

# MECHANICAL AND THERMAL PROPERTIES OF UV CURABLE POLYURETHANE ACRYLATE COMPOSITE COATINGS

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## ABSTRACT

UV curable coating formulation comprises urethane acrylate resin and nanosilica as filler were synthesized to develop UV curable inorganic organic hybrid composite (PUA). The surface of the nanosilica was chemically modified to improve its chemical interaction within the urethane acrylate matrix. The modification had been undertaken by applying vinyltrimetoxysilane (VTMOS) that acted as a coupling agent to produce organophilic silica shell (SIMA). The shell is linked to the silica via reaction with the surface silanol group of the silica. The disappearance of methoxy groups in VTMOS was demonstrated by FTIR spectrum. The percentage of silica particles in UV curable hybrid formulation were varied on 5%, 10%, 15%, 20% and 25wt% respectively. In this work, the formulation was applied on medium density fiber board (MDF) substrate and subsequent has been irradiated under UV light. Then, the coated MDF were characterized by several testing equipments (TGA, DSC, scratch tester, Instron, SEM). From the result, we found that the addition of silica nanoparticles exhibit significant improvement in coating film properties as compared to film without silica nanoparticle includes significant improvement in its modulus and scratch resistance. This make them as promising coating candidate for MDF product. On the other hand, we also found that an increase of silica particle up to 25 wt%, the viscosity has increased rapidly indicates that it is not suitable for acrylate coating formulation due to disappearance of desired effect known as thixotropy.

## ABSTRAK

Resin uretana akrilat telah disintesis bersama pengisi silika bagi menghasilkan salutan hibrid organik-inorganik (PUA) dengan menggunakan teknik pematangan sinaran Ultra Lembayung (UV). Permukaan pengisi silika dimodifikasi secara kimia bagi meningkatkan interaksi kimia diantara matrik uretana akrilat dan partikel silika. Proses modifikasi dilakukan dengan menggunakan viniltrimetoksisilana (VTMOS) sebagai agen pengkupel bagi menghasilkan kerangka silika organofilik (SIMA). Kerangka SIMA terbentuk dari tindakbalas kumpulan silanol yang terdapat dipermukaan silika bersama kumpulan metoksi dari VTMOS. Kehilangan spektrum kumpulan berfungsi metoksi dari agen pengkupel (VTMOS) dibuktikan melalui analisis FTIR. Bagi tujuan kajian peratus partikel silika di dalam resin akrilat pematangan sinaran telah divariasikan kepada 5 wt%, 10 wt%, 15 wt%, 20 wt% dan 25 wt%. Dalam kajian ini resin yang diformulasi telah diaplikasikan ke atas permukaan substrat papan serpi (MDF) dan seterusnya didedahkan di bawah sinaran lampu ultra lembayung (UV). Substrat MDF yang telah disalut didedahkan di bawah sinara UV kemudiannya dianalisis menggunakan ujian terma (DSC dan TGA), ujian calaran, fleksural dan ujikaji SEM. Hasil ujikaji menunjukkan salutan akrilat berpengisi silika memiliki sifat salutan yang lebih baik berbanding salutan akrilat tanpa pengisi silika. Ini dapat

*dilihat pada peningkatan mendadak pada sifat modulus dan kerintangan terhadap calaran. Disamping itu juga dalam kajian ini didapati penambahan partikel silika sehingga 25 wt% akan meningkatkan kelikatan resin akrilat dan seterusnya menurunkan sifat kebolehaliran bahan salutan di permukaan substrat (tixotrophy).*

**Keywords :** UV curable, hybrid materials, urethane acrylate resin, silica.

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## INTRODUCTION

Inorganic-organic hybrid materials have become one of the most interesting research fields in radiation curing and polymers (Salleh et. al., 2002). The combination of these materials (i.e. inorganic and organic) provide toughness, flexibility and enhance their resistance towards physical contact, chemicals and ambient. Such materials give great potential application especially in surface finishing, coatings, electronics and biomedical fields (Amerio et. al., 2009).

Radiation curing technology is expanding rapidly with respect in volume production or in advance application (Decker 1998). The advantage of this technology includes high quality coatings, environmental friendly, instantaneous curing time and less energy required that has made it a promising choice for commercialization as compared to conventional technique. On the other hand since conventional technique which deals mostly with solvent and the resulted high emission of volatile organic compounds (VOCs), the trend at present is started to change in order to comply with international standards that becomes stricter as well as to meet with customers demand which is seen more technology conscious (Al- mahdi et. al., 2007) .

In this paper, UV cured polyurethane acrylate-silica hybrid coatings (PUA) were synthesized to be used as a high performance coating materials. To improve the physical resistance of clear coatings, silica, nanoparticles were used for reinforcement of polymer composite. Due to their small size and their large active surface area, a homogenous distribution of the nanoparticles within the polymer matrix is believed can be achieved. To overcome the problem of the incompatibility of urethane acrylates with silica, the surface composition of the nanoparticles has to be altered from hydrophilic to organophilic. Therefore, the modification of the filler surface by coupling agents namely vinyl trimethoxysilane (VTMOS) was employed. VTMOS can be used to modify the filler surface due to their advantage that it capable to undergo hydrolysis and condensation reactions (Bauer et. al., 2003). The formation of chemical bonds between the inorganic and organic components is expected to be of great importance in guarantee a durable chemical junction between these two incompatible phases. Therefore better properties of coatings will be obtained which could become a best candidate to replace conventional coatings in various applications.

## MATERIALS AND METHOD

### *Materials*

Nano-sized silica (Aerosil OX 50) and coupling agent vinyltrimethoxysilane (VTMOS) were supplied by Degussa. Aromatic urethane acrylate as oligomer and tripropyleneglycol diacrylate (TPGDA) as monomer, were purchased from CYTEC Surface Specialties. The photoinitiator Irgacure 184 were obtained from Ciba Specialty Chemicals. MDF were received from Fakulti Perhutanan, Universiti Putra Malaysia (UPM). Maleic anhydride was used as catalyst and 4-hydroxyanisol as a stabilizer were obtained from Sigma Aldrich. All chemicals were used as received.

### Grafting Of Silane Coupling Agents On The Silica Nanoparticle

The grafting onto silica particle was prepared in oligomer and monomer mixture under heating temperature at 65 – 70 °C. Maleic anhydride, dissolved in water and 4-hydroxyanisol was introduced as catalyst and stabilizer. Meanwhile Vinyltrimethoxysilane (VTMOS) as coupling agent was added within 30 min. Finally silica particle were dispersed under intensive stirring during 1-2 hours using a dispermate dissolver. The product was immediately cooled to room temperature.

### Preparation of Inorganic Organic Hybrid Coatings (PUA composite coating film)

5 wt.% Photoinitiator was added into acrylate resin before UV irradiation. Subsequently Inorganic organic hybrid coating films (thickness = 200µm) with different percentage of silica (5 wt.% to 25 wt.% ) were prepared on MDF and plastic substrate by using bar coater applicator. After that the wet film were cured with the conventional medium pressure Hg lamp ( $120\text{Wcm}^{-1}$ ) for the polymerization process.

### Characterization

FT-IR spectra of UV hybrid coatings were recorded on a Perkin Elmer IR Spectrometer equipped with a diamond Golden Gate ATR adapter (Specac). Thermogravimetric analysis was carried out by using TGA (Mettler Toledo 851). 5 mg of each sample was used with a heating rate of 5 °C under inert atmosphere from 20 °C up to 600 °C. Meanwhile, the glass transition temperature ( $T_g$ ) were investigated by using DSC. 10 mg of each sample were heating from 0 °C to 200 °C with a heating rate of 10 °C. The scratch resistance and flexural strength of the samples were measured by using Erichsen Scratch Tester model 413 and Instron model 4301. SEM images were recorded by using SEM Philips XL 300. The morphology of coating sample as well as substrate was investigated. Prior to that, the samples were coated with gold coating by sputtering process using coater model SC 500.

## RESULT AND DISCUSSION

### Infrared Spectroscopy (FTIR)

FTIR analysis was carried out to monitor the changing of spectrum for metoxy group and acrylate group which involve in grafting and polymerization process.

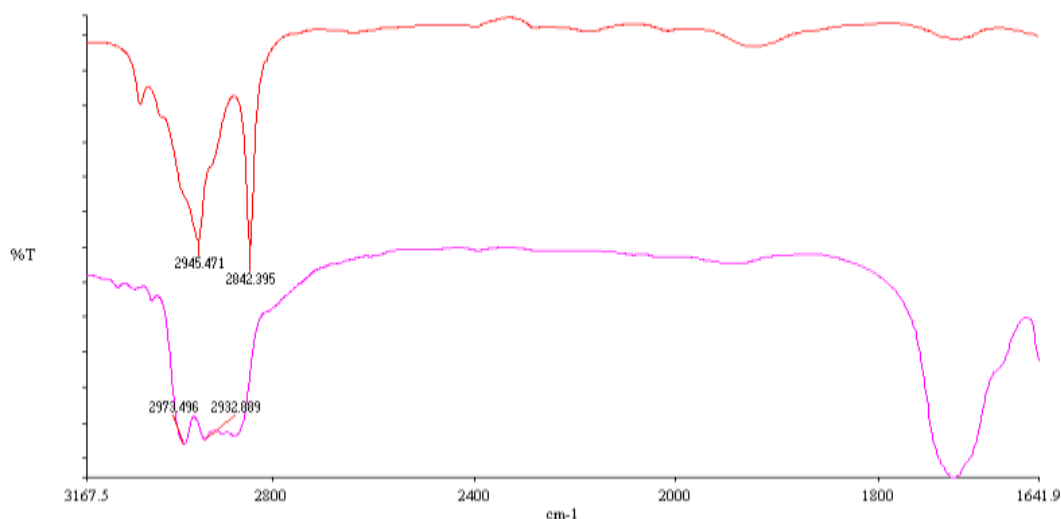
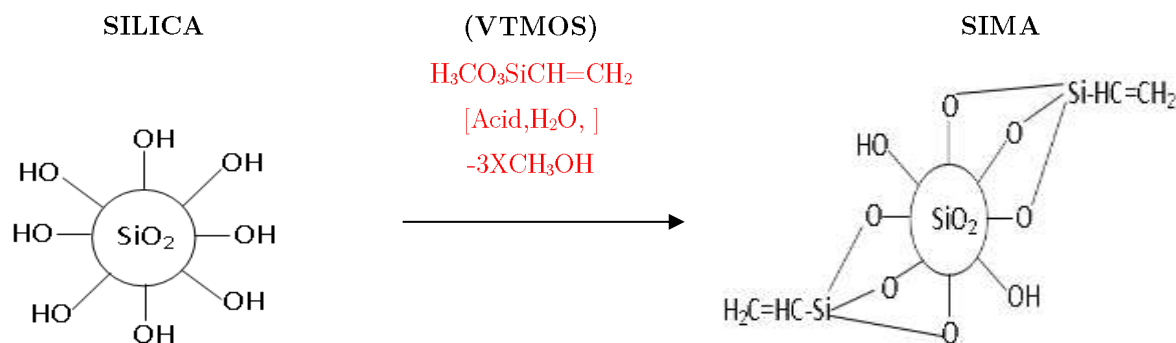


Figure 1. FTIR spectrum of VTMOS ( —) and SIMA( —)

Fig . 1 shows that the disappearance of metoxy group spectrum of VTMOS at band  $2842\text{cm}^{-1}$  were indicated the grafting process between VTMOS and silica particles. In this process the hydroxy group on silica particle

surface was interacted with methoxy group from VTMOs to form siloxane methacrylate (SIMA) and released a methanol as byproduct. This grafting process was undergone to alter the hydrophilic property of silica to organophilic thereby allow the silica particles to interact with urethane acrylate resin during polymerization process. The mechanism of this process is shown in Scheme 1 as depicted below which is proposed by Bauer et. al., 2002 (Tauber et. al., 2002).



Scheme 1: Formation of organophilic silica (SIMA) after treated with VTMOs.

In addition, the disappearance of  $810\text{cm}^{-1}$  in FTIR spectra for polyurethane acrylate in different compositions (5 – 25 wt.%) indicates that acrylate double bond has changed to single bond showing us photopolymerization process has occurred (Figure 2). As observed from the spectrum, silica composition did not influence in the reaction. It might be due to particle size of silica is so small to inhibit UV light and it not act as a radical scavenger. This observation is within the agreement with literature (Decker 1998).

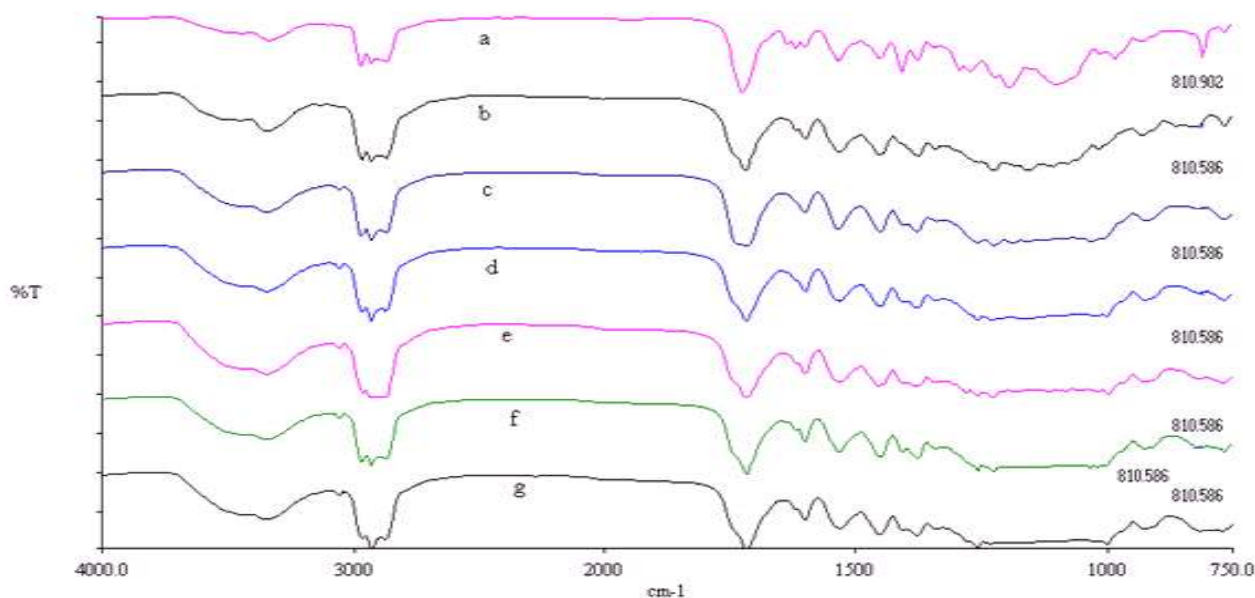


Figure 2. FTIR spectrum of uncured PUA composite resin and cured PUA composite coating. (a = 0wt%, b = 5wt%, c = 10wt%, d = 15wt% e = 20wt% and f = 25wt%).

### Scratch Resistance Study

Figure 3 shows the scratch resistance of Polyurethane acrylate coating which contained different percentage of silica particles (0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25wt%). The result clearly shows that scratch resistance increases with the composition of silica. This result is within the agreement with the previous work carried out

by Firdaus et. al 2007 and Shue et al 2002 . The incorporation of silica up to 30 % can enhance the scratch resistance of the nanocomposite coatings (Shuxue et. al., 2002). The rise of the scratch resistance is attributed to the effect of saturation of silica particle on the surface of the sample which directly resists the scratch tested to the sample (Sangermano et. al., 2005). On the other hand, the hybrid coating which comprises of urethane acrylate resin and inorganic silica has inhibited the movement of polymer chain. This effect occurred due to ability of particle silica to retard a defect propagation in polymer chain which thereby increase the scratch resistance of coating film. Furthermore the modification of particles silica by using VTMOs allow a homogeneity of silica particle dispersion inside polymer matrices. The well dispersion contributed to effectiveness of particle silica to resist the load which applied on composite coating therefore we can see that the scratch resistance was increased with the increment of silica particle amount. This observation is within the agreement with literature (Fogelstrom et. al., 2005).

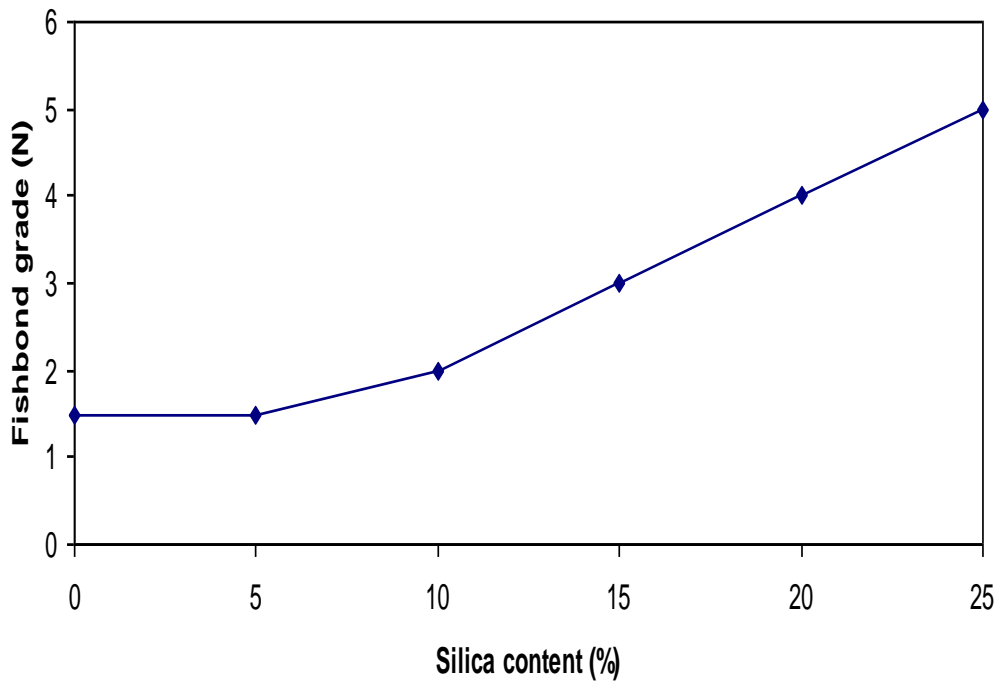


Figure 3. Scratch resistance of the PUA composite coating with different percentage of particle silica.

Additionally, the SEM image was used to provide morphological information for the sample as depicted in Figure 4. The images show us that there is no significant agglomeration of silica within the resin that indicate the silica particles are separated well from each other despite forming a clusters (Sangermano et. al., 2005). Note that, the first image is the sample without silica in which used for comparison.

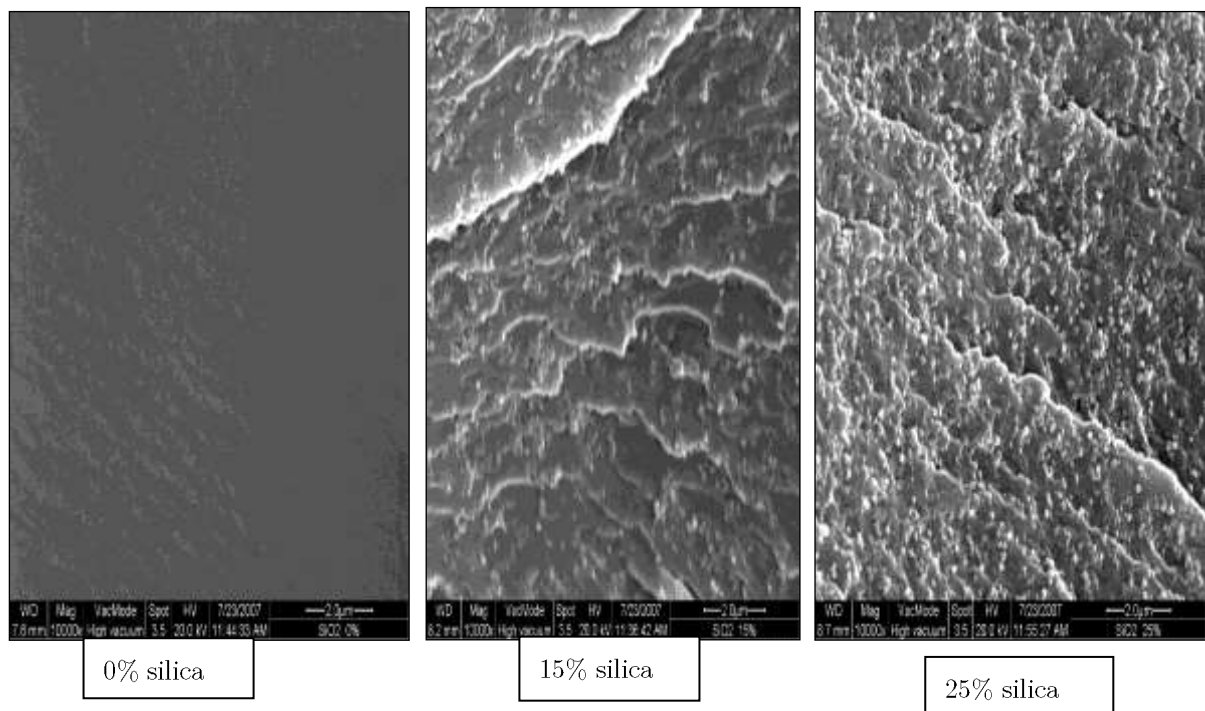


Figure 4. SEM image of PUA composite coating at different percentage of silica particle.

### Flexural Strength

Fig.5 shows that the addition of silica particles into PUA resin not more than 15% increases a flexural strength of MDF. Silica particles which embedded onto PUA resin by grafting process capable to transfer energy into particles – matrices interfaces. During a stress load, the polymer matrices allow energy to separate in polymer network meanwhile silica particles act as a energy stopper, prevent a deformation of acrylate coating. These reinforcement enhance a toughness of acrylate coating in sustaining exerted stress upon the sample (Wetzel et. al., 2003).

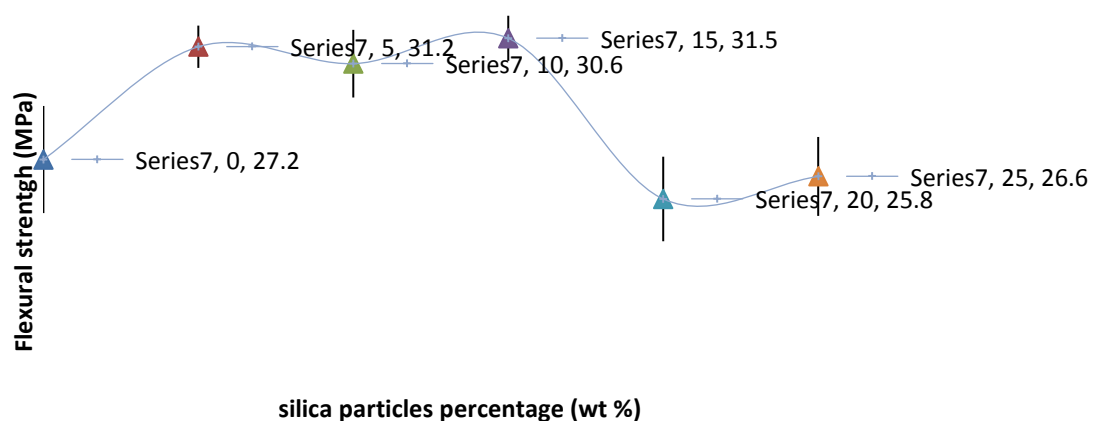


Figure 5. Flexural strength of PUA composite coating with different percentage of silica particles.

However when the silica particles is at higher concentration ( $> 15\%$ ) flexural strength start to decrease. This observation occurs due to the agglomeration of silica particles which create weak point in urethane acrylate coating. The agglomerated silica act as a strong stress concentrators induces crack propagation in acrylate coating which finally decreased the strength of polymer network (Nielsen and Landel 1994).

### Thermal Analysis Study (TGA and DSC)

Figure 5 shows that the decomposition temperature of the PUA composite coating. As can be seen, the range of decomposition is from  $280\text{ }^{\circ}\text{C}$  to  $323\text{ }^{\circ}\text{C}$ . The onset decomposition temperature occurred for the sample is at  $280\text{ }^{\circ}\text{C}$ . As compared with the decomposition temperature for polyurethane thermoplastic, the temperature usually lies around  $200\text{ }^{\circ}\text{C}$  (Masiulani and Zielinski 1985). This observation clearly shows that the significant improvement obtained by adding silica in urethane acrylate resin (Park and Cho 2003). The value of decomposition increases with increasing silica concentration. As universally known, silica contains greater heat capacity as compared with organic materials. Therefore, the rise of decomposition temperature in relation to silica content is within our expectation. It is suggested that silica adsorbs thermal energy during analysis and subsequently inhibits the scission of polymer chain (Dean et. al., 2007). With higher percentage of silica, the heat adsorption increases in which clearly seen in the figure 5.

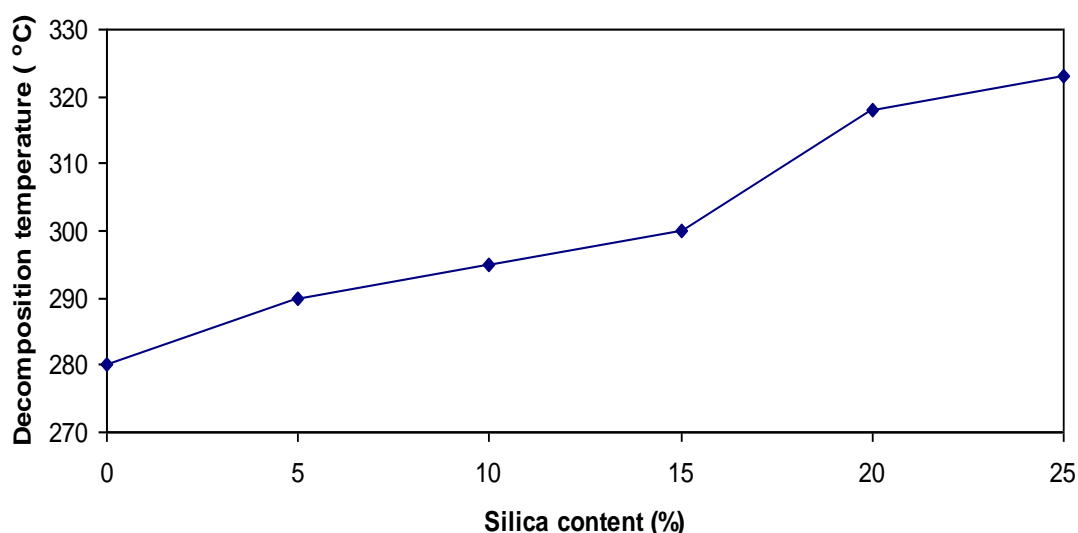


Figure 5. Decomposition temperature of PUA composite coating at different percentage of silica particle.

The similar result were also demonstrated by DSC analysis. Figure 6 shows the glass transition temperature of PUA composite coatings is proportionate with silica content. It elucidates that the movement of polymer chain (urethane acrylate) during heating process were strongly impeded by particles silica (Fragiadakis et. al., 2005). The presence of silica particles in the coating material increase the heat energy acquired to reach glass transition temperature. This effect can happen in two different ways, enhancement of heat absorption, additional of particle silica into PUA matrices will increase the heat capacity due to absorption of heat by particle silica which have higher heat capacity and homogenous dispersion of particle silica in PUA matrices, perform a protection layer which contributed to enhancement of thermal resistance of PUA composite coating. Furthermore the steric hindrance occurrence due to the presence of silica particles lead to limitation of polymer chain movement which cause more energy were required to allow the movement of polymer chain thereby contribute to the increment of glass transition temperature (Laachachi et. al., 2004).



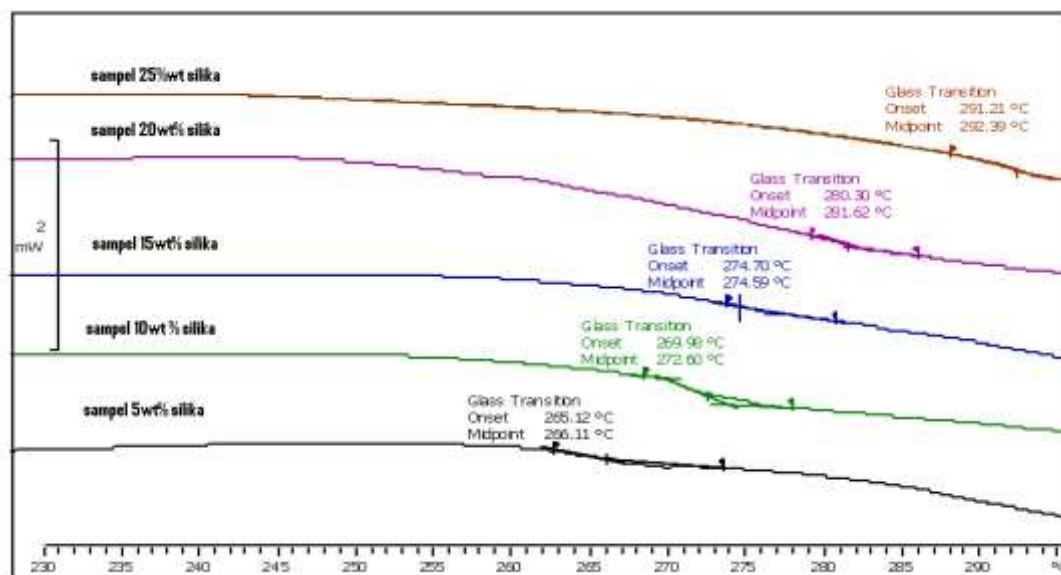


Figure 6. DSC analysis of PUA composite coating at different silica contents.

## CONCLUSIONS

PUA composite coatings film were successfully prepared by UV curing. FTIR has proved this finding with the observation of the disappearance of methoxy group and C=C indicates us that treated silica namely SIMA has successfully grafted within urethane resin with the presence of coupling agent namely VTMOs. With the presence of silica, the properties of the hybrid coatings are significantly improved and have surpassed the properties of the coating without silica. Scratch resistance, flexural strength, SEM images and TGA analysis have supported the finding. These as-prepared hybrid coatings could be used in high performance surface finishing fields.

## ACKNOWLEDGEMENT

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## REFERENCES

- Al-Mahdi, H.; Dahlan, K. Z.; Nik Salleh, N. G.; Mohd Hamzah, H.; Radtech Asia 2007 Conference and Exhibition 2007.
- Amerio, E.; Malucelli, G.; Sangermano, M.; Priola, A. (2009). Nanostructured Hybrid Materials Obtained By UV Curing And Sol-Gel Processes Involving Alkoxysilane Groups. E-Polymers. 059.
- Bauer, F., Glasel, H.J., Decker, U., Ernst, H., Freyer, A., Hartmann, E., Sauerland, V. & Mehnert, R. (2003). Trialkoxysilane Grafting Onto Nanoparticles For The Preparation Of Clear Coat Polyacrylate Systems With Excellent Scratch Performance. Progress in Organic Coatings 47: 147–153.
- Dean, K.M., Bateman, S. A. & Simons R. (2007). A Comparative Study Of UV Active Silane-Grafted And Ion-Exchanged Organo-Clay For Application In Photocurable Urethane Acrylate Nano- And Micro-Composites. Polymer 48: 2231- 2240.



- Decker, C. (1998). Special Review The Use Of UV Irradiation In Polymerization. *Polymer International* 45:133–141.
- Fogelstrom, L., Per Antoni, Malmstrom, E. & Hult A. 2006. UV-Curable Hyperbranched Nanocomposite Coatings. *Progress in Organic Coatings* 55: 284-290.
- Fragiadakis D., Pissisa, P., Bokobza, L. (2005). Glass Transition And Molecular Dynamics In Poly(Dimethylsiloxane)/Silica Nanocomposites. *Polymer* 46: 6001-6008.
- Institute for Surface Modification, IOM Annual Report 2004/2005.
- Laachachi A., Cochez, M., Ferriol, M., E. Leroy, E., Lopez Cuesta, J.M. & Oget, N. (2004). Influence Of  $\text{Sb}_2\text{O}_3$  Particles As Filler On The Thermal Stability And Flammability Properties Of Poly(Methyl Methacrylate) (PMMA). *Polymer Degradation and Stability* 85: 641-646.
- Masiulonis, B. & Zielinski, R. (1985). Mechanical Thermal, And Electric Properties Of Polyurethaneimide Elastomers. *J Appl Polym Sci* 30: 2731–41
- Nielsen L.E & Landel R.F.(1994). *Mechanical Properties of Polymer and Composites*. New York. Marcel Dekker, Inc.
- Park, S-J.; Cho, K-S. (2003). Filler–Elastomer Interactions: Influence Of Silane Coupling Agent On Crosslink Density And Thermal Stability Of Silica/Rubber Composites. *J. Colloid Interface Sci.* 267:86 - 91.
- Salleh, N.G., Glasel, H.J. & Mehnert R.(2002). Development Ofhard Materials By Radiation Curing Technology. *Radiation Physics and Chemistry* 63: 475–479.
- Shuxue Zhou, Limin Wu, Jian Sun & Weidian Shen. (2002). The Change Of The Properties Of Acrylic – Based Polyurethane Via Addition Of Nano – Silica. *Progress in Organic Coatings* 45: 33-42.
- Sangermano, M., Malucelli G., Amerio, E., Priola, A., Billi, E. & Rizza, G. (2005). Photopolymerization Of Epoxy Coatings Containing Silica Nanoparticles. *Progress in Organic Coatings* 54: 134–138.
- Tauber, A.; Hartmann, E.; Glasel, H. J.; Bauer, F.; Mehnert, R; *Proceeding of International Nuclear Conference* (2002).
- Wetzel, B., Hauptert, F. & Zhang M.Q. (2003). Epoxy Nanocomposites With High Mechanical And Tribological Performance. *Composites Science and Technology* 63: 2055–2067.
- Yhaya, M. F.; Nik Salleh, N. G.; Hassan, A.; Abu Bakar, A.; Mokhtar, M.; *Radtech Asia 2007 Conference and Exhibition* 2007.