PVDF FILMS WITH OPTIMIZED POROUS STRUCTURE USING NON-SOLVENT INDUCED PHASE SEPARATION FOR PASSIVE RADIATIVE COOLING

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ABSTRACT: *Today, as personal thermal management gains importance for both increased comfort and energy saving advantages, body cooling through the clothing system by using natural energies has come to the fore. In this study, as the first step of a cooling garment design project, radiative cooling films having porous structures with tailored optical structures to enhance UV-VIS-NIR reflectivity were produced from polyvinylidene fluoride (PVDF), via non-solvent-induced phase separation method using two solvents and water. The porous structure of PVDF films was optimized by differing polymer (5 and 10wt.%), water concentrations (3-10%) and drying conditions. Besides SEM analyses to determine the pore characteristics, cooling performances were evaluated by a hotplate apparatus combined with a halogen lamb as a sun simulator. Indirect emissivity calculations were carried out from the IR camera images of the films heated at the same temperature with a fabric whose temperature was measured with sensors. According to SEM images, PVDF films having 10 wt.% polymer and 3% water concentrations had the most porous structure. The emissivity of the optimized PVDF film with a hierarchically porous structure was enhanced to 96.6% with a temperature decrease of 1.06°C under a solar irradiance of 600 W·m^{-2} indicating a good potential for a further cooling structure as a nanocomposite and coated fabric forms.*

Keywords: *Thermal management, passive cooling, phase separation, porosity, solvent.*

PVDF FILMOVI SA OPTIMIZOVANOM POROZNOM STRUKTUROM KORISTEĆI RAZDVAJANJE FAZA NERASTAVAČIMA ZA PASIVNO ZRAČENJE

APSTRAKT: *Danas, kako lično upravljanje toplotom dobija na značaju kako za povećanje udobnosti tako i za prednosti uštede energije, hlađenje tela kroz sistem odeće korišćenjem prirodnih energija je došlo do izražaja. U ovoj studiji, kao prvi korak u projektu dizajna odeće za hlađenje, filmovi za hlađenje koji imaju porozne strukture sa prilagođenim optičkim strukturama za poboljšanje UV-VIS-NIR reflektivnosti proizvedeni su od poliviniliden fluorida (PVDF), putem razdvajanja faza koje nije izazvano* *rastvaračem. metoda pomoću dva rastvarača i vode. Porozna struktura PVDF filmova je optimizovana različitim polimerima (5 i 10 tež. %), koncentracijom vode (3-10 %) i uslovima sušenja. Pored SEM analiza za određivanje karakteristika pora, performanse hlađenja su procenjene pomoću aparata za grejanje u kombinaciji sa halogenim jagnjetinom kao simulatorom sunca. Proračuni indirektne emisivnosti vršeni su na osnovu slika IR kamere filmova zagrejanih na istoj temperaturi sa tkaninom čija je temperatura merena senzorima. Prema SEM snimcima, PVDF filmovi sa koncentracijom polimera od 10 tež.% i 3% vode imali su najporozniju strukturu. Emisivnost optimizovanog PVDF filma sa hijerarhijski poroznom strukturom povećana je na 96,6% sa padom temperature od 1,06°C pod sunčevim zračenjem od 600 V•m–2, što ukazuje na dobar potencijal za dalju strukturu hlađenja kao nanokompozit i obložen. tkanine forme.*

Ključne reči: *Upravljanje toplotom, pasivno hlađenje, razdvajanje faza, poroznost, rastvarač.*

1. INTRODUCTION

With the aggravation of global warming and extreme weather, cooling demand has witnessed a continuous increase and is expected to increase tenfold by 2050 [1]. Radiative cooling without any pollution and energy consumption has drawn worldwide attention in the past few years [2]. Having a cooling feature with the management of sun and body radiation energy components, functional clothes used in sports and working environments, which have an increasing market in the world will provide higher performance due to late or less fatigue during sports/work with increased comfort. Passive radiative cooling performance could be enabled by spectrally selective materials, which simultaneously have high solar reflectance and infrared thermal emittance as these features help simultaneously reflecting sunlight and radiating infrared thermal radiation. Recently, multilayer photonic structures, composite structures with distributed particles, metamaterials, biomaterials, bio-inspired materials, and porous structures are used for cooling [3]. Nonetheless, developing these materials/structures generally requires sophisticated processing steps and costs which limits their acceptability for large-scale production and cost-effectiveness. Therefore, a facile, cost-effective, and highly efficient approach is highly desirable for widespread practical radiative cooling applications. In this respect, recent studies in developing radiative cooling materials have focused on porous polymer films for their high solar reflection and mid-IR emission. Constructing porous polymer films for passive radiative cooling has proved an efficient way to dissipate heat to cold outer space in the form of thermal radiation and concurrently reflect incident sunlight without additional energy input [4]. Among production methods of porous radiative cooling films, nonsolvent-induced phase separation has attracted considerable attention owing to their cost-effectiveness and wide applicability [5]. The passive radiative cooling performance of these porous films correlate with their porous structures and unfortunately porous structure formed by nonsolvent-induced phase separation could not be finely regulated. In this study, PVDF films with porous structures using two solvents were produced with varying solubility parameters and water.

2. MATERIALS and METHODS

2.1.Materials

For production of passive radiative cooling film, PVDF polymer (Kynar 720), a spectrally selective polymer with a high emissivity [6] was used. Additionally, PVDF offers excellent processability, resistance to aging, weathering, UV radiation, and robust mechanical properties, making it suitable for various textile applications. N, N dimethyl acetamide (Sigma Aldrich) and acetone (Acros Organics) were used as solvent/co-solvent. In one-step non-solvent-induced phase separation film formation method, deionized water was used as non-solvent.

2.2. Methods

PVDF porous films having different polymer concentrations (5 and 10 wt. %) were produced trough one-step non-solvent-induced phase separation method which is simpler and cheaper compared to the other methods [7]. In the first step, PVDF powder at 5 and 10 wt. % was dissolved in N, N dimethyl acetamide and acetone with same ratios at 50°C in a three-sipped flask for 6 h under 400 rpm magnetic stirring. Then appropriate amounts (other solvent amounts were arranged accordingly) of water (3, 5, and to 7%) were added dropwise by a syringe pump at a feeding rate of 0.2 ml/min for another 1 h until it became clear. In the last step, the solutions were cast in the form of a thin layer of 300-400 μm thickness into petri-dishes and dried for 6 h at 120°C.

2.3. Characterization

Surface morphology and cross-sections of the PVDF films were analyzed by using scanning electron microscope (SEM, Fei Quanta FEG 250) with an accelerating 20 kV voltage and 10 μA current.

Cooling performance of the PVDF films were tested using a designed hotplate system equipped with a hotplate simulating skin (34°C), 8 sensors, a halogen lamb for sun simulation and a data acquisition system. The films were placed on the hot plate face side up under the lamb (600 W m^{-2}) at a distance of 25 cm. Environmental temperature was 22-26°C and relative humidity was 49-50% during the tests. The test was starting with a 1-minute stabilising part while lamb is off followed by a 10-minute lamb-on part to see the cooling performances and another 10-minute lamb-off part to see the heat releasing performances of the films. Temperatures were recorded with a frequency of 5-second and mum three replications were conducted for each sample.

Indirect emissivity measurements of the films were carried out by the mentioned hotplate system combined with an IR camera (Fluke Ti100 Thermal Imager). The films were placed on the hotplate (34°C) which was covered with black fabric having 99% emissivity. The sensors were located both on the black fabric and the films. After a stabilizing period of 1 min, the upper surface temperatures of the films were recorded as the actual temperature.

The thermographic images of the films were taken simultaneously with the IR camera placed at a distance of 25 cm. Finally, the recorded thermographic images were processed using SmartView Classic 4.4 software and emissivity values were determined by adjusting the emissivity in the thermal camera until the apparent temperature read by the IR camera was equal to the average temperature measured with the sensors.

3. RESULTS

In this study, radiative porous cooling films were prepared trough one-step non-solvent-induced phase separation method using co-solvent and non-solvent by the multistage solvent displacement. Effects of the polymer and water concentrations on the pore formation and cooling performance were investigated. SEM images of PVDF porous films (Figure 1 and Figure 2), show that films produced without water has a dense structure. As the water content was increased, especially for 10 wt. % polymer content, heterogenous pore formation on both surface and cross-sections increased. PVDF films having 10 wt.% polymer and 3% water concentrations had the most porous structure with smaller droplets and wrinkles. 5 wt.% polymer concentration led to the formation of larger droplets and wrinkles. Within the film production plan, gelation was occurred during the process of adding 7% water and film could not be produced for 5 wt.% polymer content. The pore formation within the films may be result of accelerating N,N dimethyl acetamide evaporation with acetone having low boiling point and changing solvent polarity and solubility, hence phasing out of PVDF polymer from solvent-non-solvent system [8].

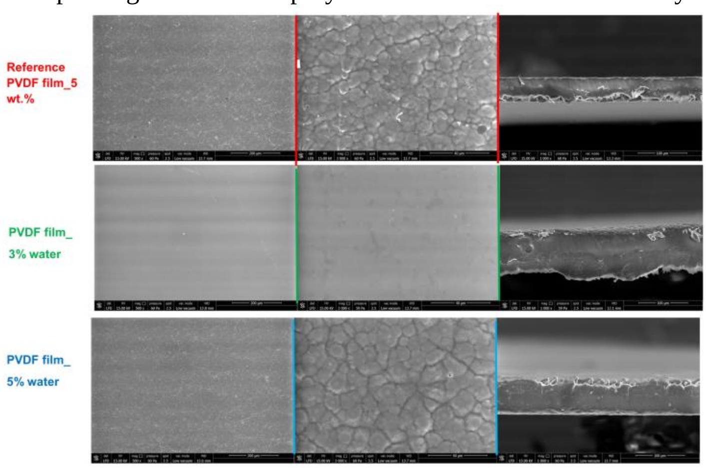

Figure 1: Surface morphology and cross-section images of PVDF films having 5 wt. % polymer and 3 and 5% water contents.

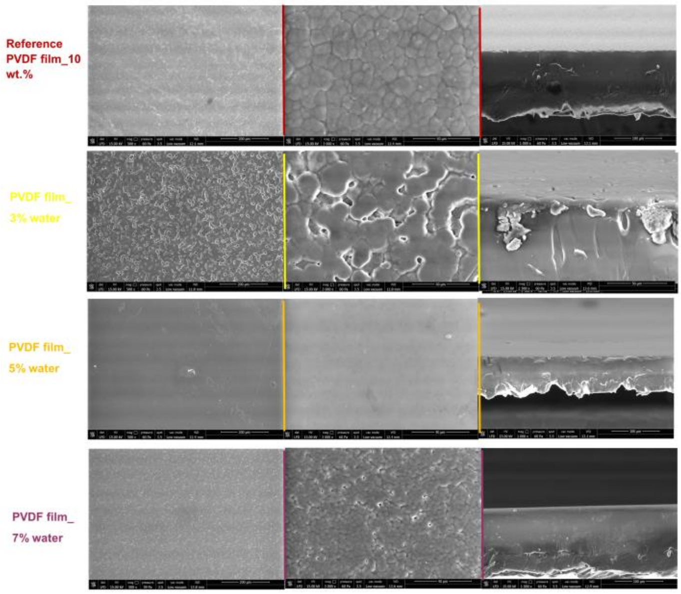

Figure 2: Surface morphology and cross-section images of PVDF films having 10 wt. % polymer and 3, 5, and 7% water contents.

Cooling performances of the PVDF films were reported in Figure 3 and 4. As can be seen in Figure 3 and Figure 4, cooling effect was obtained with the produced porous films.

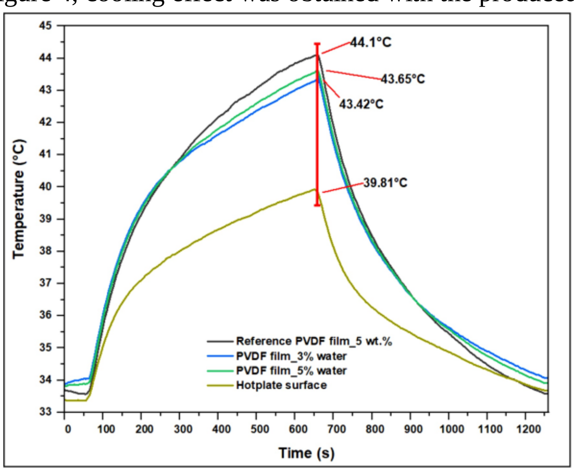

Figure 3: Cooling performance test results of PVDF films having 5 wt. % polymer and 3 and 5% water contents.

Porous films specially produced with 10 wt.% polymer and 7% water contents exhibit a temperature drop of ~1.06 °C compared to their nonporous forms. Meanwhile, this film also possess an infrared emittance of ~96.6% over the atmospheric transparency window (8-13 µm), providing a cooling effect by enabling higher heat loss to the colder outer space. On the other hand, by adding 3% water to the same polymer ratio, a porous film structure was obtained, cooling effect could not be obtained.

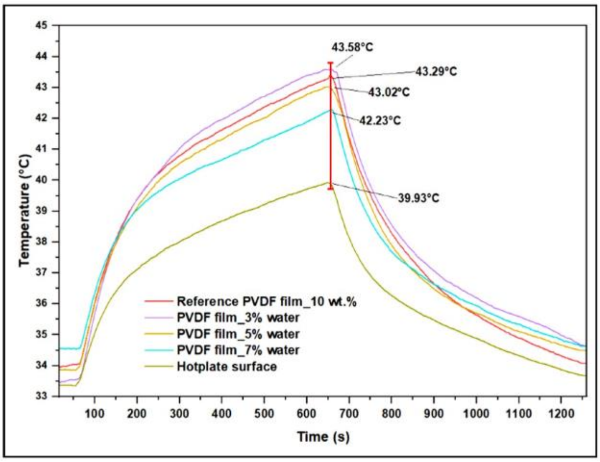

Figure 4: Cooling performance test results of PVDF films having 10 wt. % polymer and 3, 5, and 7% water contents.

According to the test results of the infrared emissivity given in Table 1, the emissivity of the films increased with polymer concentration and the pore ratio. The highest emissivity value (96.6%) was measured for the film produced with 10 wt.% polymer and 3% water concentrations while the lowest value was obtaine for sample produced with 5 wt.% polymer without water (90.6%). The produced PVDF films especially porous ones have higher infrared emissivity with the effect of many functional groups/bonds such as C-F and C-O emit overlapping with the atmospheric transmittance window and porous structure [9].

Table 1: Emissivity measurement results of the film samples

Sample code	**Emissivity (%) (at 34°C) [S.D]**
Reference PVDF film_5 wt.%	90.6 [0.19]
PVDF film_5 wt.%_3 % water	91 [0.01]
PVDF film_5 wt.%_5 % water	91.8 [0.03]
PVDF film_10 wt.%	92 [0.06]
PVDF film_10 wt.%_3 % water	92.6[1.08]

PVDF film_10 wt.%_5 % water	95 [1.08]
PVDF film_10 wt.%_7 % water	96.6 [1.08]

4. CONCLUSION

Radiative cooling PVDF films with porous structures were prepared by non-solvent induced phase separation method containing two solvents water as non-solvent. PVDF films having 10 wt.% polymer and 7% water concentrations having the most porous structure, exhibited and an infrared emissivity of 96.6%. These films achieved a maximum cooling temperature of approximately 1.06°C under a solar irradiance of 600 Wm^{-2}. The results indicate that the proposed films present a potential for radiative cooling textiles in the form of coating or lamination.

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