The Effects of Photoinitiator Addition to the Mechanical and Physical Properties of the Epoxy and Vinyl Ester Fiber Glass Laminated Composites

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ABSTRACT

Ultra-violet (UV) curing process is introduced in the curing of polymer matrix composites (PMC) for the application in producing bullet proof vest. Two types of matrix materials were used: epoxy and vinyl ester. Each of them were mixed with different types of photoinitiator; Bisacyl Phosphine Oxide (BaPO) and Alpha Hydroxyl Ketone Peroxide (AHK) at 1.0 and 10.0 per hundred of resin (phr) from the total proportion of the mixture. Sandwich construction of composite was done by hand lay-up process where the mixture was wiped on the fiber layers. The laminate was then tested to determine its characteristics of physical properties and its behavior to applied loads. Morphological observation through Scanning Electron Microscope (SEM) was performed in order to evaluate the quality of adhesion between each fiber layer and matrix wetting behavior. Vinyl ester is not recommended to be used as the matrix since two days is required to make it fully cured unlike epoxy which was rapidly cured once exposed under the UV light. The physical testing shows that optimum density for the effect of photoinitiator obtained at 1.0phr for epoxy and 10.0phr for vinyl ester. This could give benefit to the manufacturer since it gives lower weight compared to virgin matrix materials. The effect of photoinitiator to the tensile strength shows optimum results at 1.0 phr for both epoxy and vinyl ester. On the other hands, effect of photoinitiator to the hardness of the composite is found optimum at the present of 1.0 phr for both matrix materials.

Keywords*:* UV Curing; Photoinitiator; Polymer; Composite; Mechanical; Physical; Morphological

INTRODUCTION

Ultraviolet (UV) curing is known to be a hardening process of liquid material when it is exposed to UV radiation. The curing process of polymeric material by using UV light has played an important role in the processing of polymer material, since the process is more advantageous than heat cure. Although curing by this technique is relatively slow compared to heat curing, the result is high strength and high impact properties of Polymer Matrix Composites (PMC) due to crystallinity enhancement of the polymers through cross-linking mechanism. One of the applications of the curing process of polymeric material by ultraviolet light can be seen in producing personal protective equipment (PPE) for instance bullet proof vest. This research is conducted as the preliminary stage in producing the bullet proof vest where the PMC will be used to wrap an alumina plate in order to act as holder when high ballistic impact hit the bullet proof vest. This will avoid alumina plate break into pieces once bullet is triggered to hit them.

The objective of this research is to develop an outside part of bullet proof vest and to assess the ability of the UV light in converting the thermosetting material to become harden or cure under UV exposure with the assistance of photoinitiator addition. Furthermore, it is also to study the parameter involve in the UV curing process of polymeric materials and their effects to the properties of the resulted products. This study has its own importance and benefits, which are to provide the fundamental understanding on the effects of UV curing to the physical and mechanical properties for the application of bullet proof vest manufacturing technique. The output of the cured PMC will then be studied and analyzed.

Although a particular substance to be processed may vary widely depending upon its application and the final use, they are basically composed of polymer. UV curing, a conversion process of polymeric materials from a liquid to solid by UV light is a popular alternative instead of conventional drying. The number and variety of applications for UV curable inks, coatings, and adhesives, continue to expand at a rapid pace and pose new design challenges to increase cure efficiency, speed, and the physical properties of the cured polymer film. UV curing is highly adaptable to painting and coating, decorating, and assembling of a great variety of products owing to some of its key attributes. It is a low temperature process where heat is not required and a high speed process cure is nearly instantaneous. In addition, it is energy efficient processes whereby energy is invested only in the curing reaction, not in heating (Stowe, 2002). UV curing adhesive also have two components. One part is the adhesive resin itself and the second part already mixed in is called a photoinitiator. The secret of the photoinitiator is that, it will not react with the resin by itself.

The photoinitiator must absorb UV light before anything can happen. When the UV light is delivered, the photoinitiator will undergo a chemical reaction and produce products that cause the adhesive to harden better. One type of photoinitiator used in this study is BAPO with Irgacure 819 as its trade name. BAPO is a versatile photoinitiator for radical photo polymerization of unsaturated resins upon exposure to UV light. It has demonstrated useful application in white pigmented formulations, the curing of glass fiber reinforced polyester/styrene systems and for clearcoats for outdoor use with light stabilizers. The outstanding absorption properties of BAPO also allow curing of thick sections (Augustine, 2004). On the other hands, AHK is the second photoinitiator that used in this research with the trade name of Irgacure 184. This is highly efficient non yellowing photoinitiator, which is used to initiate the photopolymerisation of chemically unsaturated prepolymers in combination with mono or multifunctional vinyl monomers (Augustine, 2004).

METHODOLOGY

Raw Materials & Sample Preparation

Polymeric resins are the main raw material that was mixed together with photoinitiator. Both epoxy and vinyl ester was act as binder in the mixture. It has been bought from Wee Tee Tong Chemicals Pte. Ltd, Singapore. Meanwhile, photoinitiator material has been sponsored by Ciba Specialty Chemicals, Singapore. The photoinitiator was added to the matrix materials in the amount of part per hundred of resin (phr), with ratio of 1:3. There are three types of samples that involved in this research. Sample A is a reference sample produced without photoinitiator while sample B and C is the samples added with photoinitiator material in certain ratio. Details on sample formulation are described in the following Table 1. Each sample A, B and C was mixed together and stirred to obtain homogenous solution. The total weight of resin is 120 gram. The composition ratio of BAPO to AHK is 1:3. At the first stage of sweeping process, a layer of woven roving was placed on a flat surface. Once mixture of resin and photoinitiator is homogenized, it was swept over the top of the glass using brush. After that, another layer was put on the first glass laminate and the same procedure was repeated until a laminate of l0 layers are produced. After the 10 layers of woven roving stick together, the laminate was then undergoing vacuum bagging process where it was put in a vacuum chamber.

By performing this step, the adhesion between the layers was improved and the entrapped air was expelled. After the vacuum bagging stage, the glass laminate was exposed to UV light. Once the process completed, sample was taken out and ready for testing and analysis procedure. The exposure time under UV light for all samples A, B and C is 6 minutes.

Table 1: Details on sample formulation

Samples	Details for each sample
A	1. *Woven roving + Vinyl ester* 2. *Woven roving + Epoxy*
B	1. *Woven roving + Vinyl ester + BAPO + AHK ; (BAPO + AHK = 1.0 phr)* 2. *Woven roving + Epoxy + BAPO + AHK ; (BAPO + AHK = 1.0 phr)*
C	1. *Woven roving + Vinyl ester + BAPO + AHK ; (BAPO + AHK = 10.0 phr)* 2. *Woven roving + Epoxy + BAPO + AHK ; (BAPO + AHK = 10.0 phr)*

SAMPLE TESTING

Density test

Density test was carried out in order to study the physical properties of UV cured laminate composites produced with parameter that has been varied for instance type of adhesive used to develop laminates construction between each layer of glass as well as the amount of photoinitiator added in the adhesive resin. This test was conducted by applying the Archimedes principle.

Tensile test

Tensile test was carried out in accordance to ASTM D 3039 standards. The test was carried out at a crosshead speed of 2 mm per minute. Specimens for the tensile test were produced by cutting out laminate strips measuring 200 mm x 25 mm. The specimens were cut 3 mm oversize and final dimensions obtained by grinding and using sand paper to produce smoother end surface. Aluminum end tabs of 3.2 mm thick and measuring 50 mm x 25 mm was locally bonded onto the both ends of each laminate. A total of 6 specimen strips were cut from each of the composite laminates produced. For this testing, three series of sample were produced which are series A, B and C with 6 minutes of exposure time under UV lights exposure.

The purpose of this testing is to study the effects between the absence and presence of photoinitiator in the resin and to study the effects of the PMC by increasing the amount of photoinitiator in the mixture. The following Figure 1 shows the samples for tensile testing.

Figure 1: Specimen for tensile test ASTM D 3039

Hardness test

Hardness test was performed to the samples in order to investigate the surface penetration resistance of the glass laminates that has been cured under UV light exposure. The hardness test was conducted in the Brinell hardness test mode with diameter of indenter is 10 mm and 100 N of loads.

Morphological Observation by Scanning Electron Microscope (SEM)

The purpose of this observation is to determine if proper adhesion and fiber pull-out phenomena occurred in each of the laminates. SEM used for this observation is the variable pressure scanning electron microscope.

RESULTS AND DISCUSSION

Physical Testing of Density Behavior

The purpose of the density test is to observe the effect on the physical properties of UV cured laminate composites produced by different type of resin, to study the variation in density between the presences of photoinitiator with virgin PMC and effect on the increasing amount of photoinitiator in the polymeric resin. Generally, the density of the vinyl ester used is 1.35 g/cm^3 while for the epoxy; the density is 1.50 g/cm^3. Figure 2 shows the plotted data of density versus sample at different amount of photoinitiator addition. Samples using epoxy as an adhesive have greater density as compared to samples using vinyl ester. This result is in accordance with the density data of both virgin resins where epoxy's density has greater value than vinyl ester. The plot also indicates that the resulted density of the laminate composite is not affected by the presence of photoinitiator.

It might be due to the little amount of photoinitiator weight used. In this case, photoinitiator exists in the resin as an additive material. It acts as the catalyst to initiate the process of curing, thus, resulting in a monotonic change of density for each sample that not far varied compared to the sample produced without photoinitiator. It tells that, the presence of photoinitiator materials in the mixture is not affecting the value of density of the produced sample.

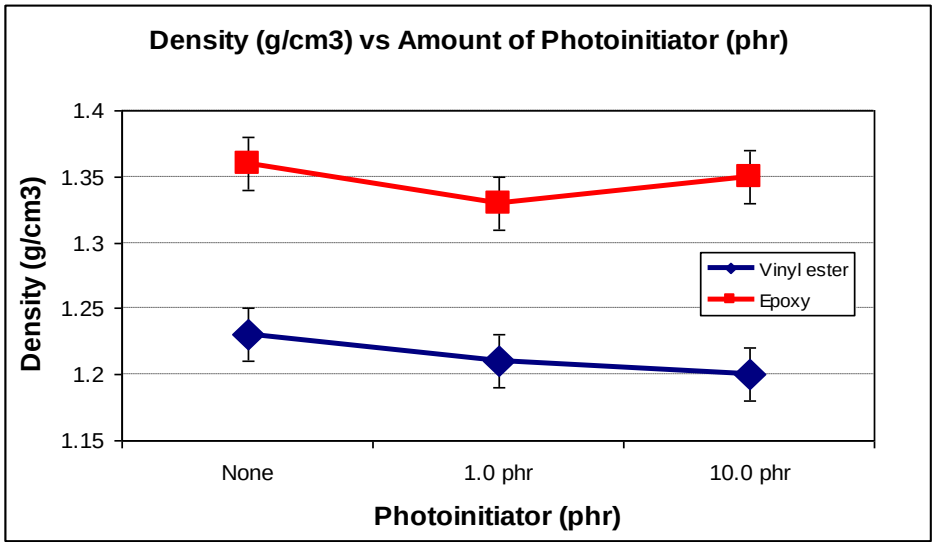


Figure 2: Density at different amount of photoinitiator addition

Tensile Strength of Laminates Composites

Figure 3 shows the plotted data for tensile strength versus samples at different amount of photoinitiator. From the graph, the tensile strength for the sample wiped with epoxy have greater values compared to sample that used vinyl ester as their adhesive material. The graph indicates that, for the series using vinyl ester resin and epoxy as adhesive, the tensile strength was optimum at 1.0 phr of photoinitiator addition. Proper adhesions between the glass fiber woven roving and the polymeric resin are achieved at this point and lead to higher value of tensile strength. Good adhesion between both phases indicates lower voids presence in the fabricated composites. However, with the presence of 10.0 phr of photoinitiator in the resin, the tensile strength was decreased significantly for both sample produced by epoxy or vinyl-ester. This indicates that, the presence of photoinitiator in higher amount will not contribute to increase the tensile strength behavior of the fabricated composites. The function of photoinitiator in the resin is to act as energy absorber to initiate the process of curing. This implies that, the presence of photoinitiator in the mixture cannot be in large amount since it is just an accelerator to initiate the curing process. This is because chain of resin that bonds the fibers together becomes weaker as the amount of photoinitiator increases to a huge amount. This is the reason why photoinitiator is added as an additive material in the mixture at a little amount. The reduction of mechanical properties might due to the part warpage caused by over-curing introduced by larger amount of photoinitiator addition (Gutowski, 1997).

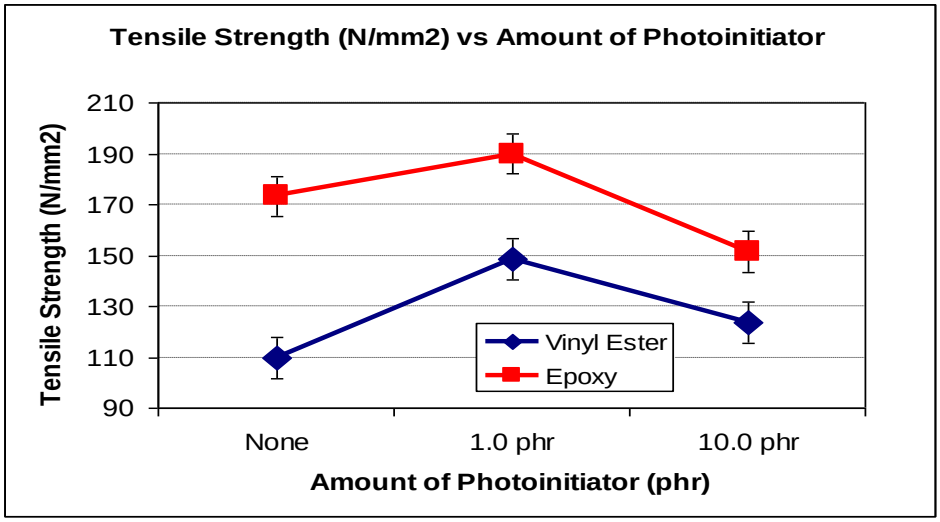


Figure 3: Tensile strength of samples at different amount of photoinitiator

Hardness Test Evaluation

Figure 4 shows the plotted data of hardness versus samples that were produced in different amount of photoinitiator addition. The graph consists of two series of samples. Series 1 is the sample that uses vinyl ester as adhesive while series 2 is the sample that uses epoxy as adhesive material and all were cured at 6 minutes under the UV light exposure. Based on the graph, for vinyl ester sample A1 which produced without photoinitiator, the hardness is lower compared to the sample that was added with photoinitiator material, which is sample C1. For series that used epoxy as adhesive resin, the hardness between sample with and without photoinitiator shows a decrement in its value. The hardness for sample A2 is much higher compared to the sample C2. This is because; the distribution of adhesive resin during the wiping process was not even from one part to another. This again contributes to the variation of hardness value for the two samples with and without photoinitiator materials. Thus, from the result, it can be concluded that the value of hardness is not affected by the presence of photoinitiator addition.

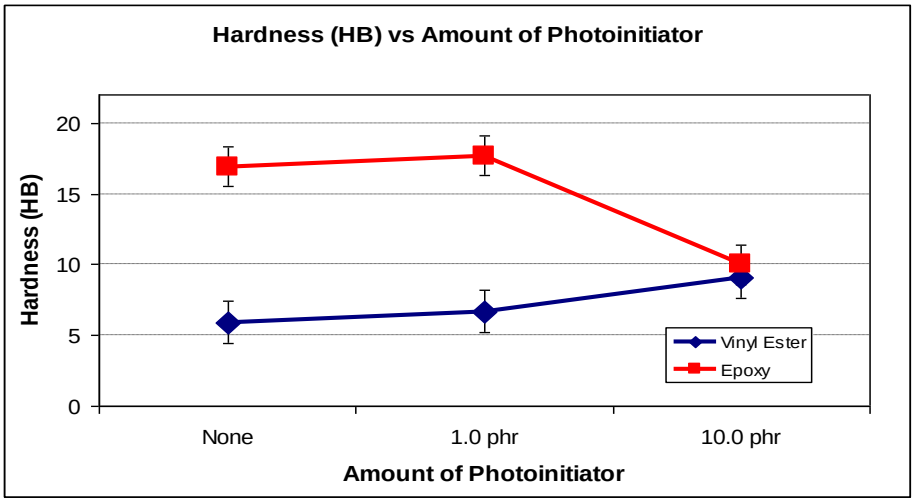


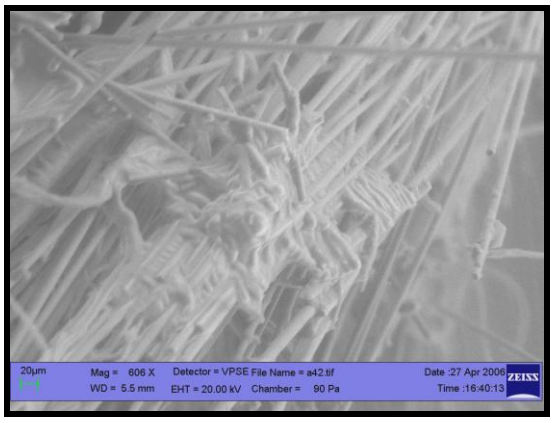
Figure 4: Hardness of Samples at Different Amount of Photoinitiator.

Based on Figure 4, the plotted graph indicates that vinyl ester have lower value in term of hardness as compared to laminate composite that used epoxy as adhesive. For sample A1, the hardness data obtained is the lowest where no photoinitiator was added to the resin. For sample B1 where 1.0 phr photoinitiator was added to the resin, the graph shows an increment. The value elevated from 5.9HB to 6.7HB. This shows that hardness of material increases with the presence of photoinitiator. Perhaps, the fibers inside the laminate were bonded tightly with the presence of photoinitiator. For sample C1, where photoinitiator was added with 10.0 phr, the hardness was increased. This might be due to the effectiveness of photoinitiator to act as energy absorber to initiate the process of curing and produces harder laminate.

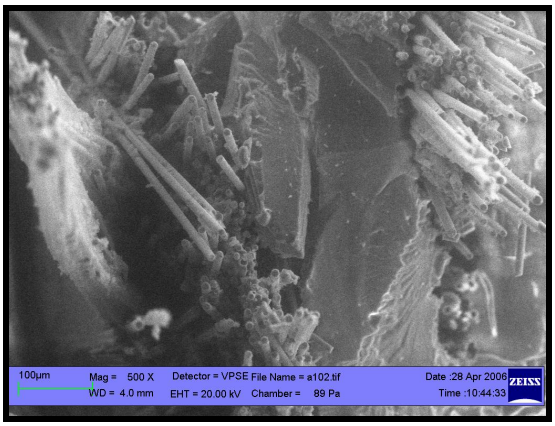
For series that using epoxy as adhesive resin, the hardness of laminate is greater as compared to laminate that used vinyl ester as adhesive. For 6 minutes of curing without photoinitiator addition, the data obtained is 16.9HB. For sample B2, with 6 minutes of curing time and the adhesive added with 1.0 phr photoinitiator, the hardness of laminate composite was increased to 17.7HB. This shows that, the presence of photoinitiator helps the composite laminate to become harder, hence, to have better properties. After 10.0 phr photoinitiator added to the resin, sample C2 shows a drastic decrement in its value. Addition of 10.0 phr of photoinitiator in the epoxy is large enough to act as accelerator where at one point it reaches yield point and out of the real function as photoinitiator.

Morphology Analysis

In addition to the physical and mechanical properties, morphological observation through the Scanning Electron Microscope (SEM) was also carried out on both of UV cured laminates that used vinyl ester and epoxy as adhesive material. The micrographs of the selected UV cured laminate are shown in the Figure 5 and it was taken at the point of tensile fracture. It clearly shows that the fiber strands have very little resin impregnated along their length. This could probably be indicative of improper adhesion between the fiber and the matrix during the curing time. The surface of fiber is covered by the matrix in an uneven condition. In addition, the existing of void can also be seen. The presence of voids affects the result especially to the mechanical properties of the UV cured laminate. However, at the point of fracture, the fiber strands appear to pull out cleanly with little evidence of resin impregnated along their length. No fiber wet out found in the fracture surface of the sample when observation was conducted. All samples have good well dried adhesives indicate that the matrix solution was cured enough before testing is conducted.



Sample B1



Sample C2

Figure 5: Micrograph of selected sample of UV cured laminates composites

CONCLUSION

In this research, several observations like mechanical and physical properties have been done to the UV cured laminated composites with respect to the effect of photoinitiator added to matrix materials. Two types of adhesive materials used indicate that the vinyl ester was not suitable to be used as adhesive since it needs two days to be cured after being exposed under the UV light. On the other hands, epoxy can cure rapidly after three minutes of exposure time under the UV light. Thus, the use of epoxy in the application of UV cured laminate composite is a right option if compared to vinyl ester. Presence of photoinitiator in the matrix materials was found not really affecting the density of the produced UV cured laminated composite. For tensile strength, the value was higher for epoxy in comparison to vinyl ester and the value was not affected by the presence of photoinitiator. An additional of 1.0phr photoinitiator shows increment in tensile strength but caused sudden decrement in its value when 10.0phr of photoinitiator was added. Hardness of UV cured laminate was found not affected by the presence of photoinitiator. Furthermore, through morphological observation by SEM, it was found that proper adhesion is not achieved between the layers of fiber and the adhesive matrix. Overall, further study need to be carried out in order to fully discover the potential of proposed materials and curing technique as well as the role of photoinitiator especially for bullet proof vest application. Results and properties obtained from this preliminary investigation is still need to be expanded by some other study to achieve the optimum information with regards to the contribution of UV light in converting the matrix materials from liquid to solid.

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