PREPARATION AND CHARACTERIZATION OF TIO_2-SILICONE NANOCOMPOSITE OBTAINED BY SOL-GEL METHOD

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Abstract: *The sol-gel process is attractive for the nanocomposite preparation due to its unique advantages such as low temperature processing, high homogeneity of final products and its capability to generate materials with controlled surface properties. The preparation of TiO_2-Silicone nanocomposite by sol–gel method, which is efficient at producing thin, transparent multi-component oxide layers, was considered due to its possible application as finishing coating on leather. In this study the preparation and characterization of TiO_2-Silicone nanocomposite were investigated. TiO_2-Silicone nanocomposite was prepared from titanium n-butoxide (TBO) and tetraethoxysilane (TEOS) catalyzed with acid. The chemical structure of the composite was evaluated by means of Raman spectroscopy. Atomic Force Microscopy (AFM) was employed to characterize the surface properties of composite films. In summary, the colloidal TiO_2–Silicone nanocomposite solution was successfully synthesized using the sol-gel method. The turbidity value of the TiO_2–Silicone nanocomposite solution was 12.7 ntu. The TiO_2–Silicone nanocomposite was mildly acidic with a pH value of 5.2. It was determined that the viscosity of the TiO_2– Silicone nanocomposite solution was approximately equal to 1-3 mPa.s. The particles sizes were approximately 5.4 nm, with the coatings being approximately 0.06 µm in thickness. From the results obtained it was revealed that the TiO_2-Silicone nanocomposite can be used as coating in leather fninshing process.*

Key words: *TiO_2-Silicone nanocomposite, Sol–gel, Leather, Coating, Finishing process.*

1. INTRODUCTION

The sol-gel process is attractive for the nanocomposite preparation due to its unique advantages such as low temperature processing, high homogeneity of final products and its capability to generate materials with controlled surface properties [1, 2]. The sol-gel process can be classified as a wet-chemical technique as it used chemical solutions (sol) as a precursor for an integrated network (gel) of either discrete particles or network polymer in order to fabricate materials (typically metal oxide) [3].

Thin transparent layers containing TiO_2 have been intensively studied due to their interesting application potential [4]. The physical and chemical properties of TiO_2 crystallite size can be controlled by adding second semiconductor into the TiO_2 matrix [5]. Silicon dioxide (SiO_2) which has high thermal stability and excellent mechanical strength being incorporated into the TiO_2 matrix helps to create new catalytic active sites due to interaction between TiO_2 and SiO_2. And at the same time, SiO_2 acts as the carrier of TiO_2 and helps to obtain a large surface area as well as suitable porous structure [6].

There are a limited number of studies related to the preparation of nanocomposites for leather finishing, where mostly nanolayered silicates and nano SiO_2 were used as inorganic fillers for binders which resulted in improved physical, mechanical and rheological properties of the materials or finished leathers [7, 8, 9, 10]. In addition there is no information about TiO_2-silicone nanocomposite used as a coating in leather finishing.

In this study, we propose to prepare TiO_2-Silicone nanocomposite via sol-gel method at ambient temperature. The chemical structure of composite was characterized by using Raman spectroscopy and surface property of the composite film was observed with Atomic Force Microscopy (AFM). Particle size was measured by a particle sizer.

2. EXPERIMENTAL

2.1 Materials

Tetraethyl orthosilicate (TEOS) was purchased from Aldrich. Titanium n-butoxide (TBO) was provided by Merck. All of these materials were used as received. Distilled water for hydrolysis of alkoxides and acetic acid (100%) as catalyst were used. Ethyl alcohol (Merck), analytical grade, was the solvent for the sol.

2.2 Preparation and Characterization of TiO_2-Silicone nanocomposite

The TiO_2-SiO_2 composite solution was produced in the following way: the amounts of required ethanol, acetic acid, distilled water and TEOS were mixed in the round-bottomed flask with stirring condition. Into this solution required amount of TBO was added dropwise. The mixture was stirred for 30 minutes to complete hydrolysis process of SiO_2 and TiO_2. The ultrasonic treatment was applied under 15 kW power. The final transparent sol was then aged to obtain gelous dispersion. To investigate the property of TiO_2-SiO_2 composite film the prepared solution was poured on glass slices (3x7 cm) at room temperature.

To determine the solution characteristics the turbidity, pH value and viscosity of the prepared solution were measured. The turbidity of the solution was measured using a Delta OHM Turbidimeter (Italy) according to the ISO 7027 nepheometric method. The measurements were taken in the range of 0–1000 nephelometric turbidity units. The pH value of the solution was measured to determine its acidic and basic characteristics with a standard pH meter (WTW Inolab, Germany). The viscosity was obtained with a Rheosys Merlin VR digital rheometer (USA). Raman Spectroscopy (Thermo DXR, USA) and Atomic Force Microscopy (XE–Nanomagnetics Instruments, UK) were employed to characterize the chemical structure and surface property of nanocomposite film. Raman spectra were obtained in the range of 4000 and 400 cm^{-1} at a resolution of 2 cm^{-1}. Particle size was measured by a particle sizer (Malvern Mastersizer 2000, UK).

3. RESULTS AND DISCUSSION

Table 1 presents the turbidity, pH and viscosity values of the prepared solution. Turbidimetric measurements were made to reveal the complete dissolution of the precursors in the solution. The turbidity value was at 12.7 nephelometric turbidity units, indicating that the chemical precursors had completely dissolved in the solution. The pH value of composite solution has a mildly acidic pH value of 5.2. It was determined that the viscosity of the TiO_2- Silicone colloidal solution was in the range of 1–3 mPa.s. The viscosity value of the solution is a key factor in controlling the film thickness. In our case, TiO_2-Silicone nanocomposite was obtained with low-viscosity. The particles were approximately 5.4 nm in size.

Table 1. *Main characteristics of TiO_2-Silicone nanocomposite solution*

TBO/TEOS (mol ratio %)	Turbidity, ntu	pH	Viscosity, mPa.s	Particle size, nm
50/50	12.7	5.20	1-3	5.94

To gain better understanding of structure of composite, we measured the Raman spectrum of TiO_2– Silicone nanocomposite. The Raman spectrum of TiO_2– Silicone nanocomposite composite is given in Fig. 1. The sharp peak at 146 cm^{-1} is indicative of the presence of TiO_2 in the anatase phase. Although the rutile phase also exhibits a peak around this area it is a normally very weak signal, therefore this peak is due to the presence of the anatase phase [11]. The SiO_2 peaks are also quite weak and hard to distinguish in this spectrum however the broad peak centered at 300 cm^{-1} in the spectrum indicates the presence of a SiO_2 shell [12].

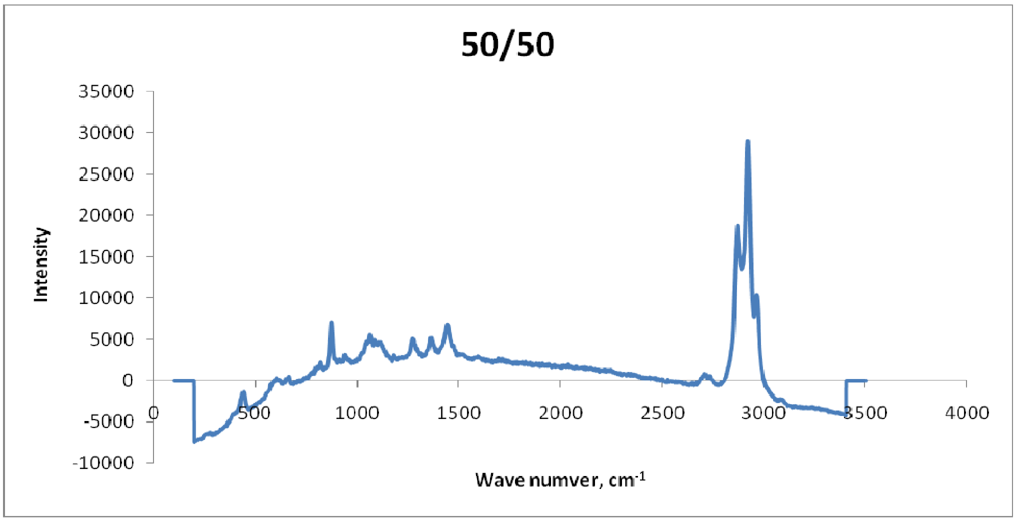

Fig 1: *Raman spectrum of TiO_2– Silicone nanocomposite*

AFM was used to characterize the surface morphology of nanocomposite film. Fig. 2 shows AFM images of the surface of the TiO_2-Silicone nanocomposite thin film. It can be seen from the Fig. 2 that films have granular microstructure. AFM gives the thickness value of TiO_2-Silicone nanocomposite film as 0.06 µm. In fact, the coating was evenly and homogenously distributed throughout the surface. Thus, it was observed that we have benefited from the advantages of the sol-gel method such as good homogeneity, ease of composition control and low processing temperature and obtained a thin, transparent and evenly distributed film on substrate.

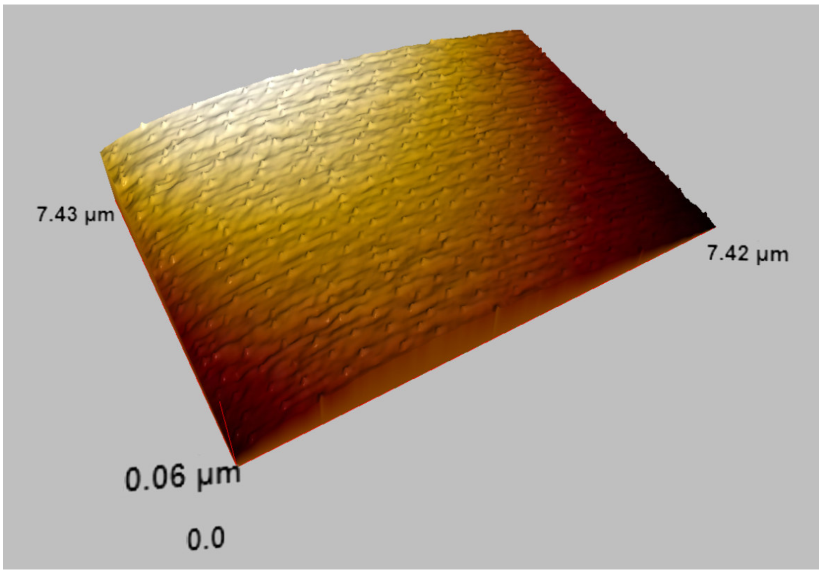

Fig. 2: *AFM image of TiO_2– Silicone nanocomposite film*

Within this framework, further studies are focusing on the investigation of the performance of colloidal TiO_2– Silicone nanocomposite as finishing coating on leather material.

4. CONCLUSIONS

In summary, the colloidal TiO_2–Silicone nanocomposite solution was successfully synthesized using the sol-gel method. The turbidity value of the TiO_2– Silicone nanocomposite solution was 12.7 ntu. The pH value of TiO_2– Silicone nanocomposite was mildly acidic with a pH value of 5.2. It was determined that the viscosity of the TiO_2– Silicone nanocomposite solution was approximately equal to 1-3 mPa.s. The particles were approximately 5.4 nm in size, with the coatings being approximately 0.06 µm in thickness. The thin and transparent coating obtained from the composite was evenly distributed. It was revealed that the TiO_2-Silicone nanocomposite can be used as leather coating material.

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REFERENCES

[1] D. Niznansky, N. Viart, J.L. Rehspringer, "*Nanocomposites Fe_2O_3/SiO_2-Preparation by Sol-Gel Method and Physical Properties*", Journal of Sol-Gel Science and Technology 8, 615-618, 1997.

[2] AS Al. Dwayyan, M. Naziruddin Khan, AA Al. Ghamdi, SS. Al-Deyab, "*Effect of DCCA on The Optical and Lasing Properties of Dye Doped Silica Gels/Ormosils*", Canadian Journal of Pure and Applied Sciences, Vol. 2, No. 1, pp. 221-226, 2008.

[3] R. Abd Aziz, N. Asyikin, I. Sopyan, "*Synthesis of TiO_2 -SiO_2 Powder Photocatalyst via Sol-Gel Method: Effect of Titanium Precursor Type on Powder Properties*", Journal - The Institution of Engineers, Malaysia, Vol. 70, No.4, pp. 34-40, 2009.

[4] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, "*Environmental Applications of Semiconductor Photocatalysis*", Chemical Reviews, Vol.95, No.1, pp. 69-96, 1995.

[5] L. Zhou, S. Yan, B. Tian, J. Zhang, M. Anpo, "*Preparation of TiO_2–SiO_2 Film with High Photocatalytic Activity on Pet Substrate*", Materials Letters, Vol. 60 No.3, pp. 396-399, 2006.

[6] P. Cheng, M. Zheng, Y. Jin, Q. Huang, M. Gu, "*Preparation and characterization of silica-doped titania photocatalyst through sol–gel method*", Materials Letters, Vol. 57, pp.2989– 2994, 2003.

[7] M. Jianzhong, Z. Zhijie, L. Lingyun, H. Jing, "*Application of Acrylic Resin Coating Agent Modified by Nano SiO_2*". JSLTC 90, 188-192, 2006.

[8] J. Ma, J. Hu, Z. Zhang, L. Liu, "*The Acrylic Resin Leather Coating Agent Modified by Nano SiO_2*", Journal of Composite Materials 40, 2189-2201, 2006.

[9] Z. Xiuli, C. Yi, F. Haojun, S. Bi, "*Waterborne Polyurethane / O-MMT Nanocomposites for Flame Retardant Leather Finishing*". JSLTC 94, 77-83, 2010.

[10] O. Yilmaz, C. N. Cheaburu, G. Gulumser, C. Vasile, "*Rheological Behavior of Acrylate /Montmorillonite Nanocomposite Latexes and Their Application in Leather Finishing as Binders*", Progress in Organic Coatings 70, 52-58, 2011.

[11] T. Ohsaka, F. Izumi, Y. Fujiki, "*Raman spectrum of anatase, TiO_2*", *J. Raman Spectrosc.* 7, 321–324, 1978.

[12] D. Greene, R. Serrano-Garcia, J. Govan, Y. K. Gun'ko, "*Synthesis Characterization and Photocatalytic Studies of Cobalt Ferrite-Silica-Titania Nanocomposites*", *Nanomaterials 4*, 331-343, 2014.