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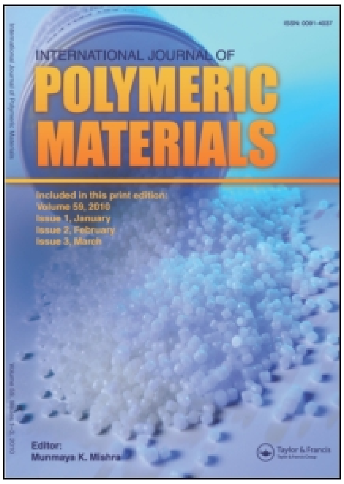

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# Development of Scratch- and Abrasion-Resistant Coating Materials Based on Nanoparticles, Cured by Radiation

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*The aim of this study was to compare the effect of monomers, prepolymers, and nanosilica on the scratch and abrasion resistance of nanocomposite coatings. Ultraviolet (UV) and electron beam (EB) curing were used to cure the nanocomposite coatings. The effect of monomers, prepolymers and nanosilica particles on the viscosity, pendulum hardness, gel content, scratch and abrasion resistance were studied. It was found that the optimum formulation for scratch and abrasion resistance contained 15% Ebecryl 600 epoxy acrylate resin with 30% monomer PETIA and 30% of Aerosil OX-50 nanosilica.*

**Keywords:** abrasion resistance, monomers, nanoparticles, prepolymers, scratch resistance

## INTRODUCTION

Coating materials are always in demand for both protective as well as decorative reasons. However, the majority of coating materials available are vulnerable to scratches and are easily abraded [1]. In the development of scratch- and abrasion-resistant surface coatings, the incorporation of nanoparticles into the coatings is gaining much popularity. Interest in radiation curing technology is also increasing, in hand with the strict regulations and environmental concerns.

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Radiation curing alone produced hard coatings with high degrees of scratch and abrasion resistance [2]. Among all radiation curing techniques available today, ultraviolet (UV) and electron beam (EB) curing are the most widely practiced. By combining radiation curing and nanocomposite technology, it is expected that the resulting radiation-cured nanocomposite coatings will have superior performance relative to readily available coatings.

Earlier works in the literature were already combining radiation curing and nanocomposite technology to produce novel scratch- and abrasion-resistant coating materials. UV or EB curing method was used to cure the nanocomposite coatings. Tauber et al. [3] had proven that polyacrylate nanocomposite films subjected to EB radiation curing showed a higher scratch and abrasion resistance. The films also had improved viscoelastic properties as compared to the neat (pure) polyacrylate. Many methods had been proposed by Fei [4] to increase the abrasion resistance of UV coatings. The improvement of abrasion resistance depends on the crosslinking density of the polymer, the use of additives such as propylene wax, aluminum oxide or nanoscaled silica. Ueda et al. [5] studied the quantitative evaluation of the scratch resistance of UV-cured organic-inorganic hybrid hard coatings by variable load scratching. They found that the UV-curable hard coatings had higher resistance against repeating abrasion than the conventional organic hard coatings. Sangermano et al. [6] reported that silica nanofillers were able to induce both a bulk and a surface modification of UV-cured coatings with an increase in $T_g$, modulus, and surface hardness. Recent works by Fogelström et al. [7] had combined three research areas, namely, nanocomposites, hyperbranched polymers, and radiation curing to produce a UV-curable coating system. They found that film with nanofiller yielded a harder surface, better scratch resistance, better adhesion to metal substrates and small improvement in flexibility. However, no research that compares the effect of monomers, prepolymers, and nanosilica on the scratch and abrasion resistance of radiation-cured nanocomposite coatings has been reported. The aim of present work is to fill in the gap in this area.

## EXPERIMENTAL

### Materials

The raw materials (Table 1) selected to produce radiation curable materials consist of prepolymer (oligomer), monomer (reactive diluent), coupling agent, filler, catalyst, stabilizer, and photoinitiators (for UV-cured coatings only). In this research, urethane acrylate

**TABLE 1** Formulations and Temperature for Synthesis

| Materials | F1 | F2 | F3 | F4 | F5 | F6 | F7 | F8 | F9 | F10 | F11 | F12 | F13 | F14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ebecryl 230 | 45 | 35 | 45 | 35 | 17.5 | – | – | – | – | – | – | – | – | – |
| Ebecryl 600 | – | – | – | – | 17.5 | 45 | 40 | 35 | 30 | 25 | 20 | 15 | 15 | 10 |
| TPGDA | 30 | 30 | – | – | – | – | – | – | – | – | – | – | 15 | 15 |
| PETIA | – | – | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 15 | 15 |
| VTMOS | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| Aerosil OX-50 | – | 10 | – | 10 | 10 | – | 5 | 10 | 15 | 20 | 25 | 30 | 30 | 35 |
| | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Water | – | 25 g | – | 25 g | 25 g | – | 25 g | 25 g | 25 g | 25 g | 25 g | 25 g | 25 g | 25 g |
| Maleic anhydride | – | 1.5 g | – | 1.5 g | 1.5 g | – | 1.5 g | 1.5 g | 1.5 g | 1.5 g | 1.5 g | 1.5 g | 1.5 g | 1.5 g |
| 4-Hydroxy anisole | 480 mg | 480 mg | 480 mg | 480 mg | 480 mg | 480 mg | 480 mg | 480 mg | 480 mg | 480 mg | 480 mg | 480 mg | 720 mg | 720 mg |
| Irgacure 500 | 2% | 2% | 2% | 2% | 2% | 2% | 2% | 2% | 2% | 2% | 2% | 2% | 2% | 2% |
| Darocur 1173 | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% | 1.5% |
| Temperature for synthesis | 65°C | 65°C | 65°C | 65°C | 65°C | 65°C | 65°C | 65°C | 65°C | 65°C | 65°C | 65°C | 60°C | 60°C |

prepolymer (Ebecryl 230) was used to impart flexibility while epoxy acrylate prepolymer (Ebecryl 600) was used to impart good hardness and abrasion resistance to the coatings. Tripropyleneglycol diacrylate (TPGDA) and pentaerythritol tri/tetraacrylate (PETIA) monomers were used to increase flexibility and crosslink density of cured film, respectively. The prepolymers and monomers used were purchased from UCB Chemicals, Belgium.

Vinyltrimethoxysilane (VTMOS) coupling agent, often used to enhance the interaction between silica nanoparticles and acrylate matrix, was selected in this study. According to Salleh et al. [1], nanocomposites treated with VTMOS showed higher abrasion resistance than propyltrimethoxysilane (PTMOS). Silica nanofiller (Aerosil OX-50) was used as reinforcing filler. This filler has low thickening and agglomeration properties compared to other types of Aerosil available in the market. The VTMOS and Aerosil OX-50 used were purchased from Degussa-Hüls, Germany.

Maleic anhydride was used as a catalyst in this study to induce crosslinking and compatibility [8]. The amount of maleic anhydride and water used for dilution was based on previous work [9]. The diluted maleic anhydride was added during the synthesis of radiation curable materials. 4-hydroxy anisole stabilizer was also added during the synthesis to prevent premature polymerization caused by heat and shearing action of the rotating blades. The amount used was also based on previous work [9]. Both maleic anhydride and 4-hydroxy anisole were purchased from Sigma-Aldrich, UK.

For UV-cured coatings, the inclusion of photoinitiators into the coating formulations was necessary. Irgacure 500 and Darocur 1173 photoinitiators purchased from CIBA Switzerland were used for UV curing. Previous work reported that the optimum amount of photoinitiators for Irgacure 500 and Darocur 1173 were 2% and 1.5%, respectively [10]. This optimum amount of both photoinitiators improved the abrasion resistance of coatings.

## Sample Formulations

Table 1 shows that VTMOS coupling agent, Irgacure 500 and Darocur 1173 photoinitiators loading were constant for all formulations. 4-hydroxy anisole stabilizer loading was constant for all formulations except for Formulation 13 (F13) and Formulation 14 (F14). The concentration of maleic anhydride in water was also constant except for Formulation 1 (F1), Formulation 3 (F3), and Formulation 6 (F6).

F1 was prepared without Aerosil OX-50 whereas 10% Aerosil OX-50 was added into Formulation 2 (F2) in order to study the effect of

Aerosil OX-50 on the coatings. According to previous work by Salleh [9], a significant improvement in scratch resistance was only achieved at 10% or more Aerosil OX-50 loading.

30% TPGDA in F1 and F2 was replaced with 30% PETIA in Formulation 3 (F3) and Formulation 4 (F4). However, F4 contained with 10% Aerosil OX-50. Both monomers, 17.5% TPGDA and 17.5% PETIA, and 10% Aerosil OX-50 were added in Formulation 5 (F5). The effect of Aerosil OX-50 and the different types of monomer on the hardness coating were investigated in these formulations.

Ebecryl 600 prepolymer and 30% PETIA monomer were used in Formulation 6 (F6) to Formulation 12 (F12). The Aerosil OX-50 loading in F6 to F12 was increased from 0 to 30%. These F6–F12 formulations were formulated in order to study the effect of Aerosil OX-50 loading on the viscosity of uncured formulations and finished coatings.

Similar to F6 to F12, Ebecryl 600 prepolymer and Aerosil OX-50 were also used in Formulation 13 (F13) and Formulation 14 (F14). However, 15% TPGDA and 15% PETIA monomers were used simultaneously in F13 and F14 instead of 30% PETIA in F6 to F12. PETIA amount was decreased from 30% in F12 to 15% in F13 and F14. The F14 has the highest Aerosil OX-50 loading (35%) compared to the rest of formulations (F1–F13). As the Aerosil OX-50 loading increased in F13 and F14, the filler loading time during the synthesizing process also increased. As a result, the use of 4-hydroxy anisole stabilizer had been increased from 480 mg for F12 to 720 mg for F13 and F14 in order to maintain the stability of F13 and F14. The stability of the formulation decreased with increasing loading time, due to the increase of time taken for the formulations to undergo the shearing action of rotating blades and the heat exposure. In this study, the reduction of stability means that the formulation either gelled immediately after the synthesis or had a shorter shelf life. To maintain the stability of F13 and F14, the temperature of synthesis also was decreased from 65°C for F1 to F12 to 60°C for F13 and F14.

All prepolymers, monomers, and filler were each weighed in a plastic container separately. Meanwhile, VTMOS coupling agent was weighed in an amber glass bottle. All materials were kept closed and stored away from light. Both maleic anhydride and 4-hydroxy anisole were ground to powder from their original pebble-like state. Distilled water and maleic anhydride were weighed in the same bottle. The sealed bottle was then immersed in Elma Transsonic T1040/H sonic water bath for about 45 min to obtain a homogenous solution. The ultrasonic sound produced a vibration that contained energy. This vibration caused molecules to collide with each other and facilitated the solution process. The molecular collisions in turn produced heat that increased the solubility of maleic anhydride in water. After the process, no more powder particles were present, indicating a homogenous solution had been formed. The bottle was then stored inside a dark cabinet.

## Mixing

The mixing process was done using the Dispermat mixer VMA-Getzmann GmbH. Neslab USA RTE-211 water bath was used to regulate the temperature of the mixing container. The water bath was allowed to stabilize at 65°C prior to the mixing process. The Dispermat mixing blades with 70 mm radius were chosen, to suit the size of the double-wall stainless steel container.

Ebecryl 230 prepolymer was poured into the mixing container. Care was taken to ensure that it did not spill to the side of the container or onto the shaft of the mixing blades. The rotation speed for the mixing blades was increased gradually in order to prevent the prepolymer from spilling out of the container. The monomer TPGDA was added to the container, followed by 4-hydroxy anisole. TPGDA reduced the viscosity of the prepolymer and facilitated the mixing process.

The maleic anhydride solution was then added, followed by dropwise addition of VTMOS. It is worth noting that during the addition, the rotation speed of the blade mixer should be increased slowly. The duration of VTMOS addition was within 30 min. Finally, the silica nanofiller was added. The mixture was allowed to mix thoroughly for an hour at 2500 rpm. After mixing, the mixture was poured into an amber glass bottle and immediately brought to the ultrasonic probe.

The ultrasonic probe was dipped into the center of the bottle. The purpose was to remove air bubbles produced during the addition and mixing process. Air bubbles scattered the light, causing the mixture to appear milky. When the ultrasonic probe stopped, the clarity of the mixture increased after air bubbles were removed. The bottle was left for at least one hour for the mixture to stabilize. The bottle was then sealed and kept in a dark cabinet.

Some content from the bottle was put into another smaller one. Then the photoinitiators were weighed based on the weight of the content in the small bottle. The photoinitiators were also weighed in the same bottle. The photoinitiators and the content in the small bottle were mixed together. The percentage of photoinitiators used is shown in Table 1. The content in the small bottle with both photoinitiators was then stirred at 200 rpm for one hour using Heidolph RZR-2000. For EB-cured coatings, the use of photoinitiators was omitted.

## Coating and Curing Process

The coating process was similar for both UV and EB curing methods; only the curing process was different. The K Paint automatic film applicator was switched on. The perforated metal base of the film applicator was vacuumized to hold the cover paper and the glass plate properly. The cover paper was used to prevent the coating materials from dripping into the vacuum holes. The slit thickness of the applicator bar used was 150 microns. The thickness of 150 microns was chosen because the coating was easier to peel for gel content measurement and reduced the possibilities of torn samples during the abrasion tests. The glass plate was put on the cover paper and the applicator bar was fixed and locked. Then the coating was poured on the glass plate and the coating process was started.

For UV curing, the coated glass was then brought to the UV machine and was put on the conveyor. The UV lamps of IST UV curing machine had been switched on and stabilized for 15 min prior to the curing process. The conveyor speed of the curing machine was set up at 10 m/min. At this speed, this machine produced 0.150 J/cm$^2$ of energy. The first coated glass was allowed to pass once under the UV light. The number of passes was 2, 3, 4, 5, 8, 10, and 12 each for the next seven coated glass plates.

For EB curing, the same formulation without photoinitiators was coated on a glass plate and subjected to electron beam curing using Curetron made by Nissin High Voltage. The dosage provided by the machine is 10 kGy (kiloGray) for each pass. The number of passes was also 2, 3, 4, 5, 8, 10, and 12 each for the next seven coated glass plates.

The purpose of the highest 12 passes (UV curing) and 120 kGy (EB curing) was to determine whether the polymerization process reached the plateau. After the irradiation, the glass plates were taken out and conditioned at 25°C under laboratory ambience for 4 h before measuring their pendulum hardness and gel content. The pendulum hardness and gel content tests were done to find the optimum curing doses for each UV and EB curing. After these dosages were determined, the whole process of coating and curing was repeated to prepare the samples for scratch and abrasion resistance measurement.

## Characterization of Nanocomposite Coatings

Byk Pendulum Hardness Tester was used to measure the surface hardness of nanocomposite coatings according to DIN 53157, by adapting the König method. After the hardness measurement, the coatings were peeled off and placed in a Soxhlet Extractor for 16 h to measure their gel contents. Results from pendulum hardness and gel content were used to determine the suitable dosages for UV/EB curing. However, the measurement of gel content for EB-cured samples was very difficult to do because they were hard and brittle. The thumb twist method was used to support the pendulum hardness and gel content results. For UV curing, 5 passes at conveyor speed of 10 m/min was chosen whereas 100 kGy was the chosen dose for EB curing. The selected dosages were then used to cure coatings for scratch and abrasion resistance tests. 150 μm-thick coatings were cured on PVC plates and decorative furniture papers for scratch and abrasion resistance tests, respectively. The scratch resistance of a coating film was measured using Erichsen Scratch Tester Model 413 according to DIN 53799. Two types of scratching needles (tip) were used, stainless steel ball tip and diamond tip. The higher the value (Newton) obtained, the better the scratch resistance. Taber Abraser 5151 was used to measure the abrasion resistance of the cured coatings according to DIN 68861.2. The testing was done at 50 wheel rotations with 500 g load for each abrasive wheel. In the case for abrasion resistance, the lower the weight loss, the better.

## RESULTS AND DISCUSSION

### The Effect of Types of Monomers on the Viscosity of Formulation

Table 2 shows that the viscosity value for F4 was higher than F2 and F3 higher than F1. The selection of monomers influenced the viscosity of formulation. PETIA with higher viscosity than TPGDA will contribute to higher formulation viscosity. PETIA (pentaerythritol tri/tetraacrylate) is a 50/50 combination of PETA (pentaerythritol triacrylate) and PETTA (pentaeryhtritol tetraacrylate).

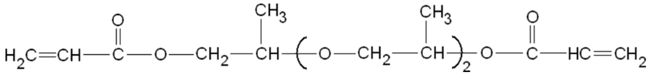
This phenomenon could be explained in terms of the chemical structures of TPGDA, PETA, and PETTA (Figures 1–3). TPGDA is a linear molecule while PETA and PETTA are both branched. Branching induced steric hindrance to the movement of molecules, thereby increasing the viscosity. Since viscosity is strongly influenced by chain branching, monomers that contain branched molecules will be more viscous than the monomers that contain linear molecules. Tri- or tetrafunctional monomer (PETA and PETTA) has relatively high viscosity compared to difunctional ones (TPGDA). This is in agreement with theory by Webster [10].

**TABLE 2** The Effect of Monomers, Prepolymers, and Nanosilica on the Viscosity

| | Monomer (%) | | Prepolymer (%) | | | |
|---|---|---|---|---|---|---|
| Formulation | TPGDA | PETIA | EB 230 | EB 600 | Nanosilica OX-50 (%) | Viscosity (mPa · s) |
| F1 | 30 | – | 45 | – | 0 | 562 mPa · s at 25°C |
| F2 | 30 | – | 35 | – | 10 | 722 mPa · s at 60°C |
| F3 | – | 30 | 45 | – | 0 | 4,748 mPa · s at 25°C |
| F4 | – | 30 | 35 | – | 10 | 2,342 mPa · s at 60°C |
| F5 | – | 30 | 17.5 | 17.5 | 10 | 3,626 mPa · s at 60°C |
| F6 | – | 30 | – | 45 | 0 | 540 mPa · s at 60°C |
| F7 | – | 30 | – | 40 | 5 | 2,074 mPa · s at 60°C |
| F8 | – | 30 | – | 35 | 10 | 3,900 mPa · s at 60°C |
| F9 | – | 30 | – | 30 | 15 | 7,522 mPa · s at 60°C |
| F10 | – | 30 | – | 25 | 20 | 31,760 mPa · s at 60°C |
| F11 | – | 30 | – | 20 | 25 | 55,025 mPa · s at 60°C |
| F12 | – | 30 | – | 15 | 30 | 78,289 mPa · s at 60°C |
| F13 | 15 | 15 | – | 15 | 30 | 4,076 mPa · s at 60°C |
| F14 | 15 | 15 | – | 10 | 35 | 5,186 mPa · s at 60°C |

## The Effect of Types of Monomers on Pendulum Hardness

Figures 4 and 5 show that F3 coatings were harder than the F1 coatings, regardless of the types of radiation used. Similarly, PETIA containing F4 were harder than TPGDA containing F2 (Figures 6 and 7). The results show that the types of monomers used also influenced the surface hardness of the coatings. Monomer with many reactive sites (double bonds) such as PETA and PETTA contributed to the coatings with higher hardness compared to the monomer which had less sites (TPGDA). When crosslinked together with prepolymer during irradiation, TPGDA cured in two dimensions since it had one double bond at both ends. On the other hand, PETIA cured in three dimensions due to its branching. As a result, PETIA produced three-dimensional network coatings that were harder than the linear ones produced by TPGDA.



$$H_2C{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}\left(O{-}CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}\right)_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}HC{=}CH_2$$

**FIGURE 1** The structure of tripropyleneglycol diacrylate (TPGDA) (Molecular weight = 300).

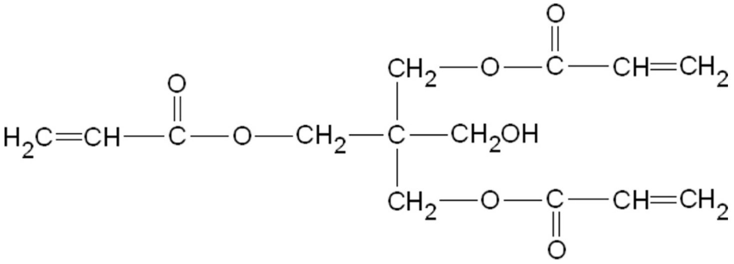


**FIGURE 2** The structure of pentaerythritol triacrylate (PETA) (Molecular weight = 298).

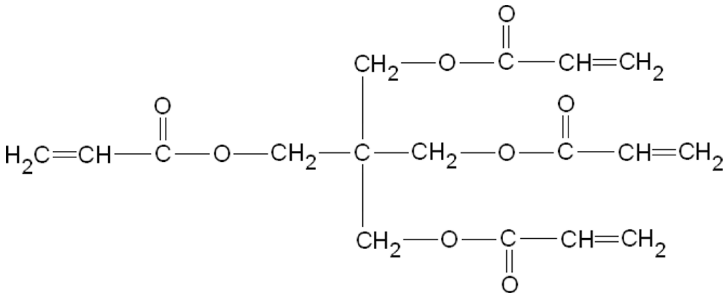


**FIGURE 3** The structure of pentaerythritol tetraacrylate (PETTA) (Molecular weight = 352).

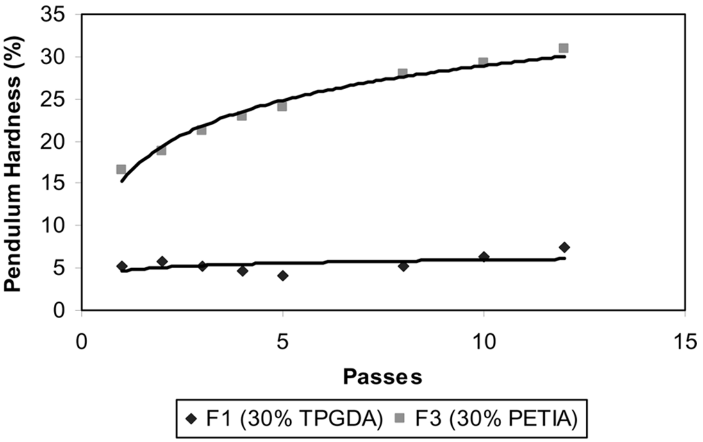


**FIGURE 4** The effect of types of monomers on the hardness of F1 and F3 cured by UV.

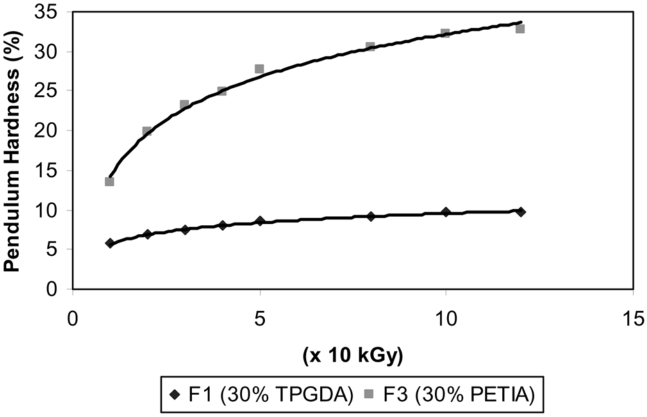


**FIGURE 5** The effect of types of monomers on the hardness of F1 and F3 cured by EB.

## The Effect of Types of Monomers on the Gel Content

As shown in Figure 8, F3 with PETIA produced coatings with higher gel content than F1 with TPGDA. Similarly, F4 with PETIA also produced coatings with higher gel content than F2 with TPGDA (Figure 9). In both figures, the gel contents of F3 and F4 coatings were always higher, right from the start of irradiation (crosslinking) processes. Higher gel content showed that formulations with PETIA were more reactive towards crosslinking. Reactivity towards crosslinking is

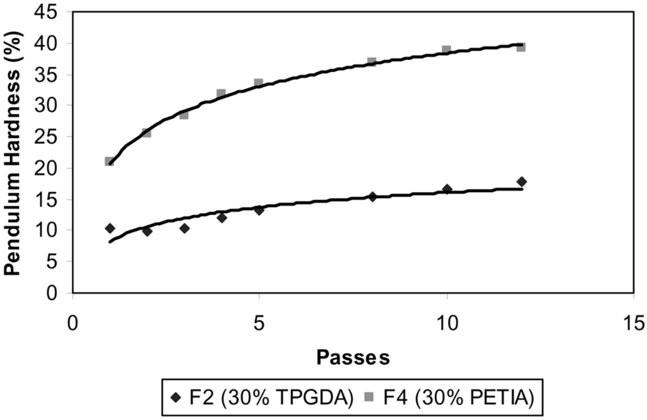


**FIGURE 6** The effect of types of monomers on the hardness of F2 and F4 cured by UV.

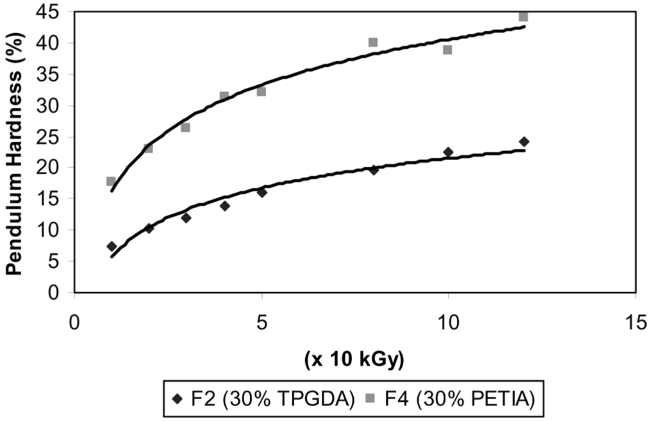


**FIGURE 7** The effect of types of monomers on the hardness of F2 and F4 cured by EB.

parallel to the increased amount of unsaturation (reactive sites). Similar finding was reported by Chattopadhyay et al. [11]. PETIA has more reactive sites than TPGDA. When crosslinked, coatings with PETIA produced higher gel content than coatings with TPGDA.

## The Effect of Types of Monomers on Scratch Resistance

Table 3 shows that the scratch resistance by stainless steel ball tip of F3 was higher than F1, for both curing methods. Similarly, F4 with

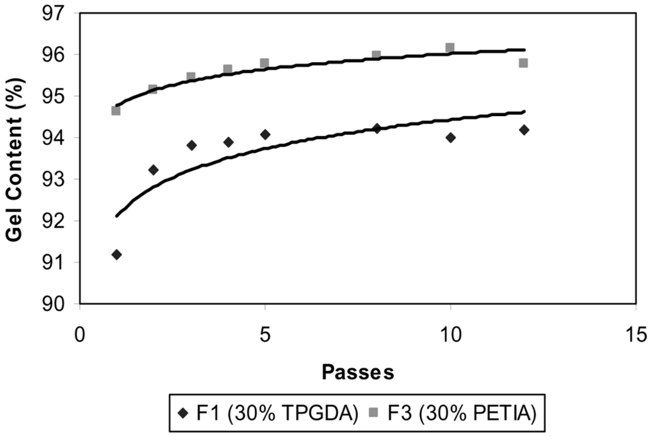


**FIGURE 8** The effect of types of monomers on the gel content of F1 and F3.

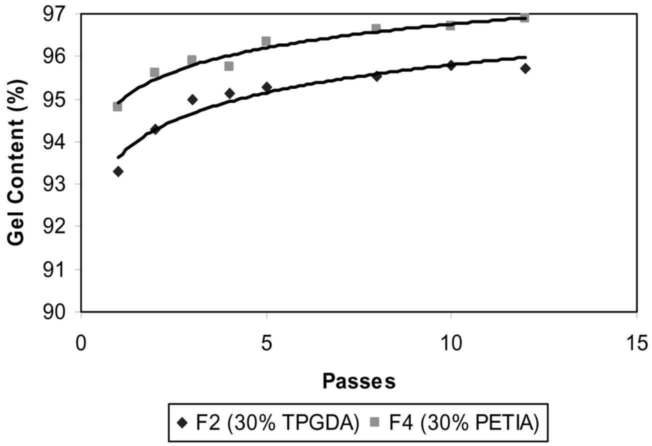


**FIGURE 9** The effect of types of monomers on the gel content of F2 and F4.

PETIA showed higher values compared to F2 with TPGDA. However, for the measurement of scratch resistance by diamond tip, the values for F3 were similar to F1. The same trend was also obtained for F4 and F2, where the values for F4 were similar to F2. This was due to the F1 and F2 coatings that were still sticky even though cured at higher dosages. Since no literature is available to support this finding, it might be possible that this tackiness provided some resistance to scratching by the diamond tip but not by the steel ball since the latter was able to roll on sticky surfaces.

The scratch resistance depended on the functionality (double bond) of the monomer (monoacrylate < diacrylate < triacrylate), similar to the report by Decker et al. [12]. The increase in scratch resistance was parallel to the increase in acrylate double bonds, as proven by Jung and Valet [13]. TPGDA was a diacrylate monomer, whereas PETIA was a combination of tri- and tetraacrylate monomer. It was expected that coatings containing PETIA to be more resistant to scratching than coatings containing TPGDA.

## The Effect of Types of Monomers on Abrasion Resistance

Table 4 shows that for UV-cured coatings, F4 coating was harder than F2 coatings. F4 coating lost 40.2 mg compared to F2 coating that lost 58.0 mg. F3 coating lost 76.4 mg compared to F1 which was torn after 20 abrasive rotations. For EB-cured samples, F4 coating with PETIA was harder than F2 coating that contained TPGDA. F4 coating lost

**TABLE 3** The Effect of Monomers, Prepolymers, and Nanosilica on the Scratch Resistance

| | | | | | | Scratch resistance (N) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Monomer (%) | | Prepolymer (%) | | | UV-cured coatings | | EB-cured coatings | |
| Formulation | TPGDA | PETIA | EB 230 | EB 600 | Nanosilica OX-50 (%) | Steel ball diameter (1 mm) | Diamond tip (90°) | Steel ball diameter (1 mm) | Diamond tip (90°) |
| F1 | 30 | – | 45 | – | 0 | ≤0.1 | 0.2 | ≤0.1 | 0.2 |
| F2 | 30 | – | 35 | – | 10 | 0.1 | 0.3 | 0.1 | 0.4 |
| F3 | – | 30 | 45 | – | 0 | 1 | 0.2 | 0.4 | 0.2 |
| F4 | – | 30 | 35 | – | 10 | 2 | 0.3 | 0.5 | 0.4 |
| F5 | – | 30 | 17.5 | 17.5 | 10 | 8 | 0.6 | 7 | 0.5 |
| F6 | – | 30 | – | 45 | 0 | >10 | 0.7 | 9 | 0.9 |
| F7 | – | 30 | – | 40 | 5 | >10 | 0.8 | >10 | 1 |
| F8 | – | 30 | – | 35 | 10 | >10 | 1.0 | >10 | 1.5 |
| F9 | – | 30 | – | 30 | 15 | >10 | 1.5 | >10 | 2.5 |
| F10 | – | 30 | – | 25 | 20 | >10 | 2 | >10 | 3.5 |
| F11 | – | 30 | – | 20 | 25 | >10 | 2.5 | >10 | 4 |
| F12 | – | 30 | – | 15 | 30 | >10 | 2.5 | >10 | 4.5 |
| F13 | 15 | 15 | – | 15 | 30 | >10 | 3 | >10 | 3 |
| F14 | 15 | 15 | – | 10 | 35 | >10 | 3 | >10 | 3.5 |

**TABLE 4** The Effect of Monomers, Prepolymers, and Nanosilica on the Abrasion Resistance

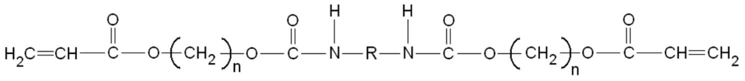
| | Monomer (%) | | Prepolymer (%) | | | Weight loss (mg) | |
|---|---|---|---|---|---|---|---|
| Formulation | TPGDA | PETIA | EB 230 | EB 600 | Nanosilica OX-50 (%) | UV-cured coatings | EB-cured coatings |
| F1 | 30 | – | 45 | – | 0 | 11.4 mg at 20 rotations | 26.8 mg at 20 rotations |
| F2 | 30 | – | 35 | – | 10 | 58.0 mg at 50 rotations | 96.7 mg at 50 rotations |
| F3 | – | 30 | 45 | – | 0 | 76.4 mg at 50 rotations | 111.2 mg at 50 rotations |
| F4 | – | 30 | 35 | – | 10 | 40.2 mg at 50 rotations | 69.8 mg at 50 rotations |
| F5 | – | 30 | 17.5 | 17.5 | 10 | 25.5 mg at 50 rotations | 46.8 mg at 50 rotations |
| F6 | – | 30 | – | 45 | 0 | 44.4 mg at 50 rotations | 44.1 mg at 50 rotations |
| F7 | – | 30 | – | 40 | 5 | 28.2 mg at 50 rotations | 30.0 mg at 50 rotations |
| F8 | – | 30 | – | 35 | 10 | 19.9 mg at 50 rotations | 22.0 mg at 50 rotations |
| F9 | – | 30 | – | 30 | 15 | 14.2 mg at 50 rotations | 15.9 mg at 50 rotations |
| F10 | – | 30 | – | 25 | 20 | 12.0 mg at 50 rotations | 13.2 mg at 50 rotations |
| F11 | – | 30 | – | 20 | 25 | 9.4 mg at 50 rotations | 10.9 mg at 50 rotations |
| F12 | – | 30 | – | 15 | 30 | 6.7 mg at 50 rotations | 8.5 mg at 50 rotations |
| F13 | 15 | 15 | – | 15 | 30 | 10.3 mg at 50 rotations | 12.8 mg at 50 rotations |
| F14 | 15 | 15 | – | 10 | 35 | 8.6 mg at 50 rotations | 8.8 mg at 50 rotations |

69.8 mg compared to F2 coating which lost 96.7 mg. F3 coating lost 111.2 mg compared with F1 which was torn after 20 abrasive rotations. These results showed that coatings with PETIA should be more resistant to abrasive forces compared to TPGDA coatings, since PETIA was a combination of multifunctional monomers compared to difunctional TPGDA. From Table 4, almost all UV-cured samples gave higher abrasion resistance than their EB counterparts.

UV coatings cured from outside towards inside but the curing was not uniform compared to EB-cured coatings. The surface might be hard because the concentration of radicals was highest at the surface, but below the surface (subsurface), the coatings were still soft. When the abrasion test was done, the flexible subsurface provided some resistance to the abrasive rotations by clogging the abrasive wheels. Meanwhile, EB-cured coatings with uniform hardness from inside to surface, performed poorly in abrasion tests.

## The Effect of Types of Prepolymers on the Viscosity of Formulations

Table 2 shows that F8 with 35% Ebecryl 600 (EB 600) was thicker than F5 with 17.5% EB 600 and 17.5% Ebecryl 230 (EB 230). F5 was thicker than F4 with 35% EB 230. F8 with 35% EB 600 was thicker than F4 with the same percentage of EB 230. F6 with 45% EB 600 was also thicker than F3 with the same percentage of EB 230. Viscosity measurements done at 60°C already showed how viscous some formulations were. These results showed that the types of prepolymers used also influenced the viscosity of formulation. EB 600 had higher viscosity than EB 230. As a result, formulations containing EB 600 were more viscous than ones containing EB 230. Higher viscosity always led to difficulties during synthesis, paint application, and cleaning up. This observation could be explained by the understanding of the chemical structures of prepolymers, since they determine the viscoelastic and physical properties of coatings (Figures 10 and 11).



$$H_2C{=}CH-\overset{\overset{\displaystyle O}{\|}}{C}-O\!\left(CH_2\right)_n\!O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-R-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O\!\left(CH_2\right)_n\!O-\overset{\overset{\displaystyle O}{\|}}{C}-CH{=}CH_2$$

with **R** = long polyol segment, **NHCOO** = urethane linkage

**FIGURE 10** The basic structure of aliphatic urethane acrylate prepolymer (Ebecryl 230).

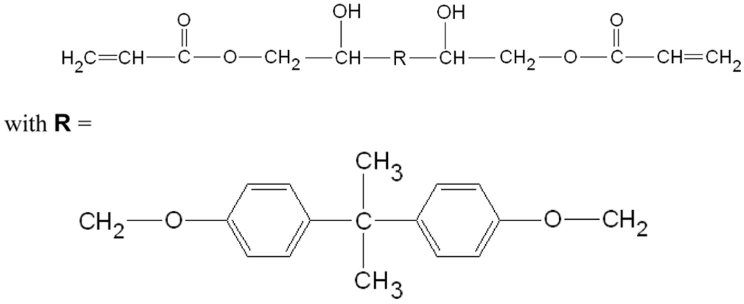


**FIGURE 11** The basic structure of aromatic epoxy acrylate prepolymer (Ebecryl 600).

Although the molecular weight of EB 230 was 10 times higher than EB 600 (5000 versus 500), EB 600 was thicker. The high viscosity of aromatic epoxy acrylates was largely due to the high degree of hydrogen bonding between secondary hydroxyl groups. Hydrogen bonds and aromatic groups play an important role in controlling the viscosity of a prepolymer. Similar observation was reported by Xu and Shi [14]. In EB 600, the combination of aromatic groups and the hydrogen bonding between molecules made the prepolymer highly viscous. In contrast, EB 230 had less viscosity since the long polyol segments and urethane linkages in the backbone were flexible.

## The Effect of Types of Prepolymers on the Pendulum Hardness Values

Figures 12 and 13 show that the hardness of F6 coatings with EB 600 was higher than F3 with EB 230, regardless of the types of radiation used. Figures 14 and 15 show the values of coating hardness in increasing order (F4 < F5 < F8) for both radiation types. From all figures, it was found that coatings with EB 600 were always harder than coatings with EB 230. Again, this was due to the chemical structure of prepolymer itself. After curing, the bulky aromatic groups in EB 600 restrained any deflections from outside forces, so the coatings became very hard. With aromatic epoxy acrylates, very hard but brittle coatings were obtained. Schwalm et al. [15] also reported similar findings. As a result, hard coatings produced higher pendulum hardness results. On the other hand, the long aliphatic polyol segments and urethane linkages in EB 230 were flexible; hence the coatings produced were soft.

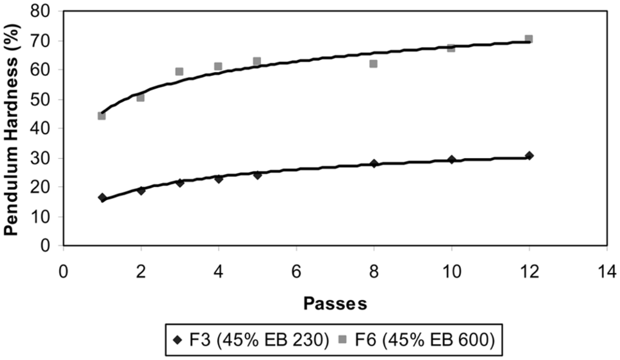


**FIGURE 12** The effect of types of prepolymers on the hardness of F3 and F6 cured by UV radiation.

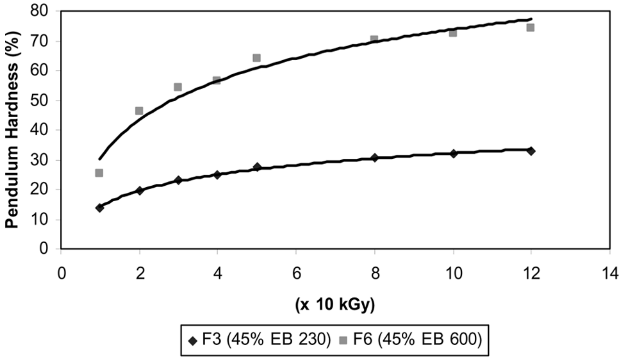


**FIGURE 13** The effect of types of prepolymers on the hardness of F3 and F6 cured by EB radiation.

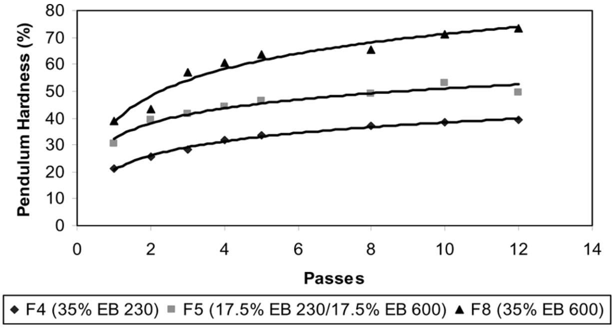


**FIGURE 14** The effect of types of prepolymers on the hardness of F4, F5, and F8 cured by UV radiation.

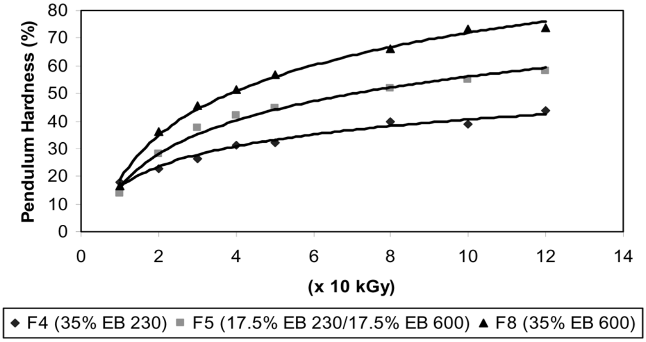


**FIGURE 15** The effect of types of prepolymers on the hardness of F4, F5, and F8 cured by EB radiation.

## The Effect of Types of Prepolymers on Gel Content

Coatings with only EB 230 were found to cure faster than the coatings with EB 600 (Figures 16 and 17). Although EB 230 has a higher molecular weight ($M_n \sim 5000$), the sum of molecular weight is due to long polyol segments. EB 600 has shorter molecular chains with bulky aromatic groups. Based on the same weight, EB 230 has less acrylate double bonds than EB 600. That was why EB 230 cured much faster at the earlier stage, because there were fewer double bonds to be crosslinked. However, as the crosslinking proceeded, coatings with EB 600 had higher gel content. This was because the participation in the cure

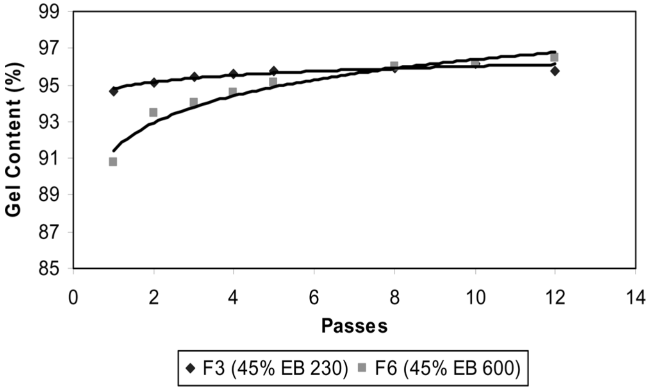


**FIGURE 16** The effect of types of prepolymers on the gel content of F3 and F6.

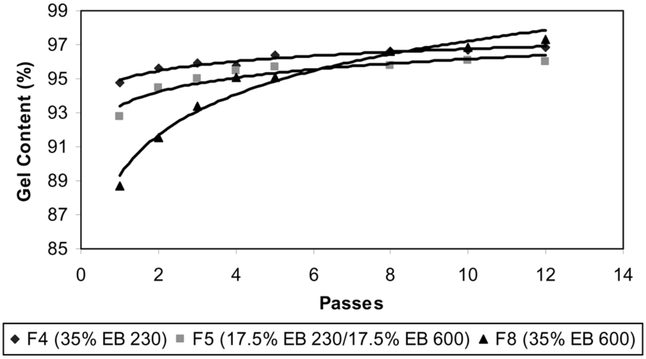


**FIGURE 17** The effect of types of prepolymers on the gel content of F4, F5, and F8.

mechanism by the secondary hydroxyl functionality in EB 600, in agreement with the theory by Webster [10]. However, F5 with half the amount of EB 600 did not follow the same trend as F6 and F8, possibly due to the influence from EB 230.

## The Effect of Types of Prepolymers on Scratch Resistance

Table 3 shows that EB 600 produced coatings that resist scratching. Regardless of the types of the radiation and the scratching tips used, F8 coating gave higher scratch resistance compared to F5 with 1:1 mixture of EB 600 and EB 230. F4 coating with EB 230 had the lowest scratch resistance among the three formulations. F6 showed higher resistance to scratch compared to F3. Although F6 had higher amount of prepolymer compared to F8, F8 coatings had higher scratch resistance. This was because F8 contained 10% nanosilica filler. Inorganic nanosilica was harder than the EB 600.

Coatings with EB 600 showed higher scratch resistance than coatings with EB 230. This was due to the backbone structure of coatings themselves. EB 230 with flexible urethane linkages and polyol segments gave lower resistance to scratching compared to the bulky aromatic rings in EB 600.

## The Effect of Types of Prepolymers on Abrasion Resistance

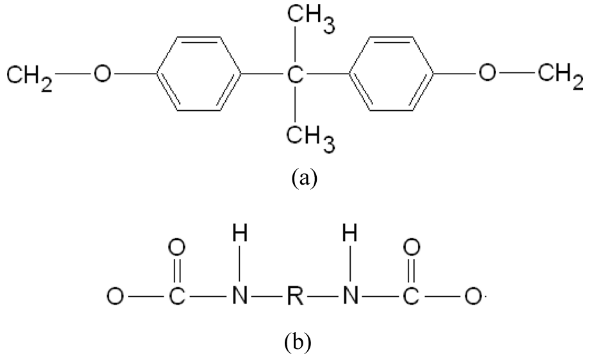
Table 4 shows that coatings containing more EB 600 had better abrasion resistance than coatings containing EB 230. For UV-cured coatings, F6 with EB 600 lost 44.4 mg whereas F3 with EB 230 lost

76.4 mg. F8 coating lost only 19.9 mg compared to F5 and F4, which lost 25.5 and 40.2 mg, respectively. For EB-cured coatings, the trend was similar. F6 with EB 600 lost 44.1 mg whereas F3 with EB 230 lost 111.2 mg. F8 coating lost only 22 mg compared to F5 and F4, which lost 46.8 and 69.8 mg, respectively. Abrasion resistance is a property related to the flexibility and strength of a polymeric backbone. The polymer backbone maintains a linearity of molecular connections and generates materials flexibility, strength, or high viscosity. This is in agreement with the theory by Allcock et al. [16]. EB 600 is an epoxy acrylate resin with aromatic rings in a polymer backbone (Figure 18a) that produces a hard surface when cured. On the other hand, EB 230 is an aliphatic urethane acrylate resin with urethane linkage and long polyol segments (Figure 18b), well-known for their flexibility and softness.

## The Effect of Nanosilica on the Viscosity of Formulations

Table 2 and Figure 19 show that the increase of nanosilica filler content increased the viscosity of formulations, i.e., the thickening effect. High viscosity tends to create problems during handling, application, and cleaning up. The viscosity values were measured at 60°C, except for F1 and F3. Figure 19 shows that above 15% nanosilica content, the viscosity increases drastically. A similar trend was also reported by Zhou et al. [17].

Bauer et al. [18] reported that even after trimethoxysilane grafting on the surface of nanosilica particles, there were still a few hydroxyl



(a)

(b)

with **R** = long polyol segment, **NHCOO** = urethane linkage

**FIGURE 18** The effect of polymer backbone on the abrasion resistance of prepolymers.

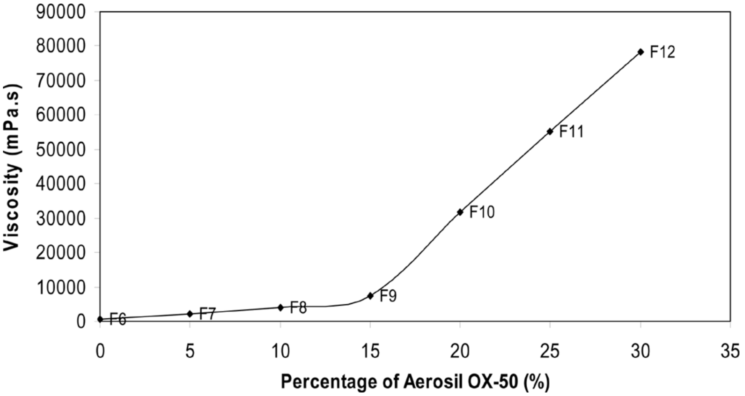


**FIGURE 19** The effect of percentage of nanosilica on the viscosity of formulations (F6–F12).

(–OH) groups remaining. These hydroxyl groups have high potential of forming hydrogen bonds. Hydrogen bonds could be formed between

a. Nanosilica [19].
b. Nanosilica and monomer.
c. Nanosilica and prepolymer [17].

Schematic illustrations of hydrogen bonding in formulations are shown in Figures 20–22. From F6 to F12, prepolymer (EB 600) was continuously replaced by nanosilica, therefore the hydrogen bonding between nanosilica particles became more dominant than hydrogen bonding between nanosilica and monomer/prepolymer.

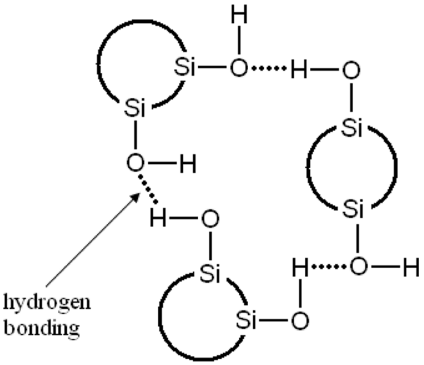


**FIGURE 20** The hydrogen bonding between nanosilica particles.

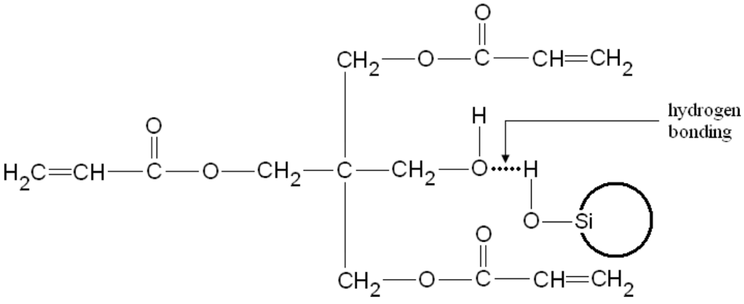


**FIGURE 21** The hydrogen bonding between nanosilica and monomer PETA.

Hydrogen bonding between nanosilica particles restricted the movement of prepolymer molecules, thereby increased the formulation viscosities. The purpose of prepolymer replacement with maximum possible nanosilica was to determine the limit of nanosilica loading for PETIA/EB 600 systems (Figure 19). This was done to cheapen the cost of formulations. Since the F12 (30% nanosilica) was already too viscous and difficult to apply (78 289 mPa · s), half of the amount of the monomer was replaced by TPGDA (F13). It was also difficult to remove air bubbles from F12 due to its high viscosity. For F13 and F14, the temperature during synthesis was reduced from 65°C to 60°C to avoid early polymerization due to longer nanosilica loading time. The amount of stabilizer was also increased by 50%. By changing the monomer, the viscosity of F13 (30% nanosilica) was 4 076 mPa · s and the next 35% of loading (F14) was possible (5 186 mPa · s). This proved that the viscosity of monomer/prepolymer influenced the ease of loading of nanosilica. Lower viscosity formulation facilitated nanosilica loading.

The limit of nanosilica addition achieved in this research was 35%. The same percentage was also reported by Bauer et al. [20]. This was

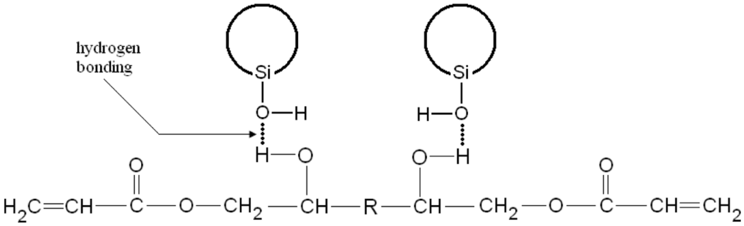


**FIGURE 22** The hydrogen bonding between nanosilica and prepolymer EB 600.

possibly due to nanosilica aggregation within the coatings. TEM study done by Bauer and Mehnert [21] had proven this observation. They had found that at 30% nanosilica loading, the nanosilica particles started to aggregate, although homogeneously distributed. This was attributable to the fact that there were still some hydroxyl groups remaining on the surface of nanosilica particles, which were capable of forming hydrogen bonds. At 40%, the nanosilica loading took longer time to finish and the formulation gelled immediately after synthesis, rendering it useless for coating applications.

## The Effect of Nanosilica on Pendulum Hardness

Overall, the inclusion of silica nanoparticles improved the surface hardness of coatings, exceptions were F6 and F13 (Figures 23 and 24). The effect of prepolymer curing came first before the effect of curing by nanosilica took place. Similar trend was also observed with EB-cured coatings. Since these formulations contained EB 600, it is possible that this is a unique curing characteristic of EB 600.

Work reported by Frings et al. [22] has confirmed that there was a clear increase in hardness with increasing silica content. Outstanding surface hardness of composite materials can only be achieved with the aid of rigid filler materials coupled with a high crosslinking density of the polymer. According to Mohs's scale of hardness, silica (quartz) can be recommended having hardness scale of 7. To put that into perspective, diamond, the hardest material known to man, tops the scale at hardness scale of 10. As an inorganic filler, nanosilica imparted

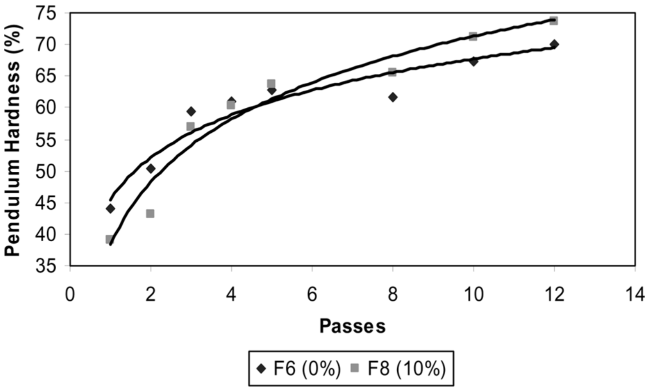


**FIGURE 23** The effect of nanosilica on pendulum hardness of UV-cured F6 and F8.

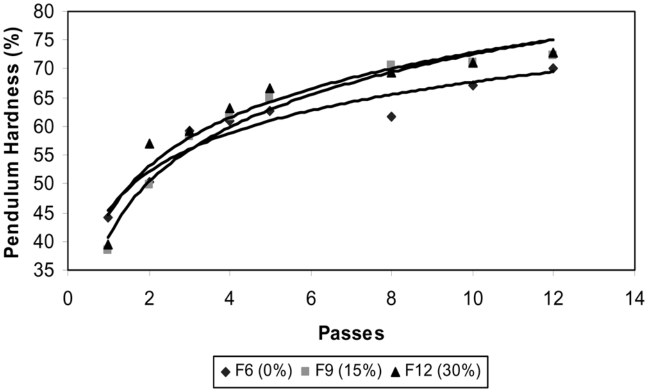


**FIGURE 24** The effect of nanosilica on pendulum hardness of UV-cured F6, F9, and F12.

hardness to the organic resin since coatings needed some degree of hardness to function properly.

## The Effect of Nanosilica on Gel Content

Figures 25–27 show that the coatings with higher nanosilica content had higher gel content. Exceptions were Figures 28 and 29. In these two figures, F6 without nanosilica cured much earlier and had higher gel content than F8 and F9. This was because F6 had more prepolymer than both F8 and F9. However, at a latter stage, the gel content of F8 and F9 were much higher than F6. This was where

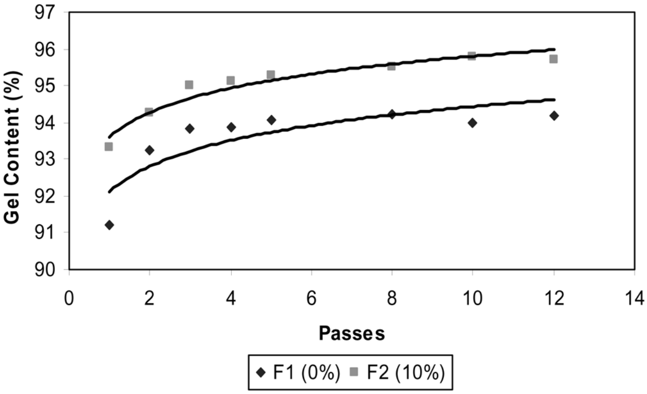


**FIGURE 25** The effect of nanosilica on the gel content of F1 and F2.

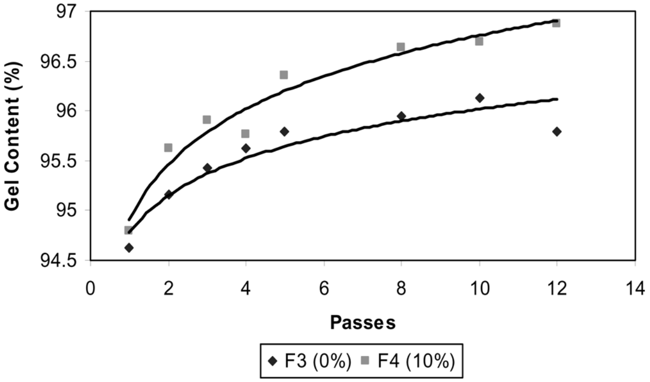


**FIGURE 26** The effect of nanosilica on the gel content of F3 and F4.

nanosilica played a role in accelerating the cure rate and reaction. This finding supports previous discussions about the effect of nanosilica on pendulum hardness. Once again, this trend was observed with all coatings containing Ebecryl 600.

Gel content measurement provided an insight into the actual cure state of a coating compared to pendulum hardness. Nanosilica increased the gel content of a coating by three ways

a. accelerated the cure reaction and cure rate of the UV-curable acrylate system [23]
b. restricted the segmental motion of the polymeric chains and increased the crosslinking density [24]

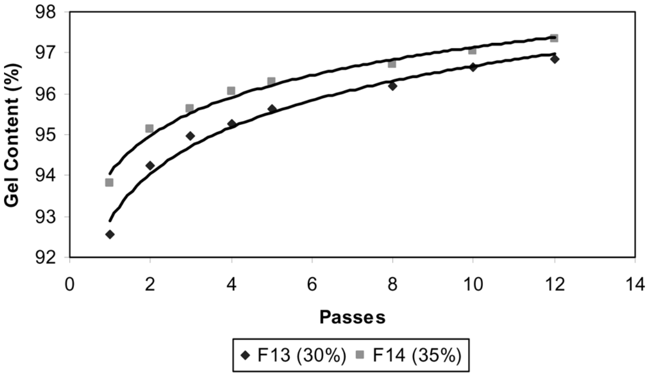


**FIGURE 27** The effect of nanosilica on the gel content of F13 and F14.

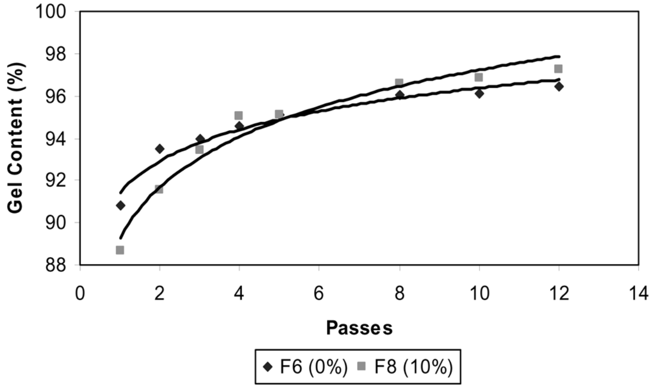


**FIGURE 28** The effect of nanosilica on the gel content of F6 and F8.

c. nanosilica itself added to the percentage of insoluble solids in the coatings.

When more nanosilica was loaded, the hydrogen bonding became dominant and increase in viscosity was observed. This means that the segmental motion of the polymeric chains also became restricted. When radiated, these restricted chains were easily crosslinked and contributed to higher gel content. After irradiation, the nanosilica was trapped inside the coatings. From the gel content measurement, it was confirmed that the nanosilica particles were completely embedded inside the matrix, since no silica precipitation was found in the acetone after the extraction.

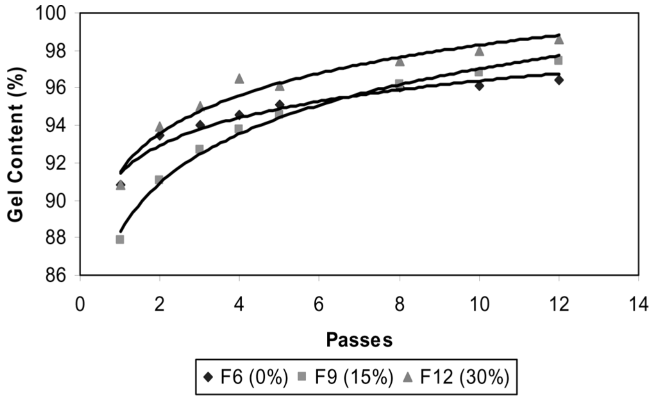


**FIGURE 29** The effect of nanosilica on the gel content of F6, F9, and F12.

## The Effect of Nanosilica on Scratch Resistance

Coatings cured by EB and scratched by diamond tip (Table 3) are used to discuss the effect of nanosilica. Both F2 and F4 with 10% nanosilica gave higher scratch resistance compared to both F1 and F3 without nanosilica. For F6 to F12, the effect of nanosilica increment from 0 to 30% was obvious. The scratch resistance was found to increase with every addition of 5% nanosilica. F12 showed the highest resistant to scratch with 4.5 Newton. Meanwhile, F14 with 35% nanosilica also had higher scratch resistance compared to F13 with 30% of similar filler loading. Discussion is based on EB-cured coatings because curing by EB removed the effect of photoinitiators. Since the coatings were very hard, it was difficult to study scratch resistance by using the stainless steel ball tip alone. The diamond tip was used because it produced more reliable results.

From the results, it was found that increasing the content of nanosilica improved the scratch resistance of coatings, similar to reports by Zhou et al. [25]. Works by Bajpai et al. [26] also found that scratch hardness of samples with a higher percentage of silicon compound was higher. Works by Sangermano et al. [6] showed that the hardness increase was due to the increase of modulus as well as the presence of the hard silica nanoparticles. Surface hardness is related to an increase in scratch resistance. Amerio et al. [24] claimed that the increase in hardness for the hybrid systems could be attributed to the increase in modulus and to the presence of hard silica domains, which tended to segregate towards the film surface. Messori et al. [27] had already proven this phenomenon by photoelectron spectroscopy (XPS) study. They stated that the silica segregated onto the outer surface, making the very surface of the coating almost completely inorganic. All these evidence proved that nanosilica increased the scratch resistances of surface coatings by migrating towards the surface of the film, as indicated by the observation that resistance to scratching tips increased during testing.

## The Effect of Nanosilica on Abrasion Resistance

Table 4 shows that the increase of nanosilica filler content increased the abrasion resistance of coatings. Again, in Table 4, the sequence of addition of 5% nanosilica from F6 (0%) to F12 (30%) could be observed. From this, it is clear that the increase of percentage of nanosilica increased the coatings abrasion resistance. A similar trend was also reported by Tauber et al. [3]. F12 coating cured by UV light showed the highest resistance to abrasion, which only lost 6.7 mg after 50 abrasive cycles (rotations).

From the results, when nanosilica was included as a filler, the coating hardness was also increased. Hard coatings resisted abrasive forces better. The weight loss gradually decreased as nanosilica content increased, indicating that nanosilica improved the abrasion resistance of the coating film. These findings are in agreement with the work by Zhou et al. [25]. Work by Chen et al. [28] also supported the mentioned findings. They found that introducing nanosilica into the polymer dramatically enhanced the abrasion resistance of polymer films no matter which preparation method was used. The higher the nanosilica content, the better the abrasion resistance.

## CONCLUSION

Monomer PETIA, prepolymer Ebecryl 600, and higher nanosilica content led to higher formulation viscosity, pendulum hardness, gel content, scratch, and abrasion resistance of surface coatings. F12 was selected as the optimum formulation because it has the highest scratch and abrasion resistance. Another factor which was considered is the viscosity. Further increase of nanosilica content would make it impractical in terms of processing. F12 contained 15% Ebecryl 600 (epoxy acrylate) resin with 30% monomer PETIA and 30% nanosilica content.

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