Supplemental Online Material for "Combining responsiveness and durability in liquid crystal-functionalized electrospun fibers with crosslinked sheath"

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A. Supplementary Figures

Figure S1. Test of how high ethanol fraction can be used in the solvent to dissolve an equimolar ratio of PVA and PAA at 7% by mass. A clear solution is obtained with 25% by mass ethanol, while some phase separation is seen at 50% by mass. At higher ethanol fractions, the samples appear a turbid white due to the strong phase separation.

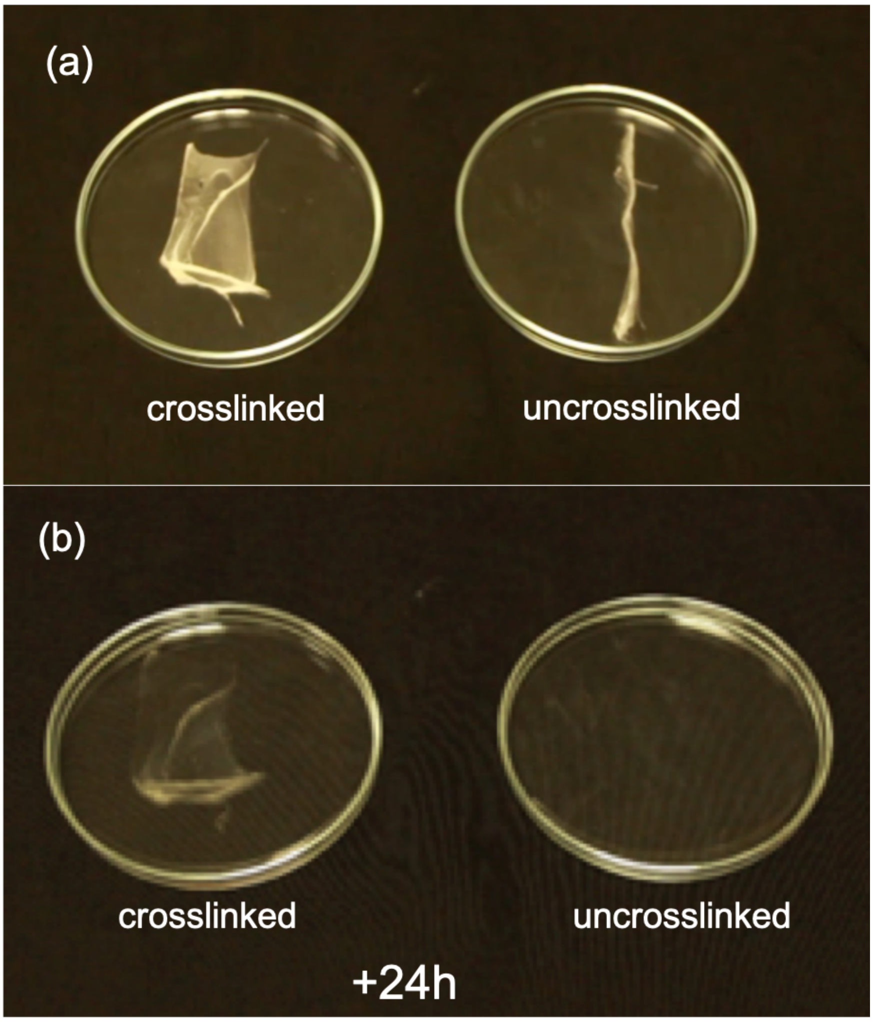

Figure S2. Macroscopic images of pure PVA-PAA fiber mats (no LC core) both crosslinked and uncrosslinked before (a) immersion in water and (b) 24 hours after immersion. Upon water immersion of both mats, the uncrosslinked mat dissolves immediately while the crosslinked mat remained intact; panel (c) shows it after 12 hours of water immersion.

B. Calculation of polymer mixture ratios

We consider masses of PVA, PAA, ethanol and water are m_{PVA}, m_{PAA}, m_E and m_W, respectively. The corresponding molar masses are $M_{PVA} = 44.05$ g/mol, $M_{PAA} = 72.06$ g/mol, $M_E = 46.07$ g/mol and $M_W = 18.02$ g/mol. PVA stock solutions in water with x mass-percent and PAA stock solutions in ethanol with y mass-percent, were prepared by i.e.:

$$x = \frac{100 m_{PVA}}{m_{PVA} + m_W} \tag{1}$$

and

$$y = \frac{100 m_{PAA}}{m_{PAA} + m_E}. \tag{2}$$

To have three different *molar* ratios R of ethanol to water, specifically, 25:75, 50:50 and 75:25. Since $n_E = m_E/M_E$ and $n_W = m_W/M_W$, we can write:

$$R = \frac{m_E/M_E}{m_W/M_W} = \frac{m_E M_W}{m_W M_E}, \tag{3}$$

which means that:

$$\Rightarrow m_W = \frac{m_E M_W}{R M_E}. \tag{4}$$

Inserting (4) into (1):

$$x = \frac{100 m_{PVA}}{m_{PVA} + \frac{m_E M_W}{R M_E}} \Leftrightarrow x(m_{PVA} + \frac{m_E M_W}{R M_E}) = 100 m_{PVA} \tag{5}$$

$$\Rightarrow m_{PVA}(100 - x) = \frac{x m_E M_W}{R M_E} \Rightarrow m_{PVA} = \frac{x m_E M_W}{(100 - x) R M_E}$$

In order to optimize the crosslinking of the fibers, equal fraction PVA monomers and PAA monomers needs to be considered. Since PVA is only 85% hydrolyzed, and the remaining 15% polyvinylacetate is not crosslinkable with PAA. This means that only $0.85 m_{PVA}$ is considered when we calculate the number of moles of each polymer. We thus get:

$$n_{PVA} = \frac{0.85 m_{PVA}}{M_{PVA}} = \frac{0.85}{44.05} m_{PVA} \text{ moles} \tag{6}$$

and

$$n_{PAA} = \frac{m_{PAA}}{M_{PAA}} = \frac{1}{72.06} m_{PAA} \text{ moles}, \tag{7}$$

provided that all masses are given in grams. to have an equimolar ratio, these must be set equal, thus:

$$\frac{0.85}{44.05}m_{PVA} = \frac{1}{72.06}m_{PAA} \Rightarrow m_{PVA} = \frac{44.05}{0.85 \cdot 72.06}m_{PAA} \tag{8}$$

There are now two different expressions for the mass of PVA, (5) and (8), are set equal:

$$m_{PVA} = \frac{xm_E M_W}{(100-x)RM_E} = \frac{44.05}{0.85 \cdot 72.06}m_{PAA} \Rightarrow m_{PAA} = \frac{0.85 \cdot 72.06 xm_E M_W}{44.05(100-x)RM_E} \tag{9}$$

The concentration of PVA solution can be written as:

$$y = \frac{100m_{PAA}}{m_{PAA}+m_E} = 100\frac{\frac{0.85 \cdot 72.06xm_E M_W}{44.05(100-x)RM_E}}{\frac{0.85 \cdot 72.06xm_E M_W}{44.05(100-x)RM_E}+m_E} = 100\frac{\frac{0.85 \cdot 72.06xM_W}{44.05(100-x)RM_E}}{\frac{0.85 \cdot 72.06xM_W}{44.05(100-x)RM_E}+1} = \tag{10}$$

$$= \frac{85 \cdot 72.06xM_W}{44.05(100-x)RM_E} \cdot \frac{44.05(100-x)RM_E}{0.85 \cdot 72.06xM_W + 44.05(100-x)RM_E} =$$

$$= \frac{85 \cdot 72.06xM_W}{0.85 \cdot 72.06xM_W + 44.05(100-x)RM_E} = \frac{6125xM_W}{61.25xM_W + 44.05(100-x)RM_E}$$

The overall polymer mass fraction P could be selected to a certain value, say 7%, by the following calculations:

$$P = \frac{100(m_{PVA}+m_{PAA})}{m_{PVA}+m_{PAA}+m_E+m_W} = \frac{100(\frac{xm_E M_W}{(100-x)RM_E}+\frac{0.85 \cdot 72.06xm_E M_W}{44.05(100-x)RM_E})}{\frac{xm_E M_W}{(100-x)RM_E}+\frac{0.85 \cdot 72.06xm_E M_W}{44.05(100-x)RM_E}+m_E+\frac{m_E M_W}{RM_E}} = \tag{11}$$

$$= \frac{100x(\frac{1}{(100-x)RM_E}+\frac{0.85 \cdot 72.06}{44.05(100-x)RM_E})}{\frac{x}{(100-x)RM_E}+\frac{0.85 \cdot 72.06x}{44.05(100-x)RM_E}+\frac{1}{M_W}+\frac{1}{RM_E}} = \frac{100x(\frac{1}{(100-x)RM_E}+\frac{1.39}{(100-x)RM_E})}{\frac{x}{(100-x)RM_E}+\frac{1.39x}{(100-x)RM_E}+\frac{1}{M_W}+\frac{1}{RM_E}} =$$

$$= \frac{100x(\frac{2.39}{(100-x)RM_E}}{\frac{2.39x}{(100-x)RM_E}+\frac{1}{M_W}+\frac{1}{RM_E}}$$

To keep P and R freely choosable, keeping them independent variables, (11) can be rewritten in order to get x as a function of P and R:

$$\frac{239x}{(100-x)RM_E} = P\left(\frac{2.39x}{(100-x)RM_E}+\frac{1}{M_W}+\frac{1}{RM_E}\right) \tag{12}$$

$$\Leftrightarrow \frac{x(239-2.39P)}{(100-x)RM_E} = P\left(\frac{1}{M_W}+\frac{1}{RM_E}\right) \Leftrightarrow \frac{x(239-2.39P)}{RM_E} = P\left(\frac{1}{M_W}+\frac{1}{RM_E}\right)(100-x)$$

$$\Leftrightarrow x\left[\frac{(239-2.39P)}{RM_E}+P\left(\frac{1}{M_W}+\frac{1}{RM_E}\right)\right]=100P\left(\frac{1}{M_W}+\frac{1}{RM_E}\right)$$

$$\Rightarrow x=\frac{100P\left(\frac{1}{M_W}+\frac{1}{RM_E}\right)}{\left[\frac{(239-2.39P)}{RM_E}+P\left(\frac{1}{M_W}+\frac{1}{RM_E}\right)\right]}=\frac{100}{\frac{239-2.39P}{RM_E}\cdot\frac{1}{P\left(\frac{1}{M_W}+\frac{1}{RM_E}\right)}+1}=$$

$$=\frac{100}{1+\frac{239-2.39P}{PRM_E\left(\frac{1}{M_W}+\frac{1}{RM_E}\right)}}=\frac{100}{1+\frac{239-2.39P}{P\left(\frac{RM_E}{M_W}+1\right)}}$$

We now have all we need, because we have chosen R and we have an equation for x, so we can get y from equation (10).

As for the volumes/masses of each solution, we can freely choose m_E and then equation (4) gives us m_W. Note that we do not yet have the masses of the *solutions*, only of each respective pure solvent. To get the solution mass, we need to add the polymer mass, but these are given in equations (5) and (8):

$$m_1=m_{PVA}+m_W=\frac{xm_EM_W}{(100-x)RM_E}+\frac{m_EM_W}{RM_E}=\frac{m_EM_W}{RM_E}\left(\frac{x}{100-x}+1\right)=\frac{m_EM_W}{RM_E}\left(\frac{100}{100-x}\right)\tag{13}$$

and

$$m_2=m_{PAA}+m_E=\frac{0.85\cdot 72.06m_{PVA}}{44.05}+m_E=\frac{0.85\cdot 72.06\frac{xm_EM_W}{(100-x)RM_E}}{44.05}+m_E=\tag{14}$$

$$=m_E\left[1.39\frac{xM_W}{(100-x)RM_E}+1\right]$$

Table S1. Calculated mass percentages of sheath and core used for electrospinning.

	Sheath		Core	
	Polymer	Solvent	LC	Solvent
Nematic	10% PVA-PAA	90% 1:3 EtOH:water	70% RO-TN 651	30% EtOH
Cholesteric	10% PVA-PAA	90% 1:3 EtOH:water	90% 1:3 CB15:RO-TN 651	10% 1,4-dioxane

Table S2. Parameters and conditions for electrospinning with nematic LC core

Relative Humidity(%)	Temperature (°C)	Distance (cm)	Voltage (kV)	Flow rate (ml/h)	
				Sheath	Core
30	22.5	9	12.5	0.0021	0.029

Table S3. Parameters and conditions for electrospinning with cholesteric LC mixture as the core

Relative Humidity(%)	Temperature (°C)	Distance (cm)	Voltage (kV)	Flow rate (ml/h)	
				Sheath	Core
31	23.6	9	7.5	0.002	0.021

C. Description of ESI movies

(1) Movie of Taylor cone while spinning with RO-TN-651 nematic LC as core. The continuous spinning cycle with core injection is about 15 s, after which the spinneret must be wiped clean (end of the movie) to avoid dripping of liquid onto the fiber mat.

(2) Movie of uncrosslinked fiber with nematic LC core as it is rotated on the transmission POM between crossed polarizers. The good extinction when the fiber is along the polarizer (vertical in the movie) and the nearly uniform brightness for orientation about 45° to the polarizer confirm the good alignment of the LC director along the fiber axis.

(3) Movie of crosslinked fiber with nematic LC core, seen in transmission POM between crossed polarizers, heated above the LC clearing point and cooled back into nematic.

(4) Movie of crosslinked fiber with nematic LC core as it is rotated on the transmission POM between crossed polarizers. The fiber brightness is maximum for orientation 45° to either polarizer while it is minimum when it is along a polarizer (vertical or horizontal in the movie), confirming that LC director is aligned primarily along the fiber axis, although the lack of complete extinction when the fiber is along either polarizer shows that the alignment quality is reduced by crosslinking.

(5) Movie of Taylor cone while spinning with cholesteric LC mixture as core. Distortion of Taylor cone shape towards the end of the movie clearly shows that polymer gelation is taking place near the Taylor cone surface after about 15 s of spinning.

(6) Movie of uncrosslinked fiber with cholesteric LC core as it is rotated on the reflection POM between crossed polarizers. The red reflection color is visible independent of orientation with respect to the polarizers, as expected since the reflected light is circularly polarized.

(7) Movie of crosslinked fibers with cholesteric LC mixture as core, observed in reflection POM between crossed polarizers, while the inclined fiber is being immersed in water. Its sheath is imbibed with water, reducing the refractive index contrast with the surrounding to near zero, thus eliminating the scattering. The near vertical fiber and its branch are above the water surface and thus retain their scattering.