Fabrication of a Light-Emitting Shape Memory Polymeric Web

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Statement of Purpose: Polymers containing nanoparticles or dyes with optical activity are highly desired for a number of commercially relevant medical applications, including high-sensitivity sensors, medical device imaging, and drug delivery. Incorporation of dyes and nanoparticles by diffusion is a method that has been widely used[1]; however this approach is hampered by difficulty in achieving uniform and controllable incorporation. Polymers with unique imaging and shape memory characteristics can be prepared by incorporating dyes or nanoparticles with specific optical absorption and emission characteristics into thermoplastic polymers.[2] In this study, indocyanine green (ICG) dye, which has near-infrared (NIR) excitation and emission wavelengths, has been uniformly incorporated into a thermoplastic polymer via electrospinning.

Methods: Electrospinning is a widely used technique to fabricate nanofibers from thermoplastic polymer solutions.[3] The polymer solution for electrospinning can be prepared by dissolving any thermoplastic polymer in its respective solvent. Herein, poly(vinyl acetate) (PVAc) (Mw = 260,000 g/mol) and different concentrations of ICG were dissolved in a solution containing 80% methanol and 20% N,N-dimethylformamide (DMF) to generate a 20 wt% polymer solution. The electrospinning solution was then loaded into a glass syringe and electrospun to fabricate nanofibers containing the ICG dye. In this technique, uniform dye incorporation is achieved and the results are compared to incorporation of the dye via casting of polymer solutions of PVAc with different concentration of ICG dye. Spectrofluorometry and NIR imaging techniques have been utilized to compare electrospun fiber mats and casted polymer films with different concentration of ICG dye.

Results: The fiber mats fabricated by electrospinning technique yielded higher emission with no gradient compared to the casted polymer films. Figure 1 shows NIR imaging results of PVAc fiber mat and casted PVAc films with different ICG concentrations. The spectrofluorometry of PVAc fiber mats with different ICG concentration also showed higher intensity around 800 nm compared to casted PVAc films with different ICG concentration (data not shown).

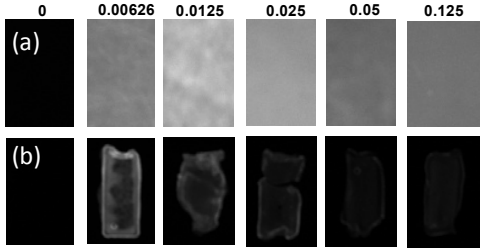

Figure 1. NIR images of PVAc/ICG in different forms: (a) fibrous mat and (b) film, each with different ICG concentrations (in mg/ml). The gain and exposure time were 1 and 140 ms respectively.

Figure 2 shows the impact of material form – film versus fiber mat – and ICG concentration on NIR emmision intensity using spectrofluorometry. PVAc fiber mats showed significantly higher intensity, whether measured by spectrofluorometry or by NIR imaging (Figure 1), when compared to the PVAc films. Moreover, the existence of an optimum dye concentration was evident from the trends, the highest NIR emission intensities being observed for samples with 0.0125 mg/ml ICG concentration. It is understood that concentrations that are higher than the optimum value lead to excessive light absorption, therefore limiting the excitation.

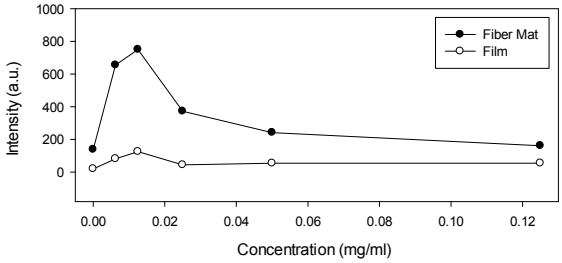

Figure 2. Graph of comparison of PVAc fiber mat and PVAc film with different ICG concentration by using spectro-fluorometry.

In addition to the light-activation imaging reported above, the electrospun PVAc fiber mats exhibited significant lateral shrinkage when heating above 40 °C, which is the glass transition (T_g) temperature of PVAc, or upon immersion in water. This shape memory effect is attributed to relaxation of molecular orientation of polymer chains along the fiber axes that is caused by elongational stresses during electrospinning.

Conclusions: PVAc fiber mats with ICG showed significantly higher intensity, whether measured by spectrofluorometry or by NIR imaging, when compared to the casted PVAc films with ICG. The combination of high intensity NIR emission and shape memory properties of PVAc fiber mats fabricated by electrospinning technique opens up application areas that include medical device imaging, temperature sensing, and light-activated shape memory effects.

Acknowledgement: We would like to acknowledge Prof. Jay E. Reeder from Upstate Medical University for assistance with the NIR Imaging studies and Prof. Mathew M. Maye from the Chemistry Department for the assistance with the spectrofluorometry studies.

References:

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