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A NEW MODELING APPROACH OF THE SURFACE PROPERTIES OF POLYMERIC SUPPORTS

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Abstract: *Sustainability and innovation in creating eco-friendly textiles are also growing areas of interest. Ozone layer depletion has been linked to a progressive increase in the incidence of skin cancer, primarily due to heightened exposure to ultraviolet (UV) radiation from the sun. A significant body of research has focused on the development of UV absorbers to mitigate this risk. However, most UV absorbers currently under investigation are water-insoluble and require emulsification or dispersion in aqueous media for effective application. This often necessitates the incorporation of organic solvents, posing challenges to formulation stability and effectiveness.*
Previous work emphasized the role of nanoparticles to modify the surface of textiles, creating new porosity and potentially improving UV protection and comfort, as
The present study aims both at the analyzsis of the relationships between the contact angle (wettability) and the concentration of the emulsion before and after UV exposure, and the development of a a mathematical model to analyze the data, for which the suggested model will identify two distinct values that describe how the concentration of the zinc oxide emulsion affects the coating after UV irradiation compared to before.
The model successfully predicts water permeability based on the engineered pore structure created by the nano-oxide coating. This paves the way for designing comfortable and potentially UV-protective textiles.
The results of this study could lead to the development of more effective and environmentally friendly UV protection strategies, reducing reliance on organic solvents and improving the efficacy of UV-blocking formulations in preventing skin cancer.
There is a linear or parabolic correlation between contact angle and nano-oxide concentration, with the lowest contact angle (least hydrophobicity) observed in uncoated fabric.

Key words: *mathematical model, polymeric textiles, nanoparticles, contact angle, porosity*

1. INTRODUCTION

To prepare UV absorber with water solubility, high affinity to cotton, satisfactory fastness properties together with good UV protection property, previous works designed novel polymeric UV absorbers by grafting benzotriazole type UV absorber onto polyvinylamine (PVAm). The prepared polymeric UV absorber not only exhibited water solubility and good anti-UV property, but it also showed very high utilization efficiency, satisfactory wash fastness and environmentally benign finishing process.
As a result, protection from sunlight, specifically ultraviolet (UV) radiation, has become a topic of

increasing interest. Methods for protecting ultraviolet sensitive materials from photo-oxidation include physically shielding the material from light (for example, clothing shielding skin), physical blockers such as titanium dioxide that scatter light, and chemical absorbers that absorb the radiation and emit it at a longer wavelength, which translates to a lower energy.

Encapsulating UV-sensitive materials within a polymer matrix offers UV protection through mechanisms such as light scattering [1-2] and limiting material movement due to restricted available free volume [3], characteristics that are not present in solution-based systems. UV absorbers, commonly used in sunscreens, are another effective means of shielding against UV radiation [4]. A combination of both encapsulation and UV absorbers could provide superior protection for materials vulnerable to UV-induced degradation [5]. Additionally, it has been demonstrated that particles incorporating protective materials with different mechanisms—such as a UV absorber and an antioxidant—can enhance the photostability of both protective agents [6]. Polymer films containing these UV-protective components have also been shown to offer UV shielding [7].

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This study investigates the protective capabilities of polymeric particles that incorporate both UV-sensitive and UV-protective materials, aiming to surpass the UV protection provided by encapsulation alone, especially when compared to solution-based systems. UV-protective particles hold significant promises for applications in sunscreens and pharmaceuticals, enhancing product stability. In addition, we propose a new technique of linearization and the proposed pseudo-power model, estimating more precisely the optimal value of the formulation of 3.5% of nano-oxide (ZnO) suspension as coating onto the polymeric support enhanced the water permeability.

2. A PSEUDO-POWER-BASED MODELING PROPOSAL

Considering the non-linear dependence between the contact angle and the concentration of the nano-oxide emulsion of the coating shown in Table 1, the shape of the data points can be parabolic, hyperbolic or logarithmic causal correlation, etc. The next step was the analyses of the degree of curvature using the linearization technique based on the probable pseudo-power behavior [15].

Table 1*. Contact angle and concentration of nano-oxides emulsion of coating before and after UV irradiation, experimental and calculated values with pseudo-power model (Eq. 1), and percentage relative deviation*

[ZnO]	$\theta_{b,exp}$	$\theta_{b,cal}$	$100(\theta_{b,cal} - \theta_{b,exp})/\theta_{b,exp}$	$\theta_{a,exp}$	$\theta_{a,cal}$	$100(\theta_{a,cal} - \theta_{a,exp})/\theta_{a,exp}$
%	°	°	%	°	°	%
0	92[a]	92.000 [a]	0.0	88[b]	88.000 [b]	0.0
0.25		105.46			98.464	
0.50		111.67			105.07	
0.75		116.25			110.42	
1.0	120	119.86	0.11843	115	114.92	0.067145
1.5		125.16			122.07	
2.0		128.66			127.28	
2.5		130.81			130.89	

3.0	131	131.86	-0.65905	135	133.11	1.3998
3.5		131.99			134.08	
4.0		131.30			133.89	
4.5		129.87			132.61	
5.0	129	127.77	0.95511	127	130.32	-2.6130
5.5		125.05			127.05	
6.0		121.74			122.85	
6.5		117.89			117.74	
7.0	113	113.53	-0.46666	116	111.77	3.6485
7.5		108.67			104.95	
8.0		103.34			97.305	
8.25		100.50			93.182	
8.55**		96.955			87.973[b]	
8.75		94.503			84.343	
8.95*		91.982[a]			80.590	

a and b: (θ_0) before and after UV irradiation, respectively. * and **: ($[ZnO]_{max}$) before and after UV irradiation, respectively.

To analyze the graphical behavior of the contact angle-concentration dependence, a linearization test is performed which consists of the optimization of an adjustable parameter (α) in the ratio $\frac{\theta-\theta_0}{[\mathrm{ZnO}]^{\alpha}}$ which can give the best linearity on the concentration [ZnO] expressed as follows.

$$\frac{\theta-\theta_0}{[\mathrm{ZnO}]^{\alpha}} = B - A \cdot [\mathrm{ZnO}] \tag{1}$$

Where A and B are two optimal adjustable positive parameters obtained by the least square method. After simplification by ($[\mathrm{ZnO}]^{1-\alpha}$) in the first derivation of Eq. 1, we obtain, at constant temperature, the following first order of a partial differential equation (PDE):

$$[\mathrm{ZnO}]\left(\frac{\partial\theta}{\partial[\mathrm{ZnO}]}\right)_T - \alpha(\theta-\theta_0) = -A[\mathrm{ZnO}]^{\alpha+1} \tag{2}$$

Where the α-power must be different in unity ($\alpha \neq 1$). Then, after simplification by ($[\mathrm{ZnO}]^{1-\alpha}$) in the second derivation of Eq. 1, at a given temperature, the partial differential equation specific to the contact angle expressed is as follows:

$$[\mathrm{ZnO}]^2\left(\frac{\partial\theta^2}{\partial[\mathrm{ZnO}]^2}\right)_T - 2\alpha[\mathrm{ZnO}]\left(\frac{\partial\theta}{\partial[\mathrm{ZnO}]}\right)_T + \alpha(1+\alpha)(\theta-\theta_0) = 0 \tag{3}$$

Where α must be different from unity ($\alpha \neq 1$) and the general solution is expressed as follows:

$$\theta = \theta_0 + \{B - A \cdot [\mathrm{ZnO}]\} \cdot [\mathrm{ZnO}]^{\alpha} \tag{4}$$

The mathematical solving of this PDE shows that there are two possible solutions; α = 0.59 and α = 0.75 related to the two situations: before and after UV irradiation, respectively. The adjustable parameters in Eq. 1 (A and B) are evaluated by the straight-line plots of the said equation;

$\frac{\theta-\theta_0}{[\text{ZnO}]^{\alpha}}$ *vs.* [ZnO] as shown in Figs. 1a and 1b. The values of adjustable optimal parameters are presented in Table 2 while the solutions for the calculated values of contact angle by Eq. 4 are presented in Table 1.

We note that we can mathematically solve the Eq. 3, as a second order homogeneous Euler-Cauchy equation specific to the contact angle by establishing its specific isobaric partial differential equation.

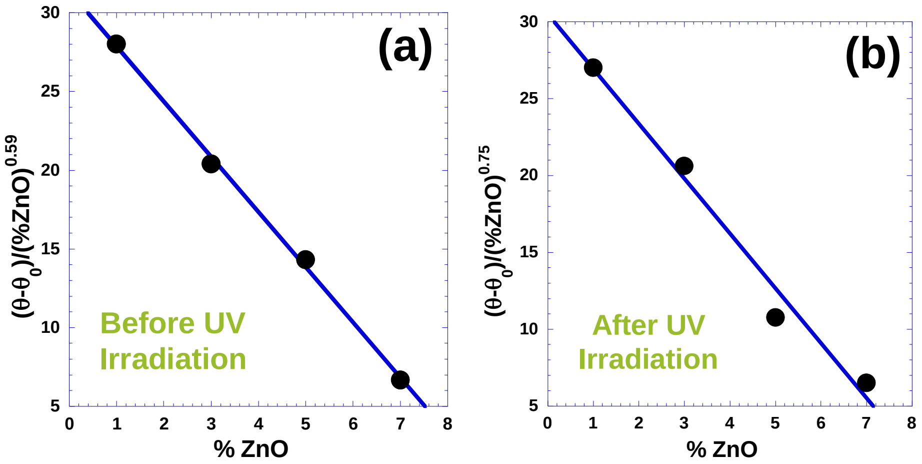

Fig. 1. *Linearization of the function* $\frac{\theta-\theta_0}{[ZnO]^{\alpha}}$ *of Eq. 1 as a function of Concentration of nano-oxides emulsion of coating [ZnO], (a): before UV irradiation and (b): after UV irradiation*

Using the Eq. 4, the concentration value ($[\text{ZnO}]_0$) corresponding to the observed maximum contact angle (θ_{max}) using simply the following derivation equation can be calculated:

$$\frac{d\theta}{d[\text{ZnO}]} = \{\alpha B - (1+\alpha)A \cdot [\text{ZnO}]\} \cdot [\text{ZnO}]^{\alpha-1} \tag{5}$$

After canceling the equation, we can write the following.

$$[\text{ZnO}]_0 = \frac{\alpha B}{(1+\alpha)A} \tag{6}$$

Table 2. *Optimal parameters values of Eq. 1 and Eq. 6.*

Parameter	θ_0	B	A	α	$[\text{ZnO}]_0$	θ_{max}	R
Before UV	92°	31.3626251	3.50474696	0.59	3.32%	132°	0.999026
After UV	88°	30.4894398	3.56665313	0.75	3.66%	134°	0.989875

CONCLUSION

In the present work, the contact angle and concentration of nano-oxides emulsion of coating before and after UV irradiation were subjected to mathematical modeling using linearization by pseudo-power technique and the partial differential equations. By combining both the linearization technique and the power law for concentration of zinc nano-oxides emulsion as the independent variable, we detected two interesting optimal exponent-values apparently characteristic and specific for the present studied zinc nano-oxides emulsion, before and after UV irradiation. The mathematical handling was done for the two values of the concentration exponent: α = 0.59 and α = 0.75, before and after UV irradiation, respectively. Moreover, future similar investigations on other nano-oxides emulsion and comparison of their specific exponents can lead to deep interpretations of this phenomenon and some novel physical meanings. Three essential points should be highlighted:

(*i*) Thanks to this technique of linearization and the proposed pseudo-power model, we estimated more precisely the optimal value of the formulation of 3.5% of nano-oxide (ZnO) suspension as coating onto the polymeric support enhanced the water permeability.

(*ii*) Using the Interpolation Methods and the proposed pseudo-power model, we estimated the maximum contact angle after UV irradiation at about 133°.

(*iii*) Using the Extrapolation Methods and the proposed pseudo-power model, we found that other than the reached minimum contact angle is recorded without nano-oxides, we can also have this minimum condition for a maximum ZnO concentration estimated at approximately 8.55%.

REFERENCES

[1]. N. Vrinceanu, N. Ouerfelli, D. Coman, *New graphical predictions of some UV radiation and water shielded attributes of polymeric supports with direct implication in comfort performance* in Msahli, S., Debbabi, F. (eds) Advances in Applied Research on Textile and Materials - IX. CIRATM. Springer Proceedings in Materials, vol 17. Springer, Cham. 2020.

[2]. Broasca G., Borcia G., Dumitrascu N., Vrinceanu N. *Characterization of ZnO coated polyester fabrics for UV protection"* in Applied Surface Science, vol. 279, pp. 272-278, 2013.

[3]. M. Iorgoaiea Guignard, C. Campagne, S. Giraud, M. Brebu, N. Vrinceanu, LI. Cioca *"Functionalization of a bamboo knitted fabric using air plasma treatment for the improvement of microcapsules embedding"*, The Journal of The Textile Institute, vol 106, nr. 2, pp. 119-132, 2015.

[4]. D.Tanasa, N.Vrinceanu, A.Nistor, C.M.Hristodor, E.Popovici, I.L.Bistricianu, F.Brinza, D.Chicet, D.Coman, P A.ui, A.M.Grigoriu, G. Broasca, *"2aQZinc oxide-linen fibrous composites: morphological, structural, chemical and humidity adsorptive attribute"* in Textile Research Journal, vol 82, nr. 12, pp. 832-844, 2012.

[5]. R.F. Popovici, I.F. Alexa, O. Novac, N. Vrinceanu, E. Popovici, C.E. Lupusoru, V.A. Voicu, *Pharmacokinetics study on mesoporous silica-captopril controlled release systems,* in Digest Journal of Nanomaterials and Biostructures, vol 6, nr. 3, pp. 1619-1630, 2012.

[6]. CM. Hristodor, N. Vrinceanu, R. Pode, et al. *Preparation and thermal stability of Al_2O_3-clay and Fe_2O_3-clay nanocomposites, with potential application as remediation of radioactive effluents.* in J. Therm. Anal. Calorim. Vol. 111, pp. 1227–1234, 2013.

[7]. N. Vrinceanu; M.I. Guignard; C. Campagne, S. Giraud, R.I. Prepelita, D. Coman, V.D. Petrescu, D.D. Dumitrascu, N. Ouerfelli, M.P. Suchea. *Correlation between surface engineering and deformation response of some natural polymer fibrous systems* in Journal of Engineered Fibers and Fabrics. vol 13, nr. 2, pp. 30-38, 2018.

[8]. K. Sukran, N. Tugba, Y. Ahmet, *"Single and hybrid effects of nano-TiO2 and -ZnO particles on multifunctional properties of textiles"* in Applied Polymer, vol. 14, nr. 10, 2023.

[9]. J. Yang, J. Wang, M. Strømme, et al. Enhanced UV protection and water adsorption properties of transparent poly(methyl methacrylate) films through incorporation of amorphous magnesium carbonate nanoparticles. J Polym Res 28, 281, 2021.

[10]. S.M. Tanyaradzwa, A. Gebrekrstos, J. Tersur O, S. S. Ray, *"An overview of recent advances in polymer composites with improved UV-shielding properties",* in Applied Polymer, vol. 14, nr.10, 2023.

[11]. R. Bagherzadeh, M. Gorji, M. Latifi, P. Payvandy, L.X. Kong,*"Evolution of moisture management behavior of high wicking 3D warp knitted spacer fabrics"* in Fibers Polym, vol. 13, nr. 4, pp. 529–534 2012.

[12]. G.E.P. Box, D.W. Behnken. Some new three level designs for the study of quantitative variables. Technometrics, vol 2, nr. 4, 455-475, 1960.

[13]. Alojz Anžlovar, Zorica Crnjak Orel, Majda Žigon. *"Nanocomposites with nano-to-sub-micrometer size zinc oxide as an effective UV absorber"*, in Polimeri vol 29, nr. 2, pp. 84-87, 2008

[14]. Chao-Hua Xue, Wei Yin, Shun-Tian Jia, Jian-Zhong Ma. *UV-durable super hydrophobic textiles with UV-shielding properties by coating fibers with ZnO/SiO_2core/shell particles* in Nanotechnology, vol 22, nr. 41, 2011.

[15]. New equation correlating nano-oxides concentration and some UV and water protection attributes of multilayer polymeric supports, N. Vrinceanu, N. Ouerfelli, preprint DOI:10.13140/RG.2.2.23320.40967