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Tailoring electrospun polymer blend carriers for nutrient delivery in seed coating for sustainable agriculture

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ABSTRACT

The fabrication of ultrathin fibrous seed coating material with focus on improving the germination potential of the seed was the aim of this work. In this effort, we have fabricated electrospun Polyvinylpyrrolidone (PVP) - poly (diethoxy) phosphazene (PPZ) nanofibers. PVP is biocompatible, biodegradable and a commonly used seed coating material while PPZ is a nitrogen and phosphorus rich, hydrophobic polymer which undergoes 74% degradation in 12 weeks. Cowpea (*Vigna unguiculata*) seeds with a harvesting time of 90 days were used as test subject. Electrospinning confers water permeability, gaseous exchange and does not have residual solvent which is an advantage over film coats. The fabricated blends were characterised by Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) etc and it showed partial compatibility of the polymers. The phase contrast microscopic images also showed two phases. A decrease in wettability with increase in the PPZ content in the fibers was seen from water contact angle measurements. The swelling and stability studies indicated that the presence of PPZ in the fibers helps retention of material on the seed. The seed viability and the degradation of the fibrous seed coating were studied using conductivity meter and pH meter. The observed experimental findings may be beneficial and of prospective use in sustainable agriculture. Such polymer blends have the potential to reduce water and soil pollution as well as protect the seed during storage and increase crop yield.

1. Introduction

With nanotechnology, a large set of materials and improved products rely on a change in the physical properties when the feature sizes are shrunk. These nanomaterials are used in many applications such as sensors, water purification, antimicrobial, catalysis, biomedical, agricultural etc (Pandey, 2016; Pandey and Ramontja, 2016a, 2016b; Pandey and Mishra, 2014; Pandey and Nanda, 2015; Masrufa et al., 2016). The potential of nanotechnology has to be explored to provide innovative solutions for the application of fertilizers and nutrients to the plants and there by confront the challenges faced by agriculture and society. Direct application of agrochemicals has limitations like continuous application, leaching through surface runoff etc. leading to environmental and economic concern (Mukhopadhyay, 2014). Seed coating is a practice of coating the seeds with a material which can also encapsulate nutrients, pesticides etc. for better stand establishment (Marcos-Filho, 2015). Polymeric seed coating adhere tightly to the seed and prevent the loss of added ingredients. Among these, Polyvinylpyrrolidone (PVP), a nontoxic, biocompatible and water soluble polymer is commonly used. It also has the advantage of environmental stability, easy processing, handling and cost effectiveness (Krishnamoorthy et al., 2016). It has numerous applications in the fields of biomedicine, adhesives, membranes, agriculture etc. as it has remarkable properties like complexing ability, bioactivity, high hydrophilicity, easy electrospinnability (Chuangchote et al., 2009). Electrospun PVP along with nutrients (Krishnamoorthy et al., 2016) and with addition of *Rhizobia* (Damasceno et al., 2013) has been applied as seed coats in leguminous plants.

The strongly hydrophilic component pyrrolidone, due to the presence of highly polar amide group makes PVP water soluble. Therefore for enhancement of PVP seed coating, it was blended with a hydrophobic polymer which would allow retention of PVP in wet soil during the complete life span of the plant. This blend can

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be applied to both seed coat and controlled release fertilizer, which would increase the nutrient use efficiency (NUE) and reduce environmental pollution due to fertilizer leaching and multiple applications. Many different polymers have been used in the form of gels, films, beads etc. which encapsulate the fertilizer like urea and super phosphate (Nair et al., 2010). The drawback with these polymer coatings is that after intake of the nutrient by the plant, a substantial amount of polymer remains, to the extent of 50 kg/ha/year which takes a long time to degrade, or has to be removed manually (Zuverza-Mena et al., 2016).

In order to address this problem, in our present study, we have attempted to blend PVP with PPZ, as both the polymers were biocompatible and biodegradable and the hydrolytic degradation of PPZ gave plant nutrient namely phosphates and ammonia (Nichol et al., 2014). PPZ are hybrid organic inorganic polymeric material whose properties are determined by the phosphorus nitrogen backbone and the substituent organic groups. These properties like low temperature flexibility, thermal and light stability, hydrophobic nature make them sought after compared to organic polymers (Nichol et al., 2014). The hexa amino substituted monomer has been efficiently used as a fertilizer in seed coats (Krishnamoorthy and Rajiv, 2017). The ethoxy substituted polyphosphazene chosen for this work undergoes about 76% decrease in molecular weight in 12 weeks (Nichol et al., 2014). The choice of seed to understand seed viability was cowpea seeds as it has a harvest time of 60–90 days and is a legume of both economic and nutritive value. The electrospun seed coat of PVP and PPZ would release incorporated nutrient due to dissolution of PVP initially, followed by slow release on degradation of PPZ. This would help during both seed germination and plant growth. Apart from imparting a hydrophobic nature to the seed coating, the blend also improves toughness, opacity etc. The blending process combines the advantages of the two polymers (Pandey and Mishra, 2013).

The process of electrospinning was used to ensure controlled release of nutrients and overcome the limitations of film coating namely low water permeability and no exchange of gases. Electrospinning is a simple and low-cost method for manufacturing ultrafine polymer fibers. These ultrafine fibers have shown amazing characteristics such as very large surface area-to-volume ratio and high porosity with very small pore size, so they are used in biomedical area (Qiu, 2002). They can be used for the release of fertilizer, pesticide or insecticide by incorporating them during electrospinning. The polymer degradation rate i.e. the rate of hydrolysis of PPZ can be tuned to the rate of uptake of nutrient by the plant, by changing the organic moiety attached to the phosphorus atom (Allcock, 2016). This ensures continuous availability of fertilizer during lifecycle of the plant. Both weak acid and basic components are released hence PPZ also acts as a buffering agent (Yin et al., 2007).

The objective of the present study was to develop and characterize the PVP and PPZ polymer blends combined in various proportions and fabricate them into electrospun nonwoven fibers. The secondary objective was to conduct a comparative study of the compositions and find the most suitable blend for sustainable agriculture. The observed facts may be indicative of the prospective use of these blends in agriculture.

2. Experimental

2.1. Materials and methods

PVP and Hexachlorocyclophosphazene (HCCP) were purchased from Sigma Aldrich India. The solvents chloroform (99.7% AR grade), hexane (99.5% AR grade), tetrahydrofuran (99.5% AR grade), were purchased from Qualigens fine chemical India Pvt. Ltd. and used without further purification. Calcium Sulphate hemihydrate, Sulphamic acid and 1, 2, 4 trichlorobenzene were obtained from Sigma Aldrich India and used without further purification.

2.2. Synthesis of poly (diethoxy) phosphazene by one pot synthesis

Poly (dichlorophosphazene) (PDCP) was prepared by the ring-opening polymerization of hexachlorocyclotriphosphazene (HCCP) in the presence of catalyst. About 2g of HCCP along with 0.35g of sulphamic acid and 0.1g calcium sulphate hemihydrate was taken in 1 mL of 1,2,4 trichlorobenzene under nitrogen (Lower the solvent amount better was the yield). The reaction was allowed to proceed for 1 h at 220 °C. 2 mL of ethanol in 5 mL of THF was added to a suspension of 1.35 g of sodium hydride in 5 mL of dry THF and allowed to run for 8 h (Huang et al., 2008). The resulting solution was added dropwise to the cooled polymer solution. The reaction mixture was stirred and refluxed for 24 h and added to hexane, when the polymer precipitated out. The polymer was concentrated and purified by precipitation into hexane from THF three times. After removal of the solvent by vacuum drying a yellow coloured solid was obtained with 55% yield. The scheme is represented in Fig. 1. The polymer was flushed with nitrogen and stored in a desiccator. Characterisation of the synthesised compound was done

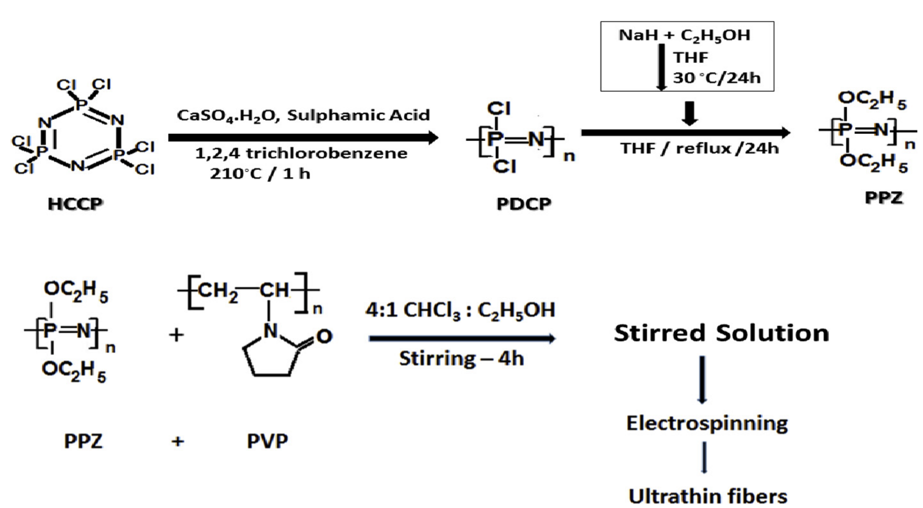

Fig. 1. Flow chart of synthesis and blend formation process through electrospinning.