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Solvent role for the electrospinning of PVDF-HFP nanofibrous coatings for passive radiative cooling applications

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Abstract. Due to the increasing demand of cooling systems, new techniques to produce materials with specific optical properties are being developed for innovative applications such as passive daytime radiative cooling (PDRC). In recent years, electrospun polymeric coatings have been proposed as one of the most promising and scalable techniques for PDRC, due to the high solar reflectivity induced by their nanofibrous structure. Specifically, electrospun poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) exhibit negligible absorption in the solar wavelength range, and a selective emissivity in the atmospheric transparency range provided by its C-F bonds. However, the production of these coatings by electrospinning involves the use of toxic or hazardous solvents. In this study, we explore the substitution of traditional solvents with a non-toxic one, i.e., dimethyl sulfoxide (DMSO), to produce PVDF-HFP electrospun coatings. Through an easy one-step electrospinning process, 35 μm -thick coatings composed of well-defined, cylindrical, uniform, and continuous fibers are obtained with comparable properties to those obtained using traditional solvents.

1 Introduction

In recent years, passive daytime radiative cooling (PDRC), which is based on maximized thermal emission and minimized absorption of incoming solar and atmospheric radiation, has been proposed as a cutting-edge cooling system [1]. Innovative materials and fabrication methods play a fundamental role in the development of this energy-free and renewable technology, through advanced coatings with ultra-high reflectance in the solar spectrum (0.3-2.5 μm) and high emittance in the atmospheric transparency window (ATW, 8-13 μm) [2].

Among the current available options, electrospun coatings (i.e., nanofibrous materials obtained by the application of a high electric field to a polymer solution) have an extremely attractive potential for PDRC applications due to their high porosity and large surface area, which promote stronger radiative heat transfer. In addition, their optical properties can be tuned by adjusting fibers diameter and pore size (to obtain high reflectivity of solar light) and by selecting high emissivity materials in the ATW [1]. PVDF-HFP (poly(vinylidene fluoride-co-hexafluoropropylene)) copolymer has been extensively studied for PDRC applications [3,4,5], due to its high transparency at solar wavelengths and selective emissivity in the ATW. However, for the production of PVDF-HFP electrospun coatings, toxic or health hazardous solvents, such as N,N-dimethylformamide (DMF), acetone or dimethylacetamide (DMA), are commonly used. Recent studies are focusing on the identification

of greener alternatives [6], and dimethyl sulfoxide (DMSO) has emerged as a valid option to dissolve fluoropolymers.

Here the feasibility of replacing traditional solvents with non-toxic DMSO to obtain electrospun PVDF-HFP nanofibrous structures to be used for PDRC applications is presented.

2 Materials and methods

2.1. Materials

PVDF-HFP Kynar Flex® 2801 copolymer pwd was kindly supplied by Arkema. DMSO and acetone were purchased from Sigma Aldrich (Milan, Italy).

2.2 Preparation of the electrospun PVDF-HFP coatings

PVDF-HFP (20 wt.%) was dissolved in pure acetone and in a DMSO/acetone mixture with a 1:1 weight ratio. After 3 h of magnetic stirring at room temperature (25 °C), a homogeneous, transparent solution was obtained in both cases.

To produce the PVDF-HFP nanofibrous coatings, an E-fiber electrospinning system by SKE Research Equipment was used. A flow rate of 1 ml/h, a working distance between the two electrodes of 15 cm, a spinneret with a diameter of 1 mm and a plane stationary collector (with an aluminium foil as substrate) were employed. A voltage of 6-8 kV and of

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12-15 kV was applied for the acetone and DMSO/acetone solutions, respectively. The process was carried out for 5 min and then the PVDF-HFP nanofibrous coatings were left to air dry overnight.

2.3 PVDF-HFP coatings characterization

A digital micrometer was used to measure the thickness of the coatings in at least five different spots.

The chemical structure of the coatings was analyzed through Fourier Transform Infrared (FTIR) spectroscopy by using a Thermo Fisher Scientific Nicolet™ iS50 spectrometer in attenuated total reflectance (ATR) mode, with an accumulation of 32 scans/spectrum at a resolution of 4 cm⁻¹ in the spectral range of 4000-400 cm⁻¹.

The morphology of the coatings was characterized by using a Supra 40 Field Emission Scanning Electron Microscopy (FE-SEM), ZEISS. The samples were previously coated with a thin film of Pt by a Quorum Q150T ES applying a current of 50 mA for 20 s. The fiber diameters were measured by ImageJ software analyzing the FE-SEM images.

3 Results and discussion

Free-standing, stable and flexible nanofibrous coatings with an average thickness of 35 μm were obtained with the use of both pure acetone and DMSO/acetone mixture as solvents.

ATR FT-IR spectroscopy was conducted on the nanofibrous coatings, as well as on the commercial PVDF-HFP powder as reference. The spectra allowed to identify the characteristic peaks of the copolymer in all samples. Specifically, peaks related to the α phase (840 and 956 cm⁻¹) were identified in the powder spectrum, while in the electrospun coatings they were not present or showed a lower intensity. On the other hand, the peaks related to the β phase (878, 1071, 1181, 1275 and 1401 cm⁻¹) were present with an increased intensity in the coatings. In fact, the electrospinning process tends to favour the β phase due to the large mechanical elongation and the strong electrical field applied [7].

FE-SEM analyses confirmed the fabrication of nanostructured coatings with both solvent systems (Figure 1). Well-defined, cylindrical, uniform, and continuous nanofibers were obtained. When pure acetone was used, the fibers were more straight and thinner, presenting a mean fiber diameter of 600 nm and a Full Width at Half Maximum (FWHM) of ~230 nm, compared to the coating produced with the DMSO/acetone mixture, which presented a mean fiber diameter of 885 nm and a significantly larger FWHM of about 400 nm. This is an interesting result for PDRC applications, as a broader diameter distribution is typically associated to a more efficient scattering across all solar wavelengths (250 - 2500 nm), leading to a higher solar reflectivity.

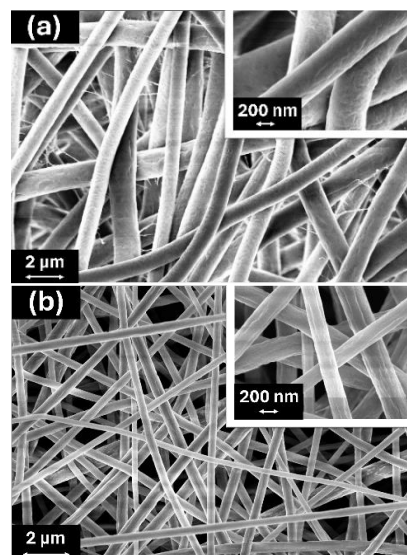


Fig. 1. FE-SEM images: PVDF-HFP electrospun coatings using (a) DMSO/acetone and (b) acetone as solvent.

4 Conclusions

The feasibility of the partial substitution of traditional toxic solvents with DMSO to produce PVDF-HFP nanofibrous coatings was confirmed since it was possible to perform a fast, facile, and efficient electrospinning process. FE-SEM analysis confirmed the correct formation of well-defined and continuous structures with an increase in the fiber diameter of approximately 300 nm with the use of the DMSO/acetone mixture as a solvent. The performance of the coating will be further evaluated in terms of optical properties and cooling capacity.

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