MEMBRANES FOR APPAREL WITH THE ADDITIONAL BARRIER FUNCTION FOR THE REDUCTION OF IRRADIATION HEAT LOSS

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ABSTRACT

A membrane is a thin layer of polymer on shell fabric of apparel. Beside waterproofing a membrane can increase the thermal protection of apparel by stopping irradiative heat loss.
We have modified a polyurethane membrane in two ways: addition of inorganic components and coating with different polymers. The addition of heat absorptive additives reduced heat transmittance of membrane from 85% to 3%. The presence of heat reflecting compounds decreased transmittance of PU film to 25%. Coating with polypyrrole revealed the highest decrease in heat transmittance (down to 1-3%) among all polymers. Both approaches made augmentation in clothing insulation when they were used in apparel.

Key Words: heat transfer, membrane, thermal insulation, apparel, irradiation heat loss

1. INTRODUCTION

The shell fabric is the most expensive component of winter apparel at mass market [1]. The shell fabric consists of a few layers; one of which is a membrane. The membrane is a thin layer of polymer in the form of a non-porous or microporous film. Nowadays, the most commonly used polymers for membrane fabrication are: poly(vinyl chloride), polyurethanes, polyacrylates, polyolefins, polytetrafluoroethylene and various types of rubbers [2]. Membranes in textiles have two main functions: water resistivity and water vapor permeability. However membrane or films for coating may have other properties and contain different additives such as pigments, heat reflecting materials, phase-change materials, flame retardant agents etc.
The membrane is located at some distance from the human body, where only two channels of heat loss play a role: irradiation and convection [3]. The membrane is an attractive layer to increase thermal insulation not only as a barrier against convectional heat loss, but playing similar barrier function towards irradiation heat loss. Such ideas have been implemented in several products. For example, a space blanket which is coated with a thin layer of silver or gold reflecting up to 80% of infrared irradiation back to the human body. Cheaper reflective surface can be made from aluminium or titanium dioxide. For example Columbia Sportswear Company developed the Omni Heat reflective coating based on aluminum, which is placed on the lining material of apparel.
While reflection is the best way to keep heat inside, in theory, the absorption of heat also may be useful. Regardless of dissipation of absorbed heat, the increase in absorption will reduce transmittance of heat through the material. Considering the constant heat flow of the human body, heat absorption by textile materials will create a higher temperature gradient at the edge of the apparel which will keep more of the heat inside the apparel.
We here report the results of studies on the influence of different additives and coatings for membrane, targeting improvement of heat reflection or heat absorption properties.

2. MEASUREMENT AND MATERIALS

Measurement of thermoinsulation property/clothing insulation or CLO has been done using Thermetrics Sweating Guarded Hotplate SGHP-8.2 according to ASTM D1518-14. Absorption and reflection measurement have been done using Perkin Elmer UV/Vis spectrometer LAMBDA 950. The structure of membranes before and after coating was studied via Field Emission Scanning Electron Microscopy (FE-SEM, jsm-6340F).
The heat retention test has been done at room temperature in the following way. Sample of membrane was placed under a 100 W lamp placed 30 cm above the sample. Time of irradiation was 1 min. The temperature of the surface was detected by IR camera Optris PI640. Specific heat capacity measurement has been made by means of MDSC TA Instruments 2920.
The following chemicals were purchased from Sigma-Aldrich: carbon black - nanoparticle size less than 500 nm (99.95%); TiO_2 - puriss; Fe_3O_4 - particle size < 5 um, 95%; Fe_2O_3 – particle size < 5 um, >99%; Graphene powder - electrical conductivity $>10^3$ S/m; Aluminium oxide (Al_2O_3) - powder, primarily α-phase, 100-325 mesh; $CaCO_3$ - >99%; Tungsten oxide (WO_3) - particle size is less than 20 um, ≥99%; quartz sand 50-70 mesh. Iron powder was supplied by Riedel-de Haën: puriss, particle size < 212 um; Nickel ~300 mesh, 99.9% and titanium powder ~325 mesh, 99.9% were purchased from Alfa Aesar; silica aerogel with particle size 2-10 um was purchased from Aspen aerogel.

3. RESULT AND DISCUSSION
3.1. Additives to membrane.

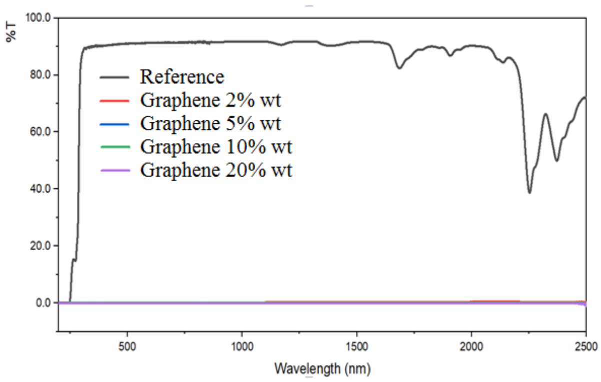
Ability of additives to influence heat transfer and to interact with heat can be evaluated in various ways. First of all, specific heat capacity shows the ability of a material to accumulate heat. Higher accumulation means that less heat will be transmitted through the material and lost. Checking temperature of the material surface, subjected to irradiation, helps to evaluate heat absorption ability of the material. Measurement of CLO simulates the real behavior of materials in contact with the human body. All above mentioned parameters were measured for 14 composites made of polyurethane (PU) containing 20 wt% of an additive (table 1). Swatch of winter apparel was made by the following way. A film with an additive was attached to polyester shell fabric by hot pressing. The layered structure of entire swatch consisted from obtained shell fabric, non-woven insulation and polyester lining woven material.

Table 1. Thermal properties of composite materials

N	Name of the additive	Specific heat capacity, J/kg×^{o}C	Temperature of film after 60 s of light exposure, ^{o}C	CLO of swatch
Reference	Pure PU film	437	29	2.94
1	Graphite	915	52	2.90
2	Graphene	951	53	3.31
3	Carbon black	980	54	3.30
4	Fe_3O_4	986	54	3.18
5	Fe_2O_3	791	48	3.03
6	$CaCO_3$	815	31	3.10
7	WO_3	863	38	2.88
8	Quartz	909	31	2.82
9	Iron	859	43	3.01
10	Nickel	826	38	3.15

11	Titanium	870	49	3.16
12	TiO_2	917	31	3.29
13	Al_2O_3	869	32	3.26
14	Silica aerogel	881	31	3.35

The highest specific heat capacity was obtained for samples containing carbon black and iron oxide - Fe_3O_4. Black additives provided good heat absorption under irradiation reaching temperature of 50 ^oC and above. Whereas white additives and generally metal particles did not absorb heat showing lower surface temperature under irradiation. CLO depends on several properties of material, but as can be seen, heat reflective and absorptive materials improve the thermal insulation property. Graphene, carbon black, titanium and aluminium oxides, used as an additive, have shown the greatest increases in thermal insulation.
It was observed that there is a big difference in the interaction with heat between graphite and graphene. It can be seen from figure 1 that even a small addition of graphene brings heat transmission down to zero, whereas graphite has to be added in significant amounts to get a similar result.



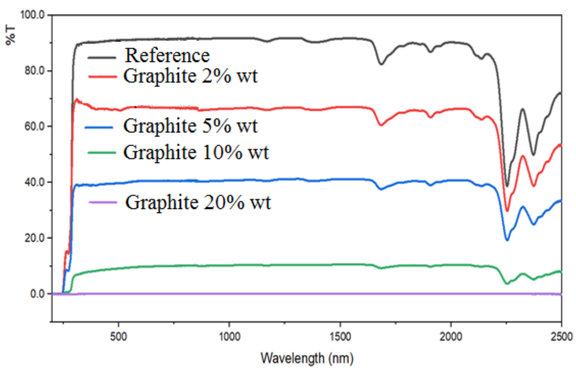


Figure 1. Heat transmittance of composites containing different amount of graphene and graphite

Heat transmittance for all additives being added to polymer in different amount is reflected in table 2. Transmittance of reference sample was 83%.

Table 2. Transmittance (%) of PU film with different amount of additives measured in the range 200-2500 nm

N	Name of the additive	Amount of the additive, wt%			
		2	5	10	20
1	Graphite	62.2	38.4	9.6	0.1
2	Graphene	0.3	0.1	0.1	0
3	Carbon black	0	0	0	0
4	Fe_3O_4	21.3	2.8	0.2	0
5	Fe_2O_3	18.5	10.3	2.3	0.1
6	$CaCO_3$	81.0	75.3	70.1	70.2
7	WO_3	72.0	64.0	59.7	47.9
8	Quartz	83.0	82.2	80.8	79.2
9	Iron	82.7	73.6	59.9	45.1
10	Nickel	81.6	80.2	80.2	69.3
11	Titanium	78.3	62.2	40.4	10.1
12	TiO_2	39.7	23.8	13.8	11.7
13	Al_2O_3	81.7	68.0	54.5	46.9
14	Silica aerogel	82.4	81.0	80.8	78.7

Carbon black has been revealed to have the best ability to stop the transmittance of light and heat. Even 2% of this additive made heat and light transmittance equal to zero. Interestingly, aerogel, which is usually regarded to be the material with the lowest thermal conductivity, has little ability to block irradiated heat.

3.2. Coating of surface by polymers interacting with heat.

A few samples of fabric with PU membrane were coated with respectively polypyrrole, polythiophene and polyaniline. All these polymers are known to efficiently absorb light and heat [4]. In addition, all of them possess good antibacterial and antistatic properties [5]. A solution of $FeCl_3$ (0.3M) in ethanol was drop cast onto a fabric sample followed by air drying. Then the fabric was placed over a layer of corresponding monomer: pyrrole, thiophene or aniline for 1.5 h. Afterwards the samples were washed and dried as in a literature procedure [6]. Transmittance of obtained samples was measured (figure 2).

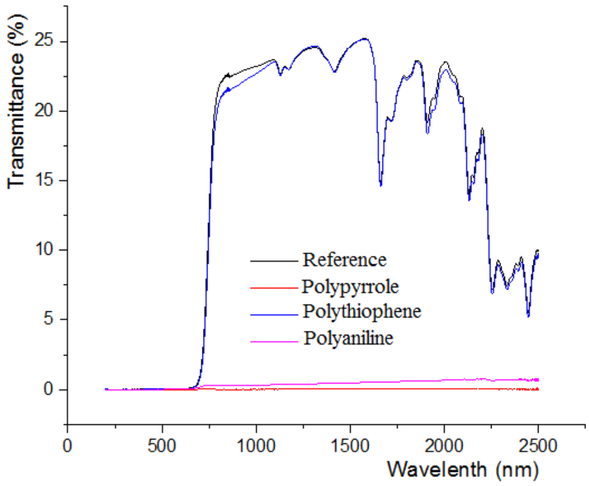


Figure 2. Transmittance of fabric with membrane coated with different polymers

The best result was obtained for samples coated with polypyrrole. Therefore more samples were made with pyrrole. Different concentrations of catalyst (iron chloride) were used and the sample weight increase, which is caused by the amount of polymer deposited on the membrane surface, was compared. Stability of coating was checked after 5 washing cycles. Results are presented in table 3.

Table 3. Properties of polypyrrole coating obtained in ethanol with the application of $FeCl_3$

Concentration of $FeCl_3$, mol/L	Weight increase after coating, % wt	Weight loss after 5 washings, % wt
Initial fabric with membrane	-	1.0
0.3	3.7	0.2
1	36.2	5.6
2	85.9	14.2
3	174	31.5
5	194	28.8

Values of heat transmittance were almost the same for all samples from table 3. Therefore, there is no need to apply high amount of polypyrrole onto the membrane surface.
Alternatively, we tried to apply polypyrrole coating in water: ethanol 1:1 ratio milieu with the application of ammonium persulfate ($(NH_4)_2S_2O_8$) as a catalyst. A solution of ammonium

persulfate in water was mixed with pyrrole and applied onto the fabric. After 30 min, the fabric was rinsed and dried. The results are presented in table 4.

Table 4. Properties of polypyrrole coating obtained in water: ethanol with the application of$(NH_4)_2S_2O_8$

Concentration of $(NH_4)_2S_2O_8$	Weight increase after coating, % wt	Weight loss after 5 washings, % wt	Specific heat capacity, J/kg×^{o}C
Initial fabric with membrane	-	1.0	1023
0.5	3.6	1.6	1131
1.0	14.8	9.1	1288
2.5	38.4	18.2	1340
3.5	30.4	-	1285

Similar to the results from table 3, data from table 4 confirms that there is no need to apply large amounts of polypyrrole to the surface, as the thermal property shows little difference for different amount of polypyrrole applied on the membrane surface. Figure 3 represents an SEM photo of the surface of initial membrane and membrane coated by polypyrrole with the application of iron chloride and ammonium persulfate. Evidently iron chloride provides more even surface of the coating.

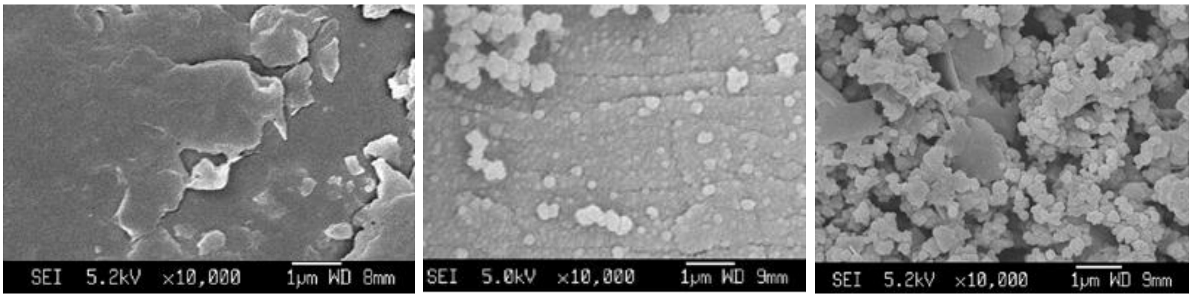


Figure 3. Initial membrane (top left), membrane coated with the application of iron chloride (top right) and with ammonium persulfate (bottom)

Measurement of CLO revealed a positive influence of polypyrrole coating on thermal insulating property of the fabric. The highest increase in CLO (75%) was obtained for shell fabric with PU membrane which contained 10% wt of polypyrrole (table 5).

Table 5. CLO value for fabric with membrane before and after coating and for swatch where fabric with membrane was used as a shell

Sample name	CLO before coating	CLO after coating	Difference in CLO, %
Fabric with membrane	0.16	0.28	75.0
CLO of swatch*	2.32	2.43	4.7

*Swatch was made by similar way like in the description for table 1.

Polypyrrole coating possesses the high ability to absorb heat and light. We compared these properties with known heat absorbing materials like graphene and carbon. Sample with membrane coated by polypyrrole has revealed the highest temperature (61^{o}C) being irradiated by 100W lamp during the 1 minute (figure 4).

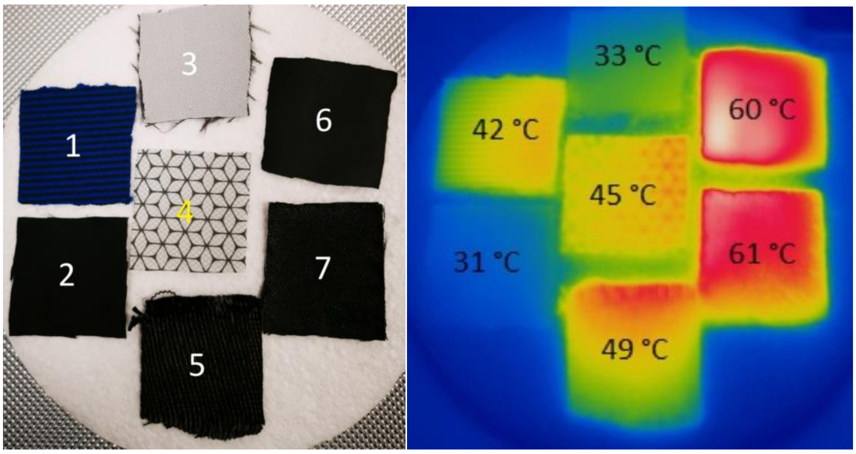


Figure 4. 1 – polyester/nylon 60/40 fabric with 20% graphene oxide; 2 – polyester lining fabric black colour; 3 – polyester shell fabric with white PU membrane; 4 – polyester fabric with 40% coverage print containing 18% graphene; 5 – pure carbon fiber fabric; 6 - polyester shell fabric with white PU membrane coated by polypyrrole; 7 – polyester fabric with PU membrane containing 18% of graphene oxide.

Sample with graphene reached almost the same value, but considering industrial applications, polypyrrole looks more attractive due to of high difference in price between graphene and pyrrole.

4. CONCLUSİONS

We have shown in our study that polypyrrole coating can be used for creation of additional heat stopping barrier being applied on the membrane surface. Regardless on thin layer which is almost non-significant for whole layered swatch of winter apparel, polypyrrole adds about 5% to total thermal insulation. In addition, polypyrrole possesses antibacterial properties and perfect antistatic property which are additional benefits for apparel. In addition, its property to raise the temperature under irradiation may be useful for nice hand feeling effect, providing a warm feeling when it is touched by customers.

5. REFERENCES

1. J.H. Hammond, A. Raman, Sport Obermeyer Ltd. *Harvard Business School Case*, N 695-022, October 1994.
2. M.E. Hall, Coating of technical textiles, in *Handbook of Technical Textile* (edited by A.R. Horrocks, S.C. Anand) Wodhead Publishing, Cambridge, 2000, 173-186.
3. G. Song, Thermal insulating properties of textile and clothing, in: J.T. Williams (Ed), *Textiles for cold weather apparel,* Woodhead Publishing Lim., New York, 2009, 19-33.
4. A. M. Rehan Abbasi, J. Militky, and J. Gregr, Heat Generation by Polypyrrole Coated Glass Fabric. *Journal of Textiles*. Volume 2013, ID 571024, 5 pages.
5. A. Varesano, C. Vineis, A. Aluigi, F. Rombaldoni, C. Tonetti, and G. Mazzuchetti, Antibacterial Efficacy of Polypyrrole in Textile Applications. *Fibers and Polymers* 2013, Vol.14, No.1, 36-42.
6. X. Zhou, et al., Facile Fabrication of Superhydrophobic Sponge with Selective Absorption and Collection of Oil from Water. *Industrial & Engineering Chemistry Research* 2013, 52 (27), 9411-9416.