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SOĞUTUCU PAMUKLU KUMAŞLAR**

**PASSIVE DAYTIME COOLING COTTON FABRIC WITH  
ADAPTIVE COMFORT FEATURES**

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## **PASSIVE DAYTIME COOLING COTTON FABRIC WITH ADAPTIVE COMFORT FEATURES**

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**ABSTRACT:** Passive daytime radiative cooling materials have attracted increasing attention due to their great potential for energy saving and the possibility to meet the need for smart clothes. However, the practical application of passive daytime cooling material in the textile industry is greatly affected by comfort components and also physical/mechanical properties that require optimization. Herein, it was aimed to develop a thermoregulating fabric using zinc oxide nanoparticles (ZnO), which provide dynamic and passive control of the infrared transmission, by adapting to the ambient temperature. For this aim, the cotton fabric was coated with a nanocomposite treatment composed of ZnO nanoparticles and temperature-responsive shape memory polyurethane (SMPU) matrix, obtaining strong scattering effects to control the wideband transmission of thermal radiation and also adaptive comfort features based on shape memory function. By reflecting sunlight of SMPU-ZnO nanocomposite coating, the cotton fabric can reach an average temperature drop of  $\Delta$  2.2°C and 0.4°C compared to the raw ones under direct sunlight and also indoor at 40°C, respectively. Also, SMPU and SMPU-ZnO nanocomposite coated cotton fabric exhibited dynamic air and water vapour permeability hence adaptive comfort features. Owing to passive cooling and also adaptive comfort features besides the simple production process, this smart fabric is promising to be widely used in sports or protective clothing areas.

**Keywords:** Passive daytime radiative cooling, zinc oxide, shape memory polyurethane, dynamic breathability

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**ÖZ:** Pasif gündüz radyatif (güneş ve vücut radyasyon enerji bileşenlerinin yönetimi) soğutucu malzemeler, büyük enerji tasarrufu potansiyelleri ve akıllı kıyafet ihtiyacını karşılama olasılıkları nedeniyle artan bir ilgi görmektedir. Bununla birlikte, pasif gündüz soğutma malzemelerinin tekstil endüstrisindeki pratik uygulaması, optimizasyon gerektiren konfor bileşenleri ve fiziksel/mekanik özelliklerden büyük ölçüde etkilenmektedir. Bu nedenle, bu çalışmada infrared iletimin pasif kontrolünü sağlayan çinko oksit nanopartikülleri kullanılarak ortam sıcaklığına uyum sağlayabilen ısı düzenleyici bir kumaşın geliştirilmesi amaçlanmıştır. Bu amaç doğrultusunda pamuklu kumaş, termal radyasyonun geniş bant iletimini kontrol etmek için güçlü saçılma etkisi sağlayan çinko oksit (ZnO) nanopartikülleri ve şekil hafıza fonksiyonuna bağlı uyarlanabilir konfor özellikleri sağlayan sıcaklık duyarlı şekil hafızalı poliüretan (SMPU) matristen oluşan nanokompozit kaplama ile kaplanmıştır. Kaplanmış pamuklu kumaşlarda SMPU-ZnO nanokompozit kaplamanın güneş ışığını yansıtması ile doğrudan güneş altında ve ayrıca 40°C'de iç mekânda ham kumaşlara kıyasla sırasıyla  $\Delta$  2,2°C ve 0,4°C'lik bir ortalama sıcaklık düşüşü elde edilmiştir. Ayrıca, SMPU ve SMPU-ZnO nanokompozit ile kaplanmış pamuklu kumaşlar dinamik hava ve su buharı geçirgenliği dolayısıyla uyarlanabilir konfor özellikleri sergilemiştir. Basit üretim sürecinin yanı sıra pasif soğutma ve uyarlanabilir konfor özellikleri sayesinde bu akıllı kumaş, spor veya koruyucu giysilerde yaygın olarak kullanılmayı vaat etmektedir.

**Anahtar kelimeler:** Pasif gündüz radyasyonlu soğutma, çinko oksit, şekil hafızalı poliüretan, dinamik nefes alabilirlik

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## 1. INTRODUCTION

With global warming, the increasing trend in outdoor temperatures and energy requirements for indoor insulation/cooling systems have forced the design of personal cooling systems by managing natural sources (solar and body radiation) without extra energy consumption. Therefore, developing advanced materials with body thermal radiation control for thermoregulation has been widely reported in recent years. Recently, passive daytime radiative cooling, one of the reported methods that can achieve the cooling effect by reflecting the sunlight (wavelengths  $\square$  0.3-2.5  $\mu\text{m}$ ) and radiating the heat to the cold outer space through the atmosphere's window (wavelengths  $\square$  8-13  $\mu\text{m}$ ) without consuming any energy has attracted considerable attention [1]. These cooling textile materials could be developed with new materials and structures, such as controlling the reflectance [2-4] and emissivity [5-10] including photonic structures [11-14], nanoparticle-doped materials [15-17], and metamaterials [18, 19]. Among these methods and materials, a common method to achieve daytime cooling fabrics is using reflective materials in micro/nanoporous films, filaments, finishing treatment for fabrics, and nanofiber [20]. Although the nanoporous composite films including nanoparticles with spectral selectivity such as titanium dioxide, zinc oxide,  $\text{FeO}_3$ , and silicon dioxide [21, 22] and filaments [23] had a cooling effect of 1.6°C-13°C compared to normal cotton fabrics, the detailed mechanical and also wearability tests were not carried out in these studies and the comfort test results did not give sufficient results due to the rigid polymer structure. Besides these nanoporous films and filaments, passive daytime cooling fabrics have been developed by coating textile materials with spectral selective nano/microparticles-polymer. According to this principle, Zhong et al. [24] fabricated a multifunctional cotton fabric for outdoor personal radiative cooling by coating fabric with spectral selective aluminium phosphate particles and superhydrophobic polydimethylsiloxane polymer. This radiative cooling textile enables simulated skin to avoid overheating by more than 4.4°C, compared to conventional textile like cotton under the same outdoor environment. Similarly, Wei et al. [25] coated cellulose acetate knitted and polyester organza woven fabric with aluminium oxide nanoparticles dispersed-cellulose acetate. These modified textiles reduced the temperature of simulated skin by 2.3°C-8°C in the sunshine and also could avoid the overheating of actual human skin by 0.6°C-1.0°C in a real-life test procedure. In these studies, the requirement for nanoparticle-containing coating/laminating thicknesses causing great decreases in permeability properties, especially in stiffness and also the necessity of having a high pore volume to reflect the sun's rays, and the inability to control the pore sizes, have attracted attention. Alternatively, the passive cooling textile materials have been fabricated by finishing treatment process which could reduce the disadvantages of coating/laminating applications in fabric properties and the chemicals used in passive cooling structures. Huang et al. [26] constructed a passive cooling and multifunctional cotton fabric with high sunlight reflectivity of 83%, infrared emissivity of nearly 90%, reducing the human body surface 3.1°C-4.7°C under direct sunlight, superhydrophobic,

UV-resistant and self-cleaning features by depositing potassium titanate whiskers-polydimethylsiloxane on cotton fibers. Also, Shams-Nateri et al. [27] developed passive cooling cotton fabric by applying titanium dioxide nanopigments with different diameters and concentrations on cotton fabric with a crosslinker. In another study [28] in which titanium-silica particles called Janus particles, were applied to cotton fabric without using polymers and a reflectance performance of 79% with a better cooling performance was obtained than reference cotton fabric as a result of near-infrared radiation reflection and heat dissipation/storage. Another similar study used different crystalline titanium dioxide particles on cotton fabric by reflecting method, and they found that oxidized titanium dioxide gave a limited cooling effect of a maximum 3.9°C. Recently, electrospinning technology was used to prepare fibers with micro-nano pores to realize daytime passive radiative cooling [29-33]. Compared with other technologies, it has obvious advantages of low production cost and the ability of adjusting fiber diameter by changing the process parameters. In addition, the secondary structure (such as porous, hollow or core-shell) and disordered arrangement of these fibers can effectively scatter visible light and emit infrared light. On the other hand, this method is not suitable for ordinary fabrics such as cotton, and the preparation process is complicated.

Despite the fact that the transfer of these cooling technologies in all the studies and methods summarized above to textile materials in the wearable form while preserving other physical/mechanical and also adaptive thermal/moisture management remains a great challenge and requires optimization. Alternatively, this study was focused to develop thermoregulating cotton fabrics through the combined use of passive daytime radiative cooling material and temperature-responsive polymer. The cotton fabric was coated by spraying nanocomposite treatment composed of ZnO nanoparticles and SMPU matrix. This nanocomposite treatment design provides strong scattering effects of ZnO nanoparticles having high solar reflectivity and refractive index  $\approx$  2 [1, 21, 34] to control the wideband transmission of thermal radiation also adaptive comfort features based on the shape memory function of the SMPU matrix. In this way, it will be possible to control the reflectivity of conventional cotton fabrics without spending any energy, and also provide comfort in all weather conditions with this process, which is promising to be widely used in sports or protective clothing areas, and so forth.

## 2. MATERIALS AND METHODS

In this study, 100% cotton fabric (areal density of 134 g/m<sup>2</sup>, yarn densities of 40 warp/cm and 38 weft/cm) was treated with ZnO reinforced SMPU nanocomposite. ZnO nanoparticles (30-50 nm particle size, Nanografi, Turkey) were used as passive cooling material due to their high solar reflectivity (nearly 80%) and high refractive index  $\approx$ 2 as well as little absorption from visible (400 nm) up to mid-infrared wavelengths (16  $\mu\text{m}$ ) [21]. SMPU (pellet-type MM-3520, SMP Technologies Inc., Japan), having a suitable transition temperature  $\sim$ 32°C for body applications, was used as a temperature-responsive polymer leading to adaptive comfort

features. Cotton fabric was treated with SMPU-ZnO nanocomposites by spraying method. For preparing nanocomposite solution, SMPU solution was prepared in N, N-dimethylformamide (DMF) (Sigma Aldrich, USA) with 5 wt% polymer concentration by mixing at 60°C for 6 h. Then, this solution was reinforced by dispersing 3 wt% of ZnO nanoparticles via ultrasonic stirring (Sonopuls HD 2200, Bandelin Sonopuls Corp.) for 1 h at room temperature. Finally, the prepared SMPU-ZnO nanocomposite solution was applied to the cotton fabric homogeneously with a spraying system (Alfajet W-77S, Turkey) at a pressure of about 0.3 MPa and a distance of 60 cm. The amount of solution sprayed was 0.1 mL/cm<sup>2</sup>. The SMPU and nanocomposite treated cotton fabrics were dried at 85°C for 3 min and cured at 120°C for 2 min.

The areal density and bending rigidity of the fabrics were assessed according to TS 251:2008 and ASTM D 1388-92:2002, respectively. To observe the breathability and changes in pore structures of the treated fabrics with temperature, dynamic air permeability was determined according to ASTM D737-04:2012 by FX Textest 3300 under 100 Pa pressure (James Heal Corp., UK) at different fabric temperatures (20°C, 40°C, and 60°C) obtained by a heated plate and controlled by a thermal camera (Fluke Ti100 Thermal Imager). Water vapour permeability of the fabrics was also measured under different environmental temperatures (20°C, 40°C, and 60°C). Passive radiative cooling performances of the treated fabrics were determined for indoor and outdoor/daylight environments. The indoor cooling performance was tested by a hot plate with surface temperatures of 25°C and 40°C under an ambient temperature of ≈21°C and 59 RH%. Measurements were conducted from the outer faces of the fabrics on a hotplate by a data logger system (MA25903S, Ahlborn) including two K-type thermocouples, and a probe for ambient temperature and humidity. The samples were placed on the hot plate and the upper surface temperature of the fabrics was recorded by the thermocouples after stabilizing the outer surface temperature for 25 min. The outdoor cooling performances were determined for a real outdoor scenario (Isparta, Turkey) during a clear and sunny autumn day with a temperature between 26-28°C with a relative humidity of 13-14% by decreasing the convective effect as much as possible. After the outer surface temperature was stabilized, the bottom surface temperature of the samples placed on a black surface was detected and recorded by the thermocouples.

### 3. RESULTS AND DISCUSSION

The areal density and bending rigidity of raw and treated fabrics were compiled in Table 1 with their statistical analysis results. According to the results, significantly minimum areal density values belonged to the raw cotton fabric as expected. SMPU and SMPU-ZnO nanocomposite treatments created statistically identical areal density values, which are significantly higher than the value of raw fabric. On the other hand, bending rigidity values increased significantly for SMPU and SMPU-ZnO nanocomposite treated fabrics. Increased bending rigidity can be attributed to the polymer/nanocomposite coating on fiber surface and deposition

among the fibers causing more difficult chain movements and preventing their relative motion during bending [35].

**Table 1.** Areal density and bending rigidity of the fabrics

Samples	Areal density (g/m <sup>2</sup> ) [SD]	Bending rigidity (mg.cm) [SD]
Raw cotton fabric	134 <sup>a</sup> [1.69]	108.29 <sup>a</sup> [12.06]
CO-SMPU	152 <sup>b</sup> [2.64]	477.53 <sup>b</sup> [48.07]
CO-SMPU-ZnO	155 <sup>b</sup> [1.35]	577.45 <sup>c</sup> [37.05]

Note: Letters show statistical differences among the results ( $p < 0.05$ ).

Air permeability, which gives an idea about porous structure, hence both heat and sweat transfer within the fabric, was dynamically measured at different fabric temperatures. The effect of SMPU/SMPU-ZnO nanocomposite treatment and temperature on air permeability was evaluated by Univariate ANOVA analysis. According to the results, SMPU/SMPU-ZnO nanocomposite treatment, temperature, and two-way interactions of treatment-temperature all have statistically significant effects ( $p < 0.05$ ) on the air permeability, meaning dynamic pore structure change based on temperature-responsive shape memory function. Results of air permeability measurements and differences among results at different temperatures are given in Figure 1(a) and (b), respectively. At temperatures (20°C) below  $T_g$  of SMPU (32°C), the air permeability results of the treated fabrics were lower than the raw ones as expected due to the polymer covering spaces among yarns. The temperature-responsive performance of the SMPU and SMPU-ZnO treatments was apparent for the temperatures above  $T_g$  of SMPU (40°C and 65°C) and there are increase trends for both applications, SMPU-ZnO being lower (Figure 1 (b)). The dynamic air permeability feature based on temperature-sensitive free volume [36] and micro-Brownian motion [37-39] change of SMPU matrix, enables to adjust insulation and cool down the body by air convection in extreme weather and during high activity levels.

As known, air-permeable materials allow water vapour to pass through and therefore water vapour permeability, a crucial parameter affecting the comfort properties of clothing systems is closely related to the air passing ability of the material. Similarly, water vapour permeability of the fabrics changed significantly ( $p < 0.05$ ) with SMPU/SMPU-ZnO nanocomposite treatment, temperature, and two-way interactions of them. As in the air permeability, SMPU and SMPU-ZnO treated cotton fabrics had dynamic and higher permeability at temperatures above  $T_g$  of SMPU (40°C and 65°C), based on the shape memory performance of the SMPU matrix, SMPU-ZnO being lower (Figure 2). The dynamic change of both air and water vapour permeability values with body/environment temperature shows that the adaptive comfort properties could be obtained with SMPU and SMPU-ZnO nanocomposite treatment.

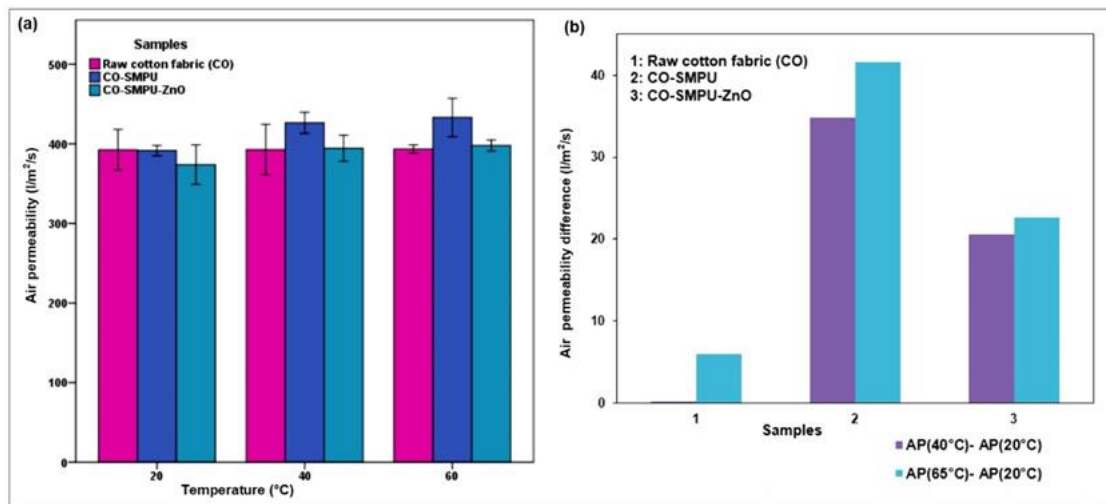


Figure 1. Adaptive air permeability values (a) and differences according to temperature (b)

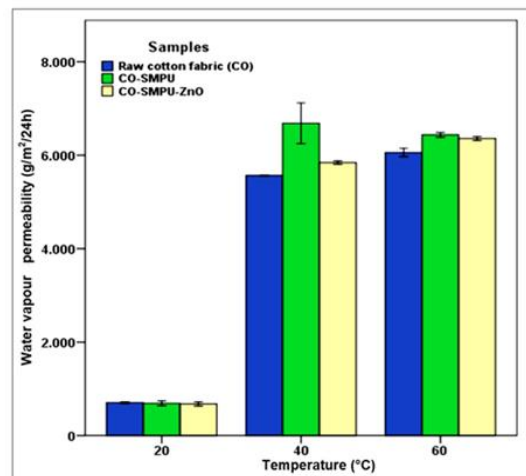


Figure 2. Adaptive water vapour permeability values at different temperatures

Passive radiative cooling performances of the treated fabrics were carried out under indoor and outdoor/daylight environments and results were given in Figure 3 and 4, respectively. According to cooling performance results (Figure 3); the indoor surface temperatures of both treated fabrics decreased more at 40°C (0.6°C lower than the raw ones) as a result of increased pore ratio within the nanocomposite polymer with temperature based on shape memory function. The increased pores including still air within the structure are thought to decrease thermal conductivity, hence lower outer surface temperature. The difference between the cooling performances of CO-SMPU and CO-SMPU-ZnO can be attributed to the higher conductivity and existence of ZnO within the pores of the nanocomposite. The outdoor results (Figure 4) are in harmony with 40°C indoor results for porosity enhancement above  $T_g$  of SMPU. Besides, the solar reflection effect of ZnO is apparent that while SMPU treatment created an increase in the inner surface of the sample, SMPU-ZnO created a temperature decrease of 2.2°C, 0.5°C lower than the raw fabric. Moreover, as the particle volume fraction increases with ZnO within SMPU matrix, conductivity of the nanocomposite increases, leading to a cooling effect by dissipating body radiative

heat to the environment. With SMPU-ZnO treatment, the cotton fabric shares a part of the heat dissipation assignment of the human body, and the conventional fabric changes into a passive radiative cooling textile, enhancing comfort under hot environments.

#### 4. CONCLUSIONS

In this study, a passive dynamic thermoregulation fabric was successfully designed and fabricated through the combined use of passive daytime radiative cooling material and temperature-responsive shape memory polymer. The passive cooling fabrics made of temperature-responsive SMPU-ZnO are worth investigating for both indoor and outdoor conditions besides their dynamic breathability function. The mentioned breathability and cooling performances enable improvements for two basic criteria of thermal comfort under high activity conditions of sports or protective clothing areas. The cooling performance is thought to be more apparent for daylight conditions under higher temperatures of summer days.

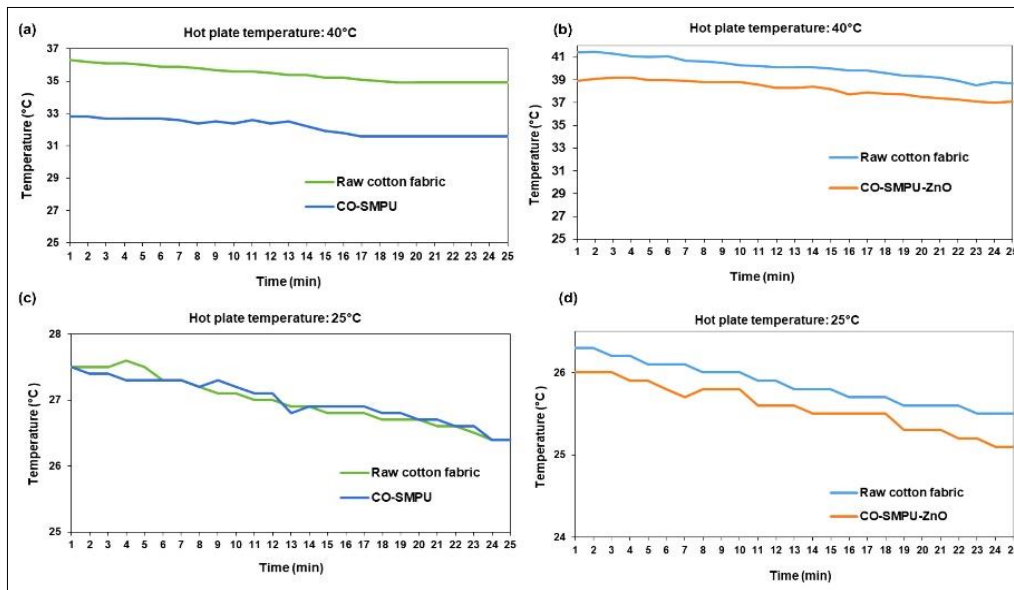


Figure 3. Indoor cooling performance measurement

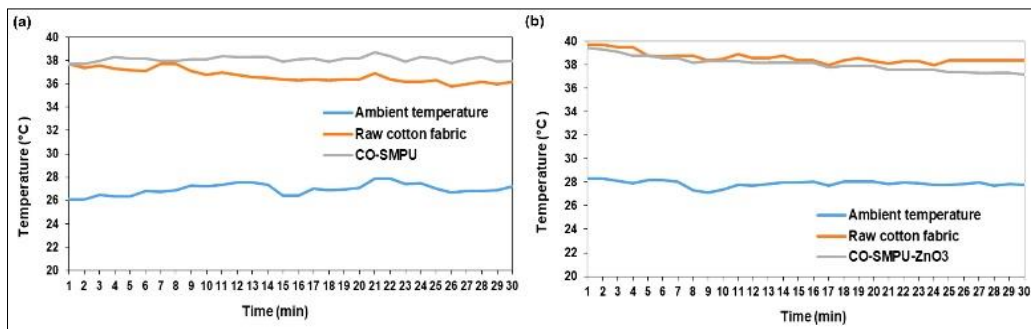


Figure 4. Outdoor cooling performance measurements

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