

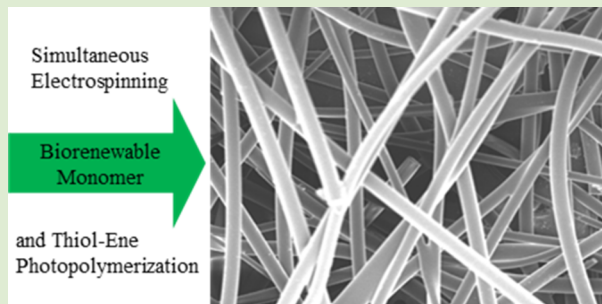
Soybean Oil Based Fibers Made Without Solvent or Heat

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S Supporting Information

ABSTRACT: Thiol–ene chemistry was harnessed to enable production of thermochemically stable thermoset fibers containing 50–87 wt % acrylated epoxidized soybean oil and 49–72% biobased carbon without using solvent or heat. In this demonstration, the fibers were made by simultaneous electrospinning and photocuring of a liquid monomer mixture, which could be translated to other fiber manufacturing processes such as melt blowing or Forcespinning. Scanning electron micrographs illustrate the fiber quality and an average diameter of about 30 μm . Photochemical conversion kinetics of functional groups during light exposure were measured by real-time Fourier transform infrared spectroscopy, providing insight into the advantages of using high-functionality monomers and thiol–ene chemistry in this application.



The vast majority of commercially produced synthetic polymers used for fiber applications are made entirely from nonrenewable, petroleum-based feedstocks. By substituting these source materials with biorenewable alternatives, the dependence on finite resources is reduced; harnessing solar energy through agriculture to transform carbon dioxide into useful monomers may be a more environmentally friendly option. Because annual worldwide production of nonwoven fibers (or “nonwovens”) is in the billions of kilograms,¹ incorporating even small amounts of biorenewable materials in these products could significantly impact the allocation of nonrenewable resources. Two important examples of commercially available polymers containing biorenewable materials from which fibers can be formed are poly(lactide) (PLA)^{2,3} and poly(trimethylene terephthalate).⁴ However, these and other preformed synthetic polymers still require heating to temperatures above their melting or glass transition temperature and solvent to reduce their viscosities for processing into functional fiber products. Polymeric fibers made at least in part from biorenewable feedstocks and processed without applied heat or solvent would likely be “greener” than conventional, petroleum-derived fibers formed using heat and solvent.

Recently, our group demonstrated a general method for the manufacture of nonwoven fibers that does not use applied heat or volatile chemical solvents.^{5,6} In that work, a mixture of relatively high molecular weight liquid monomers containing a photoinitiator was electrospun and photopolymerized in situ to produce solid crosslinked fibers with an average diameter of 25 μm . The liquid composition used to make fibers was essentially nonvolatile, because all its substituents possessed very high boiling points. Electrospinning^{7–9} is a fiber formation technique that uses a strong electric field to draw a fluid into a thin jet; other techniques such as melt blowing¹⁰ or

Forcespinning¹¹ use hot air jets or centrifugal force for fiber drawing, respectively. In principle, the general method of photopolymerizing liquid monomers during fiber formation⁵ is applicable to any of these processes. This approach is different than other reports where already formed fibers from preformed polymers were subsequently photocrosslinked.^{12–15} Notably, Kim et al. tuned the thermal addition polymerization of bulk, volatile monomers such that the resulting solution of polymer and monomer could be subsequently photopolymerized and crosslinked during electrospinning into submicrometer-diameter fibers.¹⁶

A mixture of large, nonvolatile monomers bearing multiple thiol or -ene functionalities can form a composition able to photocrosslink (i.e., photocure) quickly enough under ambient conditions to form solid fibers.⁵ Critical to this ability is the rapid conversion rates and relative insensitivity to oxygen inherent to a thiol–ene photopolymerization. For example, substituting a thiol–ene composition with one based entirely on acrylic or methacrylic functionalities may not photocrosslink quickly enough under ambient conditions to form solid fibers. While these addition polymerization systems can also quickly reach high conversions in certain conditions, the carbon-centered propagating radical is readily quenched by atmospheric oxygen to form a relatively unreactive peroxy radical.¹⁷ In contrast, thiol–ene photopolymerizations are more oxygen insensitive because peroxy radicals are able to extract a hydrogen from a thiol to form a more reactive thiyl radical, reinitiating the polymerization from a quenched state.^{17,18} Several recent reviews highlight the many advantages of thiol–

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ene chemistry and some other potential applications they enable.^{17,19,20}

Vegetable oils are one biorenewable source to which many useful chemical functionalities have been introduced to make useful alternatives to petroleum-based monomers.^{21,22} In the present work, the process of simultaneous photopolymerization and fiber formation⁵ is made even greener by incorporating a commercially available, biorenewable monomer, acrylated epoxidized soybean oil (AESO, Figure 1a). The manufacture

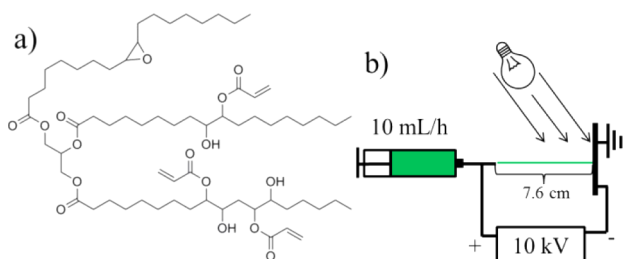


Figure 1. (a) Representative chemical structure of acrylated epoxidized soybean oil (AESO). (b) Schematic of electrospinning apparatus and conditions. The light intensity where the fluid jet meets the collector is 490 mW/cm².

of AESO from refined soybean oil, an agricultural product composed primarily of triglycerides, has previously been summarized by Lu et al.²³ Essentially, secondary alkenes present in soybean oil are converted to pendant acrylate groups in AESO to increase the molecule's reactivity, making it a more useful monomer in radiation-cure applications. AESO can be a suitable replacement for petroleum-derived multifunctional acrylates in many applications. For example, compositions containing AESO have been explored by others as biobased alternatives to conventional sheet molding compound resins,²³ thermosetting foams,^{24,25} membrane surface modifiers,²⁶ UV curable inks and coatings,^{27–29} and solar cell electrode binders.³⁰

Here fibers were made containing over 50 wt % AESO using the same electrospinning apparatus described previously,⁵ with conditions described in the Supporting Information and summarized in Figure 1b. Materials used to make the fibers other than AESO included dipentarythritol pentaacrylate (DPPA), pentaerythritol tetrakis(3-mercaptopropionate) (PETT), and Irgacure 2100 as photoinitiator (6 wt % in all cases). The AESO has, on average, a molecular weight of 1138 g/mol and 2.7 acrylate groups per molecule. DPPA has five acrylate groups per average molecule and PETT has four thiol groups per molecule. Compositions with a thiol group to an -ene group molar ratio $r = 0.28$ were used because -ene photoconversion in a mixture of DPPA, PETT, and photoinitiator with $r = 0.29$ was shown to be faster than with $r = 0.23$ or 0.18.⁵ The average -ene functionality,³¹ \bar{f}_{ene} , represents the average number of acrylate groups per -ene monomer in fiber precursor compositions containing both AESO and DPPA and is defined as

$$\bar{f}_{\text{ene}} = f_{\text{AESO}} m_{\text{AESO}} + f_{\text{DPPA}} (1 - m_{\text{AESO}}) \quad (1)$$

f_{AESO} and f_{DPPA} are the number of acrylate groups on an AESO or DPPA monomer, respectively. m_{AESO} is the mole fraction of total -ene groups in the composition contributed by the AESO monomers.

A composition that could be reproducibly electrospun and photocured into solid fibers is described in Table 1 and referred

Table 1. Summary of Compositions Used in Figures 2 and 3

composition name and representative SEM	% composition, by mass					r	\bar{f}_{ene} (eq 1)
	AESO	DPPA	PETT	Irgacure 2100			
good fibers, Figure 2a	51	29	14	6		0.28	4.3
no PETT	59	34	0	6		0	4.3
no DPPA, Figure 2d	87	0	7	6		0.28	2.7

to throughout the text as “good fibers”. In this monomer mixture an estimated 49% of the carbon is biobased (see Supporting Information). A representative micrograph of these fibers taken by scanning electron microscopy (SEM) is shown in Figure 2a. The fibers have a smooth surface without wrinkles

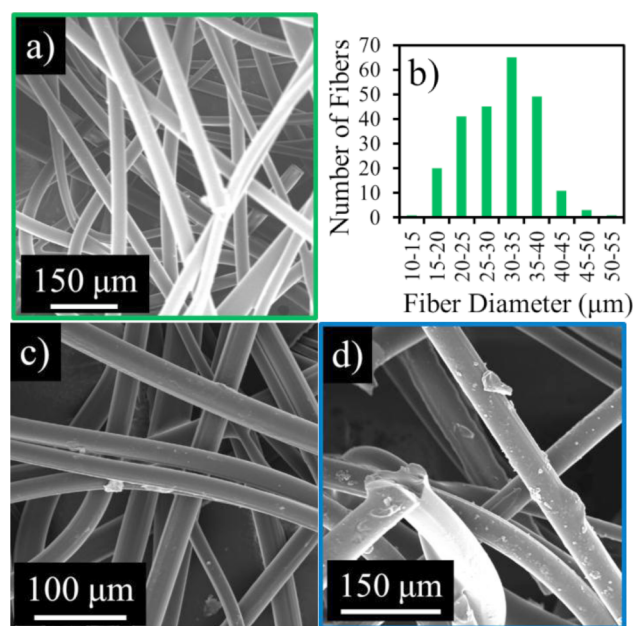


Figure 2. (a) Representative SEM micrograph of fibers made with the “good fibers” composition and (b) the resulting distribution of fiber diameters. (c) Representative SEM micrograph of fibers made from the same composition of (a) after being soaked in hot toluene and subsequently dried and (d) of fibers made with the “no DPPA” composition.

or beads, and relatively few fused junctions where fibers have become attached to one another prior to being completely cured. The diameter distribution of these fibers was taken from 236 diameter measurements and is shown in Figure 2b. The mean fiber diameter is 30 μm, with a standard deviation of 7 μm. Additional micrographs can be found in the Supporting Information.

The thermochemical stability of the fibers containing 51% AESO was explored by soaking fibers in hot toluene. The as-spun fiber mats were placed in 75 °C toluene, removed after 5 h, and then dried under vacuum. Toluene readily dissolves all of the substituents used to make the fibers, but not the final crosslinked fibers. A representative SEM micrograph of the fibers after toluene soaking is shown in Figure 2c. The fibers

retain their shape, and no new features such as wrinkling or cracking develop on the surface.

Fibers with higher biorenewable content than the composition in Figure 2a were also made. These compositions retained $r = 0.28$ and the same photoinitiator content as above but higher AESO content and lower DPPA and PETT content. However, fibers made from the compositions with higher biorenewable content appeared to have more defects and less overall fibers were made in a given electrospinning run. The compositions that did not make as many fibers was likely due to the fact that some fibers were not fully cured when they reached the collector, at which point the fluid coalesced. This could be easily remedied by implementing a more intense light source. A representative SEM micrograph of fibers made when DPPA is omitted entirely from the composition is shown in Figure 2d. This composition is described in Table 1 and referred to in the text as “no DPPA” and contains about 72% biobased carbon. The surface of many of these fibers is not smooth and contains small defects. Additionally, more fused fiber junctions are present. These features in Figure 2d are phenomenologically consistent with a slower rate of photocuring compared to compositions used to generate the highest quality fibers shown in Figure 2a. Additional SEM micrographs of these and other compositions, where the estimated biobased carbon contents ranges from 49 to 72%, can be found in the Supporting Information.

To gain greater insight into the factors influencing photocuring speed and fiber formation, real-time Fourier transform infrared spectroscopy (RTIR)³² was performed on three different monomer compositions. The results showing conversion of chemical groups at short irradiation times (<5 s) are shown in Figure 3a. This time scale is most critical for fiber formation because the fluid jet can break into droplets if it is not photocured extremely quickly. Additionally, RTIR data extending to 150 s are shown in Figure 3b. The mixtures are described in terms of composition and reaction stoichiometry in Table 1 and listed according to the data labels used in the legend of Figure 3.

The data representing the “good fibers” composition is described first. The photoconversion of thiol and -ene groups increases rapidly in the early stages of irradiation, and the photoconversions of thiol and -ene groups in this composition proceed at nearly identical rates. At any given irradiation time the conversion of -enes is no more than 4% higher than that of thiol groups. Note that because the monomer composition contains a 3.5-fold excess of -ene groups relative to thiols, this means that acrylates are homopolymerizing at a faster rate than they are reacting with thiol groups. To demonstrate the necessity of thiol–ene chemistry for this application, the photoconversion of -ene groups for a mixture that omits PETT was measured, called “no PETT”, yet has the same \bar{f}_{ene} and photoinitiator content as the “good fibers” composition. Without a thiol component, the polymerization is oxygen inhibited and the photoconversion rate is greatly suppressed.

The photoconversion kinetics of the “no DPPA” composition were also measured, which retains the same r and photoinitiator content as the “good fibers” composition. The photoconversion of the “no DPPA” composition is actually as fast as that of the “good fibers” composition for the first 0.7 s of irradiation, and for any given time after that the conversion of the “no DPPA” composition is higher than the “good fibers” composition. Initially, this may appear incompatible with our previous observation that higher quality fibers are made with a

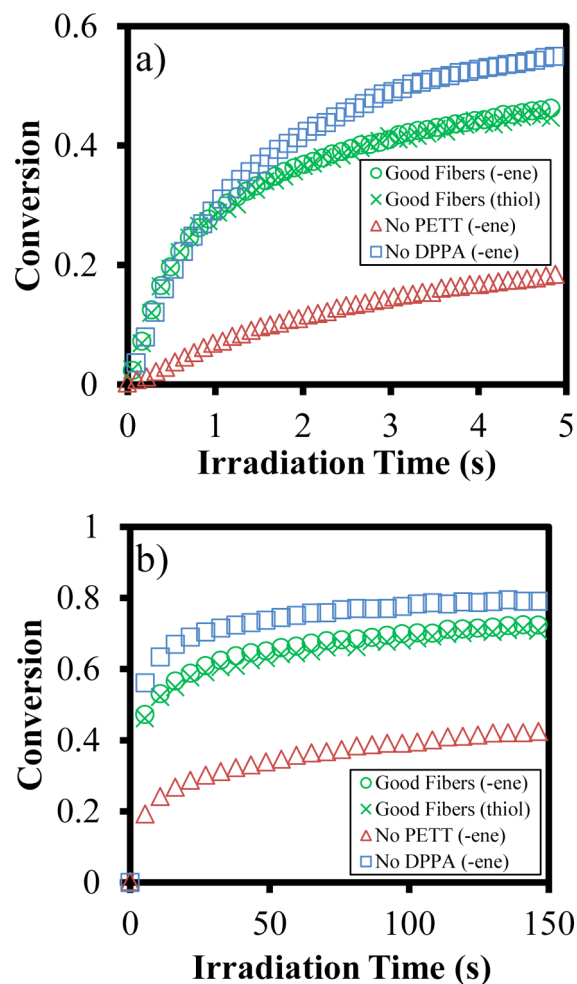


Figure 3. Photoconversion of functional groups for three samples at short (a) and long (b) irradiation times in dry air obtained by RTIR spectroscopy. The compositions of the samples are described in Table 1 according to the name used in the legend, outside of the parentheses. The designation of -ene or thiol within parentheses in the legend refers to the specific functional group to which that conversion data corresponds. For clarity, only every 50th data point is displayed in part (b). The incident light intensity was 29 mW/cm^{-2} .

composition containing both AESO and DPPA as -ene components than a composition that omits DPPA entirely (see Figure 2a,d). However, since \bar{f}_{ene} is considerably lower for the “no DPPA” composition, any prediction of the gel point will undoubtedly be higher, and the irradiation time needed to form a gel will be correspondingly longer.

To quantitatively estimate the impact of \bar{f}_{ene} on the irradiation time necessary to photocrosslink the fiber precursors, t_w the gelation theory of Bowman and co-workers³³ was applied to the RTIR data for the “good fibers” and “no DPPA” compositions. Their predictive expressions for the critical conversion to reach a gel, p_w in thiol–acrylate polymerizations (eq 38 in ref 33) are simplified by neglecting termination and cyclization effects and setting the conversion of -ene groups equal to the conversion of thiol groups, as justified by the data in Figure 3. p_w is then found by solving

$$\frac{2}{r}(\bar{f}_{\text{ene}} - 1)\frac{k_{\text{pCC}}}{k_{\text{CT}}}p_{\alpha} + (f_{\text{SH}} - 1)(\bar{f}_{\text{ene}} - 1)\left(1 + \frac{1}{r}\frac{k_{\text{pCC}}}{k_{\text{CT}}}\right)p_{\alpha}^2 = 1 \quad (2)$$

Here, $(k_{\text{pCC}})/(k_{\text{CT}}) = 1.5$ is the ratio of propagation to chain transfer kinetic parameters for thiol–acrylate systems³³ and f_{SH} is the number of thiol groups per PETT monomer. Equation 2 predicts $p_{\alpha} = 2.7\%$ for the “good fibers” composition and $p_{\alpha} = 5.0\%$ for the “no DPPA” composition. Using these values of p_{α} to extract t_{α} from RTIR data by interpolation yields $t_{\alpha} = 61$ ms for the “good fibers” composition and $t_{\alpha} = 132$ ms for the “no DPPA” composition. While higher conversions than the values of p_{α} predicted by eq 2 are undoubtedly necessary to lower the sol fraction and obtain high quality fibers, the RTIR data suggests that the “no DPPA” composition cures about twice as slow as the “good fibers” composition and is indeed consistent with the latter yielding higher quality fibers.

All of the fiber precursor compositions used here had sufficiently high viscosity for electrospinning due to AESO, the highest viscosity component, being incorporated at high contents. To produce the highest quality fibers, an -ene monomer with more acrylate groups, DPPA, was incorporated to reduce the irradiation time necessary to form a solid. As clearly demonstrated here, \bar{f}_{ene} has a large impact on fiber quality. Modification of the AESO monomer to increase functionality²³ or improving the light source to increase photopolymerization rates³⁴ could greatly enhance fiber quality at the highest biorenewable contents.

In summary, chemically stable fibers containing over 50 wt % of AESO, with an average diameter of 30 μm , can be made without applied heat or solvent by photopolymerizing a monomer composition during the fiber formation process. It is estimated that fibers with 51 wt % AESO have about 49% biobased carbon. This process can be viewed as replacing the thermal energy needed for melt processing with light energy. It is worth noting that, while the amount of thermal energy needed to render a given thermoplastic processable is a thermodynamic constant, opportunity exists to improve the energy efficiency of this photocuring-based process. By precisely tuning the light source emission spectra to the photoinitiator absorption spectra and photocuring many monomer jets in the same irradiation area, this process could be made more energy efficient.

■ ASSOCIATED CONTENT

■ Supporting Information

Materials, experimental methods, NMR characterization of AESO, estimation of biobased carbon content, and additional SEM micrographs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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