibra hilada y ⑥ tambor de bobinado.

distilled water and dried at 80 °C under vacuum for 8 h to remove DMF, leaving white PAN fibers. Finally, the fibers were stored at room temperature for further characterization and chemical activation.

Characterization

A Scanning Electron Microscope (SEM) Vega Tescan, TS-5136SB with 10 kV and x100 was used to obtain microscopy images. An LVSTD secondary electron detector and ESSENCE software were used for SEM analysis. The cross sections of fibers were characterized using the 1600X Digital Microscope. To observe the fiber under SEM, fibers were first dried to ensure liquid removal from the specimen to prevent vaporization during SEM analysis. All fibers were coated with Au to ensure higher conductivity for high-quality imaging. Finally, three images at different locations were taken on the 2 cm long part of fibers for its diameter measurement. Three fiber samples of different diameters were characterized to ensure reproducibility of the results. Effect of chemical activation on the conversion of the nitrile groups to the carboxylic acid groups of PAN fibers were evaluated by Infrared Spectroscopy through a Bruker Vertex 70 brand spectrometer (Bruker Optics Corporation, Billerica USA) with Fourier Transform, in ATR mode. Measurements were made in the mid infrared spectral region (200 – 4000 cm^{-1}), with a resolution of 4 cm^{-1} and an integration time of 60 s (1 s/scan). Data acquisition and processing were performed using OPUS software, version 6.0 (Bruker Optics, USA).

Chemical Activation

In order to prepare activated gel PAN fibers (pH-sensitive) with chemical actuation properties, thermal stabilization and alkaline hydrolysis were carried out (Samatham *et al.*, 2006). The first step was to anneal the fibers at temperatures between its glass transition temperature (above 110 °C) and the thermal degradation temperature (a 240- 300 °C). Three samples of each diameter were used for expanding/contracting application to ensure reproducibility of the results. The first step is expected to change the linear structure of raw PAN fibers in thermally stable cyclized structure containing a large number of cross links ready to withstand high temperature of alkaline hydrolysis process. This chemical structure plays a crucial role in the actuation properties (Houtz, 1950; Ouyang *et al.*, 2008). The process of activation of the PAN fibers is shown in Figure 2.

The second step converts nitrile groups of the stabilized PAN fibers into carboxylic acids by saponification with a strong base, converting the PAN fibers into gel fibers sensitive to a change in pH. Then, the resulting PAN fibers will expand when pK_a (~5) of ionizable groups are higher than the pH of the surrounding medium due to electrostatic repulsion along the chain, and will contract when exposed to an acid medium (Figure 2) (Schreyer *et al.*, 2000). Expansion and contraction behavior are based upon the exchange of counterions and solvent in/out of the gel fibers (Shahinpoor *et al.*, 2002).

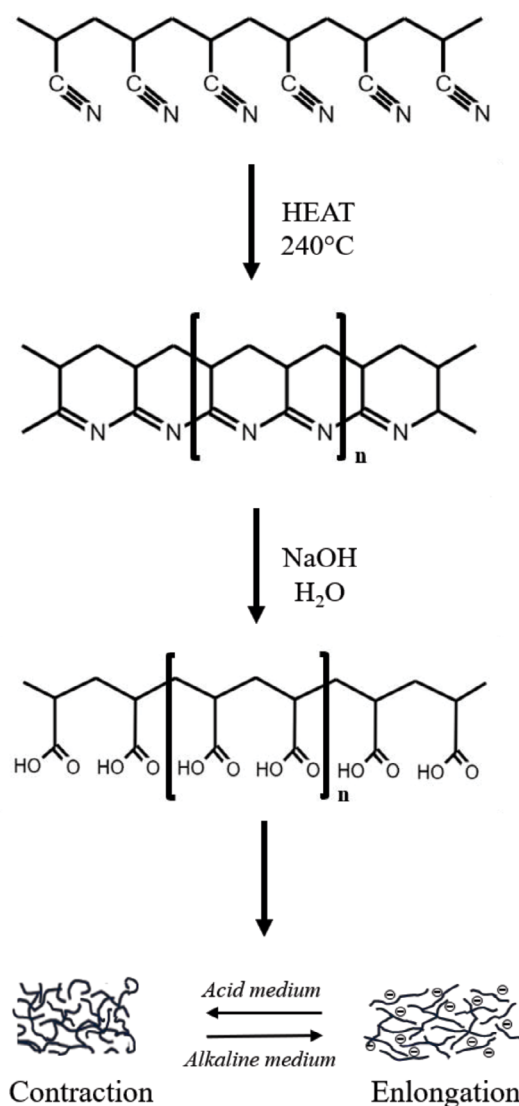


Figure 2. Schematic of reactions occurring during different activation states and contraction/elongation behavior of PAN gel fibers.

Figura 2. Esquema de las reacciones que se producen durante los diferentes estados de activación y el comportamiento de contracción/elongación de las fibras PAN de gel.

For the chemical activation process, PAN fibers were heated at 240 °C in a furnace (Barnstead Thermolyne Furnace 1300) with a heating rate of 2 °C/min in air atmosphere for 2 h. The alkaline hydrolysis process of the fibers was performed in a 1.0 N NaOH boiling solution for 30 min. Subsequently, the hydrolyzed fibers were washed thoroughly in distilled water and dried in an oven at 50 °C for 2 h for future analysis and chemical actuation behavior. PAN gel fibers were expanding/contracting using solutions with pH values from 1 to 14. To vary the pH of the solution HCl and NaOH (1 N) were used.

The force generation characteristics were investigated by preparing single strand PAN fiber in contracted state (Choe and Kim, 2006) using a tensile tester (see Figure 3) and under thermostatic conditions (temperature 25 °C); each fiber was 50 mm in length. One end of the fiber set was care-

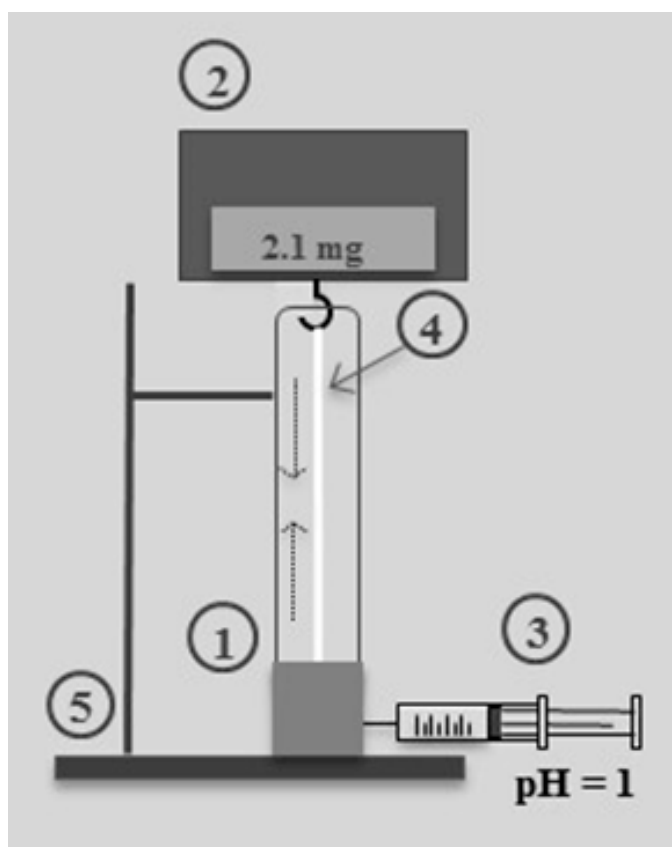


Figure 3. Schematic diagram of the force measurement system of single PAN fiber in contracted state: ① glass plate with solution batch, ② load cell, ③ syringe needle, ④ single PAN microfiber, and ⑤ universal holder.

Figura 3. Diagrama esquemático del sistema de medición de la fuerza de una sola fibra de PAN en estado contraído: ① placa de vidrio con lote de solución, ② celda de carga, ③ aguja de jeringa, ④ microfibras PAN única y ⑤ soporte universal.

fully connected to the load cell (Analytical Balance, Clarkson A S220/C/2) and the other end was fixed to the ground in the solution bath. The force generated in contracted state of the gel fiber, was calculated using the weight value reported by the analytical balance. The HCl solution was poured using a syringe, through a small nozzle to contract the fiber, after which were rinsed with distilled water. The procedure was repeated five times to ensure reproducibility of the results.

RESULTS AND DISCUSSION

As one of the most important goals was to have control over the fiber's diameter, micrographs of the samples were obtained. The effects of the metal tip in the preparation and properties can be clearly observed in Figure 4, which shows SEM of untreated PAN fibers before the stabilization and hydrolysis process. In the left inset image, the radial and continuous collection of the PAN fibers on the drum can be observed, and in the right insert the circular cross section of the fibers is shown. Fibers homogeneous in their length with solid matrix and with circular cross section were obtained using this preparation method. No crack, voids or other types of defects are observable on the fibers. These features are important to mitigate the stress concentration

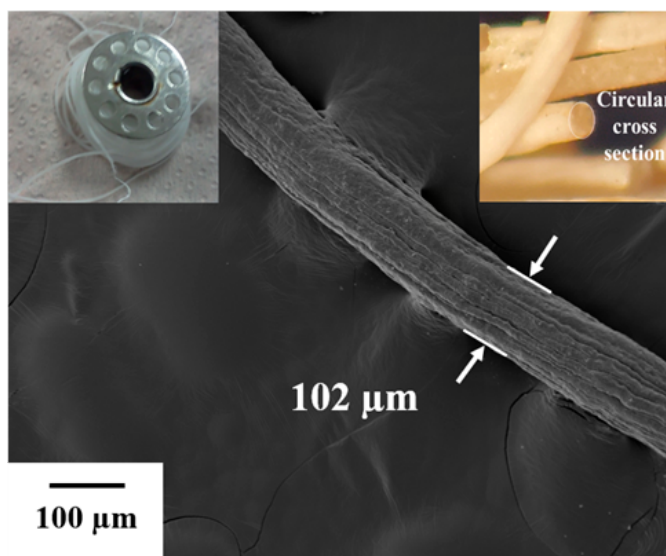


Figure 4. SEM image of raw PAN fibers obtained using the method of immersion-jet wet spinning with spinneret of inner diameter = 127 μm . Left inset: picture of PAN fibers collected radially on winding drum. Right inset: image of cross section of the fiber.

Figura 4. Imagen SEM de fibras PAN crudas obtenidas mediante el método de hilatura húmeda por in-mersión con hilera de diámetro interno = 127 μm . Inserto izquierdo: imagen de las fibras de PAN recogidas radialmente en el tambor de bobinado. Inserto derecho: Imagen de la sección transversal de la fibra.

in the fibers during the thermal stabilization and to improve chemical actuation properties of the resulting PAN fibers in linear actuators and artificial muscles applications (Lee *et al.*, 2007; Schreyer *et al.*, 2000).

To quantify the mean diameter of the PAN fibers, the distribution histogram was performed, for which ~ 150 measurements were carried out. The obtained histograms for each of the samples followed Gaussian fit with narrow size distributions; the average particle size (ϕ_n) obtained were 91, 102, 219, 237 and 287 μm for fibers M1, M2, M3, M4 and M5, respectively. A decrease in stainless steel tip diameter leads to a decrease of average fiber diameter as revealed in the size histograms obtained from the analysis of SEM micrographs of each sample (see Figure 5). It is worth mentioning that the diameter of all samples was approximately 18 % smaller than that of the spinner, due to the reduction of mass loss during diffusion of the solvent out of the precursor solution during gelation. These results demonstrate that stainless steel tip characteristic is transcendental in controlling the diameter in the scale micrometric of PAN fibers.

The preparation of activated fibers is an important step in the production of pH responsive PAN fibers for chemical actuation applications. Figure 6 show the raw, stabilized and hydrolyzed PAN fibers, respectively. On thermal stabilization, the fibers are contracted and their color changed from white to black (Figure 6b). This coloration is attributed to a change from linear structure of raw PAN fibers to cross-linked structures of pyridine ring (Friedlander *et al.*, 1968; Brandrup and Peebles, 1968). On the other hand, as alkali treatment begins the fibers change remarkably in color from black to dark brown, with texture like wet seaweed (Figure 6c), as a result

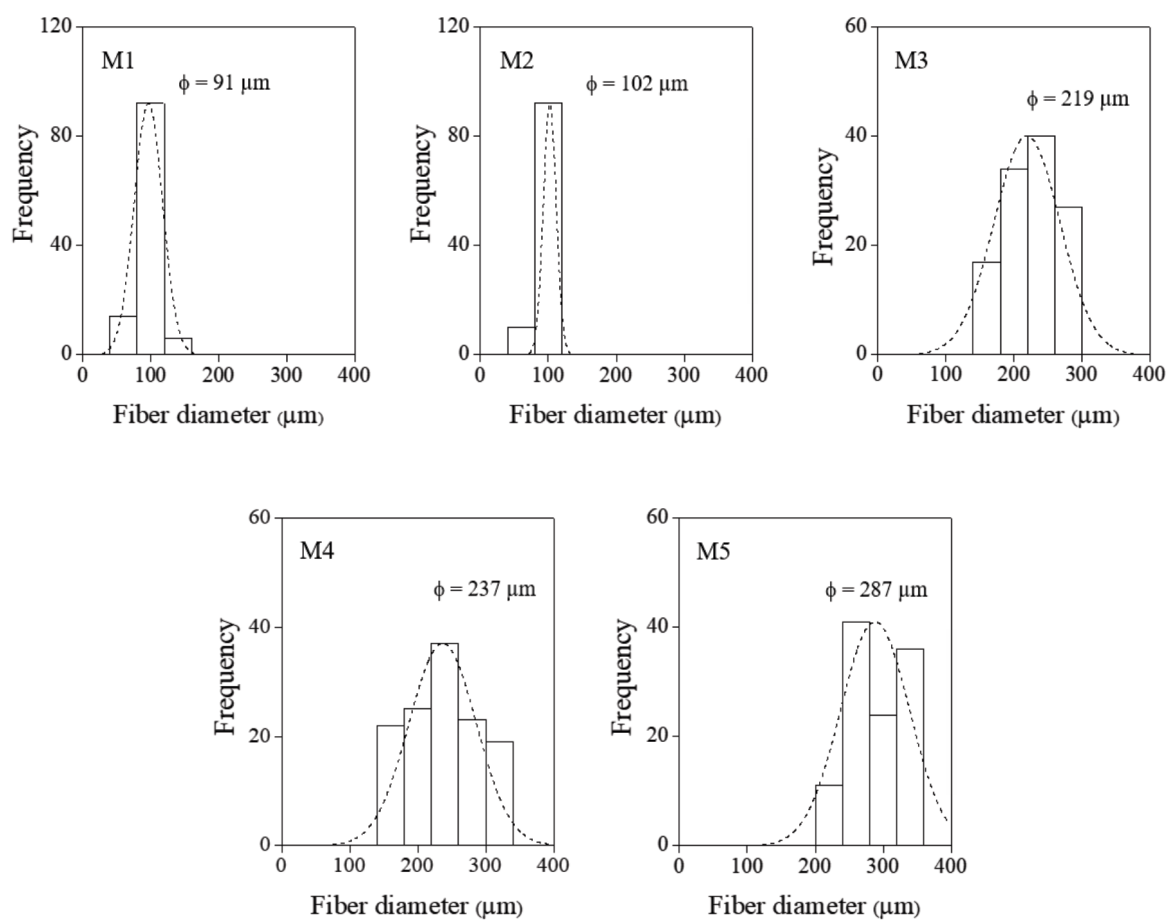


Figure 5. Normalized size distribution of raw PAN microfibers obtained with spinneret of inner diameters: a) 108 μm (M1), b) 127 μm (M2), c) 260 μm (M3), d) 311 μm (M4) y d) 337 μm (M5). Average fiber di-amer (ϕ) is calculated from Gaussian fitting of the histograms.
Figura 5. Distribución normalizada del tamaño de las microfibras crudas de PAN obtenidas con hilas de diámetros interiores: a) 108 μm (M1), b) 127 μm (M2), c) 260 μm (M3), d) 311 μm (M4) y d) 337 μm (M5). El diámetro medio de las fibras (ϕ) se ha calculado a partir del ajuste gaussiano de los histogramas.

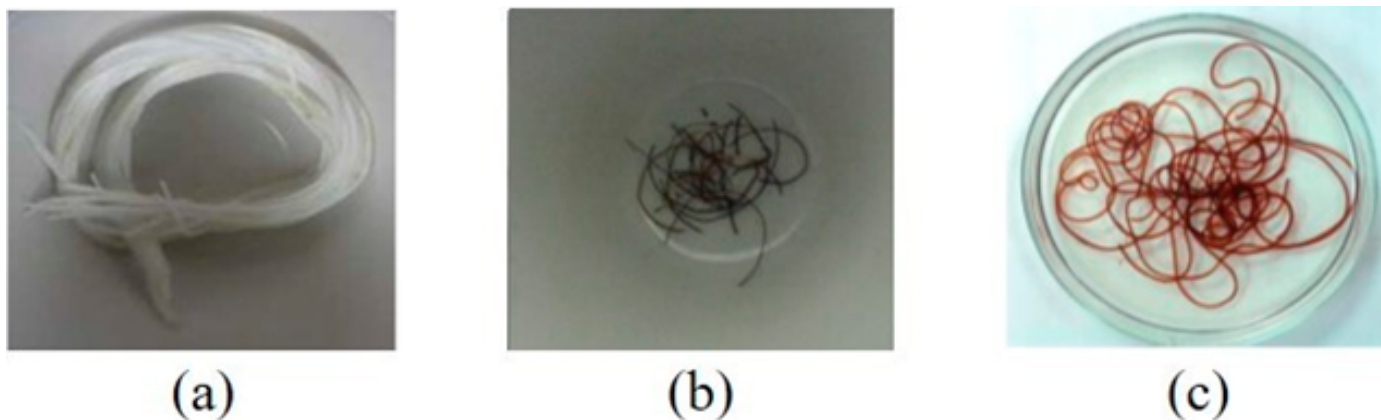


Figure 6. Images of PAN fibers: (a) in raw state, (b) after thermal stabilization process and (c) after alka-line hydrolysis process.
Figura 6. Imágenes de fibras de PAN: (a) en estado crudo, (b) tras proceso de estabilización térmica y (c) tras proceso de hidrólisis alcalina.

of displacement of nitrile groups on annealing to carboxylic acids (Mirbaha *et al.*, 2013).

To verify the chemical composition of the fibers at different activation state, FT-IR spectra were measured. Figure 7 shows the spectra of stabilized and hydrolyzed PAN fibers. The spectrum of raw PAN fiber is presented as reference, in Figure 7a. Typically, PAN fibers spectrum shows the bands in the region of $k\text{ cm}^{-1}$, 2227 - 2257 cm^{-1} , 1472 - 1427 cm^{-1} and 1397 - 1200 cm^{-1} indicating the characteristics of CH, CH₂ and CH₃ group vibrations, stretching vibration of the C≡N group, deformation vibration of CH₂ and other vibrations (Farsani *et al.*, 2009), respectively. The 2948, 1660 and 1354 cm^{-1} peaks correspond to DMF used as solvent. The absence of these peaks in Figure 7c, corroborates the chemical quality of gel fibers. Of particular interest is the C≡N group band. When raw fibers were heated at 240 °C as shown in Figure 7b, a gradual drop in the intensity of 2245 cm^{-1} band of the C≡N group can be observed, with a simultaneously presence of a new band at 1598 cm^{-1} related to C=N, which implies the cyclization of nitrile groups and formation of cross-linked structures in the polymer chain (Lee *et al.*, 2007). The drop in the intensity of the nitrile peak can be used to estimate the extent of stabilization. The spectrum of the heated and then saponified fiber (Figure 7c) exhibit a gradual increase in the intensity of the absorption band at 1731 cm^{-1} , which is attributed to the conversion of the nitrile groups to carboxylic acid groups, which is necessary to provide a large deformation of the PAN microfibers.

Actuation properties of PAN fiber

The actuation properties of the activated PAN microfibers were investigated in terms of length change characteristics under the influence of pH solution ranging from 1 to 14. The measurements are made with sufficient time (5 min) and at ambient temperature. We also investigated the generated force characteristics under the influence of pH = 2.

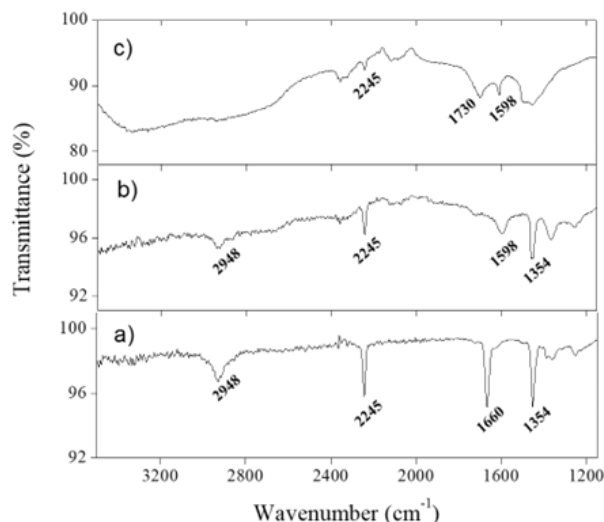


Figure 7. FT-IR spectra of PAN microfibers at different activation states: a) raw fibers, b) stabilized fi-bers and c) stabilized and hydrolyzed fibers.

Figura 7. Espectros FT-IR de microfibras de PAN en diferentes estados de activación: a) fibras crudas, b) fibras estabilizadas y c) fibras estabilizadas e hidrolizadas.

The length change of PAN microfiber with a 287 μm diameter and as function of pH variation (1 to 14) is shown in Figure 8, where the fiber length is plotted against pH. The length change ratio was calculated from Eq. (1):

$$\Delta L = \left(\frac{L_f - L_0}{L_0} \right) (100) \quad (1)$$

where the ΔL , L_f and L_0 are the length change ratio, swelling state length at pH predetermined and original length ($L_0 = 5\text{ cm}$), after two-step activation and washing in distilled water for 30 min. For length change characteristics under the influence of pH solution, the activated PAN fibers were immersed in an initial pH solution of 1. The pH was gradually increased by one pH level (solid square). When the solution reached pH 14, the solution concentration was decreased by one pH = 1 level (solid circle). Length PAN microfibers were monitored for each pH value. Fibers reacted with a length change in function of the pH solution bathing. A negative length change (contraction) was observed ~ 32.8 % for pH = 2 and pH greater than the length change was positive up to a maximum (expansion) of ~ 85.7 % for pH = 8. Increasing the pH (> 8) of the aqueous solution, a progressive decrement was again observed in the fiber length. The same length change was observed between pH 14 and 1 while the pH was decreasing. A hysteresis was noted in the elongation and contraction during all pH values of the aqueous solution, product of the difference in the diffusion rate of the water and ions into and out of the structure of PAN fibers (Schreyer *et al.*, 2000). A similar behavior of the length change characteristics under the influence of pH solution was observed for fiber with other diameters. Also, for smaller diameters the microfibers have a faster response, for example, for microfibers with an average diameter of 91 μm , the length change was completed within 2 s, while for microfibers with an average diameter of 237 μm the response was developed in about 3 s. When fibers were removed from an aqueous environment and allowed to dry, they became rigid with a length close to the original length.

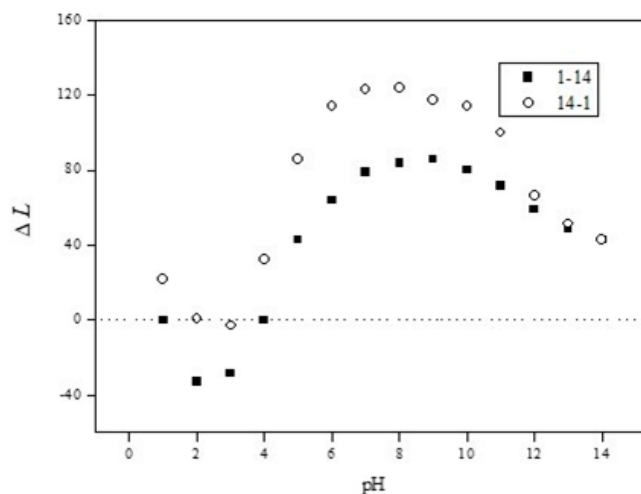


Figure 8. Length variation (ΔL) of PAN gel fibers as a function of pH.

Figura 8. Variación de la longitud (ΔL) de las fibras de gel de PAN en función del pH.

For generative force characteristics, single strand PAN fibers with 5 cm in length and with different diameters were used with a chemically induced method; pH =2 was used for the chemical activation system. The solution was poured through a small nozzle to contract the fiber after which was rinsed with distilled water. Figure 9 shows the profile of contractile force development for the actuation system. The maximum forces generated for each fiber are summarized in the Table 1. The contractile force developed gradual increases as the diameter of fibers increased suggesting that PAN microfibers with greater diameter possess more elastic flexibility. The maximum force is 0.4561 mN for PAN microfiber with a diameter of 287 μm . This value is smaller than that of the commercial PAN microfibers and PAN nanofibers (Choe and Kim, 2006). The discrepancy of generative force between the present and the other fibers may be due to the use of different additives and the diameter of fibers which is two orders of magnitude higher than that of the commercial PAN fibers. Figure 9 also shows that the response time for the maximum force generation in the force measurement system is faster for fibers smaller diameter, for example, for microfibers with a 91 μm average diameter, the force generation was completed within 46 s, while for microfibers with an average diameter of 237 μm the response was developed in about 136 s. For applications as development of biomimetic actuator, the actuation behavior of sensitive pure PAN microfibers should be improved probably adding a small amount known of other polymers. However, it requires further investigations.

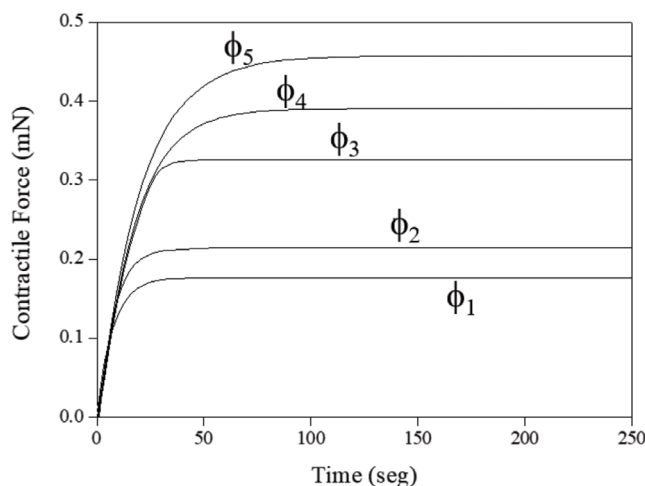


Figure 9. Generative force at pH = 2 of a single PAN fiber with different diameters: $\phi_1 = 91 \mu\text{m}$, $\phi_2 = 102 \mu\text{m}$, $\phi_3 = 219 \mu\text{m}$, $\phi_4 = 237 \mu\text{m}$ and $\phi_5 = 287 \mu\text{m}$

Figura 9. Fuerza generativa a pH = 2 de una sola fibra de PAN con diferentes diámetros: $\phi_1 = 91 \mu\text{m}$, $\phi_2 = 102 \mu\text{m}$, $\phi_3 = 219 \mu\text{m}$, $\phi_4 = 237 \mu\text{m}$ y $\phi_5 = 287 \mu\text{m}$.

Table 1. Maximum generative force of different microfiber diameters.

Tabla 1. Fuerza generativa máxima de diferentes diámetros de microfibra.

Inner diameter of spinneret (μm)	Fiber diameter (μm)	Maximum generative force ($\times 10^{-5}$ mN)
115	91	0.176
125	102	0.215
263	219	0.325
275	237	0.390
344	287	0.456

CONCLUSIONS

We have prepared pure PAN fibers with different diameters in the micrometric scale (91 – 287 μm) using an immersion-jet wet spinning system. The fiber diameter is controlled through variations in the spinner size. Uniform, smooth and continuous PAN microfibers were collected radially and were suitable modified by thermal stabilization and alkaline saponification to obtain fibers responsive to pH levels. The activated PAN microfibers show a maximum contraction of about 32.8 % for pH=2 and a maximum expansion of about 85.7 % for pH = 8. The contractile force increases with a maximum value of 0.4561 mN as the fiber diameter increases, suggesting that PAN microfibers with larger diameter have greater elastic flexibility. The response time for expanding/contracting behavior and for maximum force generation is improved by decreasing the diameter of the gel fibers.

CONFLICTS OF INTEREST

There is no conflict of interest.

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