

UV/EB Curing of Nanocomposites for Enhancing the Functionality and Utility in Coatings Industry

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Abstract--Composite materials combine properties of the individual components in a synergetic manner to produce a variety of materials in an efficient and cost effective manner. Thus, composite materials are being used in various applications from automotive to furniture industries. Materials reinforced with nanoscale components are adding new dimensions to composite materials and enable further major improvements in functional and structural properties. The incorporation of only a few percent of nano-sized particles can make dramatic property changes that may result in enhancing physical and mechanical properties of the resulting composite. Several major issues need to be addressed to utilize the full potential of such nanofillers i.e. incompatibility or weak interfacial bonding between the matrix and the nanoscale component, and agglomeration of nanosized component during processing resulting in inhomogeneous distribution. UV/EB technology offers a way of overcoming these challenges by grafting of monomers/polymers including natural polymer onto the nanofiller surface thereby fixing their morphology and at the same time making them compatible with the host polymer.

I. INTRODUCTION

Recently, there has been a strong and increasing demand for scratch and abrasion resistance composite materials that can be applied to various substrates such as plastic and wood products. For example, plastics have been widely used as motor vehicle parts, optical lenses etc. due to their characteristic features such as lightness, toughness, easy processing and low production costs. However, they are vulnerable to scratch and abrasion resistance. Another application is in the furniture and panels industry where the industry needs high scratch and abrasion resistant coating materials especially for table top and parquets.

Over 90% of all wooden furniture made in Malaysia is exported and paint companies involved in this lucrative export market must adapt to changes in global trade patterns and technology trends to survive. The wood coatings industry is attracting a lot of interest in Asia lately due to its high growth potential. In Malaysia, with a market size of over US\$60m, this is an important segment in overall coatings market. Coatings suppliers have to comply with international standards to be competitive in this market. The wood coatings market in Malaysia comprises mainly of nitrocellulose based coatings, acid cured coatings and polyurethane coatings. UV/EB curing and waterborne wood coatings are also present but have a relatively small share. In general, solvent-based wood coatings (which include acid-cured) are likely to lose share to waterborne and UV/EB curing coatings worldwide as the latter are more

environmental friendly. The stringent regulations against volatile organic compound (VOC) in developed regions like Europe are forcing the industry to move towards use of environmental friendly coatings in furniture exported from Malaysia. In Malaysia, there are about 750 furniture suppliers and over 15 wood coatings suppliers. In order to meet the expectations of their customer base, maintain their market share and conform to environmental legislation, the manufacturers need access to a low solvent-based solution. Therefore, there is a need for research and development work in this area to replace the conventional solvent technology. The instant cure of the coating materials by UV/EB and the ease with which the technology fits into highly automated production processes is seen as a great commercial advantage¹.

At present, coating materials without reinforced filler (nanoparticles) are used to provide a highly glossy and luxurious finish to specific products. In this research work, the incorporation of nanoparticles into coating materials is aimed at improving scratch and abrasion resistant properties while retaining transparency and glossiness. Mineral charges such as silica and alumina nanoparticles can be introduced into UV/EB curable resins to get hard and abrasion resistant materials, which can be used as clear coatings and fiber reinforced plastics^{2,4}. From the structural point of view, the role of inorganic filler, usually as particles or fibers, is to provide intrinsic strength and stiffness while the polymer matrix can adhere to and bind the inorganic component so that forces applied to the composite are transmitted evenly to the filler. UV/EB curable nanoparticles can be prepared and synthesized by heterogeneous hydrolytic condensation technique using acrylated oligomers such as epoxy acrylates and urethane acrylates including palm oil polyols (natural polymers) with the incorporation of nanoparticles.

In conventional composite materials, filler and the polymer are combined on micronic scale, which often leads to insufficient adhesion between the organic matrix and the reinforcing filler. Composite materials that exhibit a change in structure and composition over nanometer length scale (< 100nm) have been proven in imparting remarkable property enhancement with respect to stiffness and strength, heat resistance and gas barrier properties⁵. Several major issues need to be addressed to utilize the full potential of such nanofillers can be realized, among them, (i) weak interfacial bonding between the matrix and the nanoscale component, and (ii) agglomeration of nanosized component during processing resulting in inhomogeneous distribution.

The proposed radiation curing technique by free radical polymerization using UV light or electron beam as the source of radiation is the most suitable process and it offers several advantages including curing process can be done at ambient temperature. Other benefits of this technique^{6,10} are (i) a solvent free-formulation, with essentially no emission of volatile organic compounds to the environment and user friendly i.e. green technology; (ii) an ultra-fast curing by free radical polymerization reaction and using the highly reactive acrylate based resins; (iii) operations at ambient temperature particularly suitable for heat sensitive substrates such as plastic and wood based products; and (iv) improved productivity and increased product performance.

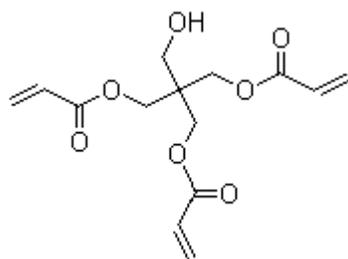
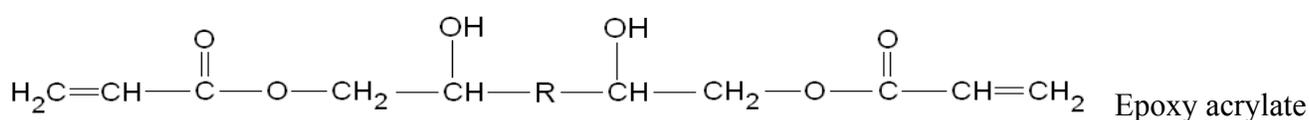
II. EXPERIMENTAL

All chemicals were used as received. The prepolymer such as epoxy acrylate (EB600) was obtained from Cytec Specialty Chemicals, Belgium. Monomer such as acrylated pentaerythritol with 3–4 functional group (PETIA) was also obtained from the same manufacturer as above. The chemical structures of the compounds used in this study are shown in Figure 1.

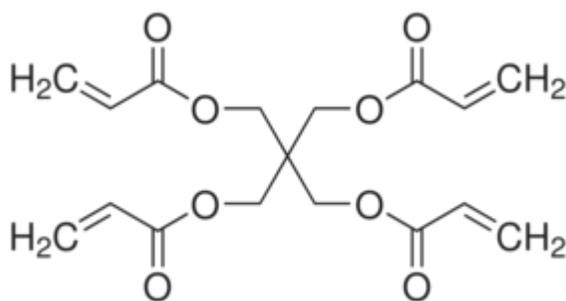
4-hydroxyanisole or 4-methoxyphenol was of gas chromatography (GC) grade quality and used as a stabilizer. Meanwhile, maleic anhydride was of analar grade quality and used as a catalyst in the heterogeneous condensation reaction. Both chemicals were obtained from Sigma-Aldrich Chemical Company Limited, UK.

All the nanoparticles of silicium dioxide such as AEROSIL OX50 used in this work were obtained from Degussa-Hüls AG, Germany. They were normally used as fillers for polymer reinforcement and scratch resistant coatings. Meanwhile, the silane such as VT MOS was obtained from the same manufacturer and used as coupling agent.

Finally, most of the photoinitiators such as DC1173 and IC500 used in the ultraviolet (UV) curing were obtained from Ciba Specialty Chemicals, Switzerland.



Pentaerythritol triacrylate



Pentaerythritol tetraacrylate

Figure 1 Chemical structures of the compounds used in this study

A. Preparation of Silico-Organic Nanoparticles

Siloxane methacrylate nanoparticles from the silica/acrylate systems were synthesized in a small batch reactor. Maleic anhydride, dissolved in water, was introduced in a mixture of several acrylates and 4-methoxyphenol. The coupling agent such as VT MOS was added within 30 minutes. Finally, nano-sized silica particles were dispersed under intensive stirring during 1–2 hours using a Dispermat dissolver.

The process for preparing these nanoparticles is proton catalyzed and efficiently proceeds at 60–65°C. Thereafter, the product was immediately cooled to room temperature.

Table 1 Percentage of materials in the formulations

Formulation	Materials (%)			
	PETIA	VTMOS	SiO ₂	EB600
Lack 1	30	25	–	45
Lack 2	30	25	5	40
Lack 3	30	25	10	35
Lack 4	30	25	15	30
Lack 5	30	25	20	25
Lack 6	30	25	25	20
Lack 7	30	25	30	15

B. Preparation of Polymeric Nanocomposites by UV/EB Curing

The polymeric nanocomposite materials were prepared basically from several acrylates and AEROSIL OX50 as shown in Table 1. These materials were coated on different types of substrates such as lamination paper, polyvinyl chloride (PVC) and glass panel using automatic film applicator. They were cured using a low energy electron beam (EB) accelerator and UV irradiator. Furthermore, in spite of relatively high nanopowder content in the nanodispersions, UV induced polymerization with the aid of conventional mercury lamps proved to be an efficient alternative to EB curing. During irradiation, the chambers were degassed by inert gas such as nitrogen. Films of these UV/EB cured nanocomposites were characterized by several methods such as scratch test and Taber abrasion test.

III. RESULTS AND DISCUSSION

Silico-organic nanoparticles have relatively large surface areas than microparticles, therefore modification effects from the polymerization activity should have a great influence to the properties of the composites. In these investigations, we use radiation such as ultraviolet and electron beam to initiate polymerization and interaction at the interface between the nanoparticles and the monomeric materials. These polymerization active nanoparticles were obtained by heterogeneous hydrolytic condensation of the silane to the silanol groups of the AEROSIL particles.

The above reaction could be verified by the application of FT-Raman spectroscopy (intensity measurements of the C=C vibration band at 1640 cm⁻¹) and gel permeation chromatography to show that the polymerization activity of the nanoparticles imparts to the silico/acrylate dispersion¹¹. In the curing

process, the nanoparticles form cross-linkages to produce radiation cured polymeric composites with improved scratch and abrasion resistance.

After soxhlet extraction, all the coated materials show very high gel content (see Table 2). These coating materials also show high pendulum hardness property as shown in Table 3. In Table 4, the weight loss of the UV/EB cured materials significantly reduced when the amount of silica particles increases i.e. up to 30% of SiO₂. These nanoparticles improve the abrasion property of the coating materials.

Table 2 Gel content UV cured materials

Formulation	Gel Content (%)
Lack 1	96.4
Lack 2	96.7
Lack 3	97.3
Lack 4	97.5
Lack 5	98.3
Lack 6	98.4
Lack 7	98.6

Table 3 Pendulum hardness of UV/EB cured materials

Formulation	Pendulum Hardness (%)	
	UV	EB
Lack 1	70.1	74.0
Lack 2	74.0	80.3
Lack 3	73.6	73.7
Lack 4	72.3	76.0
Lack 5	73.7	73.1
Lack 6	74.0	65.3
Lack 7	72.9	65.1

Table 4 Abrasion resistant of UV/EB cured materials

Formulations	Weight Loss (mg)	
	UV	EB
Lack 1	44.4	44.1
Lack 2	28.2	30.0
Lack 3	19.9	22.0
Lack 4	14.2	15.9
Lack 5	12.0	13.2
Lack 6	9.4	10.9
Lack 7	6.7	8.5

Finally, the performance of these composites is also related to other factor such as resistance to scratch. Two types of needles were used for determining the resistance of a single coat system of the composites to penetration by scratching i.e. using diamond tip and steel ball (spherically tipped needle). The method used was by applying increasing loads to the needle to determine the minimum load at which the coating was penetrated. The nanoparticles added into the coating materials improve the scratch property of the composite materials as shown in Table 5 whereas in Table 6, most of the composites exhibit excellent resistance to scratch property including Lack 1.

Table 5 Scratch resistant of UV/EB cured materials using diamond tip with 90°

Formulations	Resistant to scratch (N)	
	UV	EB
Lack 1	0.7	0.9
Lack 2	0.8	1.0
Lack 3	1.0	1.5
Lack 4	1.5	2.5
Lack 5	2.0	3.5
Lack 6	2.5	4.0
Lack 7	2.5	4.5

Table 6 Scratch resistant of UV/EB cured materials using steel ball tip with diameter 1 mm

Formulations	Resistant to scratch (N)	
	UV	EB
Lack 1	>10	9
Lack 2	>10	>10
Lack 3	>10	>10
Lack 4	>10	>10
Lack 5	>10	>10
Lack 6	>10	>10
Lack 7	>10	>10

IV. CONCLUSIONS

Polymerization active silico-organic nanoparticles could be prepared by heterogeneous condensation (in situ reaction) and formed crosslinking in the polymeric substrates. With a relatively high nanopowder content of the nanodispersions, these coating materials could still be cured by UV light and electron beam (EB) to produce excellent polymeric composites. These coating materials show better resistances toward scratch and abrasion properties compared to pure acrylates.

ACKNOWLEDGMENT

The author would like to thank the Ministry of Science, Technology and Innovation (MOSTI) and the Malaysian Nuclear Agency for funding the project.

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