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POLYESTER KNITWEAR IMPREGNATED WITH PVB/IF-WS$_2$ SYSTEM AS POTENTIAL CAMOUFLAGE MATERIAL

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Abstract: *This paper presents the results of research on the application of nanomaterials on knitwear intended for camouflage protection. Polyester fibers that had already been dyed in camouflage shades (light green, beige green and dark green) were additionally treated with poly(vinyl butyral) (PVB) with or without incorporated nanoparticles of tungsten disulfide (WS$_2$). This impregnation has proven to be successful in improving the camouflage characteristics of some other materials, like glass or cotton. For the prepared samples, the diffuse reflection, specular gloss and color coordinates of both treated samples and untreated samples were determined. Also, the samples were observed in the medium and long wavelength infrared spectrum using IR thermography. The obtained results indicated that there is a possibility of using this new impregnated knitwear in the wider area of the EMS.*

Keywords: *polyester knitwear, poly(vinyl butyral), tungsten disulfide nanoparticles, camouflage protection, IR thermography.*

1. INTRODUCTION

In earlier research, the influence of tungsten disulfide structures on the physical-mechanical and spectrophotometric properties of polyurethane camouflage coatings was examined. Since the favorable influence of the nanoparticles and nanotubes of tungsten disulfide (IF-WS$_2$ and INT-WS$_2$, respectively) was proven, both on the mechanical and the camouflage characteristics [1-3], it was encouraging to use these particles on textile materials as well. First choice was to work with natural, cotton, textile materials and application to materials with a digital camouflage pattern that is already in use in the Serbian army. The results obtained at that time spoke in favor of the fact that the use of nanoparticles had a favorable effect on camouflage properties and on obtaining the so-called multispectrality, i.e. the possibility of this material for meeting the camouflage requirements in a wider area of the electromagnetic spectrum (EMS) [4].

In this research, analysis of the influence of tungsten disulfide nanostructures on the camouflage properties of a synthetic fabric - polyester knitwear was performed. These nanostructures were previously dispersed in the chosen impregnating medium poly(vinyl butyral) (PVB). It is known that PVB as a thermoplastic elastomer is added to other polymer materials, brittle thermosetting resins such as epoxy and phenolic resin, to increase toughness [5]. PVB is a highly flexible material, compatible with numerous resins and additives, non-toxic, has very good adhesion to many substrates. PVB has very good impact resistance, tensile strength and elasticity, it is resistant to freezing and aging, it dissolves well in alcohols and organic solvents, it is transparent and colorless [6]. It releases solvents quickly so it is good for impregnation of materials, since it easily forms films and foils.

Dichalcogenides of transition metals (MoS$_2$, WS$_2$, NbS$_2$, etc.), thanks to their excellent mechanical properties, have a wide range of applications: to increase strength, reduce friction, as solid lubricants, in anti-corrosion and masking protection, etc. [3]. Due to these exceptional properties, tungsten disulfide, in the form of fullerene nanoparticles, IF-WS$_2$, and multilayer nanotubes, INT-WS$_2$, with a unique morphology and a spherical closed multilayer structure, i.e. a multilayer hollow nanotube structure, has been recognized as a potential reinforcing filler for various composites. Nanoparticles of WS_2 reduce friction and heating, and thus mechanical wear. At the same time, contact pressure causes exfoliation (flaking off) of the nanospheres, releasing tribofilms that bind to surface irregularities and voids, smoothing them out and improving overall mechanical efficiency and extending the material's service life. These multi-layered IF-WS_2 nanospheres are known to withstand extremely low and high temperatures (-270 °C to 450 °C), and as they are resistant to impact and pressure, this makes them suitable for use in extreme conditions, from low to high temperatures, high pressure to high vacuum, under high loads and rotation speeds, at high radiation and in corrosive environments [5].

2. MATERIALS AND METHODS

2.1. Samples preparation

The following materials were used to make the samples in this research: polyester knitwear in three camouflage shades (dark green, beige green and light green) that correspond to the shades already in use in the Serbian army, manufactured by "Dunav" Grocka.

For the impregnation of selected knitwear, PVBMowital B45H Kuraray was used and nanostructures of WS_2: IF-WS_2 nanoparticles, manufactured by NanoMaterials Ltd. - Nanotech Industrial Solutions Inc., Apnano Israel [7]. To disperse nanostructures and to dissolve PVB, 96% ethanol was used. The properties of the nanoparticles used are given in Table 1.

Table 1. Characteristics of IF-WS_2

Purity, %	>99
Particle density at 25 °C, g/cm^3	7,5
Apparent density, g/cm^3	0,7-1,1
Typical particle size, nm	40-300
Decomposition temperature, °C	1250
Oxidative stability in air, ° C	>350
Oxidative stability in inert, ° C	>1000
Molecular mass, g/mol	247,98

The samples were prepared as follows: first, powdered PVB was dissolved in ethanol, with or without fullerene particles of WS_2, by submerging the knitted fabric samples in the solution and evaporating the solvent. For the sample without nanoparticles, PVB was dissolved in ethanol, in a mass concentration of 3 wt.%, and for the samples with nanoparticles, they were first dispersed in the solvent by an ultrasonic processor BadelinSonoPuls, and then, with vigorous mixing, PVB powderwas added. The concentration of nanoparticles was 2 wt.%.

2.2. Camouflage efficiency characterization

Spectrophotometric properties were observed to evaluate the camouflage behavior by determining the following properties of the impregnated knitwear: specular gloss was measured at angle 85° with Elcometer 480 model T device, which is important feature for fabric materials in the field of military camouflage. Diffuse reflection was measured on UV/VIS/NIR spectrophotometer UV 3600 from a Japanese manufacturer Shimadzu with an integrating sphere in the 650 nm to 1000 nm wavelength area using UV Probe programme package [8] and color coordinates in CIE LAB system were determined as well using Color programme package with 10° and D65 observer [9].

2.3. IR Thermography

In the experiment, two measuring thermal imaging cameras operating in different ranges were used, FLIR SC620 and FLIR SC 7200. SC 7200 uses "Altair" software for data analysis and acquisition while SC 620 camera uses "ThermaCAM 2900" software package [10, 11]. The obtained images were analyzed with "ThermaCAM Researcher Professional" software [12]. In addition to the cameras, the black body TCB-4D, manufactured by Inframet, Poland, was also used in the experiment. Blackbody temperature values were controlled by the TCB TAS-T software [13]. The temperatures of the black body at which measurements were made were 45°C and 60°C. The sample was placed in front of the black body and the exposure time of the samples was 5 minutes. The goal of the experiment set up in this way was to make a comparison and insight into the process that takes place between the sample and electromagnetic energy in the MWIR and LWIR spectral range of EMS.

3. RESULTS

Difuse reflection curves registered for the examined material are given in Figure 1.

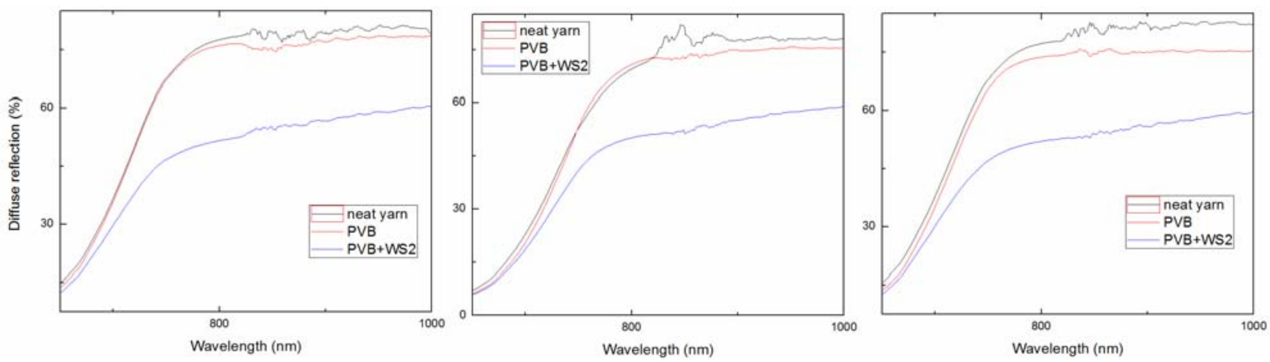

Figure 1. Difuse reflection for: light green, dark green and beige green shade, from left to right

The results show that impregnation did affected camouflage behavior of the material and for the better. There can be observed a significant drop in values of the diffuse reflection. Before impregnation the diffuse reflectance values were very high but the IF-WS$_2$ changed these values resulting in obtaining lower diffuse reflectance curves. Moreover, visually the change was not observed, and that was confirmed by colour coordinates values, given in Table 2.

Table 2. Color coordinates

Shade	With PVB			With PVB/IF-WS$_2$		
CIE Lab	L*	a*	b*	L*	a*	b*
Light green	45.3	-6.4	14.8	39.0	-4.4	11.3
Beige green	43.4	-2.6	13.5	37.3	-1.4	10.6
Dark green	33.6	-9.7	11.5	29.5	-8.1	10.1

Table 3 shows obtained values of specular gloss, which, as it may be observed, practically did not change. This means that PVB/IF-WS$_2$ could be used for the camouflage improvement not just for the natural fabrics but for the polymer threads and yarns as well.

Table 3. Specular gloss at 85°

Shade	With PVB	With PVB/IF-WS$_2$
Light green	0.0	0.0
Beige green	0.0	0.2
Dark green	0.1	0.0

Temperature values were read from the obtained thermograms and used for comparison in order to determine relative temperature differences as a measure of the camouflage effect in the IR spectral range. Tables 4 and 5 show these results. The first column represents the ambient temperature, which ranged between 19ºC and 21ºC. The second and third columns represent the temperature of the material when the black body is heated to 45ºC and 60ºC, respectively. ΔT_1 represents the temperature difference of the material when the temperature of the black body was 45ºC and when the black body was not heated while analogously ΔT_2 is the temperature difference when the black body was heated to 60ºC and when it was not heated. The last two columns are the mutual quotients of these temperature differences obtained for the impregnated samples in relation to the non-impregnated sample that represents the reference sample.

Table 4. Results obtained with the FLIR SC620 camera

Sample	T_{amb} (ºC)	T_{bb} (45ºC)	T_{bb} (60ºC)	ΔT_1 (ºC)	ΔT_2 (ºC)	$\Delta T_1/\Delta T_{ref}$	$\Delta T_2/\Delta T_{ref}$
dark green	19.43	31.93	38.99	12.50	19.56	1.00	1.00
dark green+PVB	20.27	29.27	35.1	9.00	14.83	**0.72**	0.76
dark green+PVB+ IF WS$_2$	20.51	30.06	36.21	9.55	15.7	0.76	0.80
beige green	19.6	30.1	36.66	10.5	17.06	1.00	1.00
beige green +PVB	20.44	28.89	37.22	8.45	16.78	**0.80**	0.98
beige green +PVB+ IF WS$_2$	20.77	31.11	37.66	10.34	16.89	0.98	0.99
light green	19.31	29.52	36.36	10.21	17.05	1.00	1.00
light green+PVB	20.36	31.91	39.61	11.55	19.25	1.13	1.13
light green+PVB+ IF WS$_2$	20.51	30.44	37.97	9.93	17.46	0.97	1.02

Table 5. Results obtained with the FLIR SC7200 camera

Sample	T_{amb} (ºC)	T_{bb} (45ºC)	T_{bb} (60ºC)	ΔT_1 (ºC)	ΔT_2 (ºC)	$\Delta T_1/\Delta T_{ref}$	$\Delta T_2/\Delta T_{ref}$
dark green	19,43	27,80	34,10	8,37	14,67	1,00	1,00
dark green+PVB	20,27	26,40	29,50	6,13	9,23	**0,73**	**0,63**
dark green+PVB+ IF WS$_2$	20,51	27,20	30,10	6,69	9,59	**0,80**	**0,66**
beige green	19,6	28,00	31,30	8,40	11,70	1,00	1,00
beige green+PVB	20,44	26,70	31,30	6,26	10,86	**0,74**	0,93
beige green+PVB+ IF WS$_2$	20,77	28,80	33,10	8,03	12,33	0,96	1,05
light green	19,31	26,50	31,60	7,19	12,29	1,00	1,00
light green+PVB	20,36	26,40	31,70	6,04	11,34	**0,84**	0,92
light green+PVB+ IF WS$_2$	20,51	26,80	30,90	6,29	10,39	**0,87**	**0,84**

The results do not show consistent behavior. Namely, the results obtained with the FLIR SC620 camera show better suppression when the blackbody is heated to 45ºC. Samples of light green color in this part of the spectrum, recorded by this measuring camera, do not behave in the manner required for camouflage protection. In contrast, dark green and beige green samples have better suppression when impregnated with PVB alone with similar percentage suppression.

On the other hand, the results obtained with the FLIR SC7200 camera show that the reduction of thermal reflection occurs in almost all treated samples. The reductions are larger and range up to almost 40%.

These results are quite different from the results obtained by measuring the diffuse reflectance in the VIS and NIR part of the EMS [4, 14]. Namely, it was shown that all three shades of green behave best when impregnated with nanoparticles, lowering the reflection curve thus, improving the camouflage performance of the material. It remains to be seen why there were such results, that is, such differences in the behavior of samples. Performing additional analyzes (SEM, TEM, AFM, FTIR) could provide answers. It should also be emphasized that it is not unusual for the material to behave differently in different parts of the EMS, which is why obtaining the desired multispectrality is a demanding task.

5. CONCLUSION

Examination of the influence of tungsten disulfide nanostructures on the camouflage properties of polyester knitwear was conducted. Samples were prepared by impregnating polyester knitwer with camouflage pattern in PVB/IF-WS_2 from ethanol solution. The results show that impregnation has improved camouflage behavior of the material. The significant drop in values of the diffuse reflection was observed due to added IF-WS_2. Visual appearance of the samples did not change, what was confirmed by colour coordinates values. Specular gloss did not significantly change. In results obtained by recording with a FLIR SC620 camera, it was observed that the addition of nanoparticles in beige green and dark green shades, show better reduction of thermal reflection in knitted fabrics impregnated only with polyvinyl butyral. The behavior of the light green shade is not adequate for application in this part of the EMS. On the other hand, the results obtained with another type of measuring camera (FLIR SC7200) show a significantly greater drop in the temperature difference between treated and untreated samples. It was observed that almost all samples show a difference in behavior in this part of the EMS compared to untreated samples.

Overall, nanoparticle-impregnated polyester knitwear show potential for use in the field of multispectral camouflage protection. However, future research should encompass impregnation of more camouflage shades/colors, as well as other synthetic fabrics or knitwears.

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