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Effect of Nano Silica on Moisture Absorption of Polyurethane Clear Coats as Studied by EIS and Gravimetric Methods

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ABSTRACT

Electrochemical impedance spectroscopy and gravimetric methods were carried out to analyze water uptake of thin polyurethane films separately filled with either hydrophobic or hydrophilic nano-silica. Correspondingly the impedance spectra and gravimetric data were interpreted in terms of movement of water within the coating and/or to the coating/metal interface. Although the obtained results from gravimetric and EIS (Electrochemical Impedance Spectroscopy) methods followed generally a same trend, the water uptake values were not exactly identical. Type and content of nano silica had significant effects on the capability of water absorption of thin filled coatings. Indeed, it was found that rate and maximum level of moisture absorption of polyurethane coatings "strongly depended on the type and loads of nano-silica within the clear coat. To the other words, nano-particles with different nature affects on hydrophilicity and hydrophobicity of the organic matrix resulting in increasing or decreasing of water absorption of the resulted coating. Prog. Color Colorants Coat. 3(2010), 92-100. © Institute for Color Science and Technology.

1. Introduction

Electrochemical impedance spectroscopy has been used by several authors for the determination of water content in organic coatings [1-3]. The reason for this interest lies on the fact that the capacitance of a coating is affected by penetration of water [4].

Many factors influence water absorption of polymeric coatings, such as temperature, geometry of exposed surface, polymer nature (permeable or impermeable) and diffusivity [5-7]. One of the most important mechanisms of water absorption in polymeric coating is diffusion [7-9]. In diffusion mechanism, water diffuses into the matrix and water solubility in the coating matrix is significant.

The Fick's first law of diffusion expresses the rate of species diffusing into materials (equation 1).

$$J=-D\ \delta c/\delta x \quad (1)$$

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*Corresponding author: moradian@aut.ac.ir where D is the diffusion coefficient, J is the rate of transfer per unit area, C is the local concentration of water in the coating and x is the directional distance [10].

The absorption process of liquids into thermoset polymers are complex. However, water diffusion in polyurethane above Tg follows a Fickian behavior. In contrast, diffusion bellow Tg is non-Fickian and it is very complicated and unusual [11-13].

Water permeation in a coating increases polarity which is reflected increases in the coating capacitance. The following expression shows the relationship between permeability and capacitance of a coating (equation 2).

$$C=\varepsilon\,\varepsilon_0 A/d \qquad (2)$$

where C is the capacitance of coating, ε is the dielectric constant of coating, ε_0 is the permittivity of vacuum (8.854×10^{-12} Fm^{-1}), A is the surface area of a coating and d is the coating thickness.

In this study, the effects of moisture absorption in a two pack polyurethane in the presence of two types and various contents of nano silica were investigated. The objective of the present study was to determine to what extend types and content of nano silica would influence on the water uptake properties of polyurethane coatings. Therefore, surface treated and untreated nano silica were incorporated into these coatings in order to investigate the variation of moisture absorption in the resultant coatings.

2. Experimental

2.1. Raw materials

For the purpose of studying the effect of hydrophobicity and hydrophilicity of nano silica within a thin film of a two pack polyurethane, two different types of nano silica were chosen : i.e. Aerosil 300 (hydrophilic fumed silica) and Aerosil R 812 (hydrophobic fund silica). Both were purchased from Evonic in Germany and had an average particle size of 7nm. The hydrophilic untreated 300 had specific surface area (BET) of 300±30 m²/g. The hydrophobic equivalent e.g. R 812 was based on Aerosil 300 after treatment with Hexamethyldisilane (HMDS) having a BET of 260 ±30 m²/g. The acrylic polyol, i.e. Uracron CY 433 (a solution of 60% in xylene) butyl acetate mixture was provided by DSM company (Netherland) and the isocyanate hardener, i.e. Desmodure N 75 (a solution of 75% in xylene/MPA mixture) was obtained from Bayer company (Germany). The recommended mixture ratio CY 433: N75 was 2.5:1 according to the products' data sheets. The solvent i.e. methoxy propyl acetate (MPA) was provided from Sasol company (South Africa).

2.2. Preparation of nano coating free films

Both types of nano silica were separately added at various loads to the acrylic polyol to obtain the final nano coatings. Dispersing the mixture was achieved by pearl milling. Various amounts of hydrophilic or hydrophobic nano silica powders were separately added to the acrylic resin so that the amount of pure silica in the final solid films would turn out to be 4, 6 and 8% by weight respectively. The reference control was a pure polyurethane film having nano silica content. In this way, 7 samples in three replicates were prepared based on type and content of nano silica. For coding purposes, R-812-6% for instance represents 6% by weight of hydrophobic R-812 nano silica in the final solid nano coating's film. In general, free films are required for conducting tests to evaluate physical properties such as tensile or other physical properties. Since, the evaluations of the free films for physical properties are more accurate than evaluating the films on substrate. The substrate may interfere with the determination when physical properties of organic coatings were measured. According to the ASTM D 4708 standard, procedures are given for preparing free films on three alternative substrates. These substrates are treated FEP (fluorinated ethylene-propylene) sheet, silicone coated paper, and halosilane coated glass plates. Accordingly, free films were provided after mixing of suitable amounts of the iso-cyanate component (N75) separately to acrylic/nano-silica mixtures according to the mentioned mixture ratio. The mixtures were then stirred by spatula for 20min. Consequently, 200 µm wet film of each mixture was applied with a film applicator (BYK-Gardner, Germany) on to glass substrates. After 2 weeks at ambient conditions, the fully cured films with a thickness of approximately, 50 ± 3µm were ready for further analysis.

2.3. Preparation of sample for EIS

Plates of mild steel having 5 mm thickness were used as substrate. For surface cleaning all plates were abraded and then degreased in acetone. Polyurethane / nano silica mixtures were then applied on degreased plates by using a film applicator (BYK-Gardner). The coated plates were subsequently dried at ambient condition for 2 weeks. The thicknesses of dried coated films were 20 ± 2 µm as measured by a thickness gauge on a set of three different replicate films on the steel substrate.

2.4. Electrochemical impedance spectroscopy (EIS)

A three electrode arrangement i.e. a reference Ag/AgCl electrode, a platinum counter electrode and the exposed area 2mm x 2 mm of a coated plate, immersed in 3.5% NaCl solution. EIS was used at the open circuit potential, using on Ac impedance instrument (AUTOLAB) and a frequency range from 10 KHz to 10 MHz was selected.

2.5. Water uptake measurement by EIS

Water uptake measurements were carried out according to the following Brasher and Kingsbury equation (3)[14-17].

$$X = \frac{\log (C_t / C_0)}{\log \varepsilon_w} = \frac{\log C_t / C_0}{\log 80} \qquad (3)$$

where X is the percentage water uptake, C_t and C_0 are the coating capacitance at time t and time 0, respectively, and ε_w is the dielectric constant of water (80 at 20 °C).

2.6. Water uptake measurement by gravimetric method

Water uptake measurement was obtained by weighing free films of the filled coatings before and after immersing in distilled water. For this purpose, an analytical balance with an accuracy of 0.0001 ae (the grade of balance) (ADM) balance model PW 184 was used. The percentage water uptake was calculated according to the ASTM D-570 standard [18] by using equation (4).

$$Xv\ \% = 100d(Ww-WD)/WD \qquad (4)$$

where Ww is the wet weight of specimen (water-absorbed Matrix), and WD is the initial weight of dry specimen. Xv is water uptake (%V) (volume percentage) and d is the density of dry film.

3. Results and discussion

3.1. Gravimetric method

As it was shown in Figure 1(a) and (b) percentage water uptake increased rapidly in the first few hours and then tending to become constant in the last stages of immersion.

Many scientists believe that in the first few hours, films tend to absorb water into their pores or capillaries. It is the first stage that coatings are filled with water. Therefore, the water absorption is fast. Since, the exposure time is too short. In the next stage, the water uptake process is considerable decreased and takes a long time the coatings matrix. Since, the coating is saturated. In fact, in water penetration the coatings tend to be saturated while in water absorption, surface of the coatings absorb water due to capillaries. At the last stage the coatings are fully saturated with water and hence, the rate of water uptake becomes constant. Figure 1(a) shows that increasing the content of hydrophilic nano silica up to 8%, gives rise to maximum water uptake with time.

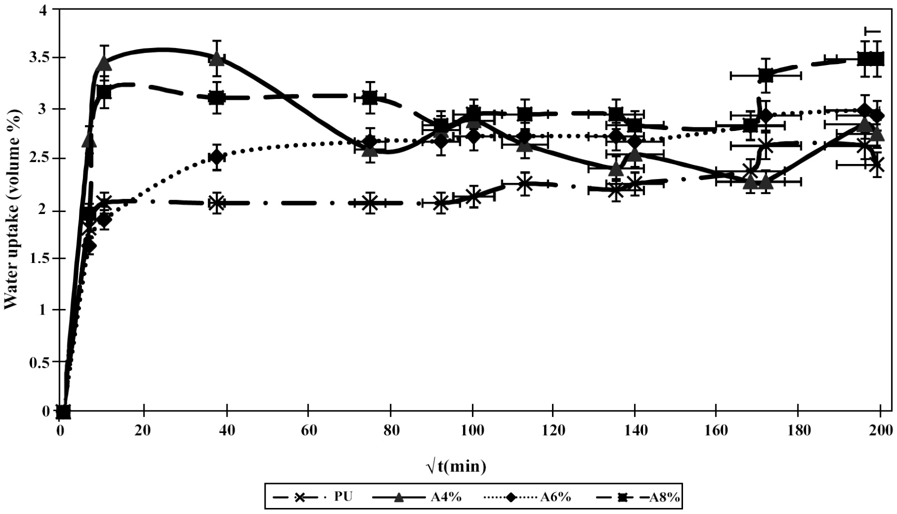

Figure 1(a): Percentage water uptake (V %) for samples containing hydrophilic nano silica.

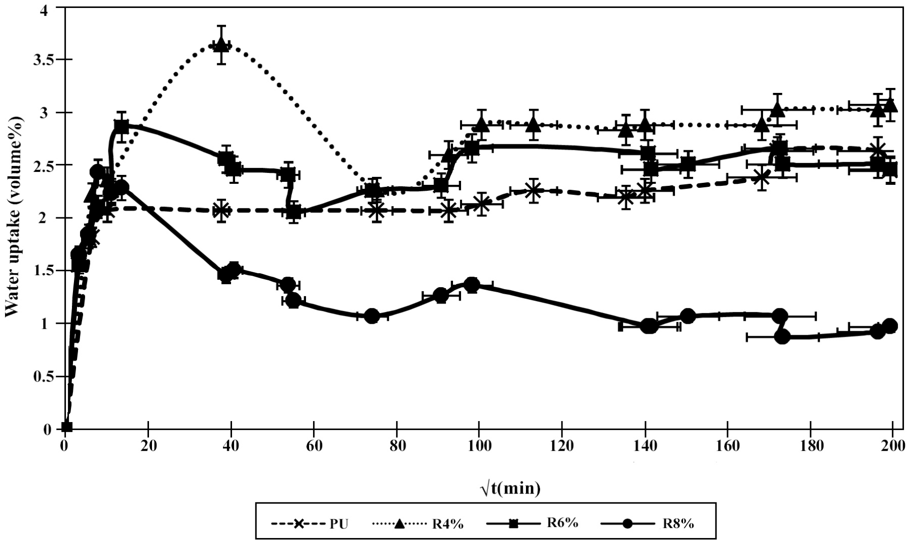

Figure 1(b): Percentage water uptake (V %) for samples containing hydrophobic nano silica.

This can be attributed to the polar groups such as OH present at the surface of nano silica. These groups have a high inclination to absorb water and increase the amount of water uptake. Therefore, a general decrease in water uptake of A300-6% was observed. This could be attributed to a good packing at this load. Although, at 200 ($t^{1/2}$) minutes the water uptake equals the 4% load.

Figure 1(b) depicts the water uptake of coatings containing hydrophobic nano silica.Three methyl groups surrounding hydrophobic nano silica make it less active to interact with the matrix. Therefore, this system has less water uptake .It must also be stated that the 8% hydrophobic nano silica has minimum water uptake at all stage of the process. This is attributed to maximum hydrophobicity and also possibly to the best possible packing and the good packing. It may be attributed to the release of polar solvent (i.e. methoxy propyl acetate) that was pushed by water, and it had been added in more percent to the formulas of coatings containing nano-silica in order to adjust solid content. Furthermore it may be related to the extraction of non-cured polymer chain with low permittivity which is often the case with large organic molecules [4]. For example, the likelihood of presence of some non-reacted isocynate or polyol molecules strongly increases because of the presence of silica particles having high surface area throughout the organic matrix. This hypothesis has been investigated elsewhere (elsewhere should be omitted) in previous study resulting in the interference of nano-particles in curing reactions of polyurethane especially for treated nano-silica (i.e. hydrophobic grade) [5]. Therefore, leaching processes of soluble species are acting in parallel with the water ingress, and are predominant particularly for coatings embedded with hydrophobic nano-silica particles.

3.2. EIS spectroscopy

An equivalent circuit model, proposed by many authors [6, 7] for water uptake is presented in Figure 2. This model manifests R_s, the electrolyte resistance. C_{dl}, double layer resistance. R_{pf}, the coating resistance. EIS data was interpreted based on the equivalent electrical circuits with suitable fitting curves by the aid of the FRA V4.9.009 software.

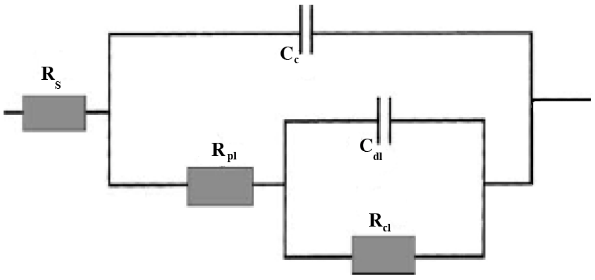

Figure 2: An equivalent circuit mode.

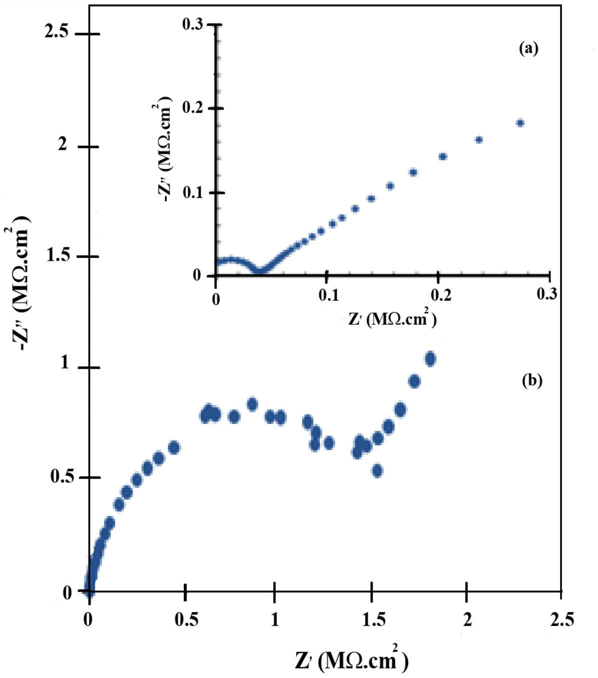

Figure 3: (a) Nyquist plot for a polyurethane coating containing 8% of hydrophilic nano-silica (i.e. A8%) after 45 days of immersion in 0.62 M NaCl electrolyte and (b) Nyquist plot for a pure polyurethane coating after 45 days of immersion in 0.62 M NaCl electrolyte.

Also, Nyquest plot for pure polyurethane and polyurethane containing hydrophilic nano silica was shown in Figure 3. As it can be seen from Figures. 3(a) and (b) the resistance of the coating containing 8% hydrophilic nano-silica is very low in contrast to pure polyurethane. Figure 3(b) lies on the beginning of double layer formation at coating/metal interface. Also, in Figure 3(a) the impedance starts above the zero point and the continuation appears as a rising line. In other words, a deviation at low frequency occurs several weeks after immersion, which is related to diffusion (Warburg).

3.3. Capacitance

Figure 4 represents that the coating capacitance values increasing in the first minutes which are indicative of absorption of water by the coatings. Subsequently, the capacitance remains almost constant on account of the fact that the coating layer is saturated with water. In this manner, the capacitance of sample with 8% hydrophilic nano silica (Figure 4(a)) is higher than its hydrophobic countertype in Figure 4(b).

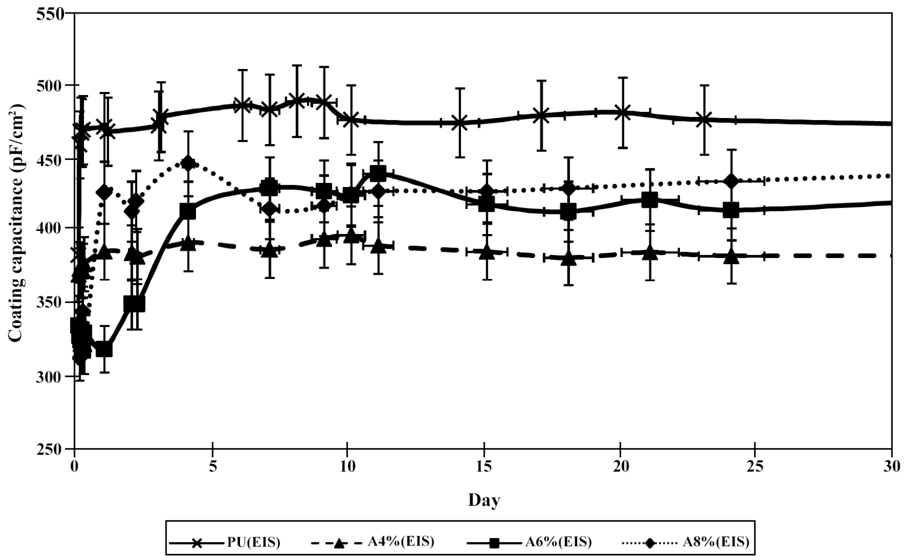

Figure 4(a): Coating capacitance vs. time of immersion for samples containing hydrophilic nano silica.

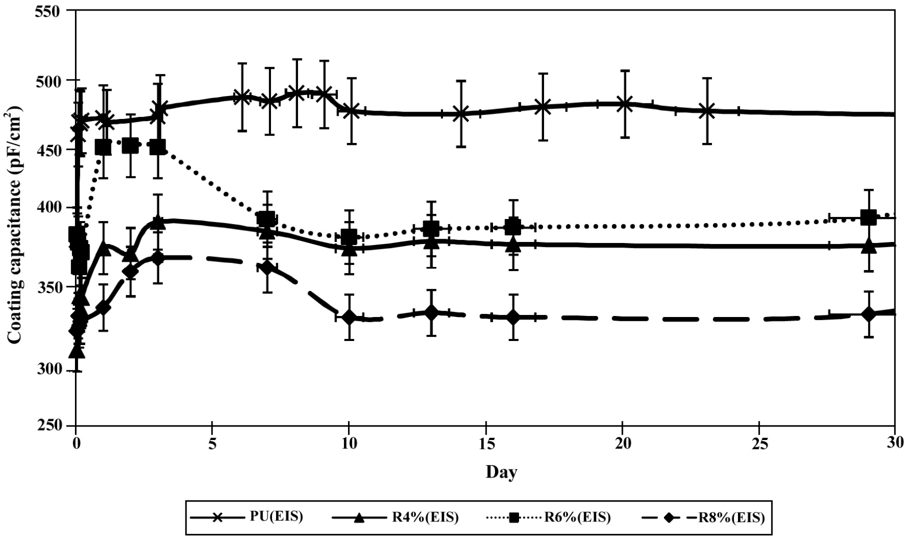

Figure 4(b): Coating capacitance vs. time of immersion for samples containing hydrophobic nano silica.

Table 1: Capacitance (pF/cm^2) versus various times of immersion for coating containing hydrophilic or hydrophobic nano silica.

t(hr)	PU	A4%	A6%	A8%	R4%	R6%	R8%
2	460	385	386	381	365	382	329
6	470	392	442	390	364	378	325
24	472	408	457	427	372	375	335
48	471	407	417	418	378	451	361
98	479	438	414	428	385	452	371
170	487	416	424	421	397	451	364
242	488	409	425	426	390	399	328
362	477	409	419	428	382	392	328
434	475	393	414	430	381	393	330
890	480	395	415	443	380	395	329
1250	477	402	427	454	379	397	328

These figures divulge that the capacitance of the control sample pure polyurethanewithout any nano silica is highest which is decreased with additions of both type of nano silica.

Since release of soluble species are acting in parallel with the water ingress, and are predominant particularly for coatings embedded with hydrophobic nano-silica particles, a reduction in coating capacitance was observed after 7 days of immersion. Similarly this behavior was also perceived for water absorption values obtained from gravimetric method. Also, Table 1 depicts the capacitance with the time for coatings loaded with various percentages of hydrophilic or hydrophobic nano silica.

3.4. Water uptake

C_0 can be calculated from the extrapolation of coating capacitance vs. √t. When the coating resistance is high, the water uptake is low which is confirmed in the Figures 5(a, b) and maybe due to lesser possibility of transferring ions. In general, water is the main component to cause swelling by transport of hydrated ions into the coating. As soon as, the coating resistance is decreased the diffusion rate would tend to increase and hence the water permeation becomes relatively high.

Figure 5 depicts four different stages for water uptake by the coatings.

- In the first day of immersion an enormous increase was shown up to 4%, indicate the tendency of a coating to absorb water.
- In the second stage (1 to 6 days) the rate of water uptake is again increased but with a slower rate. This may be interpreted as limited sites for absorbing water.
- In the third stage the coating is saturated with water hence the rate of water permeation is constant.
- In the last stage, a further increase is observed.

Also, these Figures 5(a) and 5(b) reveal the influence of type and content of nano silica. In Figure 5(a) the permeation in polyurethane clear coat is less than samples containing hydrophilic nano silica. When, the percentage of nano silica is increased to 4, 6 and 8% (by weight), the rate of water permeation is enlarged accordingly. This can be interpreted with the following reasons.

1-In the initial time of immersion, the water permeation is depended on the type of coating matrix. Polyurethane matrix is homogeneous with an organic medium whereas additions of nano silica imports heterogeneity .Since, nano-silica is inorganic material and inserting it into the organic medium makes heterogeneous medium. Also, in heterogeneous medium nano-silica were dispersed throughout the organic medium due to the fact that organic and inorganic materials have different characteristics and cannot solve into each other observed in Figure 5(b)

2-With increased the times of immersion, water permeation is under the influence of the nature and content of nano silica and its interaction with the matrix. Figure 5(a) presents the water uptake of loadings containing hydrophilic nano silica with increased the times of immersion, the water uptake increased with increased nano silica content. Such increase in water uptake by increased time could be justified through the presence of hydrophilic sites which intensively absorb water causing exceeding coating swelling and finally coating deterioration.

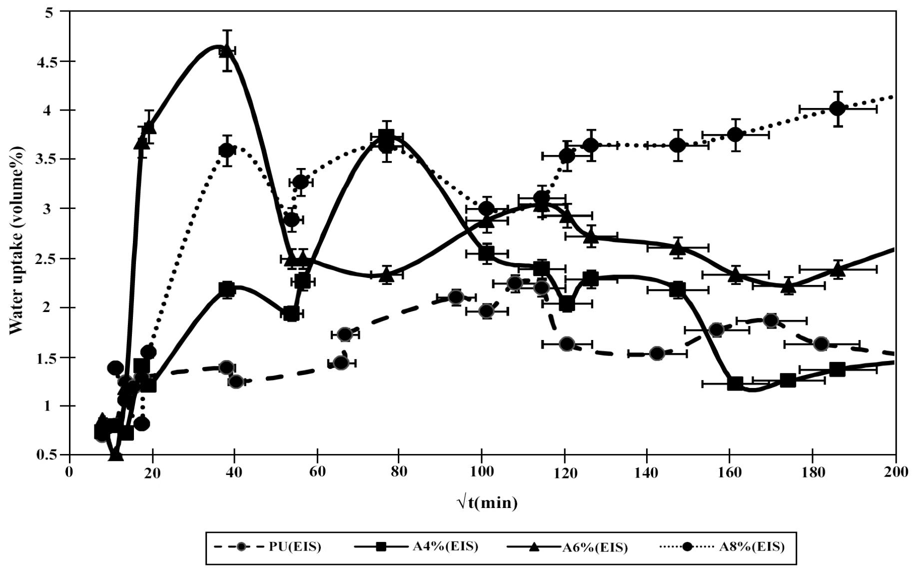

Figure 5(a): Water uptake vs. (√t) time of immersion for samples containing hydrophilic nano silica.

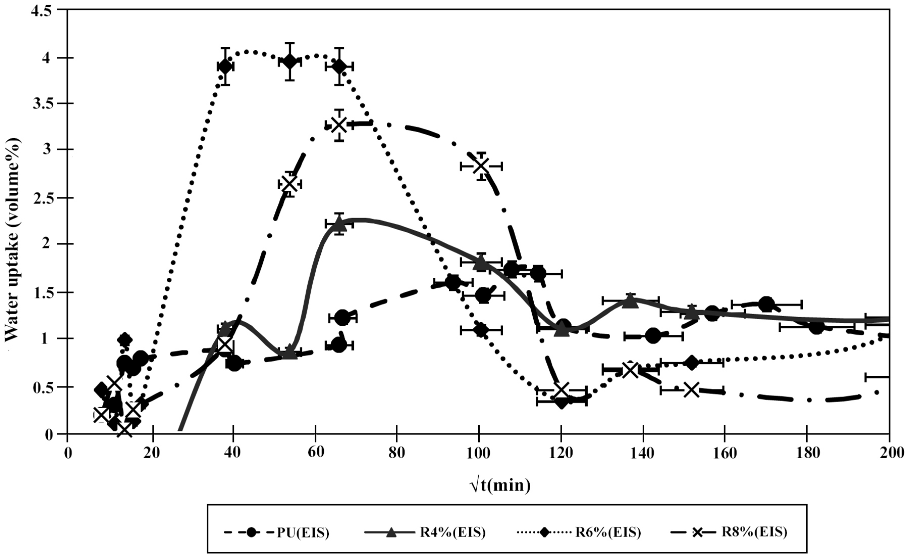

Figure 5(b): Water uptake vs. (√t) time of immersion for samples containing hydrophobic nano silica.

This trend could be obviously seen by increased nano-silica content. For hydrophobic type in which 60% of hydroxyl groups substituted with organosilane, relative permittivity is expected to reduce. Moreover, Figure 5(b) shows decrement in water uptake of 8% hydrophobic nano silica content, water uptake at this load eventually falls below the pure polyurethane at $t^{1/2} = 100$ minus.

It should be noted that some minor errors during the water uptake measurements were avoidable in case of each approach. Although a same procedure was used for gravimetric way, some parameters such as; drying free films with soft cotton, evaporation of water during weighing time, and maybe some other hidden parameters caused a fluctuation that can be seen in Figures 1(a, b). Also, fitting errors in EIS results analyses may induce such fluctuation as seen in Figures 4 to 5.

4. Conclusions

The type and the content of nano-silica play significant roles on water uptake. Moreover, the results obtained from gravimetric method showed that the coatings tend to absorb water rapidly in the initial days after such periods a further slow increase in water uptake is initiated for hydrophilic-silica filled coatings. In spite of that water uptake of coatings embedded with hydrophobic type remained constant at the long periods of immersion. The results obtained from EIS experiments revealed that the same trend can be recognized with gravimetric ones. In general, both gravimetric and EIS studies represented that water uptake of hydrophilic filled coatings raised with increasing nano-silica content whilst a reverse effect was observed for coatings containing hydrophobic nano-silica particles. The differences between the values achieved from different methods could be assigned to the different fundamentals used for calculation water uptake.

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