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# Development of UV-Reactive Electrospinning Method Based on Poly(ethylene glycol) diacrylate Crosslinking

**Abstract:** Electrospinning is a popular method for creating nonwoven fiber materials for a wide variety of applications. In the field of biomaterials, electrospun materials are favoured because of a high surface-to-volume ratio which can be useful for drug loading and release, and because nano-scale fibers mimic native tissue structures, improving cell interactions. However limitations exist with regards to traditional solvent evaporation-based electrospinning techniques.

A new area of research into reactive electrospinning is investigating methods of electrospinning that rely on *in situ* crosslinking rather than solvent evaporation to stabilize fibers. These techniques can potentially reduce the waste of excess solvents and make it easier to electrospin water soluble polymers.

In this work, UV photocrosslinked PEGDA is evaluated as a material for reactive electrospinning. To facilitate the electrospinning process poly(ethylene glycol) diacrylate (PEGDA) is combined with polyvinyl alcohol (PVA). PEGDA/PVA solutions can be successfully electrospun under constant UV light exposure to initiate the crosslinking of the PEGDA. Reactive electrospun fibers appear more stable immediately after spinning and after washing with water, indicating successful photo crosslinking.

**Keywords:** reactive electrospinning, PEGDA, UV crosslinking

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## 1 Introduction

Electrospinning as a method of reproducibly creating nonwoven fiber mats of micro- to nano-sized fibers for application in textile, industrial and medical applications has been well-studied [1]. Traditionally, polymers are dissolved in highly volatile solvents that evaporate during the fiber time-of-flight to create stable polymer fibers, but this method does have some limitations. Usually electrospun polymer solutions are mostly composed of the solvent, which is ultimately lost via evaporation during spinning. Additionally, these solvents are often not environmentally friendly and can limit biocompatibility if any toxic residuals remain after processing [1].

As a result, there has been a shift in research to examine alternative ways to stabilize fibers that are not dependent on solvent evaporation. One broad category of these methods is known as reactive electrospinning or *in situ* crosslinking. The main idea behind reactive electrospinning is to crosslink during the spinning process. The crosslinking most often occurs during the flight of the polymer between the needle and the collector. Methods for achieving this include thermal, chemical and photo crosslinking during the electrospinning process [1]. One strategy, ultra violet (UV) photo-curing reactive electrospinning, is popular because it is compatible with a wide range of polymers and UV light is relatively easy to add to existing electrospinning setups. UV photo-curing reactive electrospinning methods have been developed for a variety of polymer solutions [2,3]. Typically, polymer solutions consist of a photo crosslinkable monomer, a photoinitiator and an additional copolymer or carrier polymer. Here we investigate the development of a UV-reactive electrospinning method based on the *in situ* crosslinking of poly(ethylene glycol) diacrylate (PEGDA). Polyvinyl alcohol (PVA) was used as a carrier molecule to facilitate electrospinning. The PEGDA/PVA nonwoven fibers made under reactive electrospinning conditions had a

normal morphology and were more stable in water than those made without UV exposure.

## 2 Materials and Methods

### 2.1 General Information

PEGDA with molecular weight 250 and 700 g/mol (PEGDA<sub>250</sub> and PEGDA<sub>700</sub>, respectively), PVA (31,000-50,000 g/mol) and the photoinitiator (PI) 2-hydroxy-4'-(2-hydroxyethoxy)-2-methyl propiophenone (Irgacure 2959) were purchased from Sigma-Aldrich (Munich, Germany). Dimethyl sulfoxide (DMSO) was purchased from Carl Roth (Karlsruhe, Germany). A 50% w/v stock solution of PI in DMSO was prepared and used in all experiments. PI stock solution was mixed directly with PEGDA solutions immediately before use to generate solutions with final PI concentrations of 5, 10 and 20% w/w (relative to the mass of PEGDA).

### 2.2 FTIR measurements

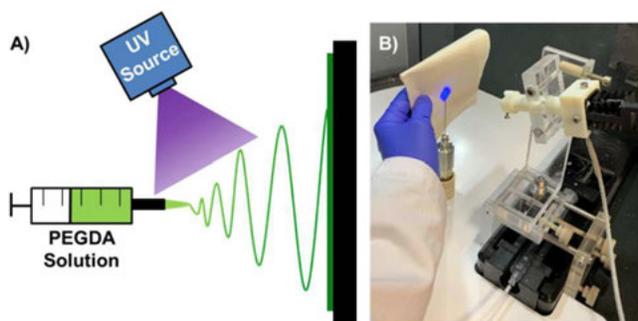
FTIR-ATR-measurements were performed using a Vertex 70 IR-Spectrometer (Bruker Corporation) with a Golden Gate™ (Specac Limited) ATR diamond insert. A spectrum was recorded at a rate of 1 measurement/second using OPUS spectroscopy software (Bruker Corporation). For each sample, 5  $\mu$ L of solution was pipetted onto the measurement surface. The 10 mW 365 nm LED UV light source (Ocean Insight, Ostfildern, Germany) was suspended approximately 4.5 cm away from the sample using a custom made cover. The FTIR measurements and UV light exposure at 100% power were started simultaneously. Peak areas between 1605 and 1651  $\text{cm}^{-1}$  were used to estimate the number of double bonds in the sample. The reaction was considered complete when the change in peak area plateaued. PEGDA<sub>250</sub> and PEGDA<sub>700</sub> with 5% and 10% (w/w) PI were analysed (each group had n=3 samples). Means were compared with ANOVA and Bonferroni post-test.  $p < 0.05$  was considered significant (GraphPad Prism).

### 2.3 Reactive electrospinning

Solutions for electrospinning were made by dissolving 15% w/w PVA and various amounts of PEGDA<sub>700</sub> in water. Solutions were mixed at 37°C for at least 12 hours. PEGDA solutions of 2.5, 5, 7.5 and 10% w/w polymer were tested.

Immediately before electrospinning, PI was added to reach a final concentration of 20% w/w.

Electrospinning was performed with a Contipro (Dolní Dobrouč, Czech Republic) 4SpinC4S LAB2 device. A solution flow rate of 16  $\mu$ L/min, collector distance of 25 cm and applied voltage of 35 kV was used in a 22°C and 24% humidity environment. UV crosslinking was initiated during the electrospinning process by exposing the area near the needle to 365 nm UV light (Fig 1A). A custom-made device held the light source and allowed for distance and angle adjustments (Fig 1B). The UV light source was used at 100% power and a distance of 18.5 cm and angle of 65° from the tip of the needle. After 30 min of spinning, nonwoven fiber mats were placed in a UV chamber (UV-Ofen CL-1000 Ultraviolet Crosslinker, Ultra-Violet Products Ltd., Cambridge, UK) for 10 min under 365 nm light.



**Figure 1:** (A) The schematic diagram shows the general UV-reactive electrospinning setup. During the electrospinning process, UV light is used to initiate crosslinking of PEGDA. (B) Pictured is the set-up used to complete this work. A custom-designed holder was utilized to control of the distance and angle of the UV light.

### 2.4 SEM imaging

Scanning electron microscopy (SEM) was performed on a Quanta FEG 250 (FEI Company, Germany). Nonwoven fiber samples were cut and mounted on aluminium carriers using graphite tape before being imaged. Samples were imaged once directly after spinning, then washed 3x in deionized water with a pipette, soaked for 5 additional minutes, rinse 3x again, dried in vacuum and imaged again.

## 3 Results and Discussion

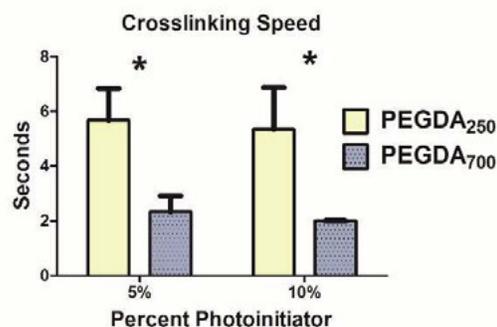
### 3.1 Relative Crosslinking Speed

FTIR measurements were used to monitor the loss of double bonds in PEGDA solutions while undergoing UV crosslinking. The crosslinking reaction was considered to be complete when the conversion of the double bonds stopped according to section 2.2. By monitoring the amount of time until the completion of the crosslinking reaction, the relative speed of the crosslinking reaction was compared between: 250 and 700 g/mol PEGDA solutions with 5 or 10% w/w photoinitiator. ANOVA analysis showed no significant affect from photoinitiator concentration, but the molecular weight of PEGDA did have a significant effect on the speed of the crosslinking reaction (Fig. 2), revealing that PEGDA<sub>700</sub> finished crosslinking significantly faster than PEGDA<sub>250</sub>. *In situ* crosslinking during electrospinning would ideally result in complete or nearly complete crosslinking before fibers reach the collector to ensure stable fibers and minimal fiber fusion. Time-of-flight for fibers is estimated to be less than 0.5 seconds, indicating the crosslinking speed is a critical factor and that polymer solutions should be optimized to have the fastest crosslinking speed possible [4]. For this reason, all further experiments were carried out using PEGDA<sub>700</sub>. Following the demonstrated pattern, higher molecular weight PEGDA solutions might have even faster crosslinking times, but we were unable to test them due to low solubility in our testing conditions.

### 3.2 UV reactive electrospinning

While the faster of the PEGDA polymers tested was higher in molecular weight, it was still too low for ideal electrospinning. PEGDA<sub>700</sub> only solutions were unable to be electrospun (data not shown). To compensate for the relatively low molecular weight of the PEGDA, a carrier polymer was included for the purpose of electrospinning. The formation of fibers during the electrospinning process has been linked to a critical threshold of viscosity related to molecular entanglement [5]. More molecular entanglement leads to better formation of fibers rather than droplets during spinning. Therefore, larger carrier molecules can be added to low molecular weight polymers to facilitate electrospinning. PVA was chosen as a carrier polymer because it has been used as a carrier with other small polymers, is biocompatible and is soluble in water [6,7].

Nonwoven fiber mats were electrospun with increasing amounts of PEGDA<sub>700</sub> relative to a constant amount of PVA. Representative SEM images from the highest and lowest tested PEGDA concentrations, with and without UV exposure are shown in Figure 3. All samples exhibit fiber formation. In 10% PEGDA samples there is a noticeable difference between samples with and without UV exposure. Without UV exposure, the fibers appear fused together, while the samples created with UV exposure has well formed, distinct fibers. This observation could be a sign of successful *in situ* crosslinking during time-of-flight. Crosslinking during



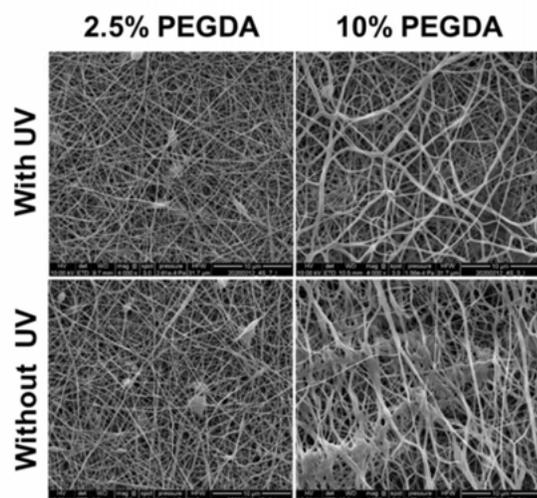
**Figure 2:** FTIR was used to measure the conversion of double bonds in PEGDA solutions. The graph displays mean time to completion of the crosslinking reaction and standard deviations. (\*) denotes significant differences between PEGDA<sub>250</sub> and PEGDA<sub>700</sub> samples at the same photoinitiator concentration ( $p < 0.05$ ).

electrospinning may be stabilizing the fibers before collection, preventing the fibers from fusing after deposition.

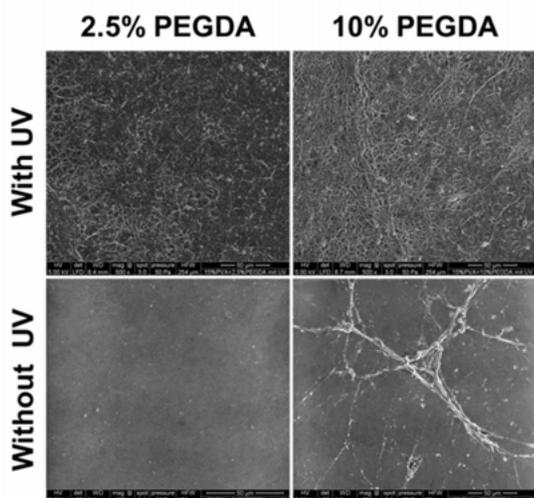
Prepared nonwoven mats were washed with deionized water briefly to further assess the materials stability. SEM images of representative nonwovens after washing are shown in Figure 4. At both PEGDA concentrations, UV exposure had a significant effect on the stability of the material in water. The UV-exposed samples have retained a generally fibrous structure while the samples that were not exposed to UV light were either completely or mostly dissolved, leaving little visible material behind. Because both PVA and PEGDA are water soluble, this experiment demonstrates that crosslinking did occur with UV exposure. PVA does not directly crosslink with the PEGDA, but rather should form an interpenetrating network with the crosslinked PEGDA [6]. Further work will need to be done to assess whether PVA is still present after washing or if it is largely removed, leaving PEGDA-only fibers.

The proof-of-concept work done in this paper demonstrated the feasibility of using reactive electrospinning to create *in situ* crosslinked PEGDA/ PVA nonwoven fiber materials. Future work will focus on optimizing polymer

solutions and UV exposure parameters to maximize crosslinking during time-of-flight of the electrospinning process.



**Figure 3:** Representative SEM images of electrospun PVA/PEGDA solutions with or without UV exposure. Fiber fusion can be seen in the 10% PEGDA samples without UV exposure, but with UV the fibers are well defined. All images are at 4000x magnification. Scale bars indicate 10  $\mu\text{m}$ .



**Figure 4:** Representative SEM images of PVA/PEGDA non-wovens with or without UV exposure after washing in water. Without UV, the fibers almost completely dissolve in water, while UV-exposed fibers maintain their general structure. Images are at 500 or 800x magnification. Scale bars indicate 50  $\mu\text{m}$ .

## 4 Conclusion

In this study, the feasibility of reactive electrospinning of PEGDA based on UV crosslinking was examined. PVA/PEGDA polymer blends could be electrospun to reliably produce nonwoven fiber mats without the need for volatile solvents. The addition of UV exposure simultaneously with the electrospinning process did not interfere with fiber formation. The reactive electrospun PVA/PEGDA fibers were more stable in water than those created without UV exposure, demonstrating evidence of PEGDA crosslinking. This work establishes a method that can be used for further optimization.

### Author Statement

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