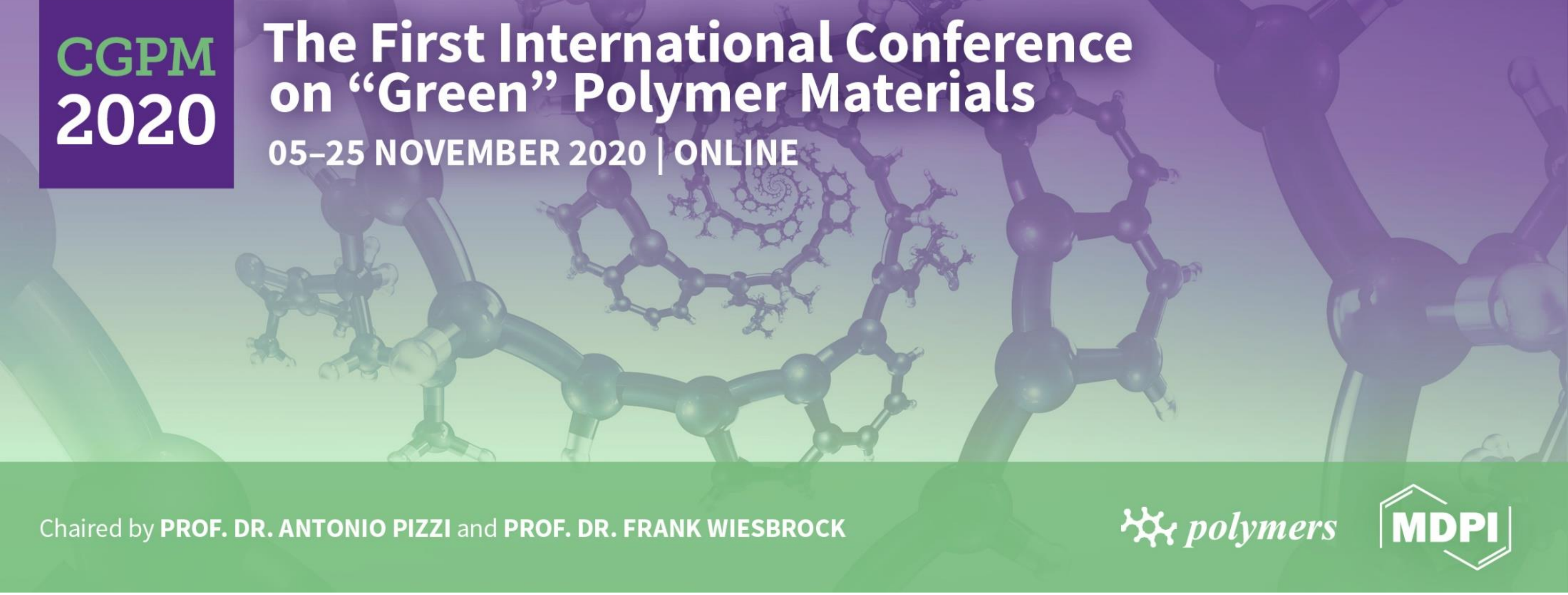

Electrospun Silk-Cellulose Composite Nanomaterials using Ionic Liquid Regenerated Films

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Abstract

In this study, 1-ethyl-3-methylimidizolium acetate (EMIMAc) ionic liquid was used and the regenerated films were coagulated in baths of EtOH or water. Because of the variability of ionic liquids, the nanomaterials produced using this technique have unique and tunable properties such as large surface area to volume ratios and low structural defects. FTIR and SEM results suggest that the structure and morphology of the final nanosized samples becomes more globular when the biopolymer composition ratio has increased cellulose content. TGA results demonstrated that the electrospun materials have better thermal stability than the original films. This two-step electrospinning method, using ionic liquid as a non-volatile solvent to first dissolve and mix raw natural materials, may lead to extensive research into its biomedical and pharmaceutical applications in the future.

Keywords: Ionic Liquids ; Electrospinning ; Biopolymers

Introduction

Electrospinning is a widely used technique to draw recalcitrant biopolymer solutions into micro to nanoscale materials in a simple and economical way. The first focus of this research involved using ionic liquids as a non-volatile solvent for natural insoluble biopolymers such as silk and cellulose (or cellulose derivatives). Compared to traditional organic solvents, ionic liquids can dissolve the biopolymers without altering the molecular weight of the biopolymer. The second focus of this research explored the dissolution of IL-regenerated composites into organic solvents and directly electrospun to produce composite nanomaterials. Various ratios of silk-cellulose bio-composite films regenerated from ionic liquids were used as the raw materials and sequentially dissolved/dispersed into Formic Acid-$CaCl_2$ solution in order to initiate electrospinning of silk-cellulose nanomaterials.

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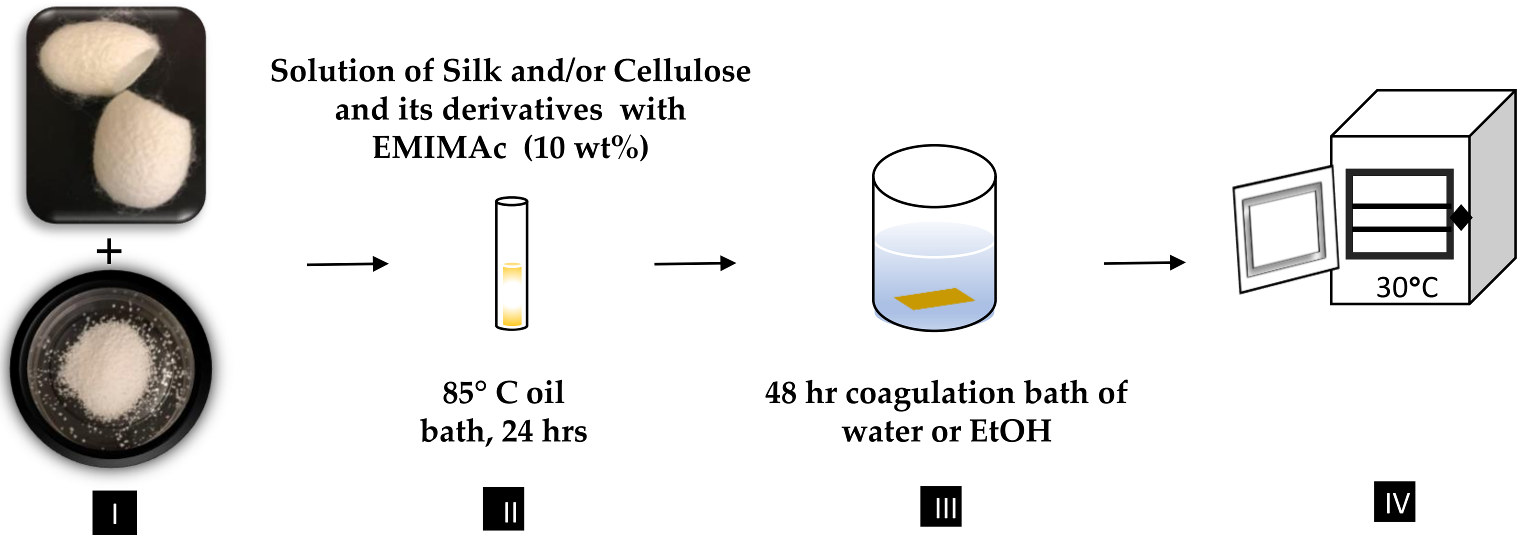
Methods- Film Production and Dissolution



- 90% Ionic Liquid: (EMIMAc) (2.7g of 3g total)
- 10% solids:
  - 100% Cellulose (Cell100)
  - 90% Cellulose 10% Silk (Cell90)
  - 75% Cellulose 25% Silk (Cell75)
  - 50% Cellulose: 50% Silk (Cell50)
  - 100% Silk (Cell0)

Mixing of Protein and Polysaccharide in Oil Silica Bath:

- Average Temperature: 85°C for 24 hours
- Coagulation Bath: 48 hours
- Vacuum Oven Time: 24 hours

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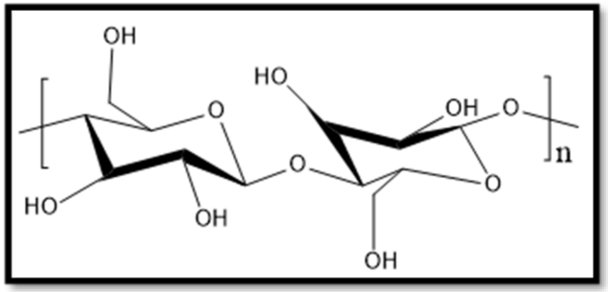
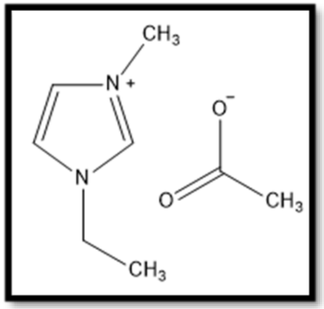
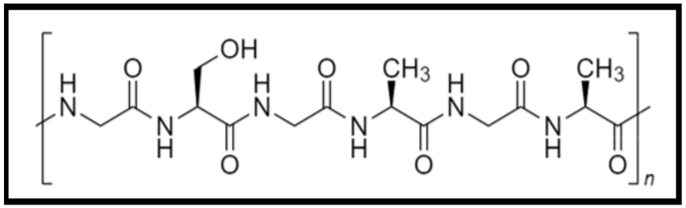
Methods-Chemical Structures



Avicel Microcrystalline Cellulose

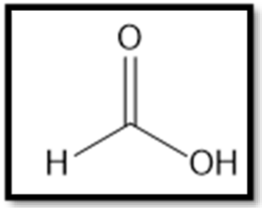


1-Ethyl 3-Methyl Imidazolium Acetate (EMIMAc)



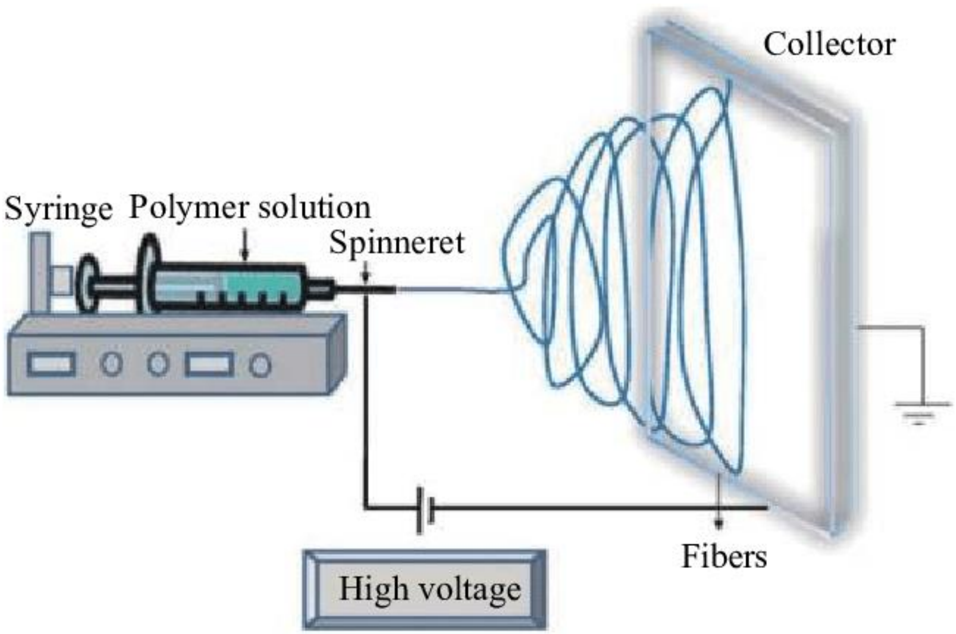
Gly Ser Gly Ala Gly Ala

B. *Mori* Silk polypeptide repeats



Formic Acid

Methods-Electrospinning



- Set Voltage Parameters: 18kV
- Flow Rate: 10 microliters per minute
- Dry film weight: 15% solids to solvent ratio
- Dissolved into Formic Acid-$CaCl_2$ solution
- Heated at average temperature: 40°C
- Transferred to BD Luer-Lok Syringe
- Collected sample on collection plate

Characterization Tests:

- SEM-Scanning Electron Microscopy,
- FTIR-Fourier Transform Infrared Spectroscopy
- TGA- Thermogravimetric Analysis

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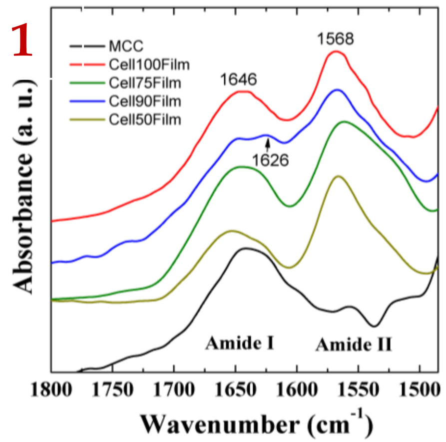
Results and Discussion - Structural Analysis

- Figure 1 and 2 depicts the FTIR spectra comparing EMIMAc generated films and their electrospun nanomaterials in the regions of 1500-1800 cm^{-1} and 800-1200 cm^{-1}.
- Figure 3 and 4 depicts the electrospun nanomaterial samples as compared to MCC.
- Figure 5 demonstrates the structural changes occurring with the Pure Silk samples.

1



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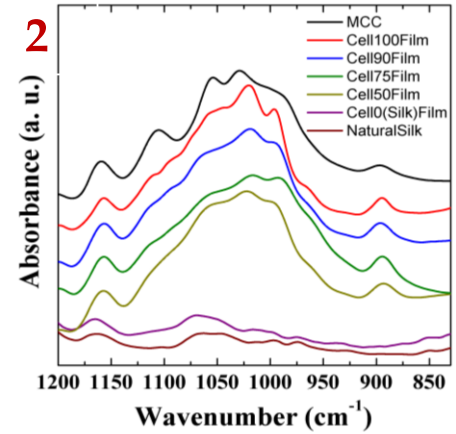

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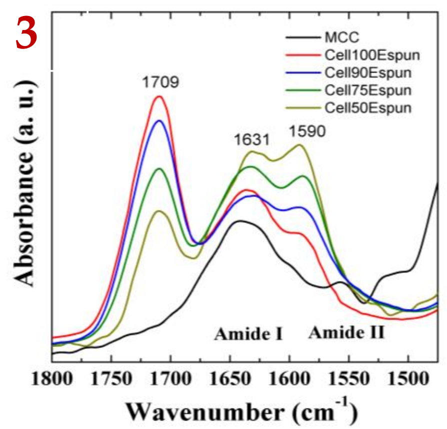

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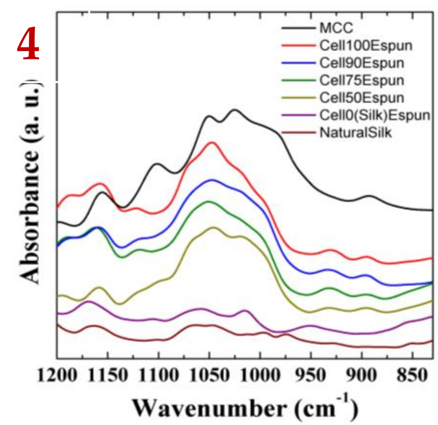

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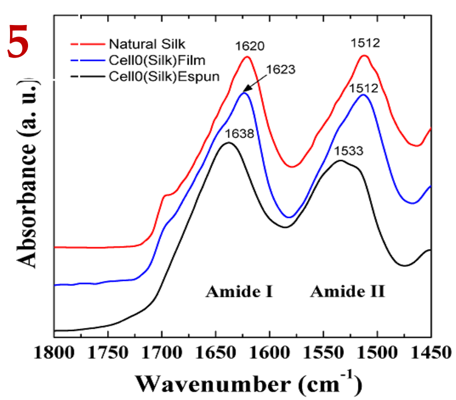

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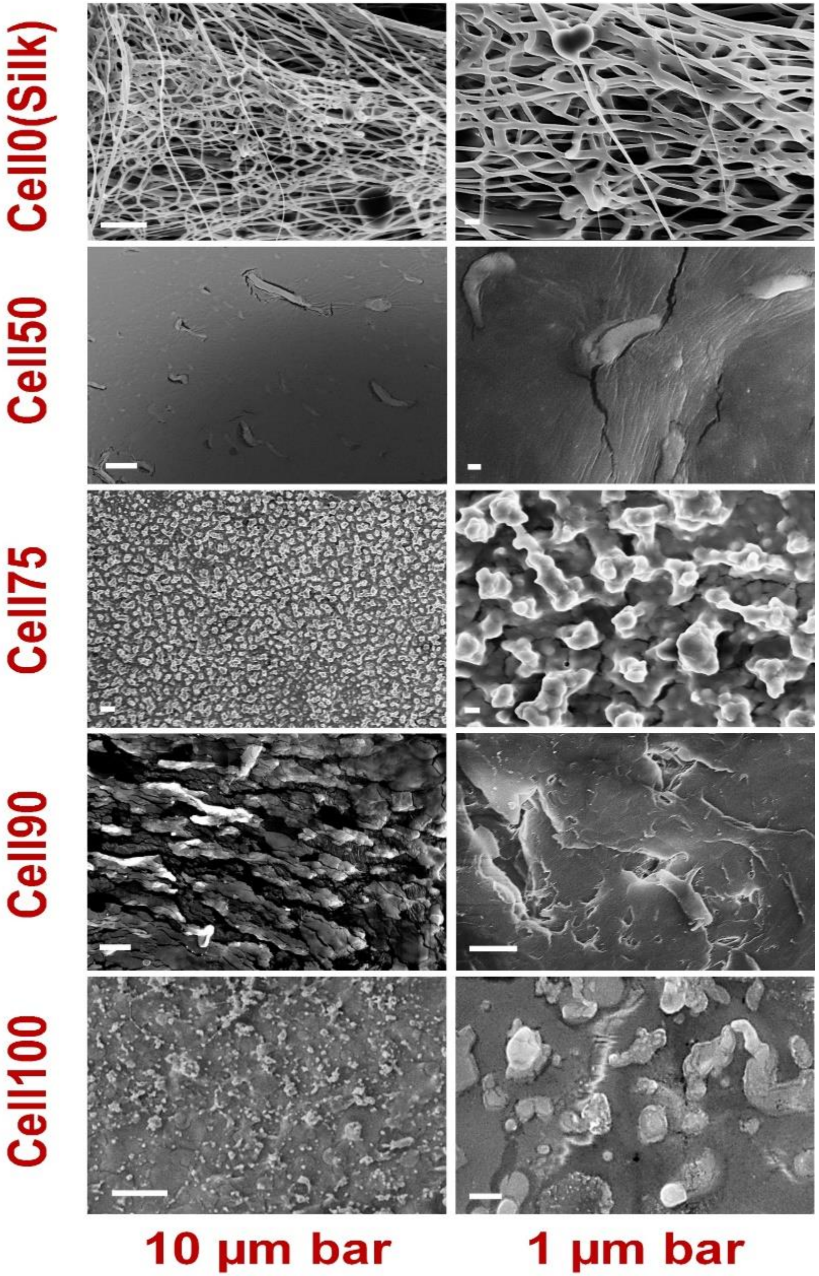
Results and Discussion - Morphology Analysis



SEM analysis shows micro and nanomaterials after electrospinning procedure. From the images we found that Pure Silk can form homogeneous nanofiber matrices using EMIMAc IL generated films as the starting materials that are similar or better to silk fibers generated from organic solvent. As the cellulose content increases, the nanofiber structures gradually disappear and become more globular-like structures.

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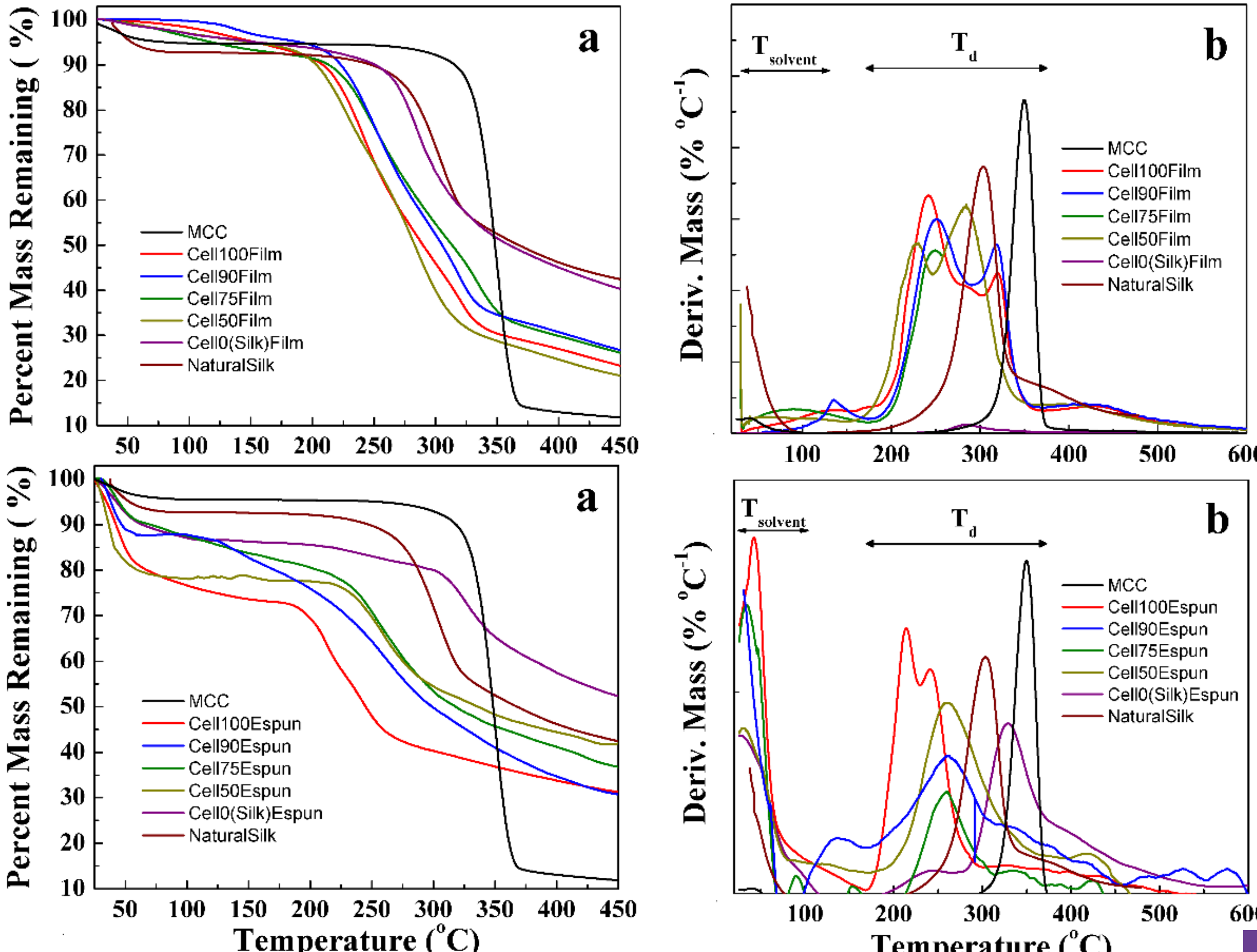
Results and Discussion-Thermal Stability Analysis



Thermogravimetric Analysis of EMIMAc Ionic Liquid generated film and E-spun nanomaterial samples: (a) percent mass remaining with respect to temperature and (b) the rate at which the sample was degraded.

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Thank you for your attention

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