Electrospinning of epoxy fibers

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A B S T R A C T

Drawn epoxy fibers possess increasingly high mechanical properties when their diameter is decreased down to a limit of about 10 μm. Smaller diameters with even higher properties can potentially be obtained by electrospinning. Yet, electrospinning of standalone epoxy fibers has not been possible so far, because of the reactivity of epoxy and the fragility of such fibers. These difficulties are overcome in the present study by dissolving the epoxy in methyl ethyl ketone solvent, and achieving suitable electrospinning conditions by controlling the degree of epoxy crosslinking in the solution. The fibers are captured on a net screen, with the positive electrode placed behind it. The resulting electrospun fibers exhibit about 80% higher strength and stiffness compared to bulk epoxy, and striking 900% higher elongation and 1200% higher toughness. Also observed is a size-dependence of the strength on the fiber diameter, which shows a sharp strength rise to more than 300 MPa (compared to about 70 MPa in bulk epoxy) in fibers of diameters down to 3 μm. This rise in properties is likely due to anisotropic molecular rearrangement resulting from the strong stretching forces induced by electrospinning. Highly performant epoxy nanofibers could find applications in diverse fields, including reinforcement in composites, sensors, coatings and electronic devices.

1. Introduction

Synthetic polymer fibers can be prepared by a number of routes including dry, wet, melt and gel spinning [1,2]. Dry spinning involves the extrusion of fibers from a polymer solution that solidifies during solvent evaporation [3], whereas wet spinning is used when the solvent cannot be evaporated and must be removed by chemical means [4]. Melt spinning uses heat to melt the polymer to a viscosity suitable for extrusion from a spinneret to generate fibers which solidify with cooling [5]. Gel spinning is a preparation method for high-strength, high--modulus fibers. Following extrusion of the polymer solution or plasti-cized gel, cooling in solvent or water is applied before stretching to a gel fiber by ultra-high extension [1]. During all these spinning processes, jets form under external shearing forces and/or under mechanical drawing when passing through spinnerets. Fibers then form upon so-lidification of the jets. Stretched jets yield fibers with 10–100 μm di-ameters, typically [1], the sub-micron scale remaining difficult to get to.

By contrast, the technique known as electrospinning, which applies a strong electrostatic field to stretch a polymer solution, opens the door for the production of ultrathin fibers with diameters down to the nanometer scale [6,7]. Extensive research has been dedicated to determining whether a particular solution is spinnable or not [8–10], indicating that

a spinnable solution is one in which the forming jet is sufficiently stable, and the filament does not break up before drying. The solution composition is key to achieving processing stability by tuning a number of parameters, including solvent properties, polymer type and concen-tration. In addition to the dielectric solvent, which makes the solution electro-responsive, a suitable polymer molecular weight is a prerequisite for solution spinnability, ensuring that the solution is sufficiently viscous and highly contiguous [10]. Therefore, the polymer system should be a percolating network, which is crucial in forming a continuous fiber. When a solution drop is exposed to an electric field with a higher force than its surface tension, it collapses and forms a Taylor cone, which further develops into an elongated jet [11]. The entangled polymer chains prevents the elongated jet from breaking apart and forming droplets [12]. Rapid evaporation of the solvent reduces the mobility of the chains within the jet and solidifies it to a fiber.

Thermoplastics are the most common polymer family used in elec-trospinning. By contrast, the other important group of polymers, the thermosetting polymers, has not been studied in electrospinning. Epoxy, the focus of our present work, is of specific interest in view of its excellent mechanical properties and wide use as a matrix in composite materials. Only one study, based on co-axial electrospinning of epoxy as an inner core surrounded by a PVP sheath, was conducted [13]. The

main reason why electrospinning was never used with epoxy is its reactive nature and small oligomer molecule. When mixed with a curing agent, which is usually an amine-based molecule, it starts to kinetically crosslink such that with time and temperature the viscosity of the resin increases, and diffusion of the molecules is reduced until a rigid 3D covalently-bonded network is formed [14]. The isothermal curing reaction of an epoxy resin is complex as a consequence of the interaction of the chemical curing reaction with other physical processes, such as gelation and vitrification, causing important changes in the macroscopic physical properties of the reacting system [15].

For electrospinning purposes, this kind of network should be fluid enough to flow through a thin nozzle, collapse into a Taylor cone when exposed to an electric field, and capable of holding shear forces during the elongation in order to form a fiber. This evidently is a challenge with epoxy, in view of its native viscosity and bonding potential, and so a different approach than that used with thermoplastics must be considered.

In our previous study, relatively simpler mechanical drawing yielded epoxy fibers with diameters in the 10–200 µm range [16]. These drawn fibers exhibited large plastic deformation of up to 150% in strain, and high strength at break and elastic modulus, compared to bulk epoxy which has brittle properties and a maximum strain of only 12% on average. Such unusual properties were attributed to re-arrangement of the molecular structure as a result of drawing. However, the small fiber diameters achievable by the drawing technique are limited. By comparison, because of its strong electrostatic stretching, electrospinning has the potential for achieving even thinner fibers and, possibly, much higher mechanical properties.

In the present work, thin epoxy fibers within a diameter range of 3–22 µm were prepared by electrospinning and examined. A new technique was developed to reach this diameter range, based on electrospinning of epoxy resin dissolved in a dielectric solvent. Since there are no previous works describing the preparation of epoxy fibers by electrospinning, an original solution and process had to be developed. The strength, stiffness and effective toughness were measured in tension and correlated with the fiber diameter. Results are discussed and compared with those of mechanically drawn epoxy fibers, prepared with and without solvent.

2. Experimental

2.1. Materials and methods

The epoxy used in this study was diglycidyl ether of bisphenol-A (DGEBA), resin EP828 and hardener EP304 (purchased from PolymerG, Israel); the hardener was a polyether amine with trifunctional primary amine. The epoxy resin was dissolved in a dielectric solvent, methyl ethyl ketone (MEK) (Sigma Aldrich), to form an electroresponsive solution for electrospinning.

Resin and hardener were added in a glass vial (weight ratio: 100:42), as recommended by the manufacturer. MEK was then added with a weight fraction of 70% of the total solution weight. The glass vial was stirred vigorously for 20 min (THINKY conditioning mixer, series ARE-250) and for an additional 76hrs on a magnetic hot plate at 70 ± 10 °C and 200–250 rpm stirring rate. During heating and mixing, the viscosity of the solution gradually increased because of crosslinking until reaching the gelation point [17,18]. Mixing continued until the solution started to show haziness, at which point the solution was ready to use. The appearance of haziness in the solution is an indication of the beginning of transition from gelation to vitrification of epoxy [15], as described in detail later. Haziness was measured by means of UV–Visible Spectrophotometer (Cary 300 Bio) and showed total absorption at 323 nm wavelength compared to 315 nm for fresh solution (see supplementary results).

2.2. Electrospinning

The homemade electrospinning system (Fig. 1) consisted of a syringe pump (Fusion 4000, Chemyx Inc.) and a DC power supply (PS/FC50R02, Glassman High Voltage, High Bridge, NJ). The nozzle included a needle with inner diameter of 0.83 mm (21 gauge) connected to a disposable syringe. The fiber collector was an aluminum net with a $15 \times 15 \text{ mm}^2$ cell size. A power supply unit was connected to a copper rod electrode 100 mm in length and 2 mm in diameter, located 10 mm behind the net. The process was conducted at room temperature, using a solution feeding rate of 0.7 ml/h and an applied voltage of 19–21 kV. Fibers accumulated on the metal net, then were left to rest for 16 h and vacuumed for another 24 h and cured in an oven at 100 °C for 6 h.

2.3. Differential scanning calorimetry (DSC)

In order to identify full curing and perceive any solvent residuals in the matrix, the thermal behavior of the epoxy samples was monitored by differential scanning calorimetry (DSC, TA DSC Q200). Samples were placed in a hermetically sealed aluminum pan. Measurements were carried out in N2 atmosphere from room temperature to 120 °C, at a heating rate of 10 °C/min^{-1}.

2.4. Tensile testing

The fibers were prepared with a gauge length of 10 mm. Prior to testing, each fiber diameter was measured under an optical microscope at 3 points along the fiber and averaged. The optical microscope was Nikon OPTIPHOT-2 connected to an IDS UI-5580CP-C-OH camera mounted on a Nikon TV lens C-0.45x. The cardboard frame supporting the fiber was connected to the load cell via a pair of fiber clamps. Prior to testing, the side edges of the cardboard frame were cut out. Mechanical tests were conducted with an Instron 5965 universal testing system (UK) equipped with a 10 N load cell, at a rate of 1 mm/min.

3. Results and discussion

3.1. Achieving the electrospinning of epoxy fibers

Electrospinning of epoxy is a challenging task, both in preparing the solution and in conducting the process. To understand the reasons for preparing the solution as described in the methods section, it is important to appreciate the differences between thermosetting and thermoplastic polymers in the context of electrospinning. This is described in Table 1.

As described in the introduction, to form a Taylor cone, the molecules in the solution should be mechanically or chemically linked to each other. In thermoplastics, this linking is achieved by the topological
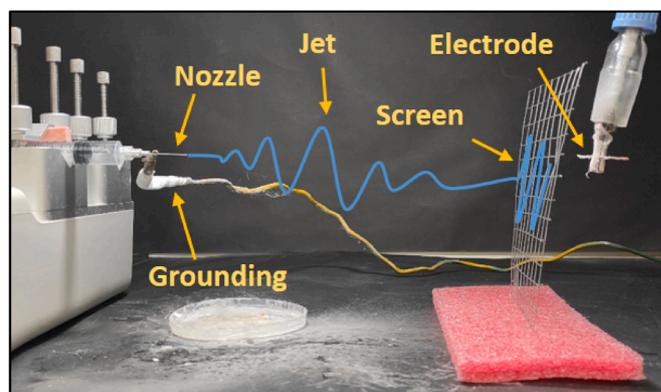

Fig. 1. Picture of the electrospinning system. The nozzle to screen distance is 19 cm, and the electrode is positioned 1 cm behind the screen.

Table 1

Differences between thermoplastic and thermosetting polymers with respect to electrospinning.

Property	Thermoplastic polymer	Thermosetting polymer
Raw material	Solid	Liquid
Components	Polymer	Polymer and curing agent
Molecular weight, Mw	Can reach high Mw	Low Mw, ~1000 kDa (kDa)
Morphology in soluble state	Linear or branched polymer chains	Oligomers
Viscosity in soluble state	Dependent on concentration	Increases as the cross-linking reaction proceeds
Molecular morphology in the bulk	Amorphous or crystalline	Cross-linked network
Thermal properties - glass Transition and melting temperatures	Tg and Tm	Only Tg
Molecular interaction in dry state	Chain entanglements, dipole and hydrogen bonds	Covalently bonded 3D network

entanglement of the long chains with each other. By contrast, in the case of epoxy, which has relatively short molecules, the crosslinking reaction forms the linkage needed for electrospinning. The approach taken was to control the degree of crosslinking and thus achieve a solution that will form a 3D percolated network, identified as gelation state [15,18]. This kind of network should be soft enough to flow through a thin nozzle, and collapse into a Taylor cone when exposed to the electric field, and at the same time strong enough to be able to sustain the tension and shear forces during the elongation in order to form a fiber (Fig. 2a).

The first step in preparing the solution is to mix epoxy, curing agent and dielectric solvent until reaching homogeneity, which is achieved by applying a high mixing rate. The second step is to apply a low mixing rate at elevated temperature for 76 h. As the epoxy and the hardener are being mixed on the hot plate, the crosslinking reaction starts but at low rate, as a result of the high fraction of solvent, which reduces the probability of the epoxy molecules meeting each other. As the mixing proceeds with time, the viscosity builds up until it reaches the gelation state [17]. At that point, the solution loses its fluidity, which indicates the joining of the epoxy branched molecules into a 3D network, but with a low degree of crosslinking. The mixing of the solution continues until a slight haziness appears, and, at that point, the epoxy crosslinking degree is sufficient for electrospinning. It is important to reach this haziness as an indicator for a specific density of crosslinking. Indeed, during fiber formation, the elongated jet will be able to sustain the extension forces by its covalent crosslinked bonds and will not break into drops, an effect that does happen with a solution that is not sufficiently gelated.

In order to better point the exact time at which the solution is ready

to use, a schematic TTT diagram is used (Fig. 2b). The TTT diagram presents the various stages the solution passes through, from the liquid state to solid state, with dependence on temperature and time [15]. As described previously, the solution reaches the gelation state (point 'a' in Fig. 2b) and as mixing continues, it slowly moves toward the vitrification region. As it gets closer to the vitrification border (point 'c' in Fig. 2b), the solution starts to lose its transparency (point 'b' in Fig. 2b), which is expressed by the haziness (Fig. 3a). Further research is needed to determine whether, at that stage, the solution is still in the gelation state or is in early vitrification.

To achieve successful electrospinning of epoxy fibers, some aspects of the epoxy solution and the characteristics of the electrospun fibers should be taken in account. When haziness appears and the solution is ready to use, it continues to crosslink with time, a reduction in temperature or an increase in mixing speed will reduce the crosslinking rate and enable better control on the solution. During electrospinning, as the solution flows out from the nozzle, it is stretched, the solvent evaporates and the fiber is formed. At that point, the fiber is flying to the collector but still contains some solvent while in the process of crosslinking. The spinning process is very fast, of the order of 10^2 msec from nozzle to collector, thus there is no sufficient time for cross-linking during the free flight. At the same time, the very rapid solvent evaporation brings the epoxy units closer together and allows faster curing once the fiber reaches the collector. At this state, the fiber has become tacky, and to collect a single fiber for a tensile test, the fiber must be deposited on a hollow frame, let to dry and continue crosslinking at room temperature. For this purpose, a system based on grounding the nozzle and applying voltage on a copper rod (electrode) placed behind the collector was devised (Fig. 1). The objective is to make the fiber fly toward the electrode but collect it on an aluminum net just before it reaches the electrode. During the process optimization, which includes tuning of the solution flow rate, electric field, nozzle diameter, and electrode and net distances, fibers were collected on a transparent glass and analyzed by means of optical microscopy. The main optimization procedure was to overcome bead formation and achieve neat fiber as showed in Fig. 3B and C. Generally, as the viscosity of the solution increased, the amount of beads was reduced.

3.2. Curing of fibers

After resting on the screen, the fibers were post-cured in an oven as described in the experimental section. DSC analysis of the fibers was performed and compared with the bulk epoxy. As seen in Fig. 4, no residual solvent is trapped in the fiber, as no additional endothermal peak around 79.6 °C is observed, which could have indicated evaporation of MEK. The glass transition (Tg) is observed at 74 °C, lower than in the bulk which was 83 °C. In the process of fiber formation, two simultaneous phenomena occur: rapid evaporation of the solvent from the fiber,
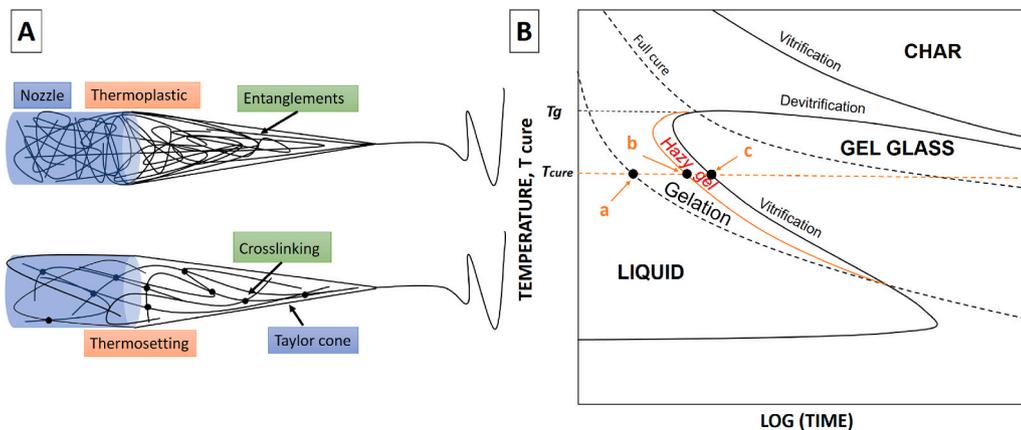

Fig. 2. (A) Illustration of a Taylor cone for thermoplastic and thermosetting solutions in electrospinning. (B) Schematic Time–Temperature Transformation (TTT) cure diagram; the orange curve represents the haziness transition. The indicated dots are: (a) The first observation of gelation in epoxy/MEK solution at 70 °C curing temperature (T_{cure}*), (b) The appearance of haziness in the solution at day 7 of mixing and heating, (c) The solution reaches the sol/gel glassy state [19]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
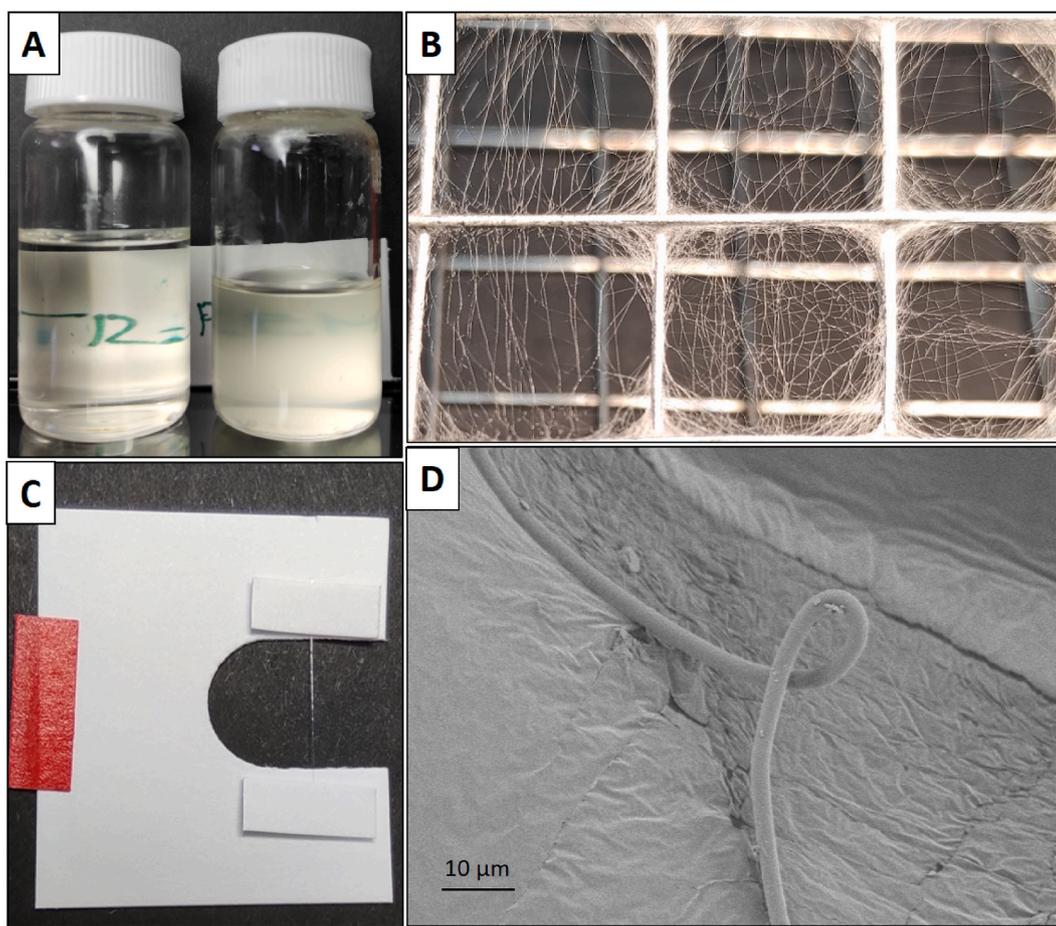
Fig. 3. (A) Epoxy solution for electrospinning: the left bottle is a clear transparent solution just prepared and the right bottle is the hazy solution ready to use after 7 days of mixing and heating, (B) electrospun epoxy fibers deposited on aluminum net (Strong light was projected to observe the fibers without magnification), (C) tensile specimen (the left bridge is cut prior to testing), (D) SEM micrograph of a single electrospun fiber.
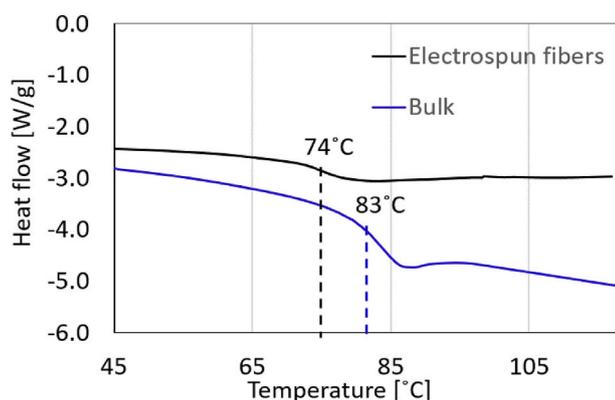

Fig. 4. DSC thermogram of electrospun epoxy fibers and bulk epoxy.

and reduction in polymer chain mobility and diffusion. As the fiber forms, the solvent evaporates very fast because of the high surface area to volume ratio [19]. The epoxy groups do not diffuse fast enough to fill the gaps left by the evaporated solvent, and the result is that these remaining gaps and the unreacted epoxy terminals effectively increase the free volume and consequently reduce Tg [20]. Possible reduction in Tg by a size effect (fiber diameter), as by Wang et al. [21], is likely not relevant here because of Wang's relatively thinner fibers (diameter below 600 nm) compared to the micrometric fibers (diameter above 3 μm) tested here. The Tg of the fibers before curing was not measured and

the question whether post-curing is necessary at all remains open.

3.3. Mechanical properties of electrospun epoxy fibers

Tensile tests performed on electrospun epoxy fibers with a diameter range of 3–21 μm are presented in Fig. 5. The results for the strength, strain (max elongation), stiffness (Young's modulus), and effective toughness are shown against fiber diameter, and average values are presented in Table 2. The mechanical properties of the electrospun fibers are much higher than those of their counterpart bulk material, showing an average increase of 78% in strength and 83% in stiffness, as well as striking increases of 900% in strain and of 1235% in toughness. Note that the strength values are in engineering scale, calculated with the fiber cross sectional area prior to necking (Fig. 6A). In addition, because of the optical lens focus limitation, diameter measurements performed by means of an optical microscope yielded slightly larger diameters compared to the actual diameter measured by SEM. Thus, the true strength is in fact significantly higher.

The wide dispersion of the results is partially due to limitations of the optical inspection of the fibers before testing. Optical microscope inspection of fibers a few microns in diameter is limited to the defects one can see on the surface. Fibers with spotted defects were removed, but it was not practical to spot all the defects. A large ratio between defect size and fiber diameter can be significant when stress is applied, because it results in high stress intensity factor causing premature fracture. We plan to improve the fiber screening method in future studies. Furthermore, the electrospinning process involves a large number of variables, including solution properties, feed rate, electric potential,
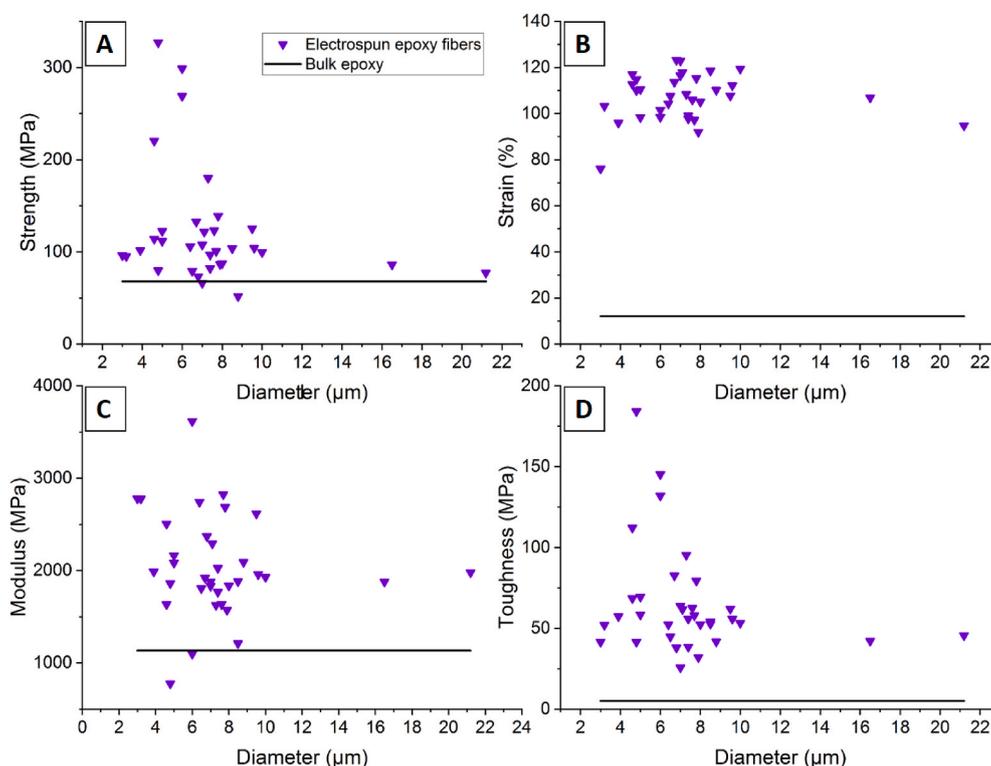
Fig. 5. Tensile test results: (A) Engineering strength, (B) Maximum strain, (C) Young's Modulus, and (D) Effective toughness (calculated as the area under the stress-strain curve) versus fiber diameter.

Table 2
Average tensile properties of fibers using different processing techniques.

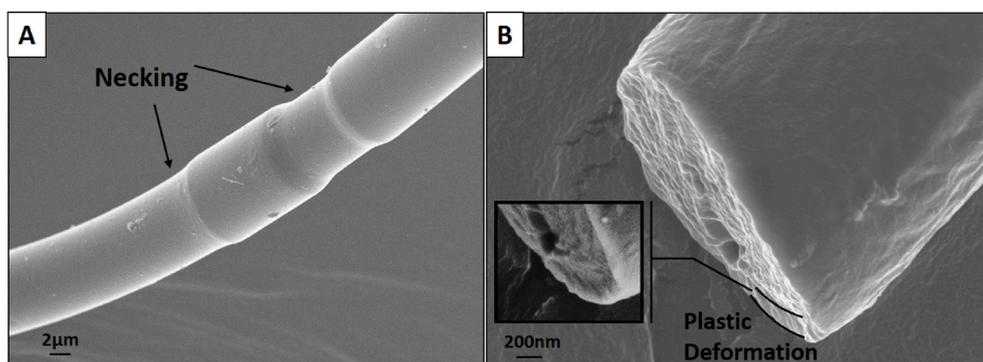| Processing Technique	Solution	Diameter [μm]	Strength [Mpa]	Strain (%)		Toughness [Mpa]	Modulus [Mpa]
Molding Bulk [16]	Neat Epoxy	–	68	12.1 ± 1.9	5.1 ± 1.1		1132 ± 161
Drawing [16]	Neat Epoxy	81 ± 65	106 ± 35	116 ± 30	72 ± 29		2510 ± 601
Drawing	Epoxy/MEK	28 ± 18	61 ± 21	68 ± 28	29 ± 19		2367 ± 649
Electrospinning	Epoxy/MEK	7 ± 3	121 ± 64	109 ± 13	63 ± 35		2073 ± 566

Fig. 6. SEM micrographs of electrospun epoxy fibers after tensile test: (A) Necking regions, (B) Cross section of the fiber surface after fracture, exhibiting a rough surface with a plastically deformed cylindrical layer surrounding the fiber core.

environmental conditions (temperature, humidity, etc.), curing conditions and more, each with its own variability, resulting in large variability of the results. That said, the trends of the measured mechanical properties are clear, regardless of the wide dispersion.

We observe an apparent trend of increasing strength at smaller diameters, although most of the results were obtained around 100 MPa. The highest values are achieved for fibers with a diameter range of 5–7 μm, with a few fibers showing a particularly high strength, up to 327

MPa for a fiber with a diameter of 4.8 μm (compared to 68 MPa for bulk epoxy). The trend of rising strength with decreasing diameter should be substantiated by further tests of fibers with yet smaller diameters. For the tested range of diameters, the elastic modulus does not exhibit a similar definitive diameter-dependence trend, although the average values are around 2.0 GPa compared to just 1.1 GPa for bulk epoxy.

The strain versus diameter shows an average relative elongation of up to 109%, but without specific correlation with the diameter. Such

high elongation is uncharacteristic for epoxy, which is considered a brittle material with typical elongation of up to 12% only. The toughness dependence on the diameter shows a behavior similar to the strength. The average toughness results are around 63 MPa compared to just 5.1 MPa for bulk epoxy, a consequence of the simultaneous improvement in both the strength and strain. Here also, a few particularly high data appear for toughness, reaching sometimes up to 184 MPa.

SEM micrographs of fibers after tensile tests (Fig. 6A) show formation of long necking regions in the epoxy, a common strain release mechanism that indicates substantial plastic deformation. This kind of behavior is not common in epoxy, usually characterized by rare, barely visible short necking prior to failure. The fiber cross sectional surface after failure is rough, as demonstrated in Fig. 6B. implying a ductile fracture, unlike the smooth surfaces characteristic of brittle failures, which are common in epoxy matrices [22]. Notice also the thin sheath (about 100 nm thick) around the fiber boundary, which seems to have a different morphology than the fiber core, implying a difference in plastic flow and mechanical properties between these regions. Notice also the large cavity, possibly a crack, inside the fiber, which is partially bridged by epoxy fibrils.

3.4. Comparison between electrospun and drawn epoxy fibers

To better understand the differences between electrospun and mechanically drawn epoxy fibers, an additional group of fibers was prepared and tested. These were fibers prepared from the same solution as in electrospinning but stretched by drawing instead of electrospinning. In so doing, it is possible to separate the effects on the mechanical properties of the solution and the preparation technique. Drawn fibers from epoxy/MEK solution were prepared and tested in the same manner as in our previous study of drawing epoxy fibers [16]. The average tensile results of four groups, each over its full diameter range, are summarized in Table 2.

As seen, fibers produced by drawing (with or without solvent) and electrospinning yield mechanical properties - strength, strain, toughness and stiffness - that are much higher than those of neat epoxy bulk. We also observe that the use of solvent in the processing of fibers by drawing (line 3 in the table) reduces the mechanical properties compared to drawing without solvent. The reason for this is likely the lower degree of crosslinking, as described in section 3.2 (DSC test), which leads to matrix softening and reduction in tensile mechanical properties [23]. Lastly, the processing of fibers by electrospinning restores the average values of the properties as for fibers made by drawing of neat epoxy. However, the impact of electrospinning on the rise of the mechanical properties at small diameters is much more significant compared to drawing of neat epoxy, as further described below.

Fig. 7a presents typical stress strain curves of the three fiber types,

compared to bulk epoxy. Notice the low strain to failure of the bulk dogbone specimen, namely 12%, compared to the fibers which exhibited large plastic deformation at a fairly constant high stress up to 80% strain, followed by a stress rise until failure slightly above 100% strain. This result may support the suggestion of a low crosslinking density in the fiber matrix, and/or a preferred crosslinking direction resulting from the stretching effect, both of which may enable larger intermolecular mobility between crosslinked centers. More generally, the molecular morphology induced in a fiber stretched by drawing or electrospinning tends to be directional, such that monomers and crosslinks are partially aligned with the stretching direction (that is, fiber direction). We recently observed anisotropy in epoxy fibers drawn from neat epoxy (thus, without solvent), for which molecular orientation was measured by wide angle X-ray scattering [16]. We also observed similar orientation and anisotropic properties in electrospun nanofibers made of thermoplastic polymers [24].

We see in Fig. 7b that the drawn and electrospun fibers made from the same solution of Epoxy/MEK can be regarded as one dataset, in which the drawn fibers occupy the region of large diameters, whereas the electrospun fibers occupy the region of small diameters, with overlap around 10 μm. The drawn neat epoxy fibers are a distinctly separate group, the strength of which rises above the bulk strength at a critical (transition) diameter around 400 μm, compared to about 80 μm in the Epoxy/MEK fibers. This large difference in critical diameters is most probably the result of the lower concentration and lower curing degree (hence lower viscosity and faster relaxation times) of the epoxy/MEK solution compared to the neat epoxy resin [24].

The trendlines of the strength-diameter data in Fig. 7b (solid curves) are power functions of the form $\sigma = \sigma_{bulk} + aD^b$, where σ_{bulk} is the strength of the bulk epoxy, D is the fiber diameter, and a and b are parameters fitted to the data. The power law slope (parameter b) of the steep trend line in the electrospun fibers is about −2, compared to about −1 in the drawn neat epoxy fibers, implying a stronger stretching effect owing to the electrospinning process. The power slope of −2 was also observed and justified analytically in our previous study of electrospun nanofibers made of thermoplastic polymers [24], which showed that the modulus and strength are proportional to the jet strain rate (due to molecular alignment), whereas the diameter is inversely proportional to the square root of the strain rate (due to volume conservation), and therefore $\sigma \sim D^{-2}$. The steep strength rise represented by the power law is attributed to the well-known coil stretch transition phenomenon, which causes polymer networks to sharply elongate above a critical jet strain rate. Hence, it seems that the potential of electrospinning in enhancing the mechanical properties of epoxy is high.

However, orientation effects in thermoset polymers as used in our study cannot be interpreted as in thermoplastic polymers. Measurements of drawn epoxy fibers obtained by X-ray scattering clearly point at
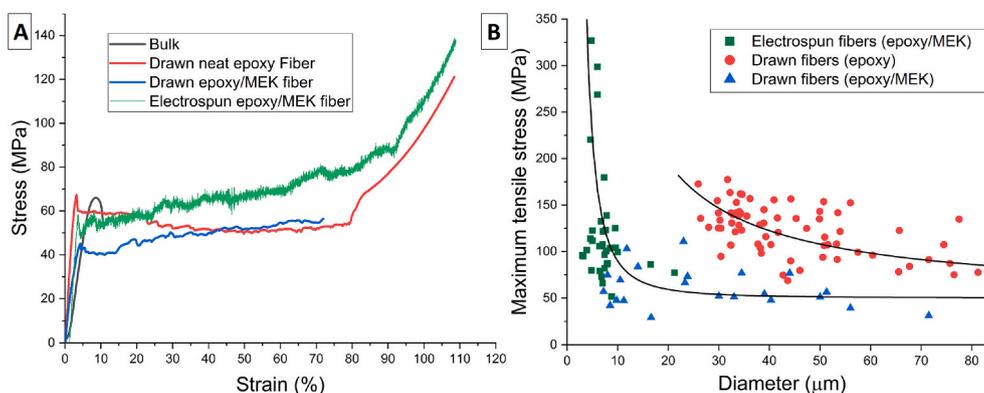

Fig. 7. Comparison between electrospun fibers and drawn fibers: (A) Stress-strain curves of a representative epoxy bulk and three types of fibers. (B) Strength against diameter of fibers electrospun from solution of epoxy with MEK solvent, and of drawn fibers with and without solvent. The trendlines are power functions fitted to the data (see details in the text).

anisotropic molecular structure along the stretching direction [16]. We expect to find a similar effect in electrospun epoxy fibers, which are subject to an even stronger stretching than drawn fibers. At the molecular scale, this orientation can be reflected by the alignment of matrix crosslinking centers in the stretching direction, as well as by alignment of individual DGEBA units or of partially crosslinked DGEBA units. After fiber solidification and full curing, this alignment is translated into long necking formation as shown in Fig. 6 and in previous studies [16,25]. Furthermore, such alignment orients a higher fraction of strong covalent bonds in the stretching direction, while decreasing the fraction of weaker intermolecular bonds in that direction, resulting in higher stiffness and strength in the stretching direction. This kind of stretching and molecular orientation is higher in electrospun fibers than in drawn fibers because of the low crosslinking degree of the electrospinning solution that increases molecular mobility, a result of the solvent presence.

4. Conclusions

The present study introduces electrospinning as a promising way for producing epoxy fibers of nanometric scale possessing supreme mechanical properties. Electrospinning of standalone epoxy fibers has not been possible so far, because of the high viscosity and reactivity of epoxy, and the fragility of the fibers. To overcome this difficulty, we developed an electrospinning method for the production of epoxy fibers with diameters down to 3 μm. To obtain electro-spinnability of epoxy, the epoxy was diluted by MEK solvent, then partially cured until the solution reached the gelation point, making the solution sufficiently liquid to flow through the nozzle and at the same time sufficiently contiguous and strong to form continuous fibers. As the epoxy fibers had to be cured following electrospinning, and in order to avoid fibers agglomeration, the fibers were collected on a metal net allowing curing and handling of individual fibers. The positive electrode was placed behind the net so that fibers could each be suspended across the gaps of the net cells.

Tensile testing of the fibers revealed much increased mechanical properties of the electrospun fibers, about 80% higher in strength and stiffness compared to bulk epoxy, and striking 900% in maximum plastic elongation and 1200% in effective toughness. The fibers exhibited a sharp rise in strength as the diameter of the fibers got smaller, roughly following a power law. These results were compared with epoxy fibers produced by mechanically drawing an epoxy gel with the without solvent, demonstrating higher strength rise for spun fibers. The change in mechanical properties is likely the result of molecular orientation of epoxy elements in the fiber direction, a consequence of the extensive stretching induced by electrospinning. Also, DSC testing showed that the Tg of the spun fibers was lower by 9°C, implying a lower degree of crosslinking which possibly contributed to plasticity.

Further research is necessary to achieve epoxy fibers with yet smaller diameters, entering the nanometric scale. This will require investigation of parameters including the solution constituents and properties, electrospinning conditions, and curing conditions. A better understanding of the governing mechanisms responsible for the properties enhancement is also necessary, by means of theoretical analysis and experimental characterization. We envision the use of such epoxy fibers in diverse applications, such as high-strength fibers, reinforcement of composites, sensors, coatings and electronic devices.

CRediT authorship contribution statement

M. Shneider: Conceptualization, Methodology, Investigation, Writing – original draft, Writing – review & editing. **X.M. Sui:** Methodology, Investigation, Writing – review & editing. **I. Greenfeld:** Methodology, Investigation, Writing – review & editing. **H.D. Wagner:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2021.124307.

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