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Electrospinning of Natural Rubber/PLA/PEO Blends: Effect of Solution and Environmental Parameters on the Material's Morphology

Salvatore Lazzara¹ | Emanuele Maccaferri^{1,2} | Emanuele Manzi¹ | Tiziana Benelli^{1,2} | Laura Mazzocchetti^{1,2} | Tommaso Maria Brugo^{1,2} | Andrea Zucchelli^{1,2} | Loris Giorgini^{1,2}

¹Department of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, Italy | ²Interdepartmental Center for Industrial Research On Advanced Applications in Mechanical Engineering and Materials Technology, CIRI-MAM, University of Bologna, Bologna, Italy

Correspondence: Salvatore Lazzara (salvatore.lazzara2@unibo.it) | Tiziana Benelli (tiziana.benelli@unibo.it)

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ABSTRACT

Nowadays, the widespread use of composite materials is limited in some applications by their low delamination resistance and low damping ability. Thermoplastic and elastomeric nano- and micro-fibers have recently been proposed to enhance the fracture toughness of Carbon Fiber Reinforced Polymer (CFRP) laminates, yielding promising results. In the present work, the morphology of microfibrillar electrospun membranes based on natural rubber/poly(lactic acid)/poly(ethylene oxide) (NR/PLA/PEO) polymer blends is investigated. It is observed that environmental parameters play a key role in determining the morphology of the fibers, allowing smooth and defect-free ones to be obtained at low humidity values while porous ones at high humidity values.

1 | Introduction

Thermoset-based composite materials are extensively utilized in the automotive, aerospace and marine industries thanks to their high mechanical properties and lightweight nature, offering an outstanding strength-to-weight ratio. Despite these attractive properties, composites usually fail due to delamination, that is the debonding of the constituent laminae because of the formation and propagation of microcracks [1]. Different methods have been proposed to increase the delamination resistance of CFRPs, producing materials with improved interlaminar fracture toughness. Among different toughening techniques, in the last two decades the interleaving of electrospun nanofibrillar mats has gained a lot of attention in the academic field [2–4].

Thermoplastic polymers, such as polyamides and polyesters, are commonly used in mats production. On the other hand, rubbery nanofibers have lately been proposed as innovative materials to mitigate composite delamination while enhancing other properties, including damping capability [5–7]. Amorphous low- T_g polymers, such as rubbers, are efficient in enhancing interlaminar fracture toughness. However, their tendency to cold-flow often results in film formation, making the production of fibers challenging. Recent studies have shown that blending elastomers with semi-crystalline thermoplastic polymers can yield to a stable fibrous morphology. In particular, nanofibers containing Nitrile Butadiene Rubber (NBR) have been proposed as highly effective toughening interlayers [8, 9].

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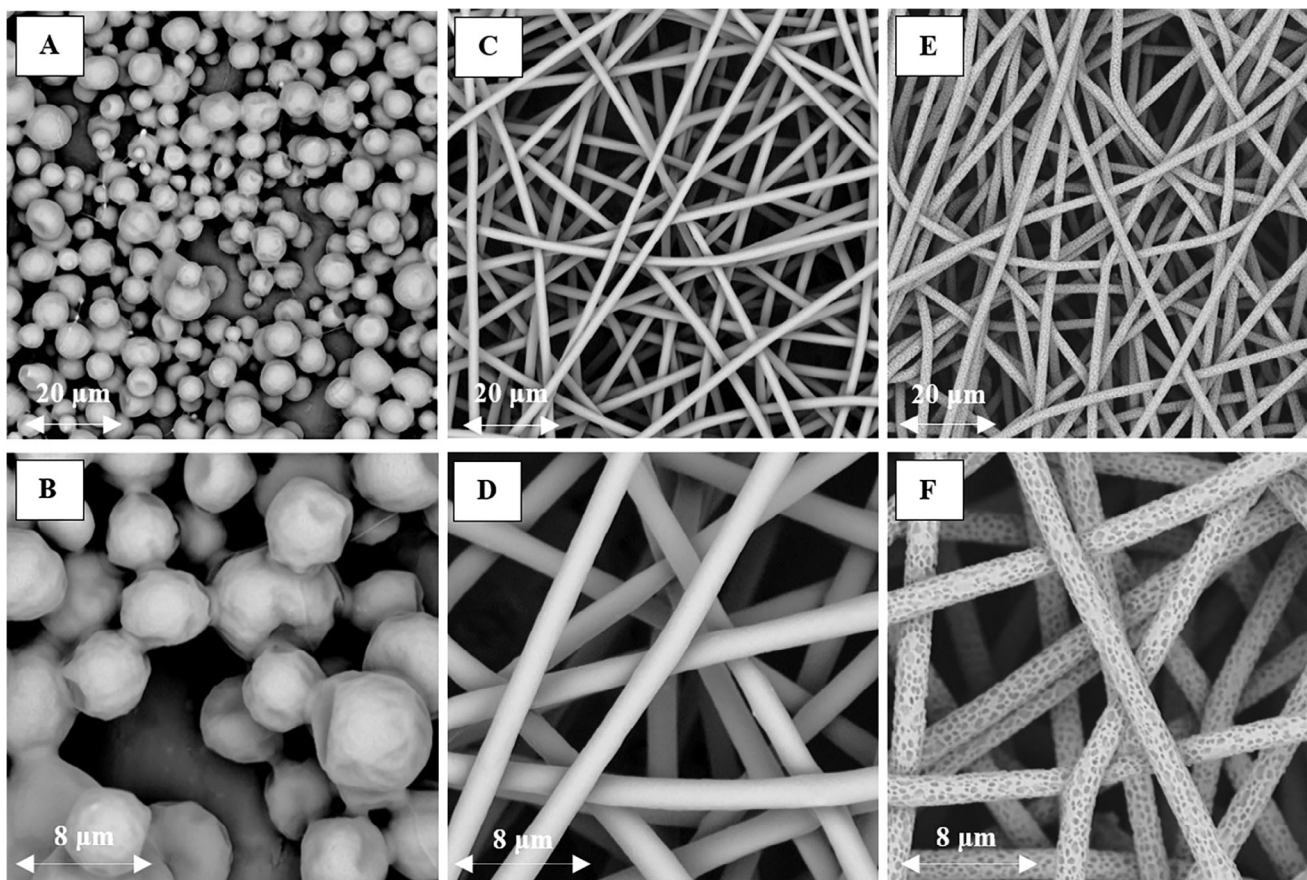


FIGURE 1 | SEM images (at different level of magnification) evidencing the morphology of electrospun mats obtained from blends: (A,B) NR/PLA 40/60; (C,D) NR/PLA/PEO 40/55/5, spun at low relative humidity (25%); (E,F) NR/PLA/PEO 40/55/5, spun at high relative humidity (70%).

The present work investigates the morphology of different elastomeric electrospun mats made from natural rubber (NR), poly(lactic acid) (PLA) and poly(ethylene oxide) (PEO) blends, that could potentially enhance the delamination resistance and damping behavior of epoxy-based CFRP laminates once integrated.

2 | Materials and Methods

Natural Rubber (NR), M_w 38,000 Da, and Poly(ethylene oxide) (PEO), M_w 1,000,000 Da, were purchased from Sigma-Aldrich and used without any preliminary treatment or purification. Poly(lactic acid) (PLA) Ingeo 4043D, with an L-lactide content of 98% and an average molecular weight of 111,000 Da, was purchased by Nature Works and used without any preliminary treatment. Chloroform (CHCl_3) was purchased from Sigma-Aldrich and was used without any preliminary treatment.

Blend solutions for electrospinning were prepared by dissolving the polymers (4 or 4.2% wt.) in chloroform under magnetic stirring at 50°C for a minimum of 4 h, until a homogeneous solution is formed. Solutions were then cooled at room temperature and electrospun using a 4-needles electrospinning machine (Spinbow) equipped with a drum collector rotating at 50 rpm and covered with baking paper, using the following process parameters: flow rate 0,60 mL/h, electric potential 10 kV, distance 12 cm.

Nanofibrous mats were analyzed by scanning electron microscopy (SEM PhenomProX) to determine the nanofiber morphology.

3 | Results and Discussion

The electrospinning process requires homogeneous and stable solutions. For this reason, at first, stable NR/PLA blends' solutions were obtained, i.e., solutions that did not give rise to the phenomena of demixing/precipitation of one or both polymers. Blends with a polymer concentration of 4% wt. remained stable with rubber content up to 40% wt. of the total polymer fraction (NR/PLA 40/60). Notably, the demixing phenomenon depends on both the rubber content in the blend and the overall polymer concentration. As the relative weight of elastomer in the blend increases, it destabilizes the solution and causes demixing to occur more quickly. The same phenomenon develops as the overall polymer concentration is raised. When the total concentration is set to 6% wt., demixing occurs at lower rubber content, beginning at just 30% wt. of NR.

The electrospinning of NR/PLA 40/60 blend results in the formation of microspheres, likely due to the solution's low viscosity (Figure 1A,B). To increase the viscosity, a small amount of high-molecular-weight PEO has been added, producing a stable solution at 4.2% wt. with an NR/PLA/PEO ratio of 40/55/5 wt. Once electrospun, morphological analysis of the resulting mats

reveals that homogeneous fibers have been obtained (diameter $2,10 \pm 0,11 \mu\text{m}$, Figure 1C,D).

The influence of environmental parameters on fiber morphology was then highlighted. Indeed, smooth and defect-free fibers were obtained at low humidity values (Figure 1C,D), while porous ones at high humidity (diameter $2,05 \pm 0,13 \mu\text{m}$, Figure 1E,F). Such porosities are generated by the breath figure mechanism, which requires both the presence of hydrophobic polymers in the system (such as NR and PLA) and volatile solvents, such as chloroform. This mechanism has already been seen in the literature for PLA-only fibers [10, 11], but it is encountered for the first time in blends with natural rubber.

4 | Conclusion

In this work, elastomeric microfibrillar membranes were produced by electrospinning, starting from polymer blends of natural rubber/poly(lactic acid)/poly(ethylene oxide) (NR/PLA/PEO). In particular, the addition of PEO allowed the obtainment of microfibrils with regular diameters, as well as showing the influence of environmental parameters on fiber morphology: smooth and defect-free fibers at low humidity values, and porous ones at high relative humidity. By contrast, just only microspheres were obtained in the absence of PEO. The obtained mats made of different microfibrils' morphologies could be potentially useful to improve the delamination resistance and the damping ability of epoxy-matrix laminated CFRPs.

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Conflicts of Interest

The authors declare no conflicts of interest.

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