POLARIZED RAMAN ANALYSIS OF POLYMER CHAIN ORIENTATION IN ULTRAFINE INDIVIDUAL NANOFIBERS WITH VARIABLE LOW CRYSTALLINITY

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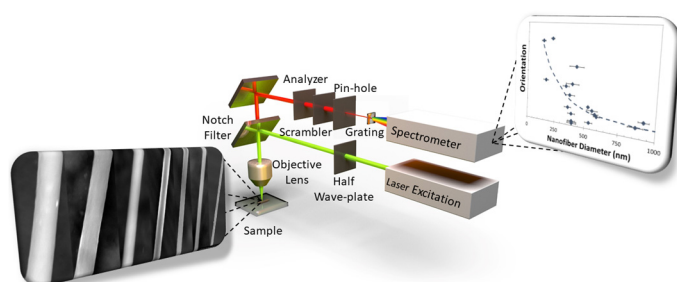
Abstract

Recent mechanical studies of ultrafine electrospun polymer nanofibers showed they can simultaneously possess high strength and toughness attributed to high degree of chain alignment coupled with low crystallinity. Quantitative analysis of macromolecular alignment in nanofibers is needed for better understanding of processing/structure/properties relationships and optimization. However, quantification of structural features in nanofibers with ultrafine diameters and low variable crystallinity is highly challenging. Here, we show that application of standard orientation analysis protocols developed for polarized Raman microscopy of bulk polymers and films can lead to severe errors in subwavelength-diameter samples. A modified polarized Raman method is proposed and implemented for study of size dependent orientation in individual nanofibers as small as 140nm. Macromolecular alignment improved significantly with the reduction of nanofiber diameter, correlating with nanofiber modulus increase. Applicability of the proposed method for quantitative comparative studies of nanofiber systems fabricated from solutions with different solvents is demonstrated.

Introduction

Unusual mechanical behavior and size effects in electrospun polyacrylonitrile (PAN) nanofibers (NFs) were recently reported by our group.[1] Simultaneous increases in strength, modulus, and toughness (as expressed by the area under the stress/strain curve) were observed with a decrease of the NFs diameter. This highly desirable combination of properties was linked to improved polymer chain alignment coupled with low and reducing crystallinity in the thinnest nanofilaments. This unique structure was attributed to peculiarities of the electrospinning process, in particular to ultrafast solvent evaporation.[2] Decreasing NF crystallinity for thinner NFs was experimentally verified on NF mats with different average diameters. Improvement in macromolecular alignment was postulated based on reduction of NF diameter and was indirectly supported by improvement in NF modulus. Direct experimental evaluation of chain orientation in nanofibers could critically enhance our understanding of their mechanical behavior and enable processing/structure/property optimization. However, such evaluation faces significant experimental problems.

Traditional methods of evaluating orientation in polymers, such as x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), rely on large quantities of material to get sufficient signal. In case of NF investigation, mats or bundles have to be used. However, diameters of electrospun NFs are usually not monodisperse. Under such conditions, the signal from NF bundle is dominated by thicker nanofilaments and beads, if some are present in the sample. Examination of individual NFs would allow to overcome this problem. However, quantitative determination of polymer chain alignment in individual NFs with low crystallinity is not easy.[3] Methods such as electron diffraction (ED) are generally applicable to highly crystalline materials. In the case of polymers, ED also faces an additional problem of radiation

damage that is difficult to quantify. One of the few tools currently available for macromolecular orientation quantification in low crystalline or amorphous NF systems is polarized Raman spectroscopy. Advances in optics and laser technology allow modern Raman microscopes to investigate small sample volumes with sufficient spatial and spectral resolution, and do not rely on sample crystallinity to produce the signal.

Application of polarized Raman microscopy to determine polymer chain orientation was first demonstrated by Bower,[4,5] and can also be found in Jasse and Koenig.[6] The complete experimental and data reduction procedures are complex. They require twelve Raman spectra in three different laser/sample/detector geometries to fully resolve the orientation functions of uniaxially oriented systems such as electrospun NFs.[7] This is generally not possible in Raman microscopy because it is limited to backscattering geometry. With some assumptions, the procedure can be reduced to acquisition of four spectra from a single location to obtain different depolarization ratios for a specific band.[8] However, data reduction to extract orientation parameters from these spectra requires either a separate experiment on an isotropic sample of the same material (usually not available) or a relatively involved probability analysis.[9,10] In the past, a simplified approach requiring only two spectra was used to obtain an indicator of orientation that was shown to correlate with the orientation function.[7] In this method, the polarizer and the analyzer are placed parallel to each other. One spectrum is obtained when they are polarized parallel to the fiber (VV), and the other when they are polarized perpendicular to the fiber (HH). The ratio of intensity I_{VV}/I_{HH} for a specific band is then used as an indicator of orientation (henceforth this method will be referred to as "simplified" method/analysis).

Here we show that a straightforward application of the traditional polarized Raman microscopy methods to study macromolecular alignment in individual electrospun NFs can

suffer from significant errors resulting from the need to acquire multiple spectra from the same location. An alternative method that provides a quantitative indicator of orientation is proposed and implemented. The orientation indicator is obtained by examining intensity ratio between two appropriately chosen bands in a single spectrum. A similar method was used in the past on amorphous systems.[8,11] Here, we show that it can be modified to account for the effects of variable NF crystallinity. Applicability of the modified method for quantitative comparative studies of size effects on macromolecular alignment in individual NFs nanomanufactured from solutions with different solvents is demonstrated.

Results and Discussion

We evaluated applicability of the simplified method by examining PAN NFs. Polarized Raman spectra were obtained from individual electrospun nanofibers. The polarization of the laser and the analyzer were parallel and the orientation of this polarization was changed relative to the fiber axis (see Fig. 1b). Results were compared to a drop-cast film, which had no preferred orientation (Fig. 1a).

All spectra exhibited a very strong, sharp band *circa* 2242 cm^{-1}, corresponding to the nitrile stretching mode in PAN, and several strong overlapping bands in the wavenumber range 2800-3000 cm^{-1}, corresponding to different CH stretching vibrations. Both regions can be used for orientation studies in PAN. However, the nitrile band is generally preferred because it is spectrally isolated from other bands.

In the case of the drop cast film (Fig. 1a), as expected, the spectra showed no change for different polarization orientations. In case of the nanofiber, the spectra were markedly different for different polarizations (see Fig. 1b). As per description above, this difference should indicate preferred orientation of the polymer chains within the NF.
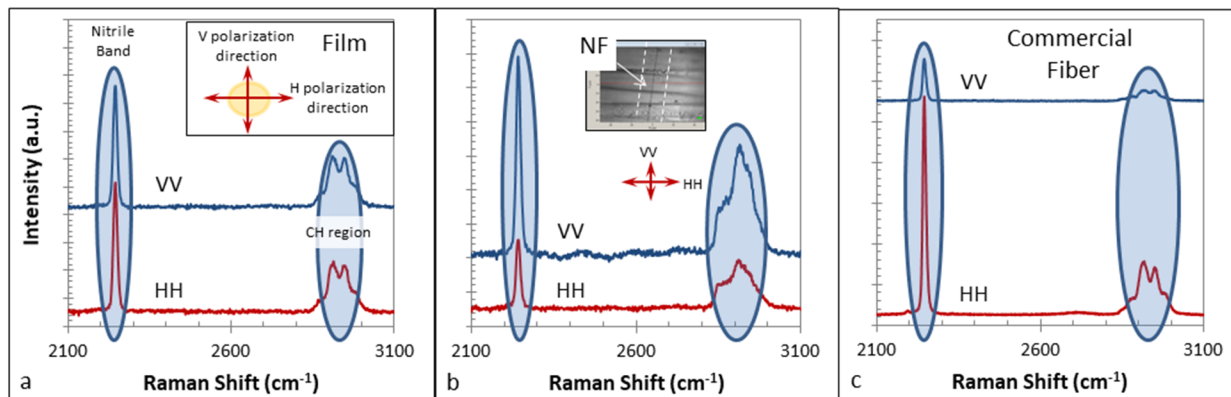
Figure 1: Polarized Raman examination of polymer chain orientation using single band at two polarizations. (a) Raman spectra of a drop-cast PAN film in two polarization orientations, showing no preferred orientation; (b) Raman spectra of an individual PAN NF (~300 nm) in two polarization orientations showing the nitrile band and the CH stretching region, indicating significant apparent orientation. The inset shows an optical microscope image of the NF and the respective polarization orientations. The relationship between the respective intensities is contrary to what is expected based on molecular models of PAN; (c) Raman spectra of a commercial PAN microfiber (~ 30 μm) in two polarization orientations (orientations are the same as in (b)). The relationship between the respective intensities is as expected based on molecular models of PAN and opposite to the one observed in NF.

However, unexpectedly, the I_{VV} intensity of the nitrile stretching mode was stronger than the I_{HH} ($I_{VV}/I_{HH}>1$). The angle between the nitrile groups and the axis of the molecular helix in PAN is not constant, but several studies have estimated the average angle to be in the vicinity of 70 degrees.[12,13] As a result, I_{VV}/I_{HH} should be smaller than 1 when preferred axial orientation of the main chain is present. Several NFs with diameters below ~500 nanometers were evaluated, producing qualitatively similar results. These results were independently replicated in two laboratories indicating a systematic nature to the artifact.

For comparison, commercial conventional PAN microfiber, Dralon X250 (approximately 30 μm in diameter) was also examined. The relation between the intensities in this case was as expected from the molecular structure of PAN – *i.e.* $I_{VV}/I_{HH}<1$ (see Fig. 1c).

Analysis of the above results indicates that the method based on two polarized spectra obtained from individual NFs with submicron diameters contains significant errors. The sources of these errors may be instrumental in nature. These include polarization dependent response of

the grating spectrograph, which is responsible for a spectral separation of the Raman signal, and a slight drift in focus distance due to mechanical switching between polarizations. The latter source can be exacerbated by limitations of the vertical step of the Raman microscope stage, which is comparable in magnitude to NF diameter in the diameter region of the highest interest. Additional potential sources of errors stem from peculiarities of light-matter interaction with the subwavelength-diameter one-dimensional cylindrical samples. The combined effect of these artifacts can lead to different reflectance of the NF when the light is polarized parallel and perpendicular to the fiber. These problems are negligible for large samples, such as the drop-cast film and the examined 30-micrometer commercial PAN fiber, but become acute when NFs with sub-wavelength diameters are analyzed. Consequently, they can lead to quantitatively and even qualitatively erroneous results. Note that these artifacts will be present or even exacerbated in the comprehensive polarized Raman analysis of orientation in nanofibers as well.

An alternative method to evaluate polymer chain orientation can be proposed. This method examines intensity ratio between two appropriately chosen bands under a single polarization combination. The two chosen bands should be differently polarized, *i.e.* their polarization should be at different angles with respect to the main chain axis (in the optimal case, one band will be polarized parallel and the other perpendicular to the main chain). As a result, when macromolecular orientation changes, the ratio of intensities between these bands changes as well (increasing or decreasing depending on the relative orientation of the fiber and the polarizer/analyzer). Both the VV and HH polarization orientations can be used. The choice of orientation should reflect maximization of the band intensity ratio to accentuate changes. The intensity ratio provides a quantitative indicator of macromolecular alignment. This method was recently demonstrated on amorphous fibers.[8,11] Since this method relies on measurements under a

single polarization combination, it avoids the polarization switching-related errors discussed above. In the case of samples with variable crystallinity, such as PAN NFs, a correction for the effects of changing crystallinity, which can also influence the intensity ratio for the selected bands, needs to be introduced.

From Huang and Koenig's work[14] the band *circa* 1355 cm^{-1} is polarized parallel to the main chain in PAN. The nitrile band is polarized close to perpendicular to the backbone chain. These two bands and their relative intensities are shown in Figure 2a. Since the nitrile band is significantly stronger, VV polarization was chosen for the experiments to maximize the $I_{1355}/I_{nitrile}$ ratio. With this geometry, an increase in orientation should lead to an increase of the 1355 cm^{-1} band and a decrease of the nitrile stretching band. An increase of the band ratio is therefore indicative of higher orientation.

Samples of individual PAN NFs in the 140-1000 nanometer diameter range were fabricated by electrospinning from solutions of PAN in dimethylformamide (DMF). Raman spectra were recorded for individual NFs under VV polarization orientation. Areas of the peaks were extracted, and the ratio $I_{1355}/I_{nitrile}$ was calculated for each spectrum (see additional experimental information in the *Methods* section). A significant increase in the $I_{1355}/I_{nitrile}$ ratio was observed with the decrease in NF diameter below 500 nm (Fig. 2b), indicating improved chain orientation in finer NFs.

As mentioned above, changes in crystallinity can also have an effect on Raman spectra.[15–21] The intensity and the position of Raman bands depend on the local environment (*i.e.* proximity of other groups, angles between the different bonds etc.). Higher crystallinity leads to a more uniform environment, and, as a result, to narrower bands (band broadening is the result, in part, of frequency shifts due to different environments present). In addition, crystalline phases

can sometimes be associated with specific macromolecular conformations. This leads to changes

in band intensity ratios for different conformations, when crystallinity changes.
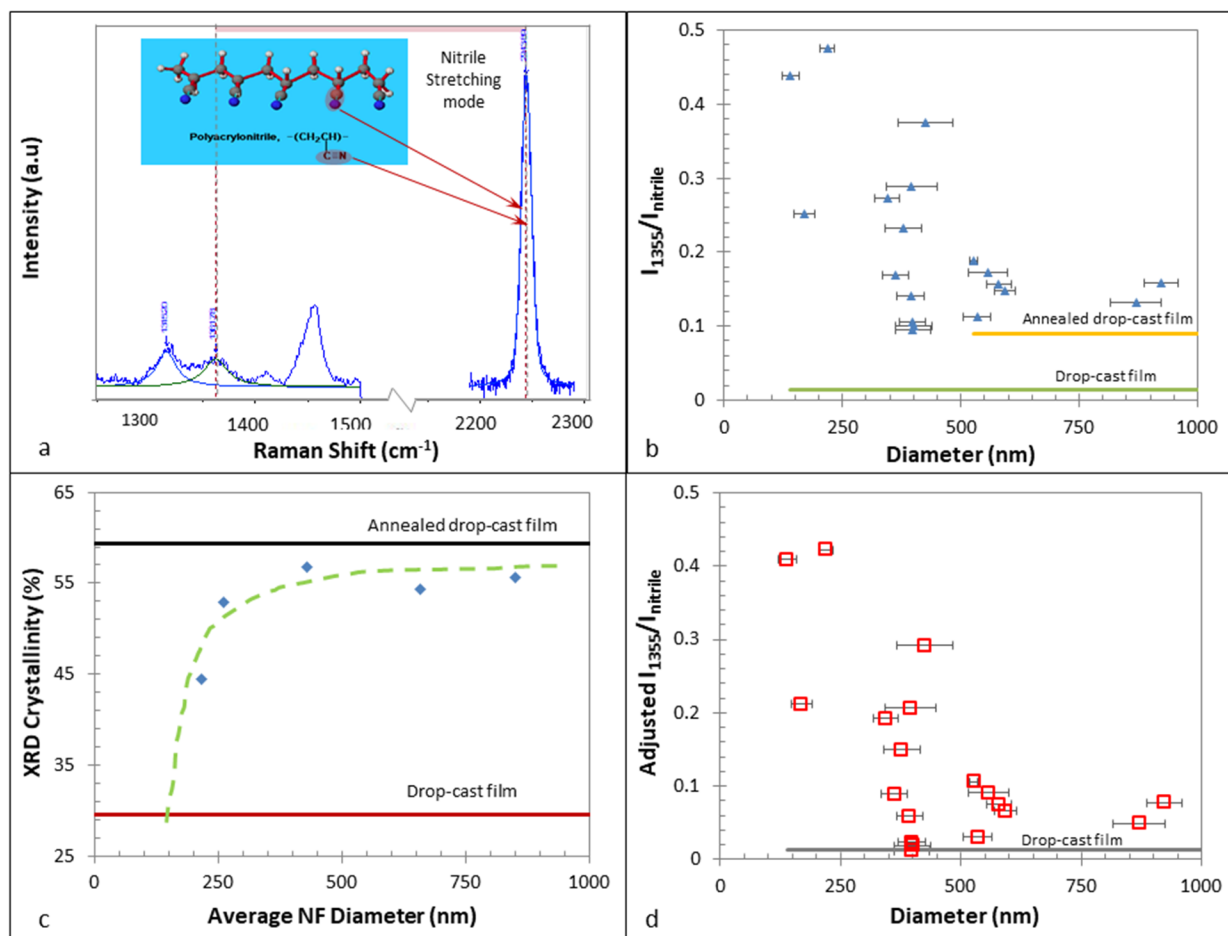
Figure 2: Polarized Raman analysis of polymer chain orientation in individual NFs with low variable crystallinity using two bands intensity ratio at single polarization combination. (a) Raman bands used to calculate intensity ratio as a measure of polymer chain orientation; (b) Size effects in the Raman band intensity ratio measured for individual nanofibers of different diameters, compared to the ratios for the as-drop-cast (green line) and annealed (orange line) PAN films; (c) Comparison of the extracted XRD crystallinity for NFs with different average diameters to the as-cast and annealed films ; (d) Size effect in the $I_{1355}/I_{nitrile}$ Raman band intensity ratio after correction for the effect of crystallinity. The line for the drop-cast film represents a system with no preferred orientation. The error bars in panels b and d correspond to standard deviation in the measured NF diameter.

The effect of crystallinity on the $I_{1355}/I_{nitrile}$ Raman intensity ratio was examined on films

with no preferred polymer chain orientation. Drop-cast film samples were prepared and dried at

60°C (below the glass transition temperature of PAN). To increase film crystallinity, samples were then annealed above the glass transition at 150°C.

Polymer crystallinity in the films and fiber mats was evaluated by XRD, following the protocol described previously.[1] The extracted crystallinity is shown in Figure 2c. Annealing resulted in significant increase in film crystallinity. Interestingly, crystallinity of the as-cast film was smaller than the crystallinity for NF mats with smallest average diameters. Normally, slower solvent evaporation in the films should have resulted in higher crystallinity. One possible reason for the higher crystallinity in NFs can be the presence of macromolecular alignment, which is not present in films. Such alignment allows for some crystallization even in the face of fast solvent evaporation from electrospun jets. The crystallinity in the annealed film was higher than that for the electrospun mats with the large average NF diameters.

Raman spectra for the films were recorded and the $I_{1355}/I_{nitrile}$ ratios were calculated. The ratio for the annealed film was higher than that for the as-cast film (see yellow and green lines in Fig. 2b) even though both films were isotropic. This result indicates that an increase in crystallinity leads to an increase in the $I_{1355}/I_{nitrile}$ band intensity ratio in addition to the effect of orientation.

As can be seen in Figure 2c, decrease in NF diameter led to decrease in NF crystallinity. Based on the examination of PAN films, this decrease should result in a decrease in the observed $I_{1355}/I_{nitrile}$ Raman intensity ratio for smaller NF diameters. Thus, decreasing crystallinity and improved orientation have opposite effects on the $I_{1355}/I_{nitrile}$ ratio so that the effect of diameter on orientation is underestimated in Figure 2b.

Data on unoriented films with different degrees of crystallinity were used to account for the effect of variable crystallinity on the Raman intensity ratio in NFs. The crystallinity of as-cast

and annealed films in this study covered the range of crystallinity in NF mats. Linear relationship between the crystallinity and the crystallinity-related changes in the band intensity ratio was assumed. Crystallinity of individual NFs was approximated from experimental data represented by the dashed line in Figure 2c. Correction to the $I_{1355}/I_{nitrile}$ ratio observed in NFs was calculated.

Figure 2d shows the variation of the two-band intensity ratio after correction for crystallinity. This corrected ratio represents intensity variation caused by changes in the degree of preferred chain orientation in nanofibers of different diameters. Scatter in the results was relatively high. Such scatter is often observed in experimental studies of nanoscale objects and individual fibers. One possible source of scatter in this work is the error in nanofiber diameter measurement. Although we attempted to accurately measure the NF diameter using markers, some uncertainty still remains. In addition, electrospinning is an instability-driven process, which can result in additional variation in structure and properties of electrospun NFs. However, despite the scatter, general trend in the Raman intensity ratio as a function of NF diameter is still readily apparent, showing significant increases for fine nanofilaments. It is important to note that the crystallinity of NF samples with larger diameters was still below that of the annealed film. Nevertheless, the $I_{1355}/I_{nitrile}$ ratio for these fibers was slightly larger than the one for the film (see Fig. 2b). This indicates presence of some preferred polymer chain orientation even in thick nanofibers. The orientation increased rapidly with the reduction of NF diameter below 500nm (see Fig. 2d).This size effect in polymer chain orientation correlated well with the increases in NF modulus observed in our previous work.[1]

Note, that the effect of crystallinity for this polymer system diminishes for small NF diameters. The crystallinity for NF samples with finest average diameters approached that of the as-cast film (see Fig. 2c). The diameters in the NF mats were not monodisperse. This means that

the crystallinity in the smallest NFs within the mats was even closer to that of the drop cast film (or possibly even below). This range of NF diameters (<250 nm) corresponds to the smallest individual NFs examined by Raman (see Fig. 2). As a result, significant increases in the $I_{1355}/I_{nitrile}$ ratio, observed for ultrafine NFs, indicate dramatic improvements in polymer chain alignment in ultrafine NFs.

In most previous studies of orientation in polymer NFs, only modest, gradual increase was demonstrated with the decrease in NF diameter (see *e.g.*[22]). This is most likely due to the fact that polydisperse NF bundles were analyzed. However, examination of the Raman intensity ratio obtained from experiments on individual nanofibers in Fig. 2d shows a sharp dependence on NF diameter. The ratio increased approximately eight-fold for NF diameter decrease from ~500 nanometers to ~140 nanometers. The observed significant increase in the $I_{1355}/I_{nitrile}$ ratio is especially impressive given the fact that the nitrile group is not fully perpendicular to the main chain. This fact reduces the changes in the $I_{1355}/I_{nitrile}$ ratio with the improved chain orientation.

Note that the smallest diameter (~140 nanometers) was approximately four and a half times smaller than the laser wavelength (633 nanometers). To our knowledge, this is the thinnest individual NF examined by polarized Raman to date. This diameter is within the range of diameters of nanofibers exhibiting simultaneously ultrahigh strength, modulus, and toughness (<250 nm).[1] Therefore, the proposed protocol is expected to be of value for the analysis of mechanisms and for mechanical properties improvement through polymer structure control during nanomanufacturing.

Finally, we evaluated applicability of the proposed polarized Raman analysis for comparative studies of size effects on chain orientation in different NF systems. A new PAN NF family was fabricated, using a different solvent (dimethylacetamide – DMAc). Changes in

solvent can affect the drawability of the system because of difference in evaporation rate,

solution viscosity, etc. As a result, they can produce different degrees of macromolecular

alignment and crystallinity in the resulting NFs. Polymer chain orientation in the new NF family

was examined on individual nanofibers and compared to the orientation in NFs produced from

PAN/DMF solutions (see Fig. 3). The dashed lines in Figures 3a, b correspond to exponential fits

of the form in equation 1:

$$I_{1355}/I_{nitrile} = I_{1355}/I_{nitrile\,\infty} + I_{1355}/I_{nitrile\,0} \, exp\left\{-d/d_o\right\} \qquad (1)$$

Where $I_{1355}/I_{nitrile\,\infty}$, $I_{1355}/I_{nitrile\,0}$, and d_0 are fitting parameters.
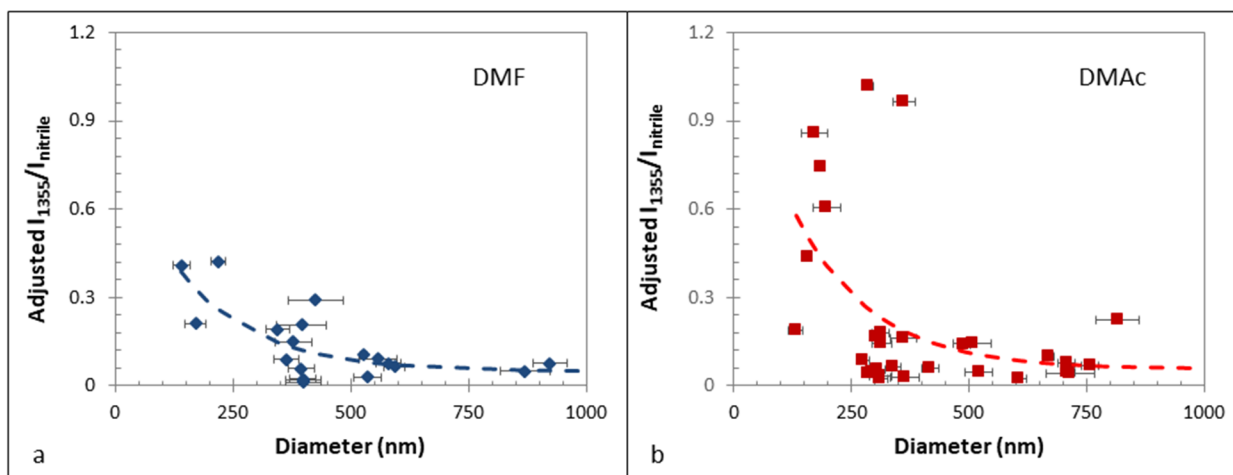
Figure 3: Comparison of size effects in polymer chain orientation in individual NFs from two
NF families electrospun from PAN solutions in (a) DMF and (b) DMAc. Dashed lines in both
panels correspond to an exponential fit.

Analysis of results shows that both families have similar degrees of macromolecular

alignment at large NF diameters (above 600 nm). The size effect in the degree of preferred

orientation for the DMAc-spun NFs is stronger and the improvement in macromolecular

alignment with diameter decrease starts at larger NF diameters. It should be noted that because

the nitrile group is not perfectly perpendicular to the backbone polymer chain, even small

changes in the $I_{1355}/I_{nitrile}$ are likely to indicate significant improvements in the degree of

macromolecular alignment. Based on these results, one can expect higher modulus and, possibly, other mechanical properties in DMAc-spun PAN nanofibers with diameters finer than 500 nm. Mechanical evaluation and a more detailed structural analysis of the two nanofiber families are in progress and the results will be reported elsewhere.

Conclusions

Electrospun NFs have recently demonstrated unique mechanical properties. Quantification of the degree of macromolecular alignment is crucial for understanding these mechanical properties, materials screening, and for properties optimization. Polymer chain orientation in individual NFs was examined using polarized Raman spectroscopy. Results from conventional polarized Raman analysis exhibited significant errors that were linked to the acquisition of multiple spectra under different polarizations from NFs with ultrafine (sub-wavelength) diameters. A modified method that relies on an intensity ratio under a single polarization combination was proposed and implemented. Correction for the effect of variable NF crystallinity was introduced for the first time. The proposed method successfully overcomes the artifacts related to the small sample size, which were observed in methods requiring multiple spectra acquisition. An indicator of polymer chain orientation in individual NFs in a broad diameter range of 140-1000 nanometers was successfully obtained and analyzed. Significant improvements in macromolecular alignment with reduction of NF diameter were experimentally demonstrated for the first time in the ultrafine (<500 nm) diameter range. Applicability of the proposed method for comparative analysis of size effects in the degree of macromolecular alignment was successfully demonstrated on two PAN NF families nanofabricated using different solvents. Good correlation between the obtained orientation indicator and previously

measured mechanical properties indicates the suitability of the proposed method for comparative and optimization studies of ultrastrong/tough fine NFs with low and variable crystallinity.

Methods

Nanomanufacturing

The nanomanufacturing process followed the protocols described in ref.[1] NFs from the two solvent systems (DMF and DMAc) were electrospun from a range of 8-12 wt% PAN (Pfaltz and Bauer, Inc.; MW 150,000) in solvent (Sigma-Aldrich), at 12 kV operating voltage, from a 20 cm spinneret/collector distance, using a 0.6 ml/h feed rate, and a 20 ga needle.

X-ray Structural Analysis

NF and film crystallinity were evaluated following protocols from ref.[1] Nanofiber mats were electrospun for structural analysis onto an aluminum substrate. Wide-angle XRD analysis was performed using a Rigaku Multiflex x-ray diffractometer with Cu Kα radiation in the range of 2θ between 10 and 50 degrees. The background was removed and the crystalline peak (or peaks in the case of annealed samples) and the amorphous halo were fitted using Lorentzian peak shapes. Crystallinity was calculated by dividing the area under the crystalline peaks by the total area.

Polarized Raman Spectroscopy

The examination was performed using HORIBA LabRam Evolution Raman microscope system with 633 nm laser as the excitation source and 600 l/mm grating.

Individual PAN NFs in the 140-1000 nanometer diameter range were electrospun from solutions of PAN and mounted on a microscope slide covered with aluminum foil. Prior to sample placement, a line grid was drawn on the sample to create reference points at grid intersections. Focusing was performed first optically under X100 magnification, and then by

maximizing the nitrile band intensity. Raman spectrum was recorded for NFs under VV polarization. Several spectra were discarded due to the loss of signal or focus as a result of NF movement observed during the experiment. The two peaks in the spectrum were fitted by a combined Lorentzian-Gaussian shape, using LabSpec6 Raman analysis software. Areas of the peaks were extracted, and the ratio $I_{1355}/I_{nitrile}$ was calculated for each spectrum. Locations of the spectrum collection were marked by measuring their distance from the reference points. Subsequently these locations were examined in an SEM to accurately measure the NF diameter.

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