Enhancing the Mechanical Properties of Electrospun Nanofiber Mats through Controllable Welding at the Cross Points

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Abstract

This communication describes a simple and effective method for welding electrospun nanofibers at the cross points to enhance the mechanical properties of their nonwoven mats. The welding is achieved by placing a nonwoven mat of the nanofibers in a capped vial with the vapor of a proper solvent. For polycaprolactone (PCL) nanofibers, the solvent is dichloromethane (DCM). The welding can be managed in a controllable fashion by simply varying the partial pressure of DCM and/or the exposure time. Relative to the pristine nanofiber mat, the mechanical strength of the welded PCL nanofiber mat can be increased by as much as 200%. Meanwhile, such a treatment does not cause any major structural changes, including morphology, fiber diameter, and pore size. This study provides a generic method for improving the mechanical properties of nonwoven nanofiber mats, holding great potential in various applications.

Graphical abstract
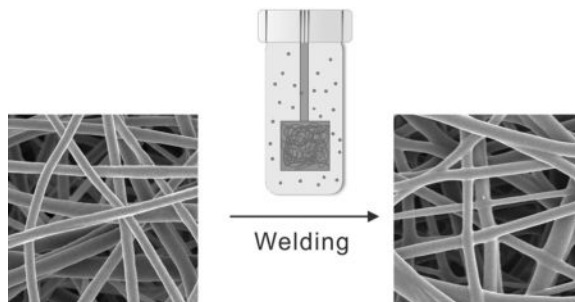
Keywords

electrospinning; mechanical properties; nanofibers; welding

1. Introduction

Electrospinning is a simple and versatile technique for the production of nanofibers with diameters ranging from nanometers to micrometers.[1] Electrospun nanofibers have attracted great attention owing to their unique features such as high specific surface areas, high porosity, and interconnected pore structure, allowing them to be used in filtration,[2,3] tissue engineering,[4–6] textiles,[7] sensing,[8] and fabrication of wearable electronic devices.[9]

Although nonwoven mats of polymer nanofibers can meet most of the requirements needed for the aforementioned applications, the inadequate mechanical strength critically limits their further development. Most nonwoven mats of electrospun nanofibers are formed via physical stacking (without interfiber connection), resulting in relatively weak mechanical properties.[10] Currently, heating[11–13] and chemical cross-linking[14–16] are the most commonly used methods of nanofiber welding to improve the mechanical properties of nonwoven mats of nanofibers. Despite the improvement in mechanical properties, these approaches typically lead to dimensional shrinkage for the nanofibers as a result of molecular chain relaxation in the amorphous region.[17] Moreover, thermal treatment is difficult to operate for polymers with relatively high melting points, and most cross-linking agents are detrimental to the environment and human health. Solvent vapor condensation at the cross points of nanofibers has been exploited for generating attoliter reactors[18] and welding nanofiber mats into conductive films.[19] Solvent vapor treatment has also been applied to introduce secondary nanostructures onto/into electrospun fibers[20] or infiltrate the channels in a porous template with a polymeric material.[21] Huang et al. used saturated *N,N*-dimethylformamide vapor to weld polyacrylonitrile and polysulfone nanofiber mats and achieved significant improvements in mechanical strength.[22] In general, this method does not cause significant changes to the fibrous structure, providing a facile and cost-effective method for nanofiber welding. To our knowledge, there is essentially no systematic study of a well-controlled system (based on the partial pressure of a solvent) for welding electrospun nanofibers made of both semicrystalline and amorphous polymers.

In this work, we demonstrated a controllable method to weld the nanofibers at their cross points using solvent vapor and further investigated their mechanical properties. As a proof of concept, semicrystalline polycaprolactone (PCL) was used as a model system because of its superior biocompatibility and spinnability.[23] In a typical experiment, a PCL solution was first electrospun into random nanofibers in the form of a nonwoven mat (Figure 1A). Since the solvent evaporated very quickly during electrospinning, the majority of the as-prepared nanofibers were in a dry and solidified state when approaching the collector. Besides physical stacking, there were no strong interactions between adjacent nanofibers.[24] The mat was cut into square stripes and placed in a closed vial with dichloromethane (DCM) vapor for a certain period of time. Such a simple treatment can effectively weld the nanofibers at the cross points (Figure 1B).

2. Results and Discussion

We first investigated the influence of DCM partial pressure on the morphology of the nanofiber mat by fixing the treatment time at 1 min. Figure S1 (Supporting Information) shows the scanning electron microscope (SEM) images of nonwoven mats of electrospun PCL nanofibers after exposure to the vapor generated from different amounts of DCM liquid. As the partial pressure of DCM (P_{DCM}) increased, the extent of welding became more prominent. When 20 and 25 μL of DCM (P_{DCM} = 31.6 and 39.5 kPa, respectively) were used to generate the vapor, the structure of the nanofibers was essentially identical to that of the nanofibers in the pristine mat (Figures S1A,B and S2A, Supporting Information). No fusion was found due to the inadequate amounts of solvent molecules to swell/dissolve the PCL nanofibers under such a short exposure time. When the amount of DCM liquid was increased to 30 μL (P_{DCM} = 47.5 kPa), the nanofibers began to show welding (Figure S1C, Supporting Information). However, the welding tended to occur on the entire nanofibers rather than just at the cross points. In particular, when the amount of DCM was further increased to 35 μL (P_{DCM} = 55.4 kPa), the porous structure of the nanofiber mat was completely lost because the PCL nanofibers evolved into a thin film (Figure S1D, Supporting Information). These results indicate that the partial pressure of DCM is a critical parameter, together with the exposure time, to manipulate the welding process in a controllable fashion.

In order to weld the nanofibers specifically at their cross points, we further optimized the exposure time by fixing the volume of DCM at 25 μL (Figure 2). When the exposure time was set to 30 min, welding of the nanofibers started to appear at their cross points (Figure 2A,B). As the exposure time increased to 60 min, fusion between crossed nanofibers became more noticeable (Figure 2C,D). Most importantly, the welding only occurred at the cross points, with no significant changes to the topological and geometric structures of the nanofibers away from the intersection. It should be pointed out that, in contrast to heat-induced fusion, exposure to solvent vapor does not influence the overall structure of the electrospun nanofiber mats other than the fusion/welding at the cross points.

Cross-point welding is strongly dependent on the molecular motion of nanofibers as well as the inter-nanofiber spacing.[11] Exposure to solvent vapor leads to partially swelling/dissolution for the PCL nanofibers. The solid–solid interface at the cross point is prone to

fusion with each other to minimize the interface free energy, while the solid–gas interface away from the cross points prefers to keep the original structure. Besides, the fiber at the cross points has smaller specific surface area (surface area/solid volume ratio) than that of fibers away from the cross points. The density of DCM vapor is the same in the air, which results in a relatively higher vapor/surface area ratio at the junctions to facilitate welding. To validate this hypothesis, we examined the cross-sections of the PCL nanofibers before and after DCM vapor treatment. Before exposure to DCM vapor, the PCL nanofibers stacked together and no interfiber bonding was found. Both paralleled and perpendicular nanofibers at the cross points could be easily identified (as indicated by arrows in Figure 2E). After the treatment with DCM vapor, the cross points exhibited an obvious change in morphology, whereas the other parts of the nanofibers still kept their original morphology. DCM vapor treatment resulted in the fusion of two parallel nanofibers, with the cross-section resembling the Arabic numeral of "8" (as indicated by the lower arrow in Figure 2F). Besides, the welding of perpendicular nanofibers was also observed at the cross points with the terminal of one nanofiber maintaining its original cylindrical shape (as marked by the upper arrow in Figure 2F). Further, we analyzed the crystallinity of the PCL nanofibers before and after DCM vapor treatment using differential scanning calorimetry (DSC) (Figure 3A,B). The melting temperature (T_m, °C) and melting enthalpy (ΔH_m, J g^{-1}) of the pristine and welded PCL nanofibers were 58.69 °C/71.10 J g^{-1} and 59.20 °C/70.80 J g^{-1}, respectively. The degrees of crystallinity were calculated from the ratios of ΔH_m to the melting enthalpy of PCL at 100% crystallinity (139.5 J g^{-1}).[25] The degrees of crystallinity for the pristine and welded PCL nanofibers were calculated to be 51.4% and 50.7%, respectively, suggesting that the treatment by DCM vapor had essentially no influence on the crystallinity of the PCL nanofibers. This conclusion was further supported by the X-ray powder diffraction (XRD) analysis (Figure 3C). Together, these data demonstrate that the welding could be induced to occur at the cross points without altering the packing of polymer chains in the fibers.

We also analyzed the average diameters before and after DCM vapor treatment. Compared to the pristine nanofibers (721 ± 199 nm), no significant difference was observed for the treated nanofibers (693 ± 192 nm). We further studied the surface pore size distributions of the pristine and welded nanofiber mats. The pore size of the pristine and welded PCL nanofiber mats had a similar distribution pattern, with the interval between 5 and 15 μm exhibiting the highest frequency (Figure 3D). Since the pore size in the surface layer was larger than that in the internal layers, the actual average pore size should be much smaller.[26] This result also confirmed that the pore size was not significantly affected after DCM vapor treatment.

Finally, we evaluated the mechanical properties of the PCL nanofiber mats before and after DCM vapor treatment. For the pristine PCL nanofiber mats, the stress increased smoothly, and then the mats broke at the maximum elongation (nearly fourfold, Figure 4A). For the welded PCL nanofiber mats, the stress increased sharply during elastic deformation, and then reached a maximum value at a greater elongation (nearly sixfold, Figure 4A). The difference between the stress–strain curves suggests that the welded nanofiber mat had higher mechanical properties compared to the pristine nanofiber mat, which is in agreement with the results from a previous report.[12] The Young's moduli were 8.41 ± 0.31 MPa and 16.5 ± 0.56 MPa for the pristine and welded PCL nanofiber mats, respectively (Figure 4B).

Since the welding at cross points of nanofibers could reduce the slipping between the nanofibers when subjected to tensions, the welded nanofiber mats had a larger Young's modulus to resist deformation. Figure 4C shows that the tensile strength changed from 11.53 ± 0.89 MPa for the pristine PCL nanofiber mat to 21.4 ± 1.08 MPa for the welded mat, suggesting the greatly enhanced tensile strength after DCM vapor treatment.

To demonstrate the generality of this method, we also examined the feasibility to weld other types of polymer fibers, including amorphous poly(D,L-lactic-*co*-glycolic acid) (PLGA) nanofibers and polystyrene (PS) microfibers. We found that the PLGA nanofibers were welded without severe structural destruction, and the initial 3D framework was retained (Figures S2B and S3A,B, Supporting Information). The average diameter changed from 749 ± 205 nm (pristine mats) to 763 ± 165 nm (welded mats), indicating the negligible impact of DCM vapor on the PLGA nanofibers (Figure S4A, Supporting Information). Besides nanofibers, the procedure based on solvent vapor treatment was also applicable to microfibers. In this case, PS microfibers with an average diameter of 1.82 ± 0.17 μm were welded at the cross points at the assistance of DCM vapor, and the average diameter of the microfibers became 1.94 ± 0.19 μm after treatment (Figures S2C, S3C,D, and S4A, Supporting Information). Furthermore, the mechanical properties of the PLGA nanofiber mats were tested before and after DCM vapor treatment. As shown in Figure S4B (Supporting Information), the tensile strength increased from 9.93 ± 1.14 MPa for the pristine PLGA nanofiber mat to 15.01 ± 0.90 MPa for the welded sample. These results indicate that the welding at the cross points of nanofibers is a general approach to improve the mechanical properties of nonwoven nanofiber mats made of both semicrystalline and amorphous polymers.

3. Conclusions

In summary, we have demonstrated a simple and versatile method to improve the mechanical properties of electrospun nanofiber mats by welding the nanofibers at their cross points. The welding was achieved by exposing the nanofiber mats to the vapor of a solvent controlled at different pressures. Such a treatment does not induce significant structural changes, such as average diameter of the fibers and pore size. This method can be applied to all polymers that can be dissolved in DCM, including PCL, PLGA, and PS. In principle, this welding technique can be extended to nanofibers made of conducting polymers to enhance the electrical conductivity of the mats.[27] This technique offers a simple and versatile approach to the fabrication of nonwoven mats of welded nanofibers, holding great potential in tissue engineering, textiles, and fabrication of sensors and electronic devices.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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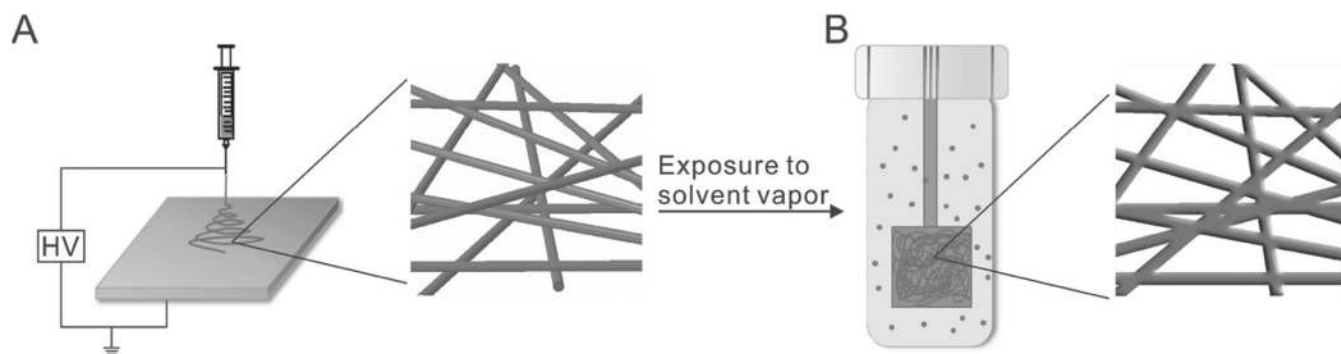
Figure 1.
Schematic illustration showing a controllable process for welding the nanofibers at their cross points: A) fabrication of nanofiber mats by electrospinning and B) nanofiber welding upon exposure to the vapor of a solvent. The gray dots indicate the solvent molecules.
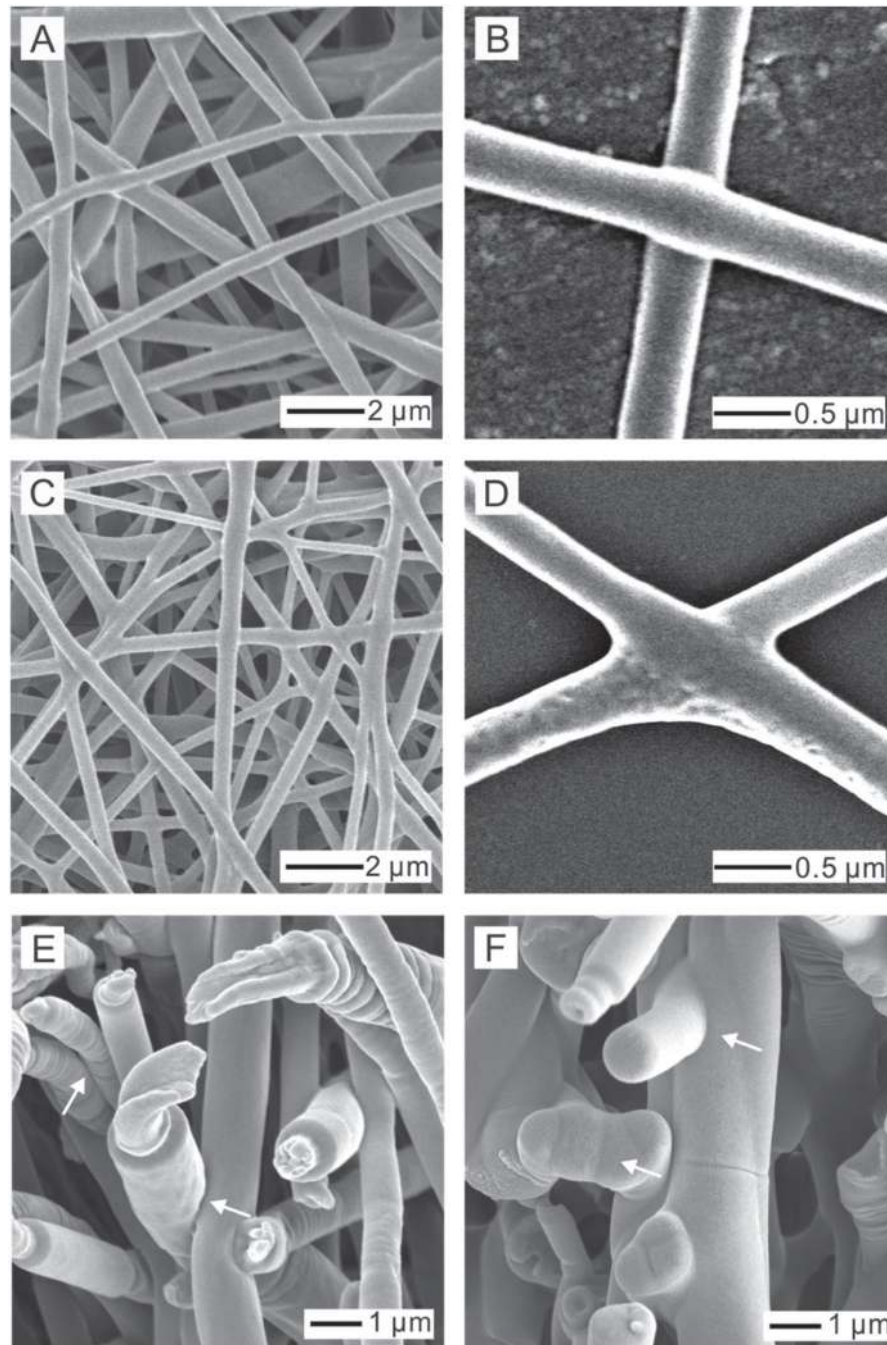
Figure 2.
SEM images of the nonwoven mats of electrospun PCL nanofibers after exposure to the vapor generated from 25 μL of DCM in a closed vial for different periods of time. A,B) 30 min and C,D) 60 min, respectively. SEM images of the cross-sections of PCL nanofibers mats E) before (the arrows indicate that the pristine PCL nanofibers mats were stacked together without interfiber bonding) and F) after the treatment with 25 μL DCM vapor for 60 min (the arrows indicate that the welding only occurred at the cross points).
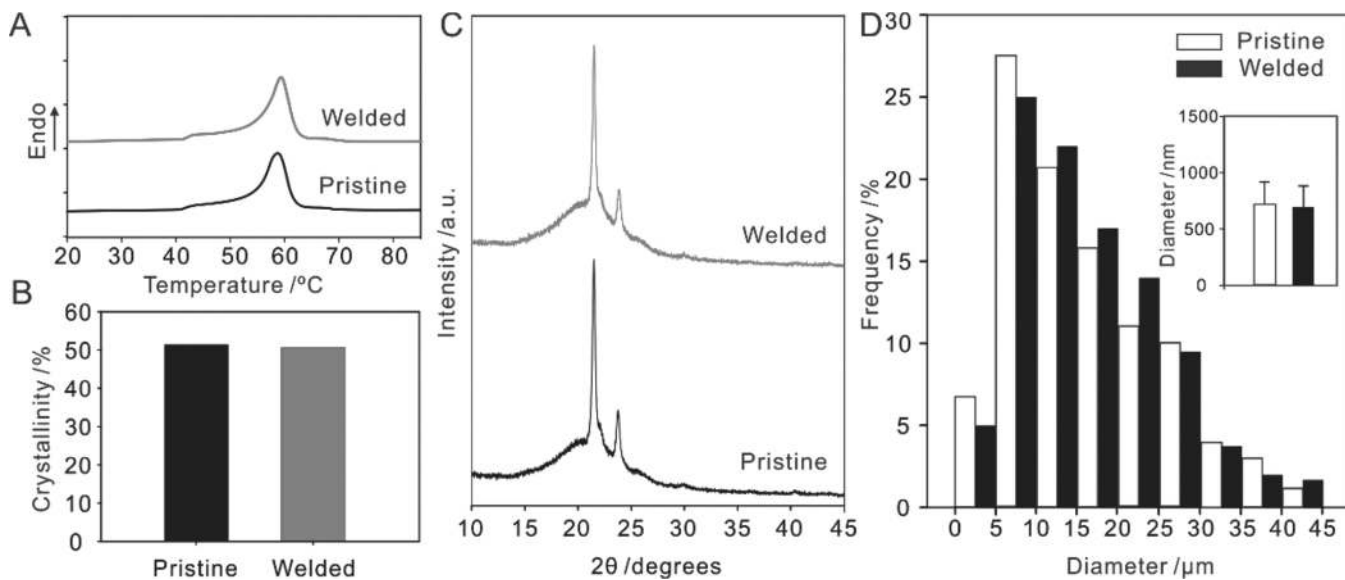
Figure 3.
A) DSC endotherms of PCL nanofiber mats before and after the treatment with 25 μL DCM vapor for 60 min. B) Crystallinity of the pristine and welded PCL nanofibers based on the DSC curves. C) XRD patterns of PCL nanofiber mats before and after the treatment with the 25 μL DCM vapor for 60 min. D) Pore size distribution of the PCL nanofiber mats before and after the treatment with 25 μL DCM vapor for 60 min. The inset shows the average diameters of pristine and welded PCL nanofibers.
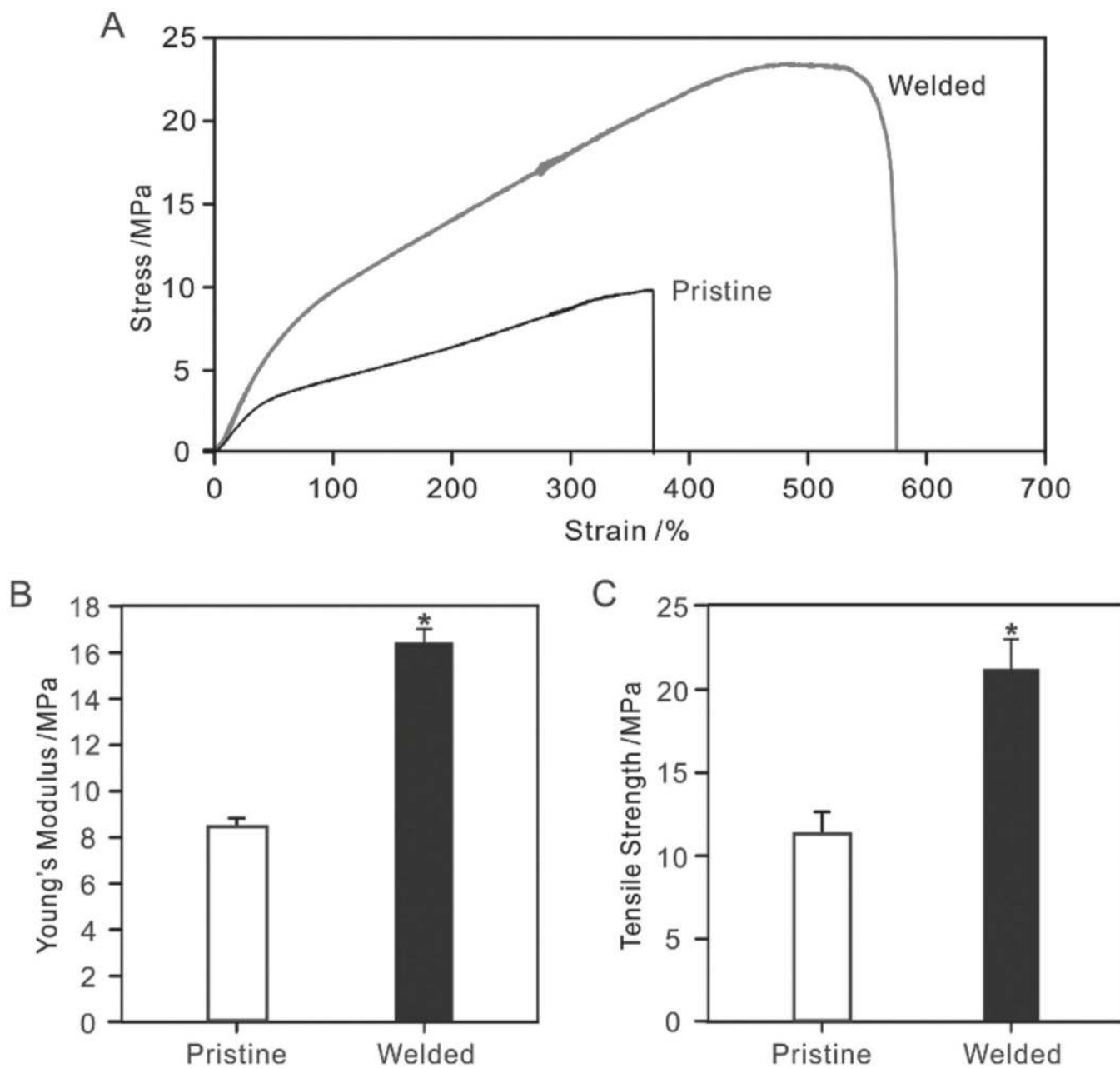
Figure 4.
Tensile mechanical assessment of electrospun PCL nanofiber mats before and after the treatment with 25 μL DCM vapor for 60 min. A) Stress-strain curves. B) Young's modulus. C) Tensile strength. $n = 5$ for each test, * indicates significant difference between the two types of samples ($p < 0.05$).