

# Nanocomposite coatings based on alkyd resin with TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles

## Abstract

Alkyd resin based nanocomposite coatings filled with different content of silicon oxide (SiO<sub>2</sub>) and titanium oxide (TiO<sub>2</sub>) nanoparticles (2 and 4<sup>wt%</sup>) were prepared by solvent casting method. Characterization of the prepared nanocomposite coatings was performed by Differential Scanning Calorimetry (DSC) and Scanning Electron Microscope (SEM). The nanocomposite coatings were also tested for their Chemical stability, Mechanical properties, Abrasion and Impact resistance. DSC analysis shown that all the characteristic temperatures (glass transition temperature-T<sub>g</sub>, reaction temperature-T<sub>r</sub>) were shifted to lower values by increasing the nanoparticle content. Mechanical characterization confirmed good elasticity with bending of f=2cm and impact resistance of 1 kg/cm<sup>2</sup>. Increasing the nanoparticle content, the wear resistance was changed as well. Better abrasion resistance was registered for nanocomposite coatings with SiO<sub>2</sub> nanoparticles compared to nanocomposites with the same content of TiO<sub>2</sub>.

**Keywords:** nanocomposite coatings, alkyd resin, TiO<sub>2</sub>, SiO<sub>2</sub>

Volume 3 Issue 6 - 2019

Anita Grozdanov,<sup>1</sup> Gennaro Gentile,<sup>2</sup>  
Maurizio Avella,<sup>2</sup> Tatyana Dobрева,<sup>3</sup> Rumiana  
Kotsilkova<sup>3</sup>

<sup>1</sup>University St. Cyril and Methodius, Republic of Macedonia

<sup>2</sup>Institute for Polymers, Composites and Biomaterials, National Research Council, Italy

<sup>3</sup>Central Laboratory of Physico-Chemical Mechanics–Bulgarian Academy of Science, Bulgaria

**Correspondence:** Anita Grozdanov, Faculty of Technology and Metallurgy, Rugjer Boskovic 16, University St. Cyril and Methodius, Skopje, Republic of Macedonia,  
Email anita.grozdonov@yahoo.com

**Received:** October 30, 2019 | **Published:** November 14, 2019

**Abbreviations:** DSC, differential scanning calorimetry; SEM, scanning electron microscope; NC, nanocomposites

## Introduction

Design and development of new types of polymer based nanocomposites (NC) is rapidly emerging as a multidisciplinary research activity whose results could broaden the applications of polymers to the great benefit of many different industries: automotive, construction, aerospace, electrical and electronics, food packaging.<sup>1-4</sup> Polymers, resins and plastics containing additives such as clays and various nanostructures have recently become widely used as replacements for conventional materials of steel and other metal products, or their coatings, especially in the field of automotive industry. The application of the polymer NC coatings for the corrosion protection of steels was reviewed by Toshiaki Ohtsuka<sup>5</sup> he reported various systems mainly based on conductive polymer matrix. The incorporation of layered silicates into polymer matrix was a research focus for many years, since the results of the Toyota research team showed that the incorporation of 2 vol% of exfoliated clay into Nylon-6 contributes to about 90°C increase in glass transition temperature and double Young's modulus.<sup>4</sup> Traditionally, alkyd resins as oil-modified polyesters, have been placed amongst the most widely used resins in exterior solvent-based inexpensive coating applications because of their high gloss and durability. Alkyd-based nanocomposite coatings were reported to exhibit better properties compared to the traditional ones.<sup>2</sup> It was shown that water vapour permeability of nanocomposite coatings remarkably decreased with respect to neat coating. For example, a decrease of water vapour permeability by a factor of 15 has been measured.<sup>1</sup> Inorganic-organic composites based on organo-alkoxysilanes and other alkoxides have demonstrated their usefulness even for hard coatings on eye-glass lenses.<sup>6</sup> It has been shown that the addition of nanoparticles, especially in combination with epoxy silanes, which act as an inorganic as well as an organic crosslinking agent, leads to a substantial increase of the abrasion resistance of such systems without losing any transparency. Therefore, due to the incorporation of nanoparticles into the certain polymer matrix, high abrasion resistance can be obtained.<sup>1,5</sup> Avella et

al.<sup>7</sup> have shown that the presence of only 2% nanoparticles strongly improves the abrasion resistance, as well as the wear of Poly(Methyl methacrylate) (PMMA).<sup>6</sup> The nanocomposites showed an average weight loss about half (2,5% against 5% of removal material) with respect to that of neat polymer.

The addition of SiO<sub>2</sub> nanoparticles into acrylic-based polyurethane coatings apparently improved the micro and macro hardness as well as abrasion resistance. Another type of nano meter SiO<sub>2</sub> is the colloid SiO<sub>2</sub>, which was also used to improve hardness, wear resistance and scratch resistance of the coatings. Literature survey also reported the improved performances of epoxy/nano-SiO<sub>2</sub> and methacrylate coating on polycarbonate substrate.<sup>2</sup> Yang et al.<sup>8</sup> have studied the influence of the nature and the size of TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles on the optical and electrical properties of Poly(p-phenylene vinylene) based nanocomposites.<sup>8</sup> Jiratumnukul et al.<sup>9</sup> have studied nanocomposite alkyd coatings prepared with organoclay, by FTIR and XRD analyses.<sup>9</sup> They have found that the X-ray profiles showed an exfoliated structure for the organoclay alkyd coating. The application of the organoclay to alkyd-based clear coatings showed a significant enhancement of the hardness and impact strength of the coating film compared with those of unmodified montmorillonite equally incorporated into the coating formulations.<sup>9</sup> Mironi-Narpaz et al.<sup>10</sup> have worked also on nanocomposite systems based on unsaturated polyester (UP)-alkyd resin (without styrene) mixed with different organo-clays.<sup>10,11</sup> Processing parameters such as mixing modes, applied shearing levels, clay contents, and mixing-temperatures were investigated. Prolonged high shear levels promoted the intercalation and exfoliation of the silicate layers, resulting in a better dispersion of clay particles.

The higher shear levels effects were achieved by vigorous mechanical mixing and they were intensified by adding large amounts of clay and optimized matrix viscosity.<sup>11</sup> Lin et al.<sup>12</sup> have worked on preparation and morphologies of the biodegradable glycerol-based alkyd resins/layered silicates nanocomposites, as well as their thermal stabilities and mechanical properties.<sup>12</sup> Although the mechanical properties of these glycerol-anhydride alkyd resins/clay nanocomposites were greatly improved, Lin et al. still had a problem

how to minimize the formation of aggregates in the case of mica or talk within the alkyd resin matrix. The properties changes of the nanocomposite coatings were attributed to the modification of coating structures and different diffusion behavior in the nanocomposite coatings compared to the conventional coatings. The most of the studies related to the nanocomposite coatings were focused on mechanical, optical or anticorrosion properties. In this work, we have examined the chemical, thermal and abrasion resistance properties of the hybrid materials using the same alkyd resin in order to check the influence of the inorganic nanoparticles on the behavior of the obtained nanocomposites. SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles of different content were selected and incorporated into alkyd resin to obtain nanocomposite coatings. However, in order to transfer the nanocoating technology from research and lab scale level into the industrial production of low-cost nanocoating materials, further efforts are needed.

## Experimental

### Materials

Alkyd resin with solid content of 44.6% and viscosity and density of  $\mu_{20}=51$ s and  $\rho_{20}=886$ kg/m<sup>3</sup> respectively was used as received. The TiO<sub>2</sub> nanoparticles were Degussa P25, ca. 80% anatase, 20% rutile; with particle size around 21 nm. SiO<sub>2</sub> nanoparticles (Aerosil 300, consists of spherically shaped primary particles, with a mean diameter of 7nm and specific surface area of 300m<sup>2</sup>/g) also from Degussa, Germany were used.

### Nanocomposite coatings preparation

Nanocomposites were prepared by incorporation of TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles in alkyd based coating formulation with a high-speed disperser at a speed of 400 rpm for 30 min at room temperature. In order to solve the dispersion problem of the nanoparticles in alkyd resin based coatings, previously the alkyd resin was mixed with dispersant agent. Two types of nanoparticles, TiO<sub>2</sub> and SiO<sub>2</sub>, have been selected and used in concentration of 2 and 4<sup>wt</sup>%. Coating films with thickness of ~60µm were obtained on Teflon sheet and allowed to dry at room temperature for 5 days.

### Characterization

Characterization protocol of the prepared nanocomposite coatings includes Differential Scanning Calorimetry (DSC), Scanning Electron Microscope (SEM), Nanoindentation and Atomic Force Microscopy (AFM), chemical stability, abrasion and flexibility test.

### Differential scanning calorimetry

Thermal properties of the coatings were analyzed using differential scanning calorimeter (Perkin Elmer DSC -7 Analyzer), from -30°C to 260°C with the heating rate of 20K/min. The measurements were performed under nitrogen.

### Scanning Electron Microscopy

The morphology of the samples was followed by Scanning Electron Microscope using the JEOL system. Vacuum Au/Pd alloy deposition of the samples in a Polaron Sputtering apparatus was performed previously.

### Chemical stability

Nanocomposite coating samples (1x1cm) were cut and they were tested in various acid and alkaline media, for different times of exposure (2, 3, and 5days) up to the moment of dissolving the samples.

### Nanoindentation

The roughness was measured by Profilometer 500. The average value was obtained from 5scannings, each of them 500 µm in contact mode with 10 mg applied contact force. The Hardness (H) was determined from nanoindentation using Berkovich Diamond indenter, with 10mN applied force (load time=15s, holding time=10s, unloading time=15s). The average value from minimum 10 measurements was done.

### Abrasion resistance

Abrasion resistance was followed by means of TABER Abraser machine under load of 10N. The abrasion resistance was reported as number of cycles up to the coating crack as well as the change in mass of the test specimen per number of performed cycles. The twist flexibility was determined using a standard method DIN 53211 by twisting a panel with a coating film over a metallic stick of defined diameter. During the specified time the coated film should not crack and separate from the panel.

## Results and discussion

### Thermal properties of nanocoatings

The incorporation of nanoparticles in appropriate polymer matrix or resin could significantly affect the thermal, barrier, mechanical and wear properties, as well as the morphology of the composites coatings.<sup>2-9</sup> The characteristic thermal parameters of the studied nanocomposite coatings obtained by DSC analysis are presented in Table 1. The presence of TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles contributed to the shifting of the characteristic temperatures: glass transition temperature (T<sub>g</sub>) and curing reaction temperature (Tr) to the lower temperatures when compared to the characteristic temperatures of the pure alkyd resin. The glass transition temperature shifting to lower temperatures could be an indication for better flexibility of the obtained nanocomposites coatings, with higher nanoparticles content. Remarkable effect was registered in alkyd resin filled with 4 wt % TiO<sub>2</sub> nanoparticles, where the T<sub>g</sub> value was lower than the T<sub>g</sub> of alkyd resin filled with the same quantity of SiO<sub>2</sub> (T<sub>g</sub> was shifted for 10 degrees). The obtained values for T<sub>g</sub> of the alkyd-based nanocomposites lower than 30°C (T<sub>g</sub><25-30°C), suggest higher durability of the obtained nanocoatings which is in agreement with the practical data. The notable T<sub>r</sub> shifting to the lower temperatures in the nanocomposite systems indicate on the catalytic effect of the nanoparticles in the alkyd reaction. The curing reaction temperature decreases as compared to the curing temperature of neat coating, also the heat of curing value increases (ΔH<sub>r</sub>). This indicate that the interaction between TiO<sub>2</sub> and SiO<sub>2</sub> nano-particles and alkyd matrix improves the curing of nanocomposite coatings. Similar results were obtained alkyd-based systems modified with other resins or nanoparticles such as ZnO.<sup>6</sup>

### Chemical stability

From practical point of view, for the nanocomposite coatings a very important practical characteristic is their chemical stability in various media. The results obtained after dipping the samples in various (neutral, acid and alkaline media) for different times of exposure are collected in Table 2. The obtained results shown that the prepared nanocomposite alkyd resin/TiO<sub>2</sub> and alkyd resin/SiO<sub>2</sub> coatings are stable in water. In organic solvents, such as acetone and chloroform, both systems swelled. After 96 h of exposure in organic solvent, the nanocomposite sample with 4% TiO<sub>2</sub> was broken, while the sample with 4 % SiO<sub>2</sub> has lost the colour and become a transparent. In the

presence of various acids, both nanocomposite coatings swelled and changed the colour to dark brown. In alkali media, both coatings were deformed and rolled, as well as changed their colour and porosity, they had yellow colour and they were porous (Table 3).

**Table 1** DSC data for the nanocomposite coatings based on alkyd resin with TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles

	$T_g$ [°C] <sup>a</sup>	$T_{Onset}$ [°C] <sup>b</sup>	$\Delta C_p$ [J/g°C] <sup>c</sup>	$T_r$ [°C] <sup>d</sup>	$T_{r-Onset}$ [°C] <sup>e</sup>	$\Delta H_r$ [J/g] <sup>f</sup>
Alkyd resin	32.30	23.50	0.40	121.30	94.50	150.00
Alkyd/2% SiO <sub>2</sub>	24.80	7.30	0.40	106.20	81.70	200.80
Alkyd/4% SiO <sub>2</sub>	22.90	1.50	0.55	102.50	76.00	213.00
Alkyd/2%TiO <sub>2</sub>	24.87	1.30	0.33	112.00	81.60	218.00
Alkyd/4%TiO <sub>2</sub>	14.87	6.80	0.30	104.00	75.50	285.00

<sup>a</sup> $T_g$  - is the glass transition temperature.

<sup>b</sup> $T_{Onset}$  - is the characteristic temperature at the beginning of the glass transition process.

<sup>c</sup> $\Delta C_p$  - is the change in the heat capacity normalized to the same alkyd resin weight reaction.

<sup>d</sup> $T_r$  - is the characteristic curing reaction temperature.

<sup>e</sup> $T_{r-Onset}$  - is the characteristic temperature at the beginning of the curing reaction process.

<sup>f</sup> $\Delta H_r$  - is the heat of curing reaction process.

**Table 2** Effects of different chemical agents

Solvent	Alkyd resin	Nanocomposite coating alkyd /4% TiO <sub>2</sub>	Nanocomposite coating alkyd /4% SiO <sub>2</sub>
Water	After 48h wave changes	Stable (unchanged) sample	Unchanged dimensions, colour changes from yellow to white
Acetone	The sample swelled	The sample swelled	The sample swelled and rolled at the bottom, transparent colour
Chloroform	The sample swelled and it become transparent	The sample swelled, and after 96 h beaks on several peaces	The sample swelled and was floating below the surface, transparent colour
Acid medium			
Acetic Acid (concentrated)	The sample swelled and it is transparent	The sample swelled, and received white milk-colour	The sample swelled and it become transparent
60% Acetic Acid	The sample was rolled at the bottom, and became transparent	The sample swelled and went down to the bottom	The sample swelled and it was break, mat-colour changes
Sulphuric Acid (concentrated)	Colour changes to brown and black, after 24h the sample was almost dissolved	Colour changes to light brown, it was floating below the surface, and after 24h the sample was almost dissolved	The sample was rolled, floated below the surface, colour changes to Cuprum-colour,
66% Sulphuric Acid	The sample was floating below the surface, after 48h swelled and colour changes to dark-brown	After 24h colour was changed to brown and the sample was rolled and floated under the surface	The sample was swelled and floated under the surface, after 48 h the colour was changed to dark brown
Alkali medium			
20 % Sodium hydroxide	The sample swelled and the colour was changed to golden, after 48 h the solvent-colour was gold	The sample was rolled and was broken , the solvent was coloured	The sample was rolled and floated under the surface, the solvent was yellow coloured

**Table 3** Nanoindentation data for the alkyd-based nanocomposite coatings with SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles

Sample	Roughness[nm] <sup>a</sup>	Hardness [MPa] <sup>b</sup>	Young's modulus [GPa] <sup>c</sup>	Depth max [μm] <sup>d</sup>	Contact area [μm.sq] <sup>e</sup>
Alkyd resin	54	51	1.681	2.834	197.300
Alkyd/2 % TiO <sub>2</sub>	98	57	2.011	2.725	184.433
Alkyd/4 % TiO <sub>2</sub>	410	45	2.179	3.020	224.571
Alkyd/2% SiO <sub>2</sub>	346	52	1.957	2.799	192.838
Alkyd/4% SiO <sub>2</sub>	344	39	1.464	3.225	255.549

<sup>a</sup> - is the nanocomposite coating roughness.

<sup>b</sup> - is the nanocomposite hardness determined from nanoindentation.

<sup>c</sup> - is the Young's modulus.

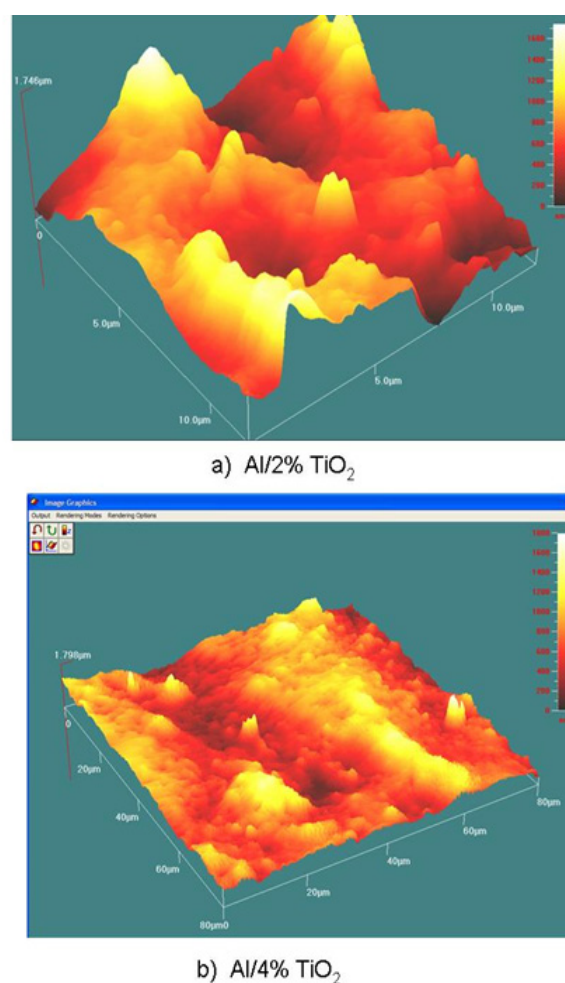
<sup>d</sup> - is the maximum contact depth.

<sup>e</sup> - is the contact area.

### Mechanical properties

The results of the mechanical properties testing shown that all coatings, obtained with both nanoparticles, exhibited very high flexibility. The obtained value of flexibility was 2cm for all studied systems, without crack registered on the nanocomposite coatings due to the characteristics of alkyd resin. Both nanoparticles have higher aspect ratio which could contribute in the higher strength and mechanical resistance of the prepared nanocomposite coatings. The obtained data from the nanoindentation testing for the surface roughness and the hardness as well as the Young's modulus are presented on Table 3. Nanoindentation data have shown that for both types of nanoparticles, the roughness of the obtained nanocomposite coatings remarkably increased, while the hardness decreased by increasing the nanoparticle content. Comparing the effect of the nanoparticle type, higher values for the hardness and the Young's modulus were obtained in the nanocomposite coatings filled with TiO<sub>2</sub> nanoparticles (Table 3). Characteristic AFM surface profiles for the studied nanocomposite coatings are shown in Figure 1 – for Alkyd/TiO<sub>2</sub> system and Figure 2 for Alkyd/SiO<sub>2</sub> system. These images confirmed that the addition of both nanoparticles increased the roughness of the surface. This indicates that nanocomposite coatings with higher amount of nanoparticles, specially TiO<sub>2</sub>, should have increased surface area resulting in enhanced adhesion<sup>13</sup> (Figure 1 & 2). The abrasion resistance of the solid body is defined as its ability to withstand the progressive removal of materials from its surface as a result of mechanical action of a rubbing, scraping or erosion.<sup>6</sup> Namely, the abrasion reduces the serviceability of the affected body and low abrasion resistance is a very important drawback that modern nanocoatings must overcome. The abrasion resistance of the nanocomposite coatings has been studied to evaluate if the presence of inorganic particles such as SiO<sub>2</sub> and TiO<sub>2</sub> could improve also the scratch resistance of the neat alkyd resin. Results for the abrasion resistance of the fabricated nanocomposite coatings are presented in Table 4. Better abrasion resistance was registered for the nanocomposites filled with SiO<sub>2</sub> compared to nanocomposites with TiO<sub>2</sub> for the mass changes after the certain number of cycles, ( $\Delta m_{2\%SiO_2}=0,0136g$ ;  $\Delta m_{2\%TiO_2}=0,0521g$ ). According to the literature, this finding could be attributed to the fact that the nanoparticles support part of the applied load, thus the penetration into the polymer surface is reduced and only

micro plugging and/or micro cutting phenomena can be generated, as can be seen in Figure 3B & Figure 4B (Table 4).



**Figure 1** AFM surface profile for the Alkyd/TiO<sub>2</sub> nanocomposite coatings.

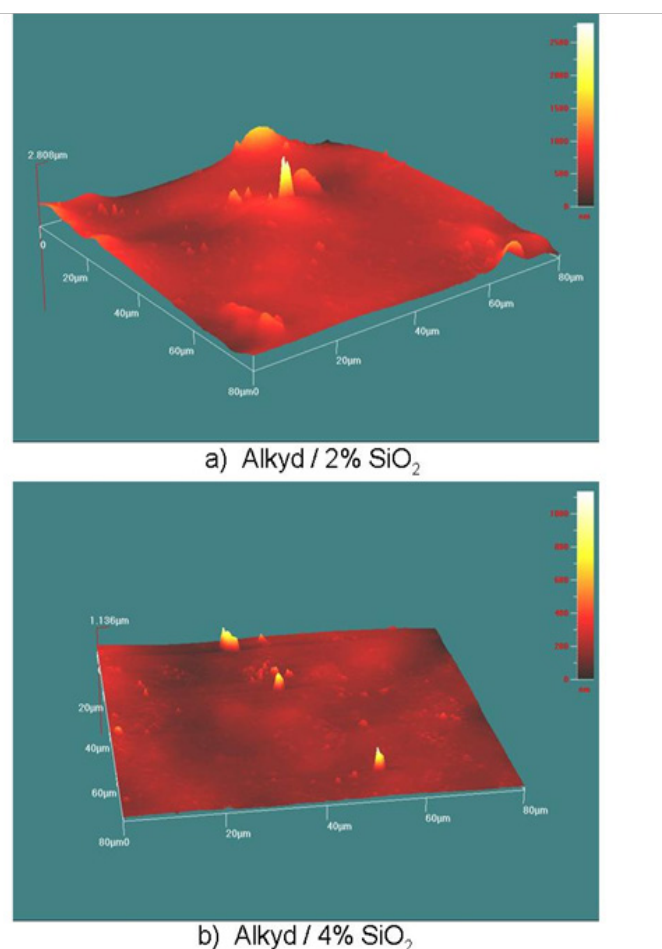


Figure 2 AFM surface profile for the Alkyd/SiO<sub>2</sub> nanocomposite coatings.

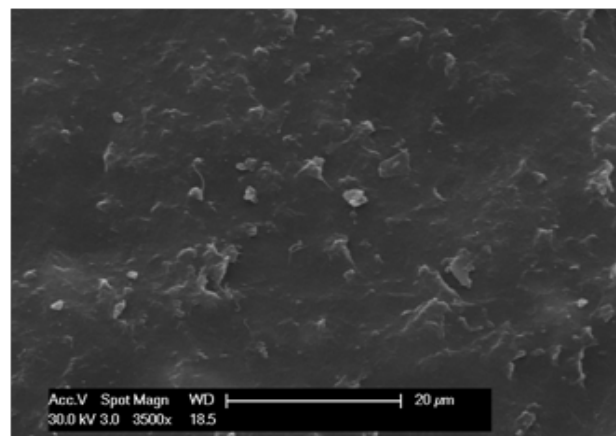
Table 4 Abrasion resistances for the nanocomposite coatings based on alkyd resin with TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles

Specimen	Number of cycles up to the coating crack
Alkyd resin	12
Alkyd / 2% SiO <sub>2</sub>	47
Alkyd / 4% SiO <sub>2</sub>	81
Alkyd / 2%TiO <sub>2</sub>	30
Alkyd / 4% TiO <sub>2</sub>	40

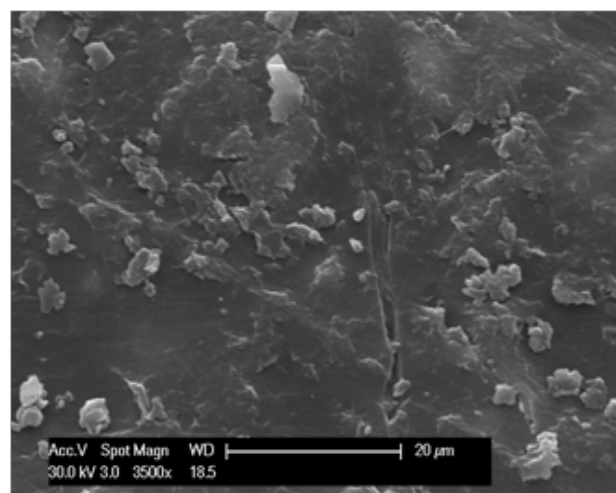
### Nanocomposite morphology

Morphology changes before and after abrasion test measurements were followed by SEM. The obtained microphotographs for Alkyd/SiO<sub>2</sub> nanocomposite coatings are shown on Figure 3A, while for the system Alkyd/TiO<sub>2</sub> nanocomposites coatings, are shown on Fig. 4a. The resulting abrasion marks and surface micro ploughing effects were registered for both investigated systems (Figure 3B & Figure 4B). Under the attack of the rough abrasive paper, the grains penetrated deeply into the surface of the polymer, removing materials from the surface by extensive micro ploughing process. During this

phase, the polymer matrix is highly plastically deformed due to the micro cutting and wear debris was formed.

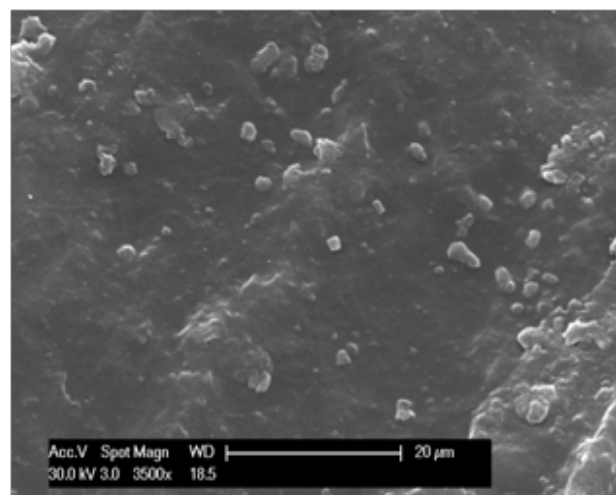


A) (x3500)

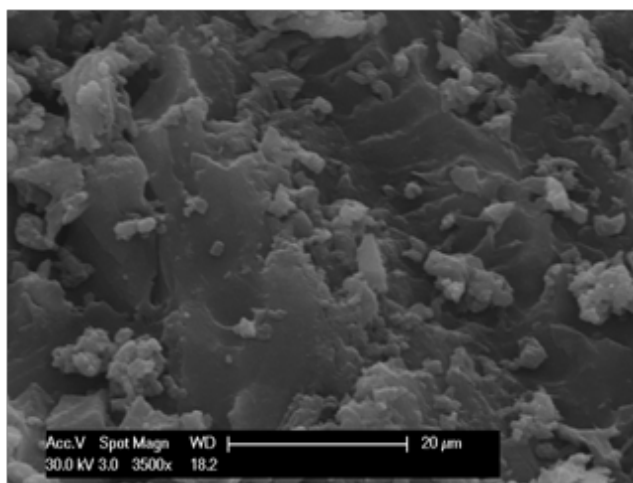


B) (x3500)

Figure 3 Morphology of Alkyd/SiO<sub>2</sub> nanocomposites coatings before (A) and after (B) abrasion test measurements.



A) (x3500)



B) (x3500)

**Figure 4** Morphology of Alkyd/TiO<sub>2</sub> nanocomposites coatings before (A) and after (B) abrasion test measurements.

## Conclusion

Using TiO<sub>2</sub> and SiO<sub>2</sub> nanoparticles, two types of nanocomposites coatings based on alkyd resin were prepared. They were characterized in terms of their thermal and mechanical behaviour. The presence of both nanoparticles, TiO<sub>2</sub> and SiO<sub>2</sub>, contributed to the shifting of the characteristic thermal parameters T<sub>g</sub> and T<sub>i</sub> to the lower temperatures indicating improved flexibility of the nanocomposite coatings. Nanoindentation data has shown that for both type of nanoparticles, the roughness of the obtained nanocomposite coatings remarkably increased, while the hardness decrease by increasing the nanoparticle content. From the studied systems, better abrasion resistance was registered for the nanocomposites with SiO<sub>2</sub> compared to nanocomposites with TiO<sub>2</sub>.

## Funding details

None.

## Acknowledgements

None.

## Conflicts of interest

The authors declare no conflict of interest.

## References

1. Dosch H, Van de Voorde MH. GENNESYS-White Paper of Grand European Initiative on Nanoscience and Nanotechnology using Neutron and Synchrotron Radiation Sources. Max-Planck Institut fur Metallforschung, Stuttgart; 2009.
2. Hongwei S, Fuchun L, Enhou H, et al. Effects of nano pigments on the corrosion resistance of alkyd coating. *J Mater Sci. Technol.* 2007;23(4):551–558.
3. Buzarovska A, Grozdanov M, Avella G, et al. Poly (hydroxy-butyrate-co-hydroxyvalerate)/titanium dioxide nanocomposites: A degradation study. *J Appl Polym Sci.* 2009;114(5):3118–3124.
4. Usuki A, Kojima Y, Kawasumi M, et al. Synthesis of nylon 6-clay hybrid. *J Mater Res.* 1993;8:1179–1184.
5. Ohtsuka T. Corrosion Protection of Steels by Conducting Polymer Coating. *Int J of Corrosion.* 2012:7.
6. Dhoke SK, Bhandari R, Khanna AS. Effect of nano-ZnO addition on the silicone-modified alkyd-based waterborne coatings on its mechanical and heat-resistance properties. *Prog Org Coat.* 2009;64(1):39–46.
7. Avella M, Errico ME, Martuscelli E. Novel PMMA/CaCO<sub>3</sub> Nanocomposites Abrasion Resistant Prepared by an in Situ Polymerization Process. *Nano Lett.* 2001;1(4):213–217.
8. Yang SH, Nguyen TP, Le Rendu P, et al. Optical and Electrical Properties of PPV/SiO<sub>2</sub> and PPV/ TiO<sub>2</sub>. *Composite Materials Composites: PA.* 2005;36(4):509–513.
9. Jiratumnukul N, Pruthipaitoon S, Pitsaroup T. Nanocomposite alkyd coating. *J Appl Polym Sci.* 2006;102(3):2639–2642.
10. Mironi-Harpaz, Narkis M, Siegmann A. Nanocomposite systems based on unsaturated polyester and organo-clay. *Polym Eng and Sci.* 2005;45(2):174–186.
11. Mironi-Harpaz, Narkis M, Siegmann A. Curing of Styrene-Free Unsaturated Polyester Alkyd and Development of Novel Related Clay Nanocomposites. *Macromolecular Symposia.* 2006;242(1):201–207.
12. Lin G, Zhang X, Li Y, et al. Some Nanocomposites Based On A Glycerol-Derived Alkyd Resin and Layered Silicates. *Mol Cryst Liq Cryst.* 2008;483:33–48.
13. Boccaccini AR, Gerhardt LC, Rebeling S, et al. Fabrication, characterisation and assessment of bioactivity of poly(d, l lactic acid) (PDLLA)/TiO<sub>2</sub> nanocomposite films. *Composites PA.* 2005;36:721–727.