Effect of nanosilica based modifying agent for hydrophobic coating application

Pengaruh agen pengubagh berasakan nanosilika bagi aplikasi salutan hidrofobik

Nurul Huda Mudri[1], Nik Ghazali Nik Salleh[1], Mek Zah Salleh[1], Khairul Azhar Abdul Halim[1], Liyana Sharilla Muhammad Faisal[1] dan Zafirah Othman[2]

[1] Bahagian Teknologi Pemprosesan Sinaran
Agensi Nuklear Malaysia (Nuklear Malaysia)
Bangi, Kajang, Selangor.

[2] Fakuti Sains dan Teknologi Sumber
Universiti Malaysia Sarawak
94300 Kota Samarahan, Sarawak

ABSTRACT

Hydrophobic coatings find wide application in industry due to their unique features such as water repellent and self-cleaning properties. In this study, modifying agent was synthesized by way of nanosilica particles dispersion in polydimethyl siloxane with addition of surfactant, catalyst and stabilizer using high speed dispermat. The modifying agent was added into coating formulation and cured under UV exposure. Scanning Electron Microscopy image of the film found that the nanosilica particles were distributed well on substrate. Contact angle measurement gave the highest reading of 116^{o} for 20% wt of the modifying agent. The optical properties of the film were evaluated via transmission and haze test.

Keyword: Nanosilica, hydrophobic, UV exposure, coating, surface analysis

ABSTRAK

Salutan hidrofobik mempunyai pelbagai aplikasi di industri disebabkan sifat-sifat uniknya seperti kalis air dan sifat auto-pembersihan. Dalam kajian ini, agen pengubah disintesis secara penyebaran partikel nanosilika di dalam polidimetil siloksana dengan penambahan pengampai, katalis, dan penstabil menggunakan dispermat berhalaju tinggi. Agen pengubah ditambah ke dalam formulasi salutan dan dimatangkan di bawah dedahan UV. Imej Scanning Elektron Mikroskopi pada filem mendapati agen pengubah tersebar sekata pada substrat. Analisis pengukuran sudut sentuh memberikan bacaan tertinggi 116^{o} bagi 20% agen pengubah. Sifat-sifat optik filem diuji melalui ujian *transmission* dan kekabutan.

Kata kunci : Nanosilika, hidrofobik, dedahan UV, salutan, kajian permukaan

1.0 Introduction

Hydrophobic coatings have attracted world's attention due to their special characteristics such as self-cleaning, anti-fogging, anti-corrosion for various applications like paints, optical devices, windshield and interior fabrics. In theory, the surface is considered as hydrophobic when the contact angle is greater than 90^o and recognized as superhydrophobic as the contact angle is more than 150^o (Latthe, 2014)

In natural environment, lotus leaf (*Nelumbo nucifera*) is the most popular example of hydrophobic surface and has been set as a benchmark for the scientists to fabricate the hydrophobic surface property. The contact angle is higher than 160^o and it can maintain its cleanliness even though it grows in muddy and dirty ponds. Lotus leaf acts as self-cleaning by beads up the water droplets into spherical form and rolls off to collect the dirt and debris along the surface. The combination of extreme water repellency and self-cleaning properties is known as "*Lotus Effect*".

Recent studies have reported various techniques to produce water repellence surface. Taurino *et al*., 2014 have produced hybrid coating containing vinyl-ester resins and vinyltriethoxysilane (VTEOS) via sol-gel process. The multi-layer approach of sol-gel process gave out surface wettability more than 150^o, mechanically stable and proven as scratch resistance. Shanhu and co-workers, 2015 provided new technique to prepare superhydrophobic silica coating using condensation of flouroalkoxysilane (17FTMS) in ethanol at room temperature. The treated silica were then embedded into the sol-gel processed silica matrix and deposited on glass plates. The coating showed superhydrophobic properties without any surface chemical modification; however low starch resistance.

Among those technologies offered for coating industry, radiation curing is an efficient and simple method to produce cross-linked materials with thickness range of a few microns to several millimeters. It is mainly consists of monomers, oligomer, additives and photoinitiators depends on the radiation sources; either ultra violet light or electron beam. The advantages of this techniques are fast, less emission of volatile organic compounds, environmental friendly and save space instead of usage of bulky machines. This techniques is now employed in industry for various applications such as paints, adhesives, inks, microelectronics, optical materials and dental resins.

In this paper, a technical route to produce hydrophobic coating using nanosilica particle is reported and the physical and optical properties of the coating will be discussed.

2.0 Experimental

2.1 Material

All chemicals were used as received. Nanosilica particle Aerosil OX50 was purchased from Degussa Co. while polydimethylsiloxane and silicon oil were purchased from Fischer Scientific. Maleic anhydrate, 4-methoxy phenol and anti terra 213 were functioned as catalyst, stabilizer and surfactant respectively. Urethane acrylate (EB 210) was used as oligomer while Trimethylolpropane triacrylate (TMPTA), Tripropylene glycol diacrylate (TPGDA), Pentaerythritol diacrylate (PETIA) were used as reactive diluents in the formulations. Irgacure 1173 and Irgacure 500 were used as photoinitiators to start the polymerization when exposed to ultraviolet light.

2.2 Preparation of modifying agent

PDMS, silicon oil, maleic anhydrate and 4-methoxyphenol were added in the 2L synthesis reactor. The temperature was fixed at 60^{o}C while the speed of the dispermat mixer was set at 1700 rpm. Nanosilica particle Aerosil OX50 was added slowly into the mixture to prevent agglomeration and continuously stirred until it became homogeneous. Finally dropwise of anti terra 213 was added and stirred for further 10 minutes. The treated nanosilica particles was leaved at room temperature for overnight before usage.

2.3 Synthesis of coating formulation

A coating formulation composed of EB210, TMPTA, TPGDA and PETIA was prepared in ratio of (30:4:3:1) by stirring using electrical stirrer (Caframo, Canada) at 300 rpm until it reach the homogeneous state. The loading of modifying agent and photoinitiators into the coating formulation is described in Table 1:

Table 1: Mixture amount of coating formulation, modifying agent and photoinitiators

Material (g)	Coating formulation	Modifying agent	Irgacure 1173	Irgacure 500
0%	30.0	-	1.5	1.5
5%	28.5	1.5	1.5	1.5
10%	27.0	3.0	1.5	1.5
15%	25.5	4.5	1.5	1.5
20%	24.0	6.0	1.5	1.5
25%	22.5	7.5	1.5	1.5

The mixtures were stirred until it form homogeneous state and leaved for overnight before usage. The sample was coated on glass plate with thickness of 30 µm and exposed to UV light prior to curing process.

2.4 Contact Angle

The wetting properties of the coating was measured using FACE contact angle. A drop of distilled water (containing 15 µl) was dropped using a syringe. The height between the syringe and the surface is set at 20 µm. The reading was taken based on the angle between the water droplet and the surface.

2.5 Scanning electron microscopy (SEM)

Scanning electron microscopy (Phenom World G2 Pro) was performed and equipped with detectors for back-scattered electrons. The applied acceleration voltage was set at 5kV with 10k magnification.

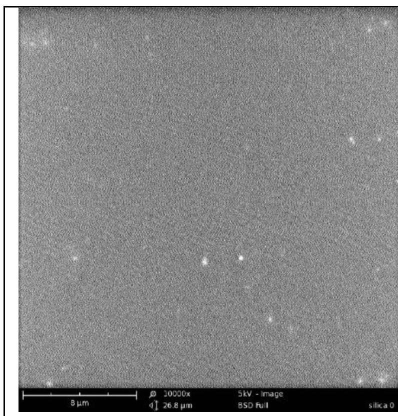
2.6 Haze and transmission test

The optical properties of the coating were evaluated using Haze Gard Dual Tester which can give both haze and transmission reading of the sample. The reading of each sample was done in triplicate.

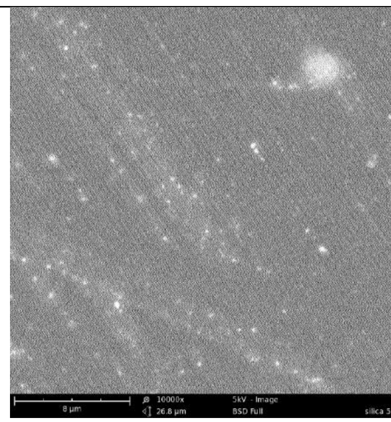
3.0 Result and Discussion

In this study, modifying agent was prepared separately before being added into urethane acrylate based coating formulation. The modifying agent contained of nanosilica particles was dispersed with silicon oil and PDMS with addition of maleic anhydrate, 4-methoxy phenol and anti terra 213 that acted as catalyst, stabilizer and surfactant respectively. The modifying agent solution does mix homogenously with no different phase after mixing for almost 1 hour 30 minutes using high speed dispermat.

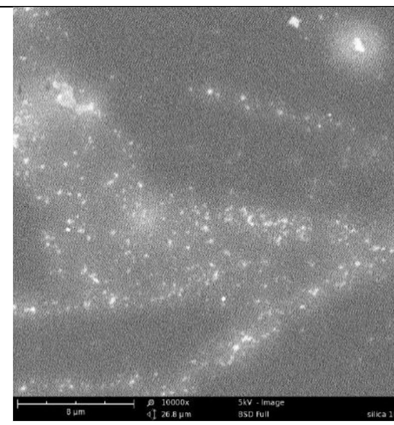
The morphology of the films containing different amount of modifying agent were analyzed using Scanning Electron Microscopy (SEM) at 10k magnification (Fig. 1). It was found that the amount of nanosilica particles increased proportionally with the amount of modifying agent loading.



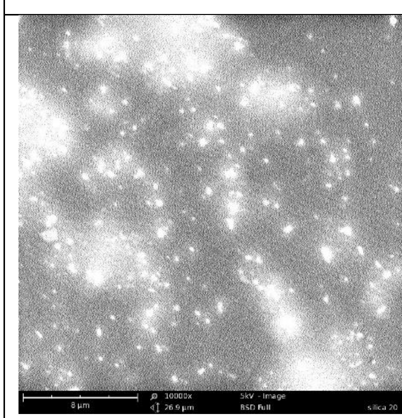
(a) 0 wt %



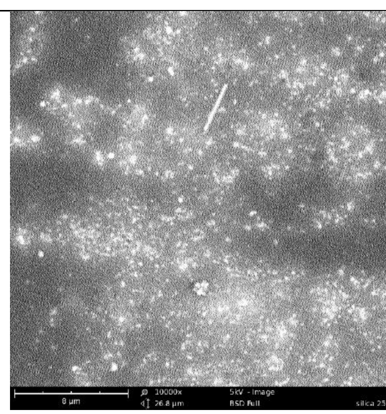
(b) 5 wt %



(c) 10 wt %



(d) 15 wt %



(e) 20 wt %

Fig. 1: Comparison of surface morphology for variation amount of modifying agent under SEM micrograph at 10k magnification

The hydrophobicity of the film is then measured using contact angle (Fig. 2). It was found that the modifying agent subsequently changed the wettability of the surface from hydrophilic to hydrophobic along with increasing amount of modifying agent. The highest contact angle value is at 116^{o} with 20% of modifying agent loading. However, at 25% loading of modifying agent, the value of contact angle is decreased to 93^{o}. Thus, it can be concluded that the optimum amount of modifying agent is at 20%.

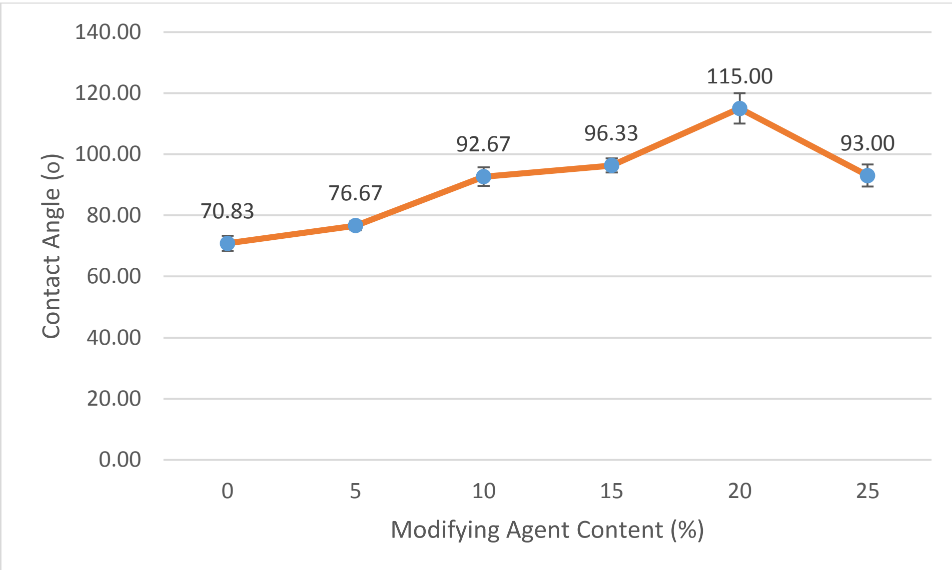


Fig. 2: Effect of various modifying agent content to the wettability property.

Haze and transmission test were conducted to determine the optical properties and hence to find it suitable application. Transmittance is defined as the amount of light energy that is transmitted through a sample. From the test result (Fig 3), all samples possess good transmittance quality as the values range between 89.4 to 90.2.

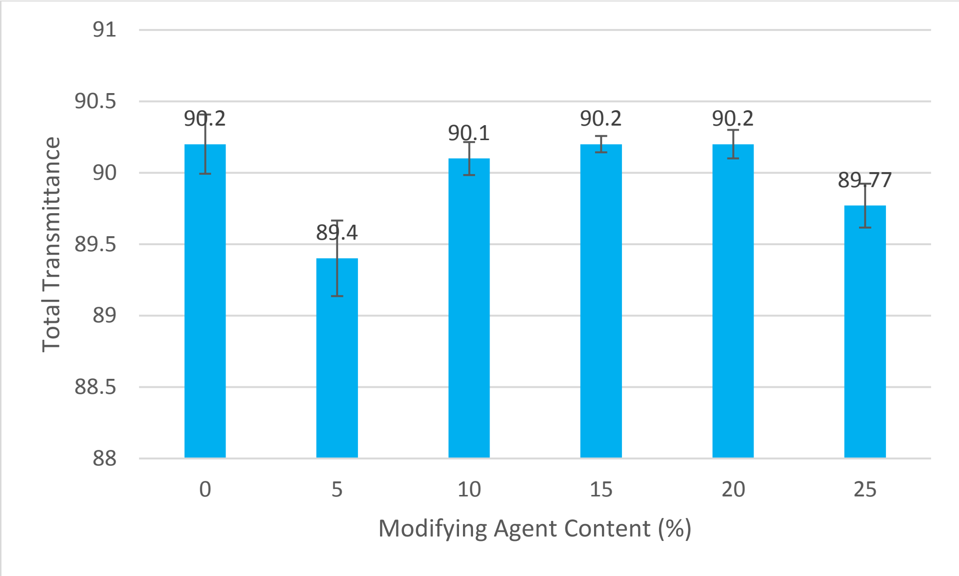


Fig 3: Variation of total transmittance for different amount of modifying agent content

From the observation, the sample tend to be cloudy as the amount of the modifying agent is increased. This is confirmed via the haze test (Fig. 4), where the hazeness increased along with increasing amount of modifying agent. The highest value of the hazeness is 40.53 for 25% of modifying agent content shows a big gap value compared with the control (no modifying agent); 0.32. This results reflect the poor transparency of the sample as more modifying agent is added into the coating formulation.

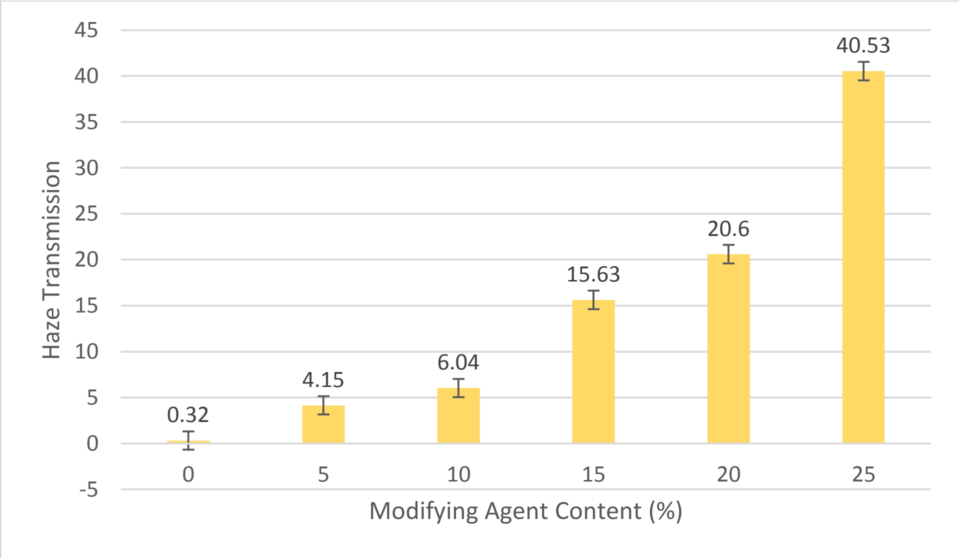


Fig. 4: Effect of modifying agent content on hazeness property

4.0 Conclusion

From this study, a simple step of preparing modifying agent was discussed. This modifying agent changed the wettability of the surface from hydrophilic to hydrophobic along with increasing amount of modifying agent. The highest contact angle value is 115^{o} for 20% amount of modifying agent added into the formulation. The addition of modifying agent maintain good transmission property, however proportionally decreased the transparency of the sample with the increasing amount of the modifying agent. With this kind of property, the modifying agent may suit for application that do not need high transparency coating such as paint industry. Further study need to be conducted to increase the hydrophobic property to superhydrophobic and evaluate the thermal and chemical properties.

5.0 References

Chen, W., Wang, X., Tao, Q., Wang, J., Zheng, Z., and Wang, X., 2013. Lotus-like Paper/Paperboard Packaging Prepared with Nano-modified Overprint Varnish, Applied Surface Science, 266, 319-325.

Latthe, S.S., Terashima , C., Nakata, K., and Fujishima, A., 2014. Superhydrophobic Surfaces Developed by Mimicking Hierarchical Surface Morphology of Lotus Leaf. Molecules, 19, 4256-4283.

Liu, S., Latthe, S.S., Yang, H., Liu, B., and Xing, R., 2015. Raspberry-like Superhydrophobic Silica Coatings with Self-cleaning Properties, Ceramic International, 41, 11719-11725.

Taurino, R., Fabbri, E., Pospiech, D., Synytska, A., and Messori, M., 2014. Preparation of Scratch Resistance Superhydrophobic Hybrid Coatings by Sol-gel Process, Progress in Organic Coatings, 77, 1635-1641.