EFFECT OF SILICA NANOPARTICLES ON PROPERTIES OF COATINGS BASED ON ACRYLIC EMULSION RESIN

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ABSTRACT

In this study, enhancing of some characterizations of water-based coating, i.e. physic-mechanical properties, thermal resistance and weathering durability by adding nanosilica were investigated. Nanocomposite coating formulas were filled by 2 wt.% nanosilica particles which were used in this study, namely: nanosilica from Sigma (10-20 nm), nansilica from rice husk (RHA) (~50-200 nm) and nanosilica from Arosil − Belgium (7-12 nm). The obtained results showed that in presence of nanosilica, coating properties were improved in comparison with neat coating. However, coating filled by nanosilica from rice husk indicated the best properties in studied coating formulas. It may be explained that nanosilica from rice husk was in hard spherical shape while other kinds of nanosilica were in porous shape.

Keywords: nanosilica, physic-mechanical properties, weathering durability, thermal stability, acrylic emulsion.

1. INTRODUCTION

Organic coatings have been using in various applications with protecting and decorating all kinds of materials surface purpose. Coatings can be divided two categories: water and solvent-based coating. In there, solvent-based coatings have been become popular in a huge range of applications due to their precisely advanced properties, such strong adhesion and chemical resistance. In spite of these advantages, a common drawback of solvent-based coatings is to cause environmental pollution. With the rise environmental awareness, many countries around the world applied law to restrict solvent based binder. As a result, coating on the base of waterborne binders have recently become more popular, especially, about 85% architectural paints are made from waterborne binder [1-4]. In comparison with solvent-based binder, waterborne binders are low negative effects on the human health.

In recent decades, using nanoparticles enhancing polymer properties is an advanced research. In there, nanosilica has been attracted of scientists as its superior properties. Hence, nanosilica has been studied and applied in a lot of hi-tech manufacturing industries such as chromatography column packing materials, adsorbents, corrosion inhibitors, photocatalysts, catalyst supports, and medicine [1, 5-8]. In presence of nanosilica, some properties of materials were significantly improved such as mechanical, electrical, thermal properties and weathering characterization [9-10]. Moreover, nanosilica is also used as corrosion inhibitor due to self-healing characterization of nano SiO_2 [6]. However, dispersion, shape, size and content of particles affect to characterizations of nanocomposite.

Influence of nano-SiO_2 on nanocomposite properties with various substrates was published in some literatures but there isn't information about the effect of nanosilia kinds on properties of the coating based on acrylic emulsion, especially reinforcing by nano- SiO_2 made from RHA. In effort of enhancing the properties of acrylic coating using architectural paint, nanosilica was added in coating formula. This work would present effect of 3 kinds of silica nanoparticles (from Sigma, Arosil and made from RHA) on physic-mechanical, thermal properties and weathering resistance of coating base on acrylic emulsion resin Plextol R4132.

2. MATERIALS AND METHODS

2.1. Materials

- *Water-based acrylic resin* Plextol R 4152 having 49 ± 1 % of solid content, pH at 7 – 8.5 was supplied by Symthomer Company. *Coalescing agent:* using Texanol was purchased by Dow Chemical Company.

- *Nanosilica:* (1) Nanosilica provided from Arosil (Belgium) has 7-12 nm of particles size; (2) Nanosilica obtained from Sigma which has 10-20 nm particle size; (3) Nanosilica which was made from rice husk ash and has 50-200 nm particles size, was supplied from Vietnam Institute of Industrial Chemistry.

2.2. Sample preparation

Ratio of constituents in studied formulas were presented on Table 1. First, nano SiO_2 was dispersed into deionized water (A component) and Texanol was dispersed into waterborne binder (B component) by using a supersonic equipment TPC-25 (Switzerland) in one hour. After that, the A and B mixture were mixed together and vibrated in 2 h.

Table 1. Compositions of coating formulas.

	Sample's name	Constituents					
		Plextol R4152	Texanol	Nanosilica			Deionized water
				Rice husk ash	Sigma	Aerosil	
11	R4152	8	0.12	0	0	0	0
22	RHA-SiO_2	8	0.12	0.08	0	0	0.8
33	Sig-SiO_2	8	0.12	0	0.08	0	0.8
44	Aro-SiO_2	8	0.12	0	0	0.08	0.8

The paint coatings were applied by using a sprayer (6 kg/cm^2 of pressure). The volume of paint on each substrate was calculated as the formula:

$$V_L = \frac{d_{\mu m} \times S_{(m^2)}}{10 \times X_{(\%)}}$$

where: V: the volume of paint (L); d: the dry paint coating (μm); S: the square of paint coating (m^2); X: the solid content (%).

Coatings with 25 ± 1.25 μm-thickness for IR, weight loss and morphology analyses were fabricated on glass sheets. Films for IR measurement after 7 days of dying at room temperature, were separated from the sheets and attached on an aluminum window. Samples for abrasion resistance and adhesion measurements were prepared on steel substrate and on concretes substrate, respectively, in accordance of test standards for each test.

2.3. Accelerated aging test

Coating formulas were exposed in accelerated weathering chamber - Atlas UVCON UC - 327 - 2 (USA). A cycle of aging process consisted of 4 h of dark water condensation (CON) at 50 ^{o}C and 8 h UVB exposure at 60 ^{o}C according to the standard ASTM G154. All coatings were dried during 24 h at 60 ^{o}C in vacuum oven.

2.4. Analysis

2.4.1. IR analysis

IR spectrum of unaged and aged coatings were recorded by NEXUS 670 (Nicolet, USA) in Institute for Tropical Technology, VAST. Changes of functional groups during aging exposure process were monitored quantitatively. Remaining functional groups was determined by formula [2]:

$$\text{Remaining group } (\%) = D_t/D_0 \times 100.$$

where: D_o: Optical density of functional groups in unaged coating; D_t: Optical density of functional groups in aged coating.

2.4.2. Weight loss

Weight loss (Δm_t) of aged coatings was calculated as follows [2]:

$$\Delta m_t (\%) = [(m_0 - m_t)/m_0] \times 100$$

where: Δm_t: the weight loss (%); m_0: the weight of unaged sample (g); m_t: the weight of aged sample (g).

2.4.3. Physico-mechanical properties

- Abrasion Resistance: the abrasion resistance of studied formula coatings were measured in accordance with standard ASTM D 968.

- Adhesion: The adhesion of the coatings to concrete substrate was determined by cutting test method in accordance with ISO 2409 standard.

2.4.4. SEM and TEM analysis

Surface morphology of samples was analyzed by S-4800 FE-SEM (Hitachi, Japan). Samples surface was coated with a very thin carbon layer to avoid the charging effect caused by the nonconductive nature of coatings.

Morphology of nano-SiO_2 was studied by HR-TEM - JEM 2100 (Jeol, Japan).

2.4.5. Thermo Gravimetric Analysis (TGA)

Thermo-gravimetry experiments used TGA- 50 (Shimadzu, Japan). Samples were heated from ambient temperature to $600^{o}C$ with $10^{o}C.min^{-1}$ rate, in an argon atmosphere with 50 $cm^3.min^{-1}$ flow rate.

3. RESULTS AND DISCUSSION

3.1. Morphology of nanosilica and nanocomposite coatings

Morphology of nanosilica particles were obtained by Transmission Electron Microscopy (TEM). TEM images of silica nanoparticles were displayed on Fig.1.

As can be seen from Fig. 1 nanosilica made from rice husk ash has size from 50 – 200 nm, in spherical shape and unequal distribution. Silica particles tend to combine/aggregate with each other to a huge cluster of particles. While nanosilica supplied by Sigma and Arosil exhibited unique particles, having size of 10-20 nm and in porous shape. These nanoparticles were not scattered but clustered together into spongy granules of relatively dense density.

FE-SEM image of coatings surfaces containing 2 wt % nanosilica were illustrated on Fig. 2. As can be seen from Fig. 2, neat coatings (without nanosilica) had smooth surface but surface of coating became rougher in presence of nanosilica. Depend on nanosilica type, the rough surface were presented in difference ways.
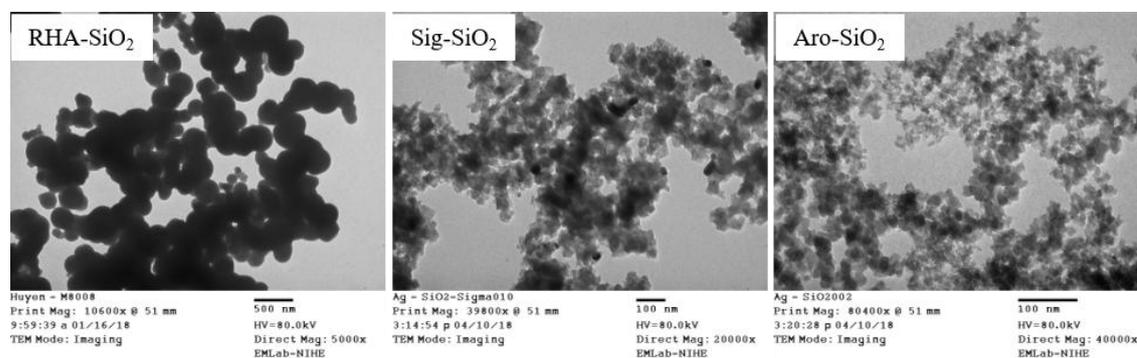
Figure 1. TEM images of nanosilica particles.

For coating containing nanosilica made from rice husk ash, the nanoparticles had nearly 50-200 nm size equaling nanoparticles diameter. It means nanosilica from rice husk ash illustrated good dispersion in acrylic polymer substrate. In contrast, surface coatings containing nanosilica from Sigma and Arosil aggregated to cluster of silica particles. Up to a point, nanosilica was not well dispersed into R4512 and thus aggregating to huge cluster of silica particles. However, coatings containing nanosilica made from rice husk ash, more or less, dispersed better than other. Nanosilica made from rice husk ash on coating observed fairly unique while coating containing nanosilica form Sigma and Arosil displayed some cluster of silica particles due to

nanosilica tending to sink. It can be explained that nanosilica made from rice husk ash has larger size in comparison with other nanosilica which studied in this work. Thus, dispersion of nanosilica made from rice husk ash may be easier than those. In addition, nanosilica from Arosil which has 7-12 nm of size and amorphous form, can easily react with water producing silicic acid [11]. As a result, creating more and stronger hydro bond to lead increasing flow viscosity and easily agglomerating nanosilica.
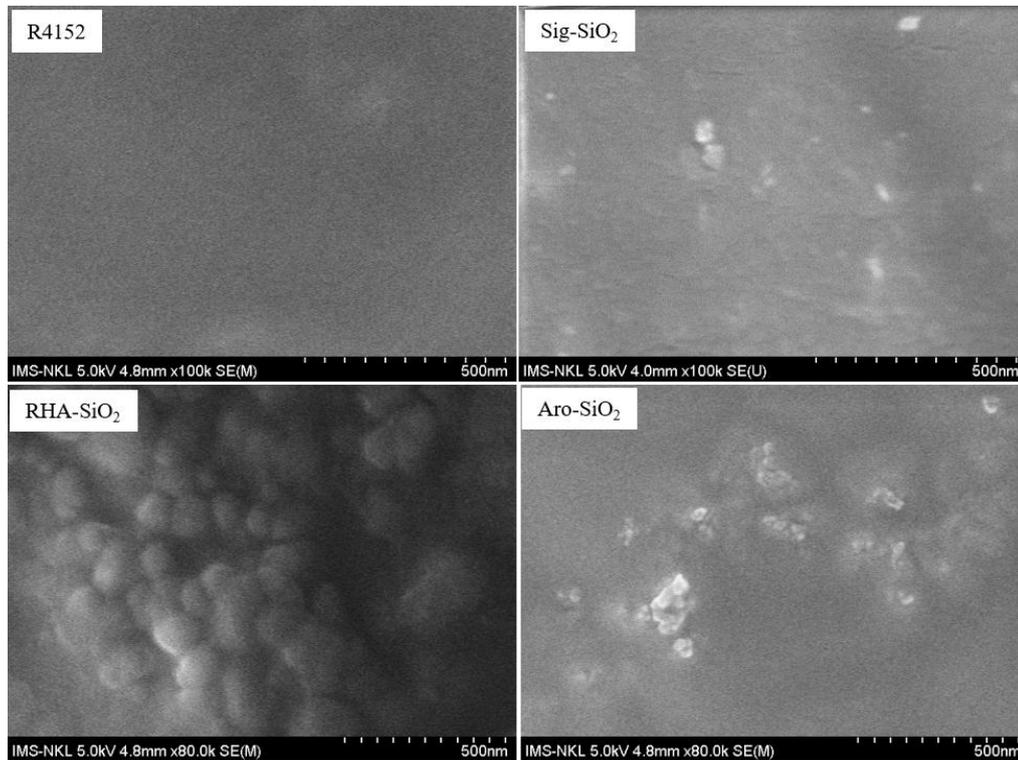
Figure 2. FE-SEM images of coatings with and without 2 wt.% nanosilica.

Dispersion and shape of nanosilica into coating formulas would affect to some properties of coating such mechanical, thermal properties and weathering durability. Effect of nanosilica would be presented on next section.

3.3. Effect of nanosilica on physico-mechanical properties of coating

Physico-mechanical properties, namely adhesion and abrasion resistance were studied. The physico-mechanical of coating filled and unfilled nanosilia were showed in Table 2.

As results in table 2, adhesion of coating was not affected by nanosilica, leveling off 1 level. However, their abrasion resistance increased if coating was filled by nanosilica. Abrasion resistance of neat coating was 47.25 litres/mil, in presence of nanosilica abrasion resistance of coating increased to 86.24 – 104.37 litres/mil depending on type of nanosilica. As can be seen, coating containing nanosilica from Sigma just reached 86.24 while coating filled nanosilica from rice husk plateaued at 104.37 litres/mil.

Table 2. Physico-mechanical properties of coating filled and unfilled nanosilia.

No	Properties	R4152	RHA-SiO$_2$	Sig-SiO$_2$	Aro-SiO$_2$
1	Adhesion, level	1	1	1	1
2	Abrasion Resistance, litres/mil	47,25	104,37	86,24	94,42

It can be explained that nanosilica enhanced physico-mechanical properties of coating and it plays as role of reinforce agent [10] and thus raising abrasion resistance of coating. Depend on of dispersion and shape of nanosilica into coating formula, abrasion resistance growth of coatings are various. As mentioned above, nanosilica made from rice husk ash saw a fairly unique distribution. In addition, rice husk ash based nanosilica was in hard spherical shape while other kinds of nanosilica in this work were in porous shape. Thus, physico-mechanical of RHA-SiO$_2$ was highest.

3.4. Effect of nanosilica on weathering durability of coating

The chemical changes and weight loss of coatings were monitored to assess on their weathering durability. IR spectrums of unaged and 42 cycles aged coating unfilled and filled 2 wt.% nanosilica were presented in Figure 3. Quantitative change of absorption were showed in Figure 4.
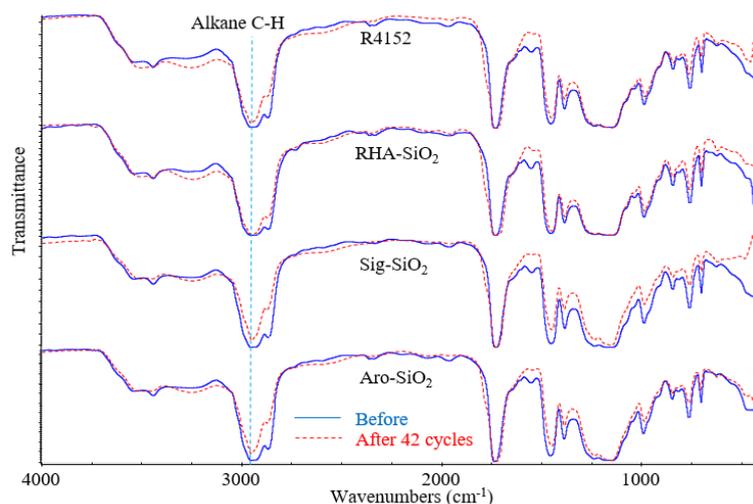
Figure 3. IR spectrums of coating unfilled and filled 2 wt.% nanosilica initial and after 42-cycle aging.

Figures 4&5 indicated that absoption intensity at 2946 cm-1 coresponding to C-H stretching reduced while optical intensity at 3520 -3400 cm^{-1} coresponding to OH group increased. The presence of SiO$_2$ nanoparticles prevented coating from aging process. In other word, this investigated that the decrease of alkane C-H band in the SiO$_2$ embedded coatings was less pronounced than that in unfilled coating during the accelerated aging process. Especially, the decrease of alkane C-H band retarded the most in the RHA-SiO$_2$ filled coating. This can be explained that RHA-SiO$_2$ nanoparticles absorbed UV radiation better than others, consequently, RHA-SiO$_2$ enhanced photostability of coatings.

Coating samples in aging process was not only monitored the chemical modifications but also assed their weight loss. Remaining weight of coating unfilled and filled 2 wt.% nanosilica during artificial weathering process were showed on Fig. 5.
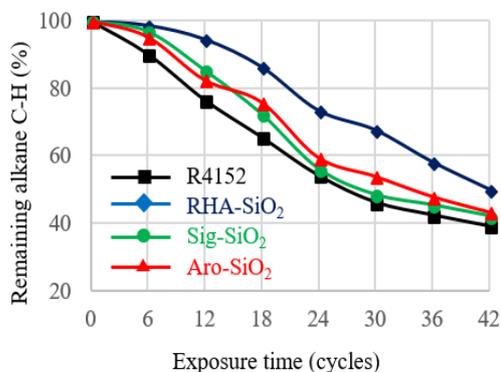
Figure 4. Effect of SiO$_2$ nanoparticles on the loss of alkane CH groups of coatings.
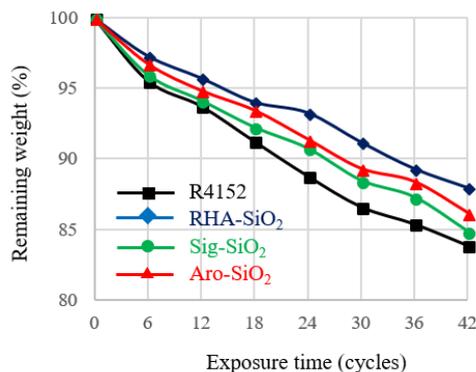
Figure 5. Remaining weight of coating unfilled and filled 2 wt. %nanosilica during artificial weathering process.

After 42 cycles testing, remaining weight of coatings containing RHA-SiO$_2$, Sig-SiO$_2$ and Aro-SiO$_2$ were 85 % - 87 %. Neat coating (R4152) having remaining weight was 83 % - reached lowest point in the studied samples. It can investigate that nanosilica enhances weathering durability of coating. However, this effect also depends on dispersion and UV absorbing ability of nanosilica into coatings formula.

3.2. Influence of nano-SiO$_2$ on the thermal durability of coating

Figure 6 shows TGA graphs of unfilled coating and its nanocomposites with 2 wt.% content of nano-SiO$_2$. Thermal degradation parameters of neat coating and nanocomposite coatings were presented in Table 3.
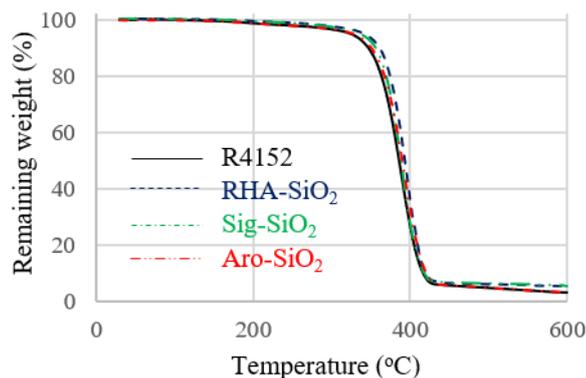
Figure 6. TGA curves of the neat and nanocomposite coatings.

Figure 6 indicated that weight loss of samples proceeds via three stages. First stage is from 30 to nearly 330 ^{o}C. It can be assumed that initial thermal degradation temperature was assigned with temperature at 5 % loss in mass (T$_{5\%}$). For that temperature, it could be attributed to the

release of adsorbed water and low molecular organic compound in the coatings, occurred at 324.14, 339.14, 334.14 and 328.14 $^{\circ}$C for the neat and the RHA-SiO$_2$, Sig-SiO$_2$ and Aro-SiO$_2$ filled coatings, respectively. Thermal stability of these coatings was relatively strong, compared to those previously reported with the onset degradation temperature of around 240-300 $^{\circ}$C [1].

Table 3. Values of T$_{5\%}$, T$_{50\%}$, T$_{75\%}$ for the neat and nanocomposite coatings.

Coatings	T$_{5\%}$ (^{o}C) (5% loss in mass)	T$_{50\%}$ (^{o}C) (50% loss in mass)	T$_{75\%}$ (^{o}C) (75% loss in mass)
R4152	324.14	386.14	401.14
RHA-SiO$_2$	339.14	393.14	406.14
Sig-SiO$_2$	334.14	388.14	402.14
Aro-SiO$_2$	328.14	390.14	405.14

The thermal decomposition with the majority of weight loss occurred at temperature > 340 $^{\circ}$C and it was probably caused by scission of backbone chain in the acrylic polymer [1]. It can be assumed that the temperature at 50 % loss in mass (T$_{50\%}$) is this thermal degradation temperature. For that temperature, it occurred at 386.14 $^{\circ}$C and 393.14, 388.14 and 390.14 $^{\circ}$C for the control and the nanocomposites, respectively. As can be seen in figure 6 the 75 % reduction of the initial weight of the samples cured at 401.14 $^{\circ}$C and 406.14, 402.14 and 405.14 $^{\circ}$C for unfilled and filled coating, respectively. At higher temperature, the char yields of coating without and with nanosilica were found to be 3.08, 5.45, 5.16 and 3.1 % at 600 $^{\circ}$C, respectively.

4. CONCLUSION

Nanocomposite formula on the base of silica nanoparticles and waterborne acrylic binder were successfully prepared by using ultrasonication. Morphology of nanosilica and of nanocomposite coatings as well as influence of nanosilica on thermal stability, weathering durability and physico-mechanical characterizations of coatings were assessed. Obtained results showed that nanosilica made from rice husk ash had size from 50 − 200 nm and in spherical shape while kinds of nanosilica from Sigma, Arosil had size of 10-20 nm and in porous shape. All three kinds of studied silica nanoparticles were able to enhance the physico-mechanical properties, thermal resistance and weathering durability of the coating. The coatings containing 2 wt.% content of nanosilica from rice husk ash expressed highest improvement of properties.

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