CHARACTERIZATION AND THERMOGRAPHIC ANALYSIS OF FIR EMITTING CERAMIC NANOPARTICLE EMBEDDED FILMS

Ashik Md Faisal[1,2,3,4], **Fabien Salaün**[1,2], **Stéphane Giraud**[1,2], **Ada Ferri**[3], **Yan Chen**[4], **Lichuan Wang**[4]

[1]*University of Lille Nord de France, F-5900 Lille, France*
[2]*ENSAIT, GMTEX, F-59100, Roubaix, France*
[3]*Politecnico di Torino, DISAT, Corso Duca degli Abruzzi 24, 10129, Turin, Italy*
[4]*Soochow University, College of Textile and Clothing Engineering, Suzhou, Jiangsu, 215123, China*
ashik-md.faisal@ensait.fr

ABSTRACT

Far-infrared (FIR) ray emitting textiles are claimed to be functional textiles improving health and well-being. FIR ray emitting textiles are derived from traditional fibers by incorporation of ceramic nanofillers with appropriate electromagnetic absorption and emission properties. The purpose of this research is to analyze the thermographic effects of ceramic nanofiller based polyurethane films and characterize their physical properties. Water-based polyurethane binder was separately incorporated with Aluminum Oxide, Silicon Dioxide, Titanium Dioxide, and Silicon Carbide to make a thin layer of film by Sonication technique. Different intense of IR-emissive layer was found with different concentration of ceramic nanofiller into the films. Reflection and transmission at the FIR range were measured with an integrating sphere by Fourier-transform infrared spectrometer. Thermal properties of films were investigated by thermogravimetric analysis (TGA) and by differential scanning calorimetry (DSC). The results showed that the thermophysical properties are strongly dependent on the nature of nanofillers. In addition, physical properties like tensile strength and contact angle were also measured to evaluate the feasibility of the films towards thermal comfort.

Key words: FIR, ceramic nanoparticle, thermal comfort, functional textiles.

1. INTRODUCTION

Far infrared radiation (FIR) is a kind of electromagnetic radiation that has been investigated for the resonance of the human body. The wavelength range of Far infrared radiation (FIR) is 0.76~1000μm and the absorption wavelength (resonance wavelength) range of most organic compounds is 6~14μm[1]. Resonance occurs when the material close to the human skin emit or reflect the same wavelength as the human skin. Resonance increases the circulation of the blood and produces heat. Ceramic nanoparticles, such as aluminum oxide, silicon dioxide, titanium dioxide, silicon carbide have been incorporated into the textile to utilize the far infrared radiation effect of ceramics[2].

Radiative thermal management has become an effective way to achieve both heating or cooling effect[3, 4]. By controlling the FIR reflectivity, transmissivity and emissivity, different heat transfer mechanism (heating or cooling) can be achieved. The purpose of this study was to enhance the thermal performance of the textile material by applying different ceramic nanoparticle to the hydrophilic polyurethane film laminate. The effect of different ceramic nanoparticles was evaluated with thermogravimetric analysis and FTIR.

2. MATERIALS AND METHODS

Water-based polyurethane binder (supplied by Archroma, in this article, indicated as B4 due to 40% solid content) was separately incorporated with Aluminum Oxide (particle size 80~120nm), Silicon Dioxide (particle size 5~50nm), Titanium Dioxide (particle size 70~100nm), and Silicon Carbide (particle size 1~20µm) to make a thin layer (~0.6mm) of film (using Teflon mold) by sonication technique. 5% of ceramic nanoparticle (on the basis of the solid content of end product) was dispersed to water using sonication for one hour and then water-based polyurethane binder (B4) was added slowly to the mixture. Further sonication and magnetic stirrer have used to make the solution more uniform. The film was then dried at room temperature for one day. Further drying was done in an incubator at 95°C and then cured at 130°C for 6 minutes. FTIR spectrometer from Pike Technologies (integrated with a reflective gold inner coating) was used[5, 6] to measure the spectral reflectance (ρ) and transmittance (τ) at the wavelength range of 2~18µm in standard atmospheric condition and then emissivity (ε) was calculated according to Kirchhoff's law by the equation $\varepsilon = 1 - \rho - \tau$ [3]. TGA test was performed at the temperature range of 20~700°C at a heating rate of 10°C per minutes with a nitrogen atmosphere. DSC test was performed at the temperature range from 30~100°C with a heating rate of 10°C per minutes and the atmosphere was purged with nitrogen at a constant flow (50 ml/min) during the experiments. The thermal program used as- isothermally held at 100°C for 3 minutes, ramp and again isothermally held at -30°C for 3 minutes (run for the dual cycle). The contact angle for different liquids was measured by DIGIDROP contact angle meter. Tensile Properties were tested according to the NF EN ISO 521 with a cell force of 1kN and a drawing speed of 1 mm/min. All the tests have been done at a standard atmosphere (20 ± 2°C temperature and 65 ± 5% relative humidity).

3. RESULTS AND DISCUSSION

The radiative properties such as transmittance and reflectance of non-conducting materials (such as textiles, ceramics, polymers) do not vary from normal for incidence angles until a certain range (less than 70°). The effect of different ceramic nanoparticle on the radiative properties of the films has been shown in Figure 1-4.Infrared property characterizations of Al2O3 incorporated films. Measured total FTIR (a) reflectance, (b) transmittance, (c) emissivity, and (d) emissivity at the resonance wavelength. Overall lower transmittance was reported for the deposition of ceramic nanoparticle even though the reflection shows no significant effect except the silicon carbide where the reflection was reported very low. Each of the samples exhibits overall similar spectral patterns with an exception between 12-14µm wavelength where the overall emissivity for the incorporated samples shows higher values than the standard one. However, these amounts of variations do not affect the conclusion of the study and the effect is less pronounced as the overall emissivity is already high at these range of wavelengths.

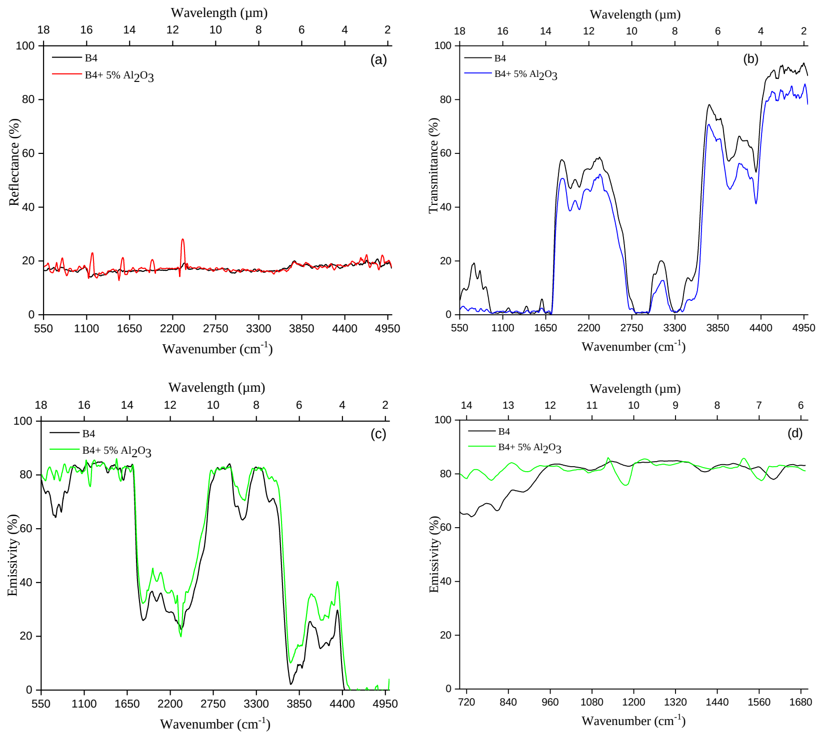

Figure 1. Infrared property characterizations of Al_2O_3 incorporated films. Measured total FTIR (a) reflectance, (b) transmittance, (c) emissivity, and (d) emissivity at the resonance wavelength

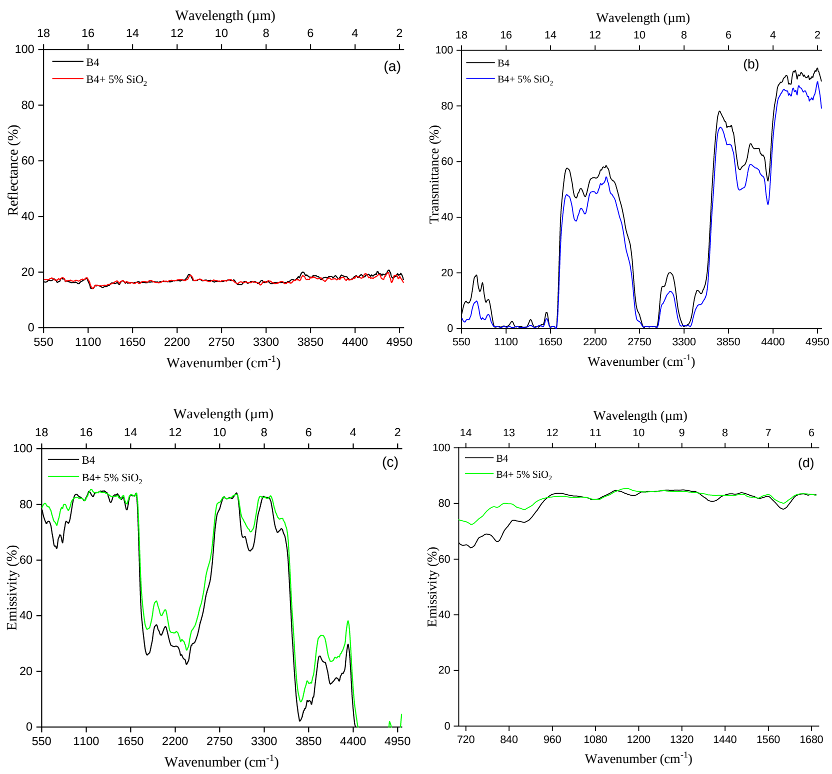

Figure 2. Infrared property characterizations of SiO_2 incorporated films. Measured total FTIR (a) reflectance, (b) transmittance, (c) emissivity, and (d) emissivity at the resonance wavelength

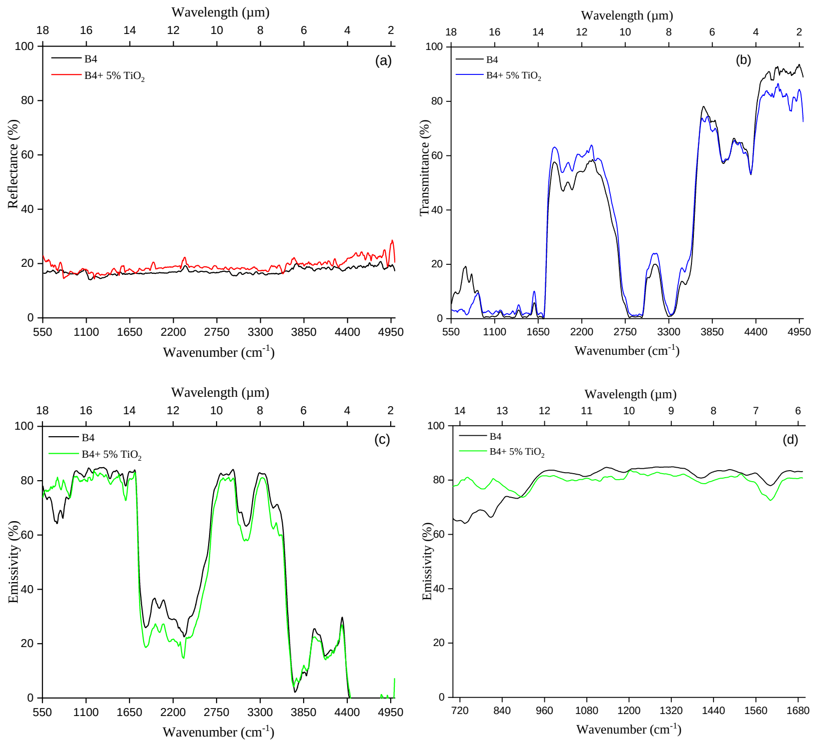

Figure 3. Infrared property characterizations of TiO_2 incorporated films. Measured total FTIR (a) reflectance, (b) transmittance, (c) emissivity, and (d) emissivity at the resonance wavelength

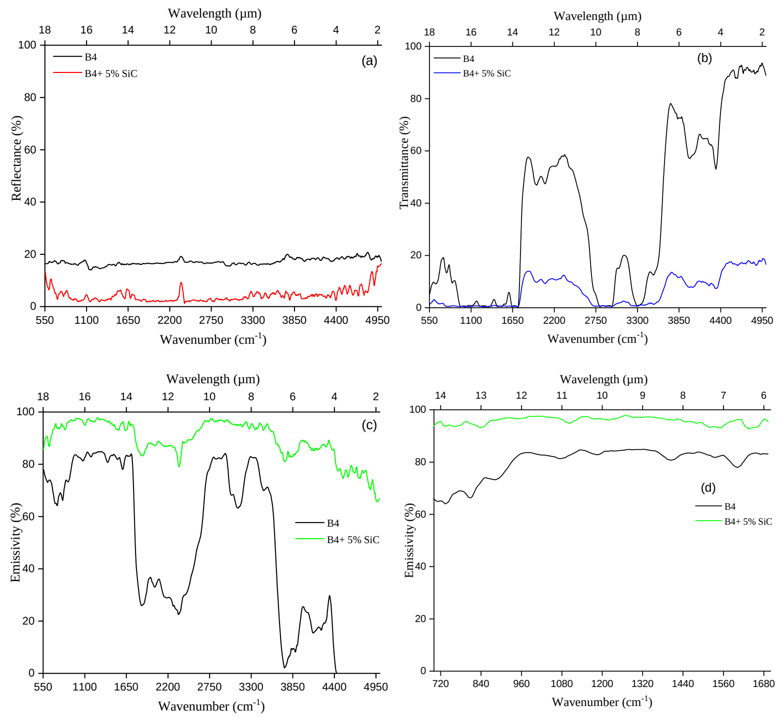

Figure 4. Infrared property characterizations of SiC incorporated films. Measured total FTIR (a) reflectance, (b) transmittance, (c) emissivity, and (d) emissivity at the resonance wavelength

Thermal behavior of B4 and other films displayed single step degradation (Figure 5). The decomposition of B4 characterized by the onset temperature at 5% weight loss ($T_{onset5\%}$) started at 316°C. $T_{onset5\%}$ for other films were reported as 315°C (Al_2O_3), 318°C (SiO_2), 312°C(TiO_2), 318°C (SiC) The main decomposition peak of B4 corresponding to the B4 backbone decomposition took place at 422°C. Furthermore, the char residue remaining in B4 at 600°C was reported lower (0.24%) than the ceramic incorporated films (2.83~5.61%). The thermogravimetry data of different films have been shown in Table 1.

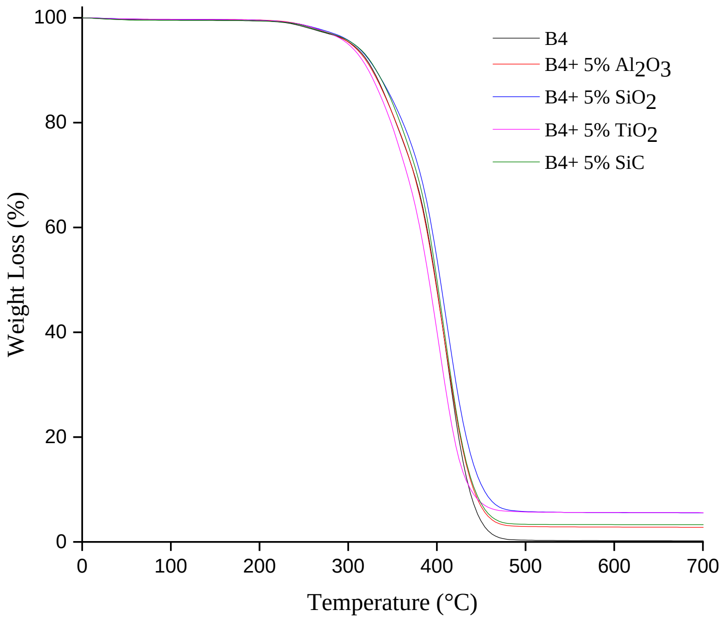

Figure 5. TG curves of different films

Table 1. Thermogravimetry data of different films

Sample ID	$T_{onset5\%}$ (°C)	T_{max} (°C)	Residue at 600°C (%)
B4	316.24	421.95	0.24
B4+ 5% Al_2O_3	315.56	419.17	2.83
B4+ 5% SiO_2	318.60	416.74	5.58
B4+ 5% TiO_2	312.88	411.75	5.61
B4+ 5% SiC	318.60	416.35	3.30

The DSC analysis graph of the B4 and the ceramics are shown in Figure 6. It is obvious from the graph that there is no distinct exothermic heat upon the first heating step. It can be concluded that all the samples were fully cured. The inflection slope of DSC graph for the glass transition process was not being reported in any literature. The lower value of inflection slope indicates that the material is more stable upon the cooling process. The first heating step shows the highest value of inflection slope compared to the second heating step. For the first heating step, aluminum oxide shows the lowest value of inflection on the other hand titanium dioxide shows the highest value of inflection slope.

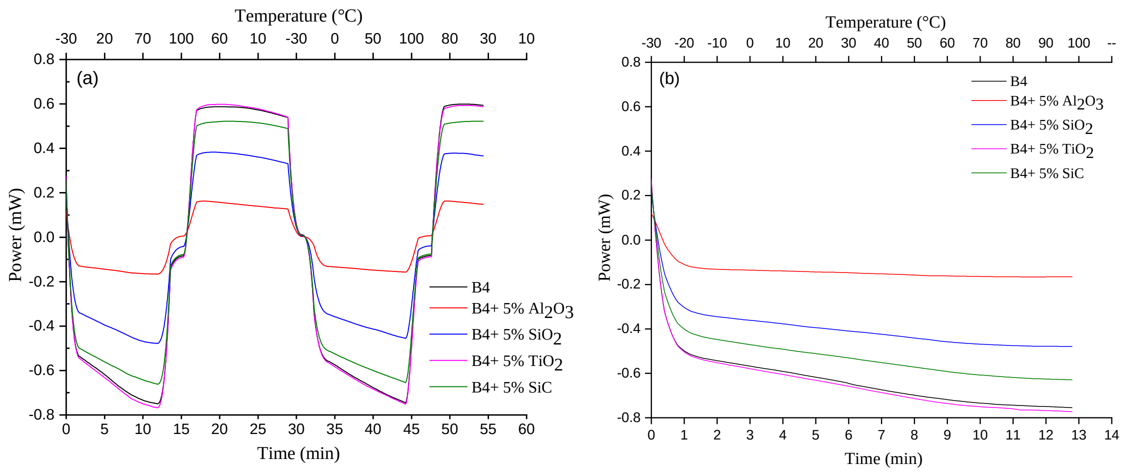

Figure 6. DSC graph of (a) different films and (b) first heating step

Contact angle (Table 2) defines the wettability of a solid surface by using liquid (water, diiodomethane, etc). Several factors i.e. surface roughness, nature of the material (hydrophobic or hydrophilic) can influence the contact angle as well as the wettability of the surface. It has been reported from our experiment that the hydrophobic nature of ceramic nanofiller have an influence on the contact angle as the contact angle has found up to 76.8º (SiC-water) where the film without nanofiller has reported up to 44.2º.

Table 2. The contact angle for different measuring liquid

Sample ID	Average contact angle (°)	
	Diiodomethane	Water
B4	39.9	44.2
B4+ 5% Al_2O_3	50.2	60.3
B4+ 5% SiO_2	48.8	54.2
B4+ 5% TiO_2	50.1	54.1
B4+ 5% SiC	66.3	76.8

The reinforcing effect of a nanofiller on the mechanical properties of polymer composites strongly depends on its particle size, surface characteristics, aspect ratio, shape, aggregate size and degree of dispersion. The effect of ceramic nanoparticles on the tensile properties of the polyurethane binder is listed in Table 3. The addition of nanoparticles affects crystallization of the polyurethane matrix and therefore changes the structural characteristics of the semi-crystalline matrix that may affect the tensile strength as in most of the cases, the addition of ceramic nanoparticle resulted in the increment of tensile strength for the films.

Table 3. Tensile Properties of different films

Tensile Properties	B4	B4+ 5% Al_2O_3	B4+ 5% SiO_2	B4+ 5% TiO_2	B4+ 5% SiC
Tensile strength (MPa)	18±0.2	21±0.4	19±0.3	20±0.8	25±0.5
Elongation at break (%)	439±1.9	233±0.8	225±0.5	228±0.2	120±0.8

4. CONCLUSION

In this paper, the radiative and thermographic effects of different ceramic nanofiller based polyurethane films has been demonstrated. The results showed that the thermophysical properties are strongly dependent on the nature of nanofillers. Though further study is required to reach a conclusive decision about the effect of nanofillers onto the surface emissivity in FIR range as it depends on many chemical and physical properties. The nanofillers also have a significant effect on the wettability, tensile strength, and film color.

5. ACKNOWLEDGMENTS

The project has been funded by the European Commission under the framework of Erasmus Mundus Sustainable Management and Design for Textile (SMDTex).

6. REFERENCES

1. Park CH, S.M., Shim HS, Far IR emission and thermal properties of ceramics coated fabrics by IR thermography, *Key Engineering Materials*, 2006. 321: p. 849-852.
2. Cai L, S.A., Wu P, Hsu PC, Peng Y, Chen J, Liu C, Catrysse PB, Liu Y, Yang A, Zhou C, Warming up human body by nanoporous metallized polyethylene textile, *Nature communications*, 2017. 8(1): p. 496.
3. Hsu PC, L.C., Song AY, Zhang Z, Peng Y, Xie J, Liu K, Wu CL, Catrysse PB, Cai L, Zhai S, A dual-mode textile for human body radiative heating and cooling, *Science advances*, 2017. 3(11): p. e1700895.
4. Abbas A, Z.Y., Ali U, Lin T, Improving heat-retaining property of cotton fabrics through surface coatings, *The Journal of The Textile Institute*, 2017. 108(10): p. 1808-14.
5. Anderson DM, F.J., Pooley MA, Seidel S, Hamblin MR, Beckham HW, Brennan JF, Infrared radiative properties and thermal modeling of ceramic-embedded textile fabrics, *Biomedical optics express*, 2017. 8(3): p. 1698-711.
6. Worobets JT, S.E., Stefanyshyn DJ, Apparel with far infrared radiation for decreasing an Athlete's oxygen consumption during submaximal exercise, *Research Journal of Textile and Apparel*, 2015. 19(3): p. 52-7.