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Controlled Release of Nonionic Compounds from Poly(lactic acid)/Cellulose Nanocrystal Nanocomposite Fibers

Chunhui Xiang,[1] Alan G. Taylor,[2] Juan P. Hinestroza,[1] Margaret W. Frey[1]

[1]Department of Fiber Science and Apparel Design, Cornell University, Ithaca, New York 14853

[2]Department of Horticultural Sciences, New York State Agricultural Experiment Station, Cornell University, Geneva, New York 14456

Correspondence to: M. W. Frey (E-mail: mfw24@cornell.edu)

ABSTRACT: Poly(lactic acid)(PLA)/cellulose nanocrystal nanocomposite fibers were prepared by electrospinning at elevated temperature. Columbia Blue, a nonionic hydrophobic dye with a molecular weight and partition coefficient that mimics a systemic agrichemical, was incorporated into the fibers as a model compound. The release of Columbia Blue into water displayed little burst release. Diffusion-controlled release of Columbia Blue was significantly influenced by the hydrophobicity of the electrospun PLA nanocomposite fibers and followed Fickian diffusion kinetics. The release of Columbia Blue by degradation-controlled mechanism followed zero-order, time-independent Case II kinetics ($n = 1.0$). Increasing cellulose nanocrystal content in the fibers increased the fiber degradation rate and the Columbia Blue release rate. The plasticizing effect of Columbia Blue on the thermal properties of the electrospun nanocomposite fibers showed the miscibility of Columbia Blue inside the electrospun nanocomposite fibers. A greenhouse trial confirmed the anticipated trends of higher pesticide dosage causing higher whitefly mortality percentage. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Nanofibers produced by electrospinning are of industrial and scientific interest due to their long lengths, small diameters, and high surface area per unit volume.[1] The simplicity of the electrospinning process itself, the ability to vary the fiber diameter by changing the solution concentration and/or the surface tension of the liquid, and the ability to incorporate active compounds into nonwoven fabrics during electrospinning afford the prospect of preparing useful systems for controlled delivery. Flat nonwoven fabrics that can be either fabricated or cut to almost any size represent an attractive form for topical delivery applications, and other shapes (e. g., tubes) can be constructed using different target geometries. Moreover, a significant implication of the mechanism of electrospinning is that the materials derived from composites will not likely be an admixture of two different fibers but rather fibers containing both components, in principle, offering another and quite unique means of controlling release rates.[2] The combination of high porosity and nanoscale pores achievable via electrospinning is also unique.

An active compound can be released from a biodegradable delivery system by diffusion through a polymer matrix or pores in the matrix and/or after the degradation of the polymer backbone and erosion of the matrix. The release may be controlled by diffusion, by a combination of diffusion and erosion, or solely by erosion of the delivery system. The influence of several fiber and active compound parameters has been studied to understand release of pharmaceuticals from polymer materials. Tuovinen et al.[3] studied the effect of hydrophobicity of a drug on its release from hydrophobic starch acetate films. The hydrophobicity of the drug affected its release rate from potato starch acetate films. Sotalol was released faster than the more hydrophobic molecule, timolol, under the same conditions. These results demonstrate the role of stronger interaction between the starch acetate films and timolol due to the hydrophobic nature. Kenawy et al.[4] reported the drug delivery potential of electrospun polymers by spinning poly(ethylene co-vinyl acetate) (PEVA) and poly(lactic acid) (PLA) fibers containing tetracycline hydrochloride as the model drug. They observed that the electrospun PEVA and 50/50 PLA/PEVA nonwoven fabrics released tetracycline at a constant rate over a period of 5 days. These observations stress the relevance of electrospun nonwoven fabrics for controlled drug delivery systems and other biomedical applications. These authors also reported the release behavior of the

tetracycline hydrochloride from PEVA, PLA, and a blend. They mentioned that the nonwoven fabrics of PLA fibers exhibited some instantaneous release, most probably from tetracycline hydrochloride on the fiber surfaces, but the total amount of drug released was negligible over 50 h. Zeng et al.[5] studied the influence of drug compatibility with polymer solutions on the release kinetics of electrospun fiber formulation. The release of paclitaxel and doxorubicin base from electrospun PLA fiber samples followed nearly zero-order kinetics associated with the degradation of the fibers. However, an obvious burst release was observed for doxorubicin hydrochloride. Maximum drug incorporation inside the polymer fibers and constant and stable drug release profiles were achieved when a hydrophobic polymer was chosen as the fiber material for a hydrophobic drug, whereas a hydrophilic polymer was employed for a hydrophilic drug. The solvents were good for both the drug and the polymer. Otherwise, the drug was only dispersed rather than dissolved in the polymer solution. The drugs were located on or near the fiber surface and the drug diffused rapidly into the release media with a significant burst release.

In our previous paper,[6] PLA/cellulose nanocomposite fibers were successfully produced during elevated temperature electrospinning. The strength of the electrospun nonwoven fabrics was improved by the incorporation of cellulose nanocrystals, which acted as nucleating agent of PLA crystallization and hence increased the crystallinity of PLA in the resulting nanocomposite fibers. We also demonstrated that the incorporation of cellulose nanocrystals accelerated the hydrolytic degradation rate of PLA.[7] The water contact angle of the electrospun nonwoven fabrics decreased as the cellulose nanocrystal content increased. The hydrophobicity of the electrospun PLA/cellulose nonwoven fabrics decreased with incorporating 0, 1, and 10% cellulose nanocrystals. On the basis of the contact angle and water absorption results, incorporation of cellulose nanocrystals is expected to increase interaction between water and the PLA/cellulose nanocomposite fibers during the hydrolytic degradation processes. Columbia Blue, a nonionic and hydrophobic dye with log K_{ow} and molecular weight within a agricultural agent range, was used as a model compound for examining release rate profiles of the electrospun nanocomposite fibers. Fifty weight percent Columbia Blue (based on the weight of PLA) was incorporated into the nanocomposite fibers electrospun from PLA containing 0, 1, and 10% w/w cellulose nanocrystals at elevated temperature. To characterize the release profiles of dye from PLA/cellulose nanocomposite fibers, the rate of release of the dye into the release media was measured. In particular, two properties were examined: the extent of the burst effect in water; and, the kinetics of dye release in both water and phosphate buffered saline (PBS, pH 7.4).

EXPERIMENTAL

Materials

Microcrystalline cellulose powder (MCC, extra pure, average particle size 90 μm) was purchased from Acros Oganics (Geel, Belgium). Poly(lactic acid) (PLA) (M_w = 211,000 Da, M_n = 109,000 Da) was supplied by Cargill Dow (Minnetonka, MN) and phosphate buffered saline (PBS) (p-5368, pH 7.4) was purchased from Sigma-Aldrich (St. Louis, MO). *N, N*-dimethyl formamide (DMF) was purchased from Mallinckrodt Laboratory Chemicals (Phillipsburg, NJ). Columbia Blue (M_w = 232 Da, Log K_{ow} = 4.1, nonionic) was from DayGlo Color Corporation (Cleveland OH). All other reagents were used without further purification.

Methods and Techniques

Elevated Temperature Electrospinning Processing. Cellulose nanocrystals were prepared from the microcrystalline cellulose by acid hydrolysis as described in our previous work.[6] Polymer suspensions, consisting of PLA and cellulose nanocrystals, were prepared in DMF solvent. The concentration of the final suspension used for electrospinning was 22 wt % PLA in DMF containing cellulose nanocrystals contents of 0, 1, and 10% w/w based on the weight of PLA. The suspensions were then electrospun at 70°C. During electrospinning, the polymer suspension was introduced into a 5 mL glass syringe (VWR Scientific, West Chester, PA). The syringe was attached with a stainless steel needle (ID = 0.60 mm) and housed in a shielded heating unit that was preheated to 70°C ± 5°C and controlled by a Watlow controller (St. Louis, Missouri). After thermal equilibration, electrospinning was started with 15 kV supplied by a high voltage supply (Gamma High Voltage Research, FL) and 10 μL/min feed rate driven by a programmable syringe micropump (Harvard Apparatus, MA). A rotating aluminum plate (Diameter = 20 cm) covered with aluminum foil was used to collect nanocomposite fibers at 10 cm distance away from the needle tip. Each sample was collected for 5 h.

Incorporation of Columbia Blue into Nanocomposite Fibers Electrospun from PLA/Cellulose Nanocrystals. On the basis of the weight of the PLA, 50% w/w Columbia Blue and 0, 1, and 10% w/w cellulose nanocrystals were incorporated into the electrospun nanocomposite fibers. Cellulose nanocrystals were first dispersed in DMF overnight with an ultrasonic liquid processor (Misonix Sonicator® 3000) in a water bath. Then the desired amount of PLA and Columbia Blue were added. Next, the suspension was heated to about 100°C for PLA dissolution in DMF under constant stirring. After the PLA thoroughly dissolved in DMF, the blended mixture was electrospun as described above.

Columbia Blue Release Measurements

Columbia Blue Release from the Nanocomposite Fibers by Diffusion. Approximately 0.2 g electrospun PLA/cellulose nonwoven fabrics containing Columbia Blue were immersed in 100 mL distilled and deionized water in closed bottles. Samples were shaken at 200 rpm using a platform shaker (Innova™ 2300, New Brunswick Scientific) at room temperature for 48 h. Triplicates of all samples were prepared. 0.5 h, 1 h, 2 h, 4 h, 6 h, 8 h, 12 h, 16 h, 24 h, 36 h, and 48 h, 1 mL aliquots were collected. After sampling, 1 mL distilled and deionized water was added to keep overall sample volume equal to 100 mL. The 1 mL sample was then mixed with 9 mL DMF for the Columbia Blue concentration measurement. Identification and qualification of Columbia Blue was achieved using Liquid Chromatography/Mass Spectroscopy (LC/MS) (Agilent Technologies 6130 Quadrupole LC/MS) with a Restek Ultra C18, 5 μm, 250 × 4.6 mm and UV detector. The mobile phase consisted of 60% acetonitrile and 40% water at a flow rate of 1.0 mL/min. Columbia Blue was detected at a wavelength of 374 nm.

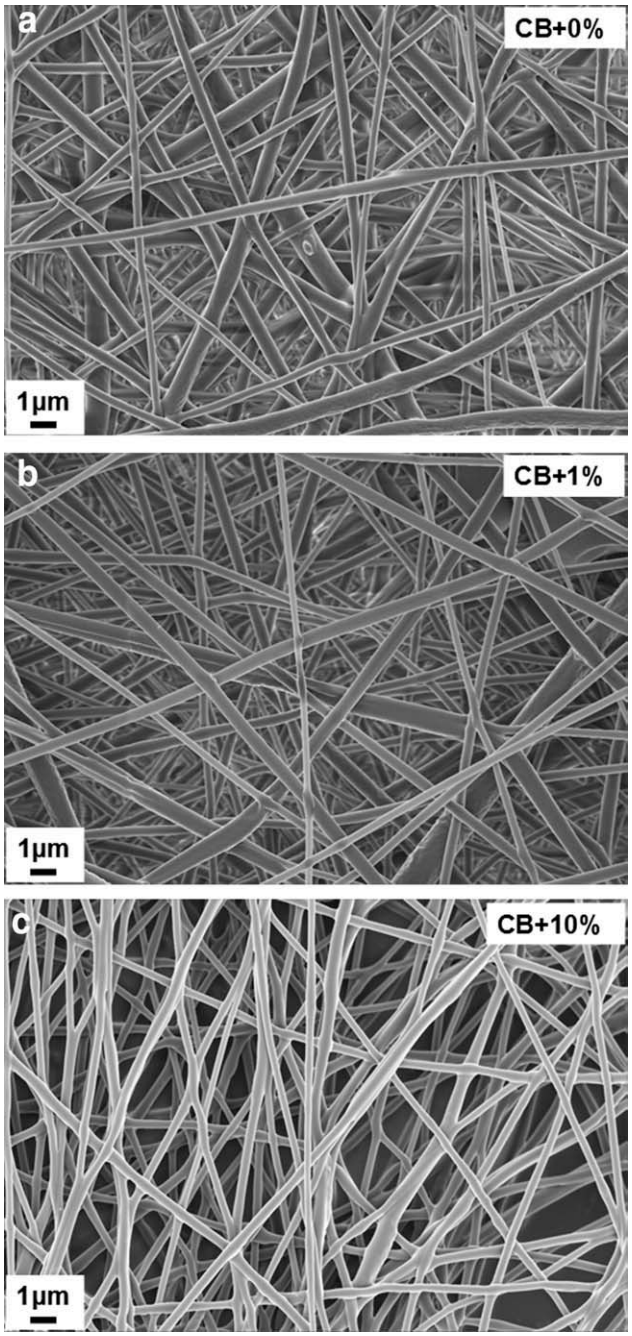

Figure 1. FESEM images of electrospun PLA/cellulose nanocomposite fibers containing Columbia Blue after dye release measurement.

Columbia Blue Release from the Nanocomposite Fibers via Fiber Hydrolytic Degradation. The release of Columbia Blue during hydrolytic degradation of PLA with 0, 1, and 10% cellulose nanocrystals was conducted by suspending about 10 mg dye-loaded electrospun nonwoven fabrics in 10 mL of phosphate buffered saline, pH 7.4, at 37°C in a shaking (100 rpm) water bath (Julabo SW 23, Seelbach, Germany). Samples were removed from the release media in 4 weeks, 8 weeks, 12 weeks, and 16 weeks. The 10 mL release media were then mixed with 90 mL DMF for Columbia Blue concentration measurement using LC/MS as described above.

Characterization of Nanocomposite Fibers Electrospun from PLA/Cellulose Nanocrystals Containing Columbia Blue

The morphology of the electrospun PLA/cellulose nanocomposite fibers containing Columbia Blue was observed with a LEO 1550 field emission scanning electron microscope (Keck SEM) at a voltage of 3 kV. The fibers were sputter-coated with a 2–3 nm layer of gold and palladium for imaging using a Desk II cold sputter/etch unit. The fiber diameters were determined using image processing and analysis in software Image J. Fifty fibers were measured for each samples. The thermal properties of the electrospun PLA/cellulose nanocomposite fibers containing Columbia Blue were investigated by Differential Scanning Calorimetry (DSC) (DSC 2920, TA Instruments) before and after the release study. Samples of approximately 10 mg were loaded and heated in a nitrogen atmosphere at a rate of 10°C/min from 0 to 200°C. The pore size of the electrospun PLA/cellulose nonwoven fabrics containing Columbia Blue was measured with an 1100-AEHXL capillary flow porometer (Porous Media). The nonwoven fabrics were cut into 25 cm in diameter circles for the porometry measurement. Three specimens for each sample were measured. The molecular weight of the PLA of the electrospun nanocomposite fibers containing Columbia Blue was determined by Size Exclusion chromatography (SEC) (a Waters 486 UV detector and a Waters 2410 differential refractive index detector, Waters Corporation), using polystyrene standards for calibration and tetrahydrofuran (THF) as the carrier solvent at 40°C with a flow rate of 0.5 mL/min. For SEC measurements, the electrospun PLA/cellulose nanocomposite fibers were dissolved in THF. The cellulose nanocrystals were removed by syringe filters with a pore size of 0.45 μm (Millipore) and the molecular weight of PLA was measured.

Real/Actual Application of the PLA System in Green House Trial

For the initial interaction, we tested the effect of a controlled-release, systemic thiomethoxan treatment on greenhouse whiteflies. For these trials four treatments were used and each treatment was replicated five times. In all the treatments, the electrospun PLA matting was placed along side Kentucky Wonder pole bean seeds during planting. The controls consisted of 3.954 cm^2 pieces of unloaded PLA matting, whereas the three experimental treatments included three varying sizes of thiomethoxan loaded PLA, which in turn equated to three different dosages (low, medium, and high dosage rates). Given that the recommended dosage for a given seed is 140 μg, we established low rate treatments in which the plants received pieces of PLA equivalent to 50% of the recommended dosage. The medium rate treatments were treated with the 100% of the recommended dosage and the high rate treatments were treated with

Table I. Average Fiber Diameter and Mean Pore Size of Electrospun PLA/Cellulose Nanocomposite Fibers Containing 50% Columbia Blue

Cellulose content	Mean fiber diameter (nm)	Mean pore size (μm)
0%	326 ± 139	0.48 ± 0.04
1%	335 ± 144	0.51 ± 0.08
10%	306 ± 90	0.94 ± 0.14

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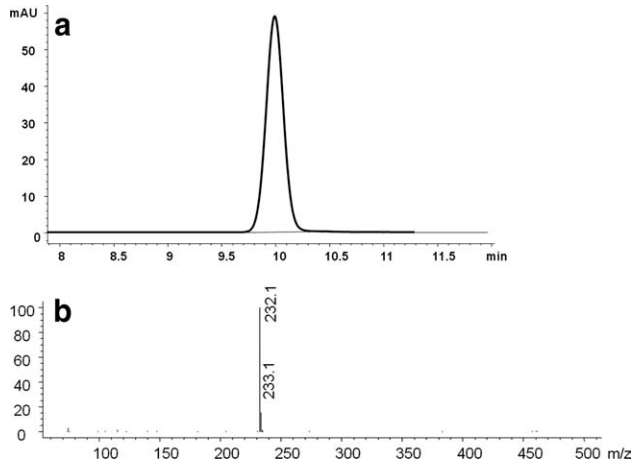

Figure 2. Identification of Columbia Blue by LC/MS: a. LC spectrum; b. mass spectrum.

200%. Since we assumed the density of thiomethoxan in the PLA mat was a uniformly distributed 834.926 $\mu g/cm^2$, these differing rates were achieved by varying the size of the PLA mat that was placed with the bean seed.

RESULTS AND DISCUSSION

Morphology of the Nanocomposite Fibers Electrospun from PLA/Cellulose Nanocrystals Containing Columbia Blue

Figure 1 shows the morphology of the nanocomposite fibers containing 50% (based on the weight of PLA) Columbia Blue electrospun from PLA containing 0, 1, and 10% cellulose nanocrystals. The mean fiber diameter, mean pore size of the nanocomposite fibers containing Columbia Blue are shown in Table I. A Student t-test was used to compare the difference of the fiber diameter and the pore size of the electrospun PLA/cellulose nonwoven fabrics containing 50% Columbia Blue. At a 0.05 significant level, no significant difference was found in the fiber diameter among the PLA nonwoven fabrics with 0, 1, and 10% cellulose nanocrystals ($p > 0.1$). There is no obvious difference in the mean pore size between the nonwoven fabrics electrospun from PLA containing 0% and 1% cellulose nanocrystals ($p = 0.5$). However, significant difference was found in the pore size of the nonwoven fabrics electrospun from PLA with 0% and 10% cellulose nanocrystals ($p < 0.0001$). The mean pore size of the PLA nonwoven fabrics with 10% cellulose nanocrystals was twice as big as the pore size of pure electrospun PLA nonwoven fabrics.

Table II. Initial Burst of Columbia Blue from the PLA/Cellulose Nanocomposite Fibers

Cellulose contents	Burst (wt % of total loading in the first 4 h)
0%	3.0 ± 0.8
1%	3.4 ± 0.1
10%	4.4 ± 0.4

Columbia Blue Release Measurement

Identification of Columbia Blue. A model pesticide, Columbia Blue, was chosen following Briggs's "rule of 3"[8] and Clarke-Delaney's "guide of 2."[9] Columbia Blue dissolved in DMF ensures a high load (50%) and homogeneous distribution of dye into the nanofibers. Nonhomogeneous active agent dispersion within the polymer is a problem as it leads to release bursts. These bursts occur most commonly during initial elution.[10] A process of dissolving Columbia Blue in DMF was developed and successfully applied to these problems.

During the release measurements, Columbia Blue was identified by the LC/MS (Figure 2). The retention time of Columbia Blue

Table III. Comparison of the Predicted Release of Columbia Blue from the Electrospun PLA Nanocomposite Fibers with 0, 1, and 10% Cellulose Nanocrystals

	0% Cellulose		1% Cellulose		10% Cellulose	
t (h)	$f(t)_{theor}$ (mg)	$f(t)_{exp}$ (mg)	$f(t)_{theor}$ (mg)	$f(t)_{exp}$ (mg)	$f(t)_{theor}$ (mg)	$f(t)_{exp}$ (mg)
0	0	0	0	0	0	0
0.5	0.6	0.3	0.6	0.3	1.0	0.3
1	0.8	0.6	0.8	0.6	1.4	0.6
2	1.2	0.9	1.2	1.0	2.0	1.2
4	1.7	1.3	1.6	1.4	2.8	2.2
6	2.1	1.8	2.0	1.8	3.4	2.9
8	2.4	2.3	2.3	2.3	3.9	3.8
12	2.9	2.8	2.8	2.8	4.8	4.7
16	3.4	3.4	3.3	3.3	5.5	5.6
24	4.1	4.1	4.0	3.9	6.8	6.9
36	5.0	4.9	4.9	4.8	8.3	8.0
48	5.8	6.0	5.7	5.7	9.6	9.6
B_1	0.84 ± 0.51 mg $h^{-0.5}$		0.82 ± 0.33 mg $h^{-0.5}$		1.38 ± 2.30 mg $h^{-0.5}$	

Using eq. (1) and the exprimental release of Columbia Blue.

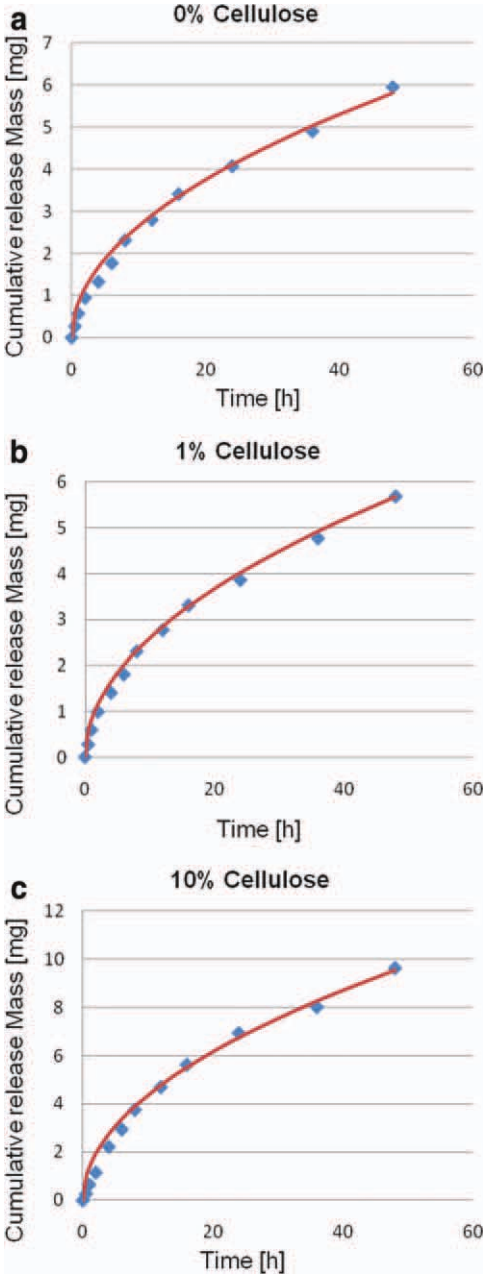

Figure 3. Comparison of the theoretical versus experimental release of Columbia Blue from the electrospun nanocomposite fibers with different cellulose nanocrystals. (■, experimental data; —, predicted release curves). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of HPLC spectrum remained unchanged at 9.8 min [Figure 2(a)]. The mass spectrum of Columbia Blue also did not change [Figure 2(b)]. Therefore, Columbia Blue did not degrade in the release media (i.e., water at room temperature, and PBS of pH 7.4 at 37°C) used in this study.1

Columbia Blue Release from the PLA/Cellulose Nanocomposite Fibers by Diffusion. To examine the extent of the burst effect and the kinetics of Columbia Blue release, the rate of

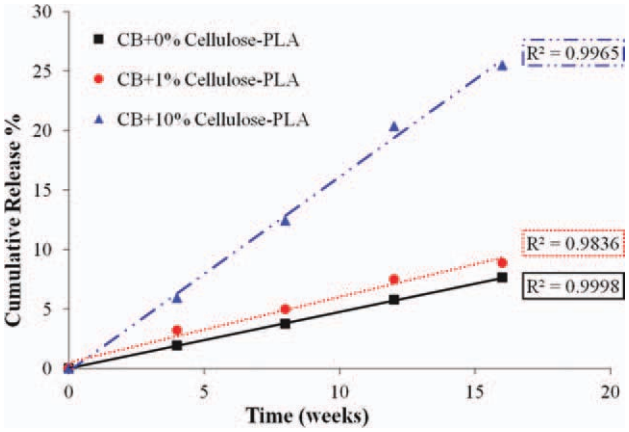

Figure 4. Cumulative release percentage of Columbia Blue from the nanocomposite fibers electrospun from PLA containing 0, 1, and 10% cellulose nanocrystals by fiber degradation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

release into distilled and deionized water was measured at room temperature. The nanofiber nonwoven fabrics of PLA with 0, 1, and 10% cellulose nanocrystals displayed little burst effect (<5% in the first 4 h, Table II). To describe the mechanism of Columbia Blue release from the nanocomposite fibers by diffusion, a model originally proposed by Higuchi[11] was applied. Brophy et al.[12] used Higuchi equation to describe the total mass released up to time t:

$$f(t) = B_1 t^{1/2} \quad (1)$$

Table III and Figure 3 show the predictions of eq. (1) of Columbia Blue from the electrospun PLA nanocomposite fibers with 0, 1, and 10% cellulose nanocrystals in comparison with the experimentally observed release of Columbia Blue. Agreement of the predictions with the experimental release results was good. The higher the cellulose nanocrystal content, the faster Columbia Blue released. The considerably higher hydrophilicity of the nanocomposite fibers containing 10% cellulose nanocrystals[7] is believed to be the predominate factor for the much faster release (B_1) of this hydrophobic model agricultural agent. For the more hydrophilic fibers, i.e., PLA nanocomposite fiber with 10% cellulose nanocrystals, Columbia Blue can migrate easily from the inside of the fibers to the surface. The different release rate should also be related with a change in the polymer matrix properties. Bigger pore size and higher water uptake[7] of the nonwoven

Table IV. The Dependency of Cumulative Release Percentage of Columbia Blue on the Molecular Weight Loss Percentage of PLA

Cellulose content	M_w loss-dependency exponent
0%	1.211 ± 0.013
1%	1.216 ± 0.006
10%	1.629 ± 0.003

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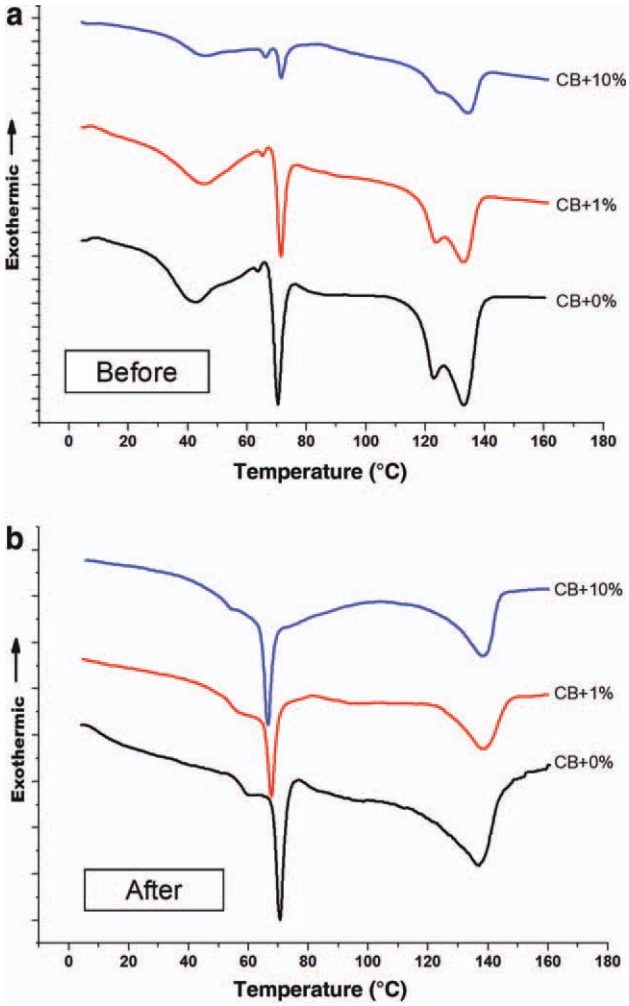

Figure 5. DSC thermographs of PLA from the electrospun PLA/cellulose nanocomposite fibers before and after the Columbia Blue release study. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fabrics electrospun from PLA with 10% cellulose nanocrystals favored Columbia Blue diffusing from the nonwoven fabrics, and hence, had a higher release percentage.

Columbia Blue Release from the Nanocomposite Fibers by Fiber Degradation. It is well-known that the drug release rate from PLA polymer matrices is mainly controlled by the diffusion of drug in the matrices in the first time, crossing over to a regime controlled by the degradation of matrices. The latter mechanism depends on the molecular of the polymer.[13] Figure 4 shows the release profiles of Columbia Blue from the electrospun nanocomposite fibers containing 0, 1, and 10% cellulose nanocrystals by fiber degradation. The release of Columbia Blue was controlled with fiber degradation. The faster the fiber degraded, the more Columbia Blue released from the nanocomposite fibers. Zero-order, time-independent Case II kinetics (n = 1.0) kinetics were confirmed. Zeng et al. [5] also reported this almost idea release of paclitaxel in the buffer containing 0.01 mg/mL proteinase K from PLLA electrospun fibers. The release profile of Columbia Blue from the nanocomposite fibers had a higher release rate. The slope of the line is determined the release rate. Zero-order, time-independent Case II kinetics (n = 1.0) is characterized by a linear mass uptake and/or release with time.[14] In non-Fickian or anomalous transport, both diffusion as well as macromolecular relaxation time scales are similar and both control the overall rate of penetrant absorption. Case II transport is the limit when relaxation predominates.

On a log–log plot, the cumulative release percentage of Columbia Blue by degradation-controlled mechanism had linear dependence on the molecular loss percentage. The slopes of the lines indicate the dependency exponents (Table IV). The M_w (loss %)-dependency exponent increased with higher cellulose nanocrystal contents. The release of Columbia Blue from PLA with 10% cellulose nanocrystals had a linear dependence on the molecular weight loss to the 1.63 power, which is higher than from PLA with 0% to the 1.21 power and PLA with 1% to the 1.22 power. Higher power indicates stronger correlation between the release and fiber degradation. The faster the fiber degraded, the more Columbia Blue was released. Our previous work[7] has demonstrated that PLA in the nanocomposite fibers electrospun from PLA with 10% cellulose nanocrystals had the fastest hydrolytic degradation rate.

The thermal properties of PLA from the electrospun PLA/cellulose nanocomposite fibers containing Columbia Blue are shown in Figure 5 before and after the Columbia Blue release study. After the sixteen-week Columbia Blue Release study, the original biomodel melting peaks represent Columbia Blue and PLA disappeared and monomodel melting peak appeared.

The temperatures of the major peaks from DSC thermographs of PLA from various nanocomposite fibers are summarized in Table V. We reported that the glass transition temperature of the nanocomposite fibers containing 0, 1, and 10% cellulose nanocrystals were 58°C, 59°C, 59°C, respectively.[6] The incorporation of Columbia Blue into PLA/cellulose nanocomposite fibers during electrospinning decreased the glass transition temperature of PLA. The reason is that Columbia Blue (T_m =

Table V. DSC Summary of PLA from the Electrospun PLA/Cellulose Nanocomposite Fibers Before and After the Columbia Blue Release Study

	T_g (°C)	T_m (°C)
CB+0% Cellulose PLA-Before	37 ± 1	65, 71, 123, 133
CB+1% Cellulose PLA-Before	40 ± 2	66, 72, 123, 133
CB+10% Cellulose PLA-Before	40 ± 1	66, 71, 124, 134
CB+0% Cellulose PLA-After	56 ± 2	69, 137
CB+1% Cellulose PLA-After	55 ± 1	68, 138
CB+10% Cellulose PLA-After	53 ± 1	66, 140

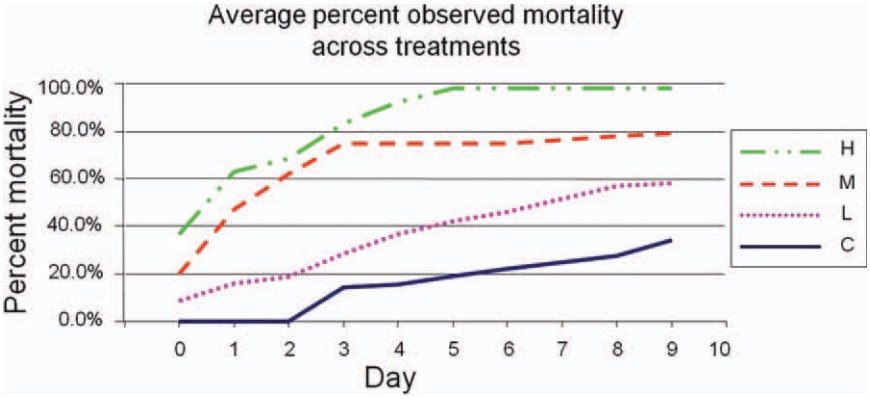

Figure 6. Average percent observed mortality across treatments. C-0 dosage of pesticide (control), M-manufacture recommended dosage; L-50% of manufacture recommended dosage; H-200% of manufacture recommended dosage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

74°C) melted at the processing temperature (70°C ± 5°C) during electrospinning. Hence, the melted Columbia Blue acted as a plasticizer and decreased the glass transition temperature of PLA in the as-spun nanocomposite fibers. After the release study, compared with PLA in the as-spun fibers, the glass transition temperature of PLA in the nanocomposite fibers increased, but these values are still lower than the T_gs of PLA in the nanocomposite fibers without Columbia Blue. This further confirmed the plasticizing effect of Columbia Blue for the PLA in the nanocomposite fibers. As the amount of Columibia Blue decreased, the plasticizing effect reduced.

Real/Actual Application of the PLA System in Green House Trial. The average percent observed mortality of the whiteflies across treatments is shown in Figure 6. To ensure that we would observe 100% germination amongst the planted bean seeds, all the seeds were primed and only seeds which had shown the emergence of a radical were planted. Upon emergence, each of the 20 bean plants was watered daily with an appropriate amount of water and once the plants were all deemed suitably large, 20 adult greenhouse whiteflies were caged to a single leaf on each plant. To measure the efficacy of the thiomethoxan release, whitefly mortality was recorded daily for 9 days. Upon conclusion of the experiment, the anticipated trends were observable where the low rate treatments showed higher mortality than the controls, the medium treatments showed higher mortality than the low rate treatments, and finally high rate treatments exhibited the most significant mortality rates.

CONCLUSIONS

Fifty percent of Columbia Blue (based on the weight of PLA) was successfully incorporated into the nanocomposite fibers electrospun from PLA containing 0, 1, and 10% cellulose nanocrystals. No statistically significant difference was found in the fiber diameter among the PLA nonwoven fabrics with 0, 1, and 10% cellulose nanocrystals. There is no obvious difference in the mean pore size between the nonwoven fabrics electrospun from PLA containing 0% and 1% cellulose nanocrystals. The mean pore size of the PLA nonwoven fabrics with 10% cellulose nanocrystals was twice as big the pore size of pure electrospun PLA nonwoven fabrics. During the release experiments, Columbia Blue did not degrade in the release media. At room temperature, the release of the nonionic dye into water displayed minimal burst release. Columbia Blue release by diffusion-controlled mechanism followed a Fickian diffusion mechanism. Diffusion-controlled release of Columbia Blue was significantly influenced by the hydrophobicity of the electrospun PLA nanocomposite fibers. The release rate profiles of Columbia Blue by degradation-controlled mechanism followed zero-order, time-independent Case II kinetics ($n = 1.0$). The M_w (loss %)-dependency exponent increased with higher cellulose nanocrystal contents. The faster the nanocomposite fiber degraded, the more Columbia Blue released from the fibers. The plasticizing effect of Columbia Blue on the thermal properties of the electrospun nanocomposite fibers showed the miscibility of Columbia Blue inside the electrospun nanocomposite fibers. Once the Columbia Blue was out of the fibers, the plasticizing effect decreased. The real/actual application of the electrospun PLA system in green house trial confirmed the anticipated trends of higher pesticide dosage caused higher whitefly mortality percentage.

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