

# Thermal Stability and Physical Properties of Epoxy Composite Reinforced with Silane Treated Basalt Fiber

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**Abstract:** This study evaluates the influence of different silane coupling agents on the thermal and physical properties of epoxy-anhydride composite reinforced with basalt fiber. The silane coupling agents were selected by their functional groups so that they could have different chemical interactions with the epoxy and anhydride curing agents. The thermal and degradation behavior of the composites with different fiber contents were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Through the evaluation of  $T_g$  and thermal degradation behavior of both systems, it was deduced that the silane coupling agents have a great influence on the thermal properties of the composites as well as interfacial improvement. Also, the tensile properties of the composites were systematically evaluated in order to further understand the effect of silane coupling agents on the interaction with basalt fiber and epoxy matrix.

**Keywords:** Epoxy composite, Anhydride curing agent, Silane coupling agent, Basalt fiber, Thermal property, Physical property

## Introduction

The use of materials obtained from renewable sources draw great attention from many industries due to the interest in the environment, recycling, biodegradation, renewable resources, etc. Consequently, research on fibers from natural resources as reinforcements in organic polymer matrices has been extensively studied. Basalt fiber is a strong candidate material which originates on volcanic, over-ground, effusive rock saturated with 45-52 %  $\text{SiO}_2$ . This formation results in several advantageous properties such as high modulus and strength as well as significant heat resistance and outstanding vibration isolators. Several articles dealing with glass and carbon fiber reinforced polymer composites mention the significance of basalt fiber as a potential new reinforcing material [1,2].

It is well known that epoxy resins have many excellent properties, including good chemical and solvent resistances, high mechanical strengths, and high distortion temperatures with an industrially competitive material cost [3-5]. Therefore, they have been widely used in many fields such as adhesives, coatings, composites as well as in advanced material areas such as electronics and aerospace industries. These epoxy composites can be reinforced with inorganic fillers including super fibers and nano particles. The increasing economic and environmental demands on the reinforcements of load-bearing polymer structural materials encourage researchers to develop new, high-strength reinforcing materials and structures. Consequently, intensive research has been carried out all over the world with regard to the applicability of different organic and inorganic reinforcing fibers in polymer matrices in the past few decades. Among such promising fibrous materials, basalt fiber spun from mineral rock has drawn great attention as a reinforcing material compared to

traditional glass and carbon fibers [6,7].

A key factor in achieving good mechanical properties in a composite material is the existence of good interactions between the polymer matrix and the fibers, which allows good load transfer from the matrix to the reinforcement. It is well known that fiber-matrix interaction can be improved by introducing particular functionalities on surface fibers by treating the fiber with plasma or by using coupling agents. The use of silane coupling agents is generalized since it is well known how these work to provide intense links between inorganic fibers, such as glass and organic matrices. These coupling agents improve the adhesion between the fiber and the matrix, increasing the physical, mechanical, and chemical properties of the fiber-matrix interface. The use of silane coupling agents is generalized since it is well known how these work to provide intense links between inorganic fibers and organic matrices.

Therefore, the interfacial modification of basalt fiber for epoxy composites has been widely investigated for many years. The poor fiber-matrix adhesion can be improved with different types of coupling agents such as silane compound [8-10] or maleic anhydride derivatives [11,12]. The key question is how to find a method for the modification of the interfacial structure that is both economic and efficient. In the same line of investigation, the derivatives of silane compounds draw a great attention to the researchers [6,7, 13-15]. However, little is known about the interaction of epoxy-anhydride composites with silane coupling agent treated basalt fiber and its influence on the physical and thermal properties.

Therefore, this study focuses on the evaluation of the effectiveness of different silane coupling agents on thermal and physical properties of basalt-epoxy composites. Physical and thermal characteristics of the resins and composites were further investigated in terms of  $T_g$ , thermal degradation, char yield, and tensile properties.

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## Experimental

### Materials

The basalt fiber, roving of 130 tex (average monofilament diameter of 11  $\mu\text{m}$ ), used in the experiment was provided by Secotech (Korea) and was chopped to 6 mm length.

All chemicals were used as received and showed in Table 1. Diglycidyl ether of bisphenol-F (DGEBF, Bakelite EPR 161) was obtained from Hexion. Tetrahydrophthalic anhydride (THPA, Sigma-Aldrich) was used as curing agents for epoxy resin. Dimethylbenzyl amine (Sigma-Aldrich) was used for anhydride as a catalyst. Different silane coupling agents were selected to improve interactions between the epoxy resin and the basalt fiber. The aminofunctional silane was 3-(aminopropyl) triethoxysilane (Sigma-Aldrich, abbreviated as APS) and the selected methacrylfunctional silane was 3-methacryloxy propyl trimethoxy silane (Sigma-Aldrich, abbreviated as MPS).

### Preparation of Basalt Fiber Reinforced Epoxy Composites

In order to remove any dirt from the fiber and sizing emulsifier attached to it during its spinning process, acetone was used as the removing solvent in an ultrasonicator for 1 hour [15]. Following completion, it was dried for 24 hours at room temperature. After this initial stage, the basalt fiber was subjected to the silane treatment. First, a water: methanol (95:5 wt%) solution containing 0.5 wt% silane controlled with pH 4.0 using acetic acid was prepared and it was left standing for 1 h to homogenize and ensure optimum silane dissolution. Then, the basalt fiber was introduced in the solution for 1 h at room temperature. Finally, the wetted basalt fiber was dried at 200 °C for 24 h until it was completely dry.

The appropriate amounts of epoxy resin, corresponding curing agent and chopped basalt fiber were weighed into a glass dish and mechanically stirred at 85 °C until well mixed. The fluid resin mixture was then poured into a preheated mould between two glass plates treated with a silicon based mould release agent. The resin filled mould was initially heated under reduced pressure at 100 °C for 1 h in order to remove any air entrapped in the mould filling process. The material was then subjected to the curing condition at 110 °C for 40 min (amine curing system, abbreviated as epoxy-amine) or 130 °C for 40 min (anhydride curing system, abbreviated as epoxy-anhydride) in a temperature controlled hot-press. The curing conditions were selected from the preliminary result of non-isothermal and isothermal experiments by differential scanning calorimetry (DSC). In order to eliminate variability due to monomer purity or cure history, all samples were prepared from single batches of epoxy and curing agent and were cured simultaneously. The amount of curing agent was calculated through the following equation (1).

Amount of curing agent (phr) =

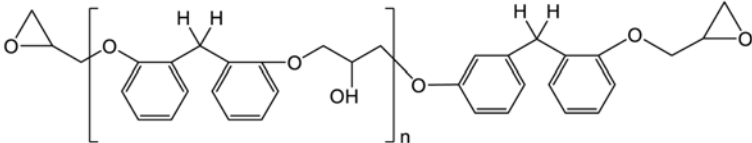
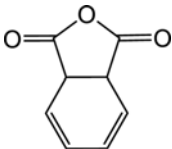
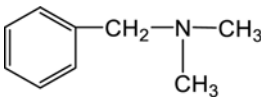
$$\alpha \times \frac{\text{Active Hydrogen Equivalent Weight (g/eq)}}{\text{Epoxy Equivalent Weight (g/eq)}} \times 100 \quad (1)$$

$\alpha$  is 1.0 for the anhydride curing system when 0.5 phr of dimethylbenzyl amine is added as a curing catalyst.

### Instrumentation

Thermal properties of the composites were analyzed by Differential Scanning Calorimeter (DSC) (TA instrument DSC2010 system, USA) using hermetic pan under nitrogen gas at a flow rate of 60 ml/min and a heating rate of 10 °C/min.

**Table 1.** Chemical structures for the resins, curing agents and silane coupling agents

| Name of chemicals                     | Chemical structure  |
|---------------------------------------|---|
| Bisphenol-F type epoxy (DGEBF)        |           |
| Tetrahydrophthalic anhydride (THPA)   |           |
| Dimethylbenzyl amine                  |           |
| 3-Aminopropyltriethoxy silane         | $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$                         |
| 3-Methacryloxypropyltrimethoxy silane | $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ |

Thermal degradation behaviors of the composites were characterized with Thermogravimetric analysis (TGA) (TA instrument Q series 50 system, USA) at a nitrogen flow rate of 90 ml/min and a heating rate of 20 °C/min.

Tensile property was evaluated by using a Universal testing machine (LR10K, LLOYD) according to the testing method of KS M 3381. The gauge length of tensile testing was 15 mm and the crosshead speed was 5 mm/min.

Scanning electron microscopy (SEM) analysis of composite was performed by using a Hitachi S-4700 microscope (acceleration voltages: 20 kV) to evaluate the fracture surface. All specimens were coated with a thin layer of gold-palladium before analysis.

## Results and Discussion

### Glass Transition Temperature ( $T_g$ ) of the Composites

As shown in Figure 1, the  $T_g$  of epoxy-anhydride composites is effectively increased with the addition of basalt fiber. This enhancement is attributed from the fact that the mobility of polymer chains in epoxy-anhydride matrix may be limited by the inorganic reinforcement.

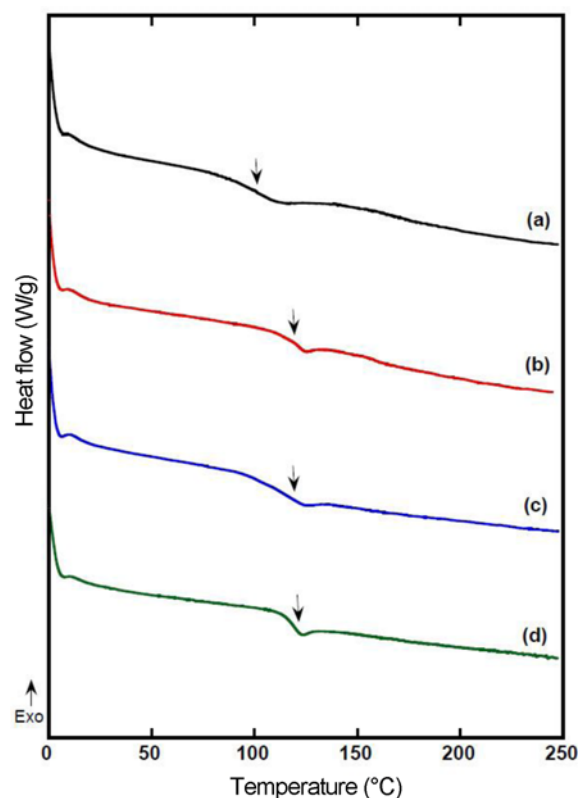
As shown in Figure 1(a), the epoxy-anhydride bulk resin showed  $T_g$  of ca. 105 °C and the  $T_g$  of epoxy-anhydride composite is increased with the 10 % addition of untreated basalt fiber from ca. 105 °C to ca. 120 °C, thus showing a  $T_g$  enhancing effect by the basalt fiber addition. This means that the mobility of epoxy-anhydride polymer chains is effectively limited and has been well reported in the previous study [16].

However, it is noticeable that the enhancing effect of  $T_g$  is not relevant to the additional treatment nor the structure of silane coupling agents. The epoxy-anhydride composites with 10 % addition of basalt fiber show similar  $T_g$ s of about 120 °C even with different types of silane coupling agents, which may have an additional interaction between basalt fiber and matrix resin. This means that the local interaction on the surface of basalt fiber does not change the  $T_g$  of bulk matrix resin. Therefore, it can be deduced that the  $T_g$  enhancement effect is dominated by the addition of basalt fiber reinforcement, which is enough to limit the molecular movement of epoxy chains rather than surface silane treatment.

### Thermal Degradation Behavior of the Composites

Thermal degradation behavior for APS treated basalt fiber reinforced epoxy-anhydride composites with different fiber contents is shown in Figure 2. A very similar behavior is also observed for MPS treated basalt fiber reinforced epoxy-anhydride composites with different fiber contents (Figure 3).

One distinctive feature is that the initial degradation temperatures at 95 % weight loss are decreased with the increase of fiber contents. The weight loss event in TGA thermograms can provide the information for 3 thermal

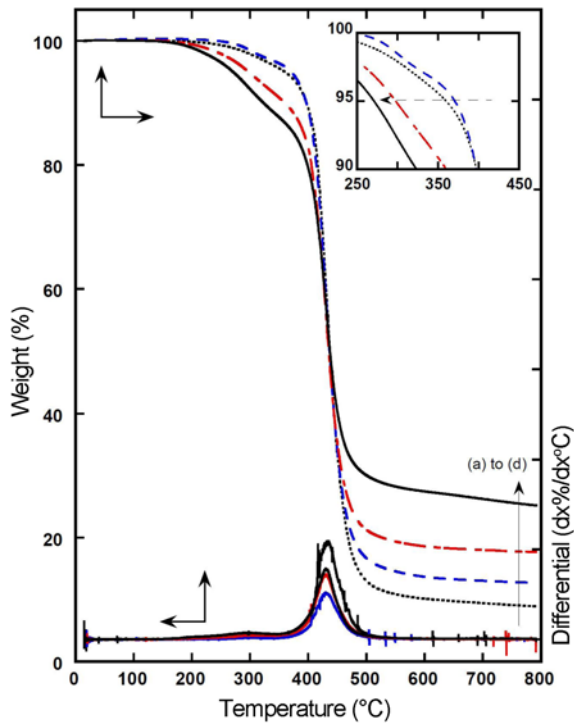


**Figure 1.** DSC thermograms of basalt fiber reinforced epoxy-anhydride composites using; (a) no basalt fiber, (b) 10 % of untreated basalt fiber, (b) 10 % of APS treated basalt fiber, and (c) 10 % of MPS treated basalt fiber.

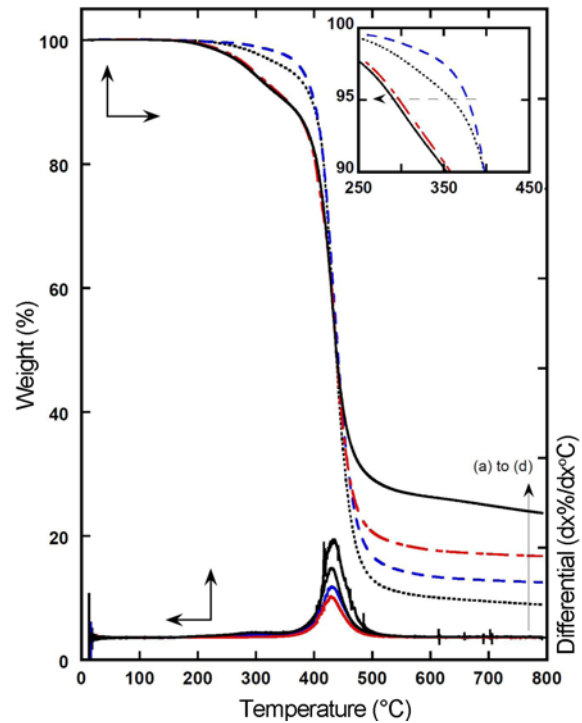
degradation steps in epoxy resin. First, the aliphatic chain loss at relatively low temperature under 300 °C. Second, the aromatic chain loss at around 400 °C. Last, the aromatic or char degradation. Consequently, the initial degradation temperatures at 95 % weight loss is closely related to this first step and it is well known that the initial weight loss is mainly due to the volatile or weak chemical bonding in the polymer network structure.

When a silane coupling agent is incorporated into the curing system of epoxy resin, three possible reactions are possible between: 1) epoxy resin and anhydride curing agent (EC, major epoxy curing reaction), 2) epoxy resin and silane coupling agent (ES), and 3) anhydride curing agent and silane coupling agent (CS). As shown in Scheme 1, it is not likely that the ES and CS reactions occur for the MPS system. The physical interaction can be enhanced in the interface between basalt fiber and EC matrix resin.

Moreover, the reactions in APS system (Scheme 2) could be more complicated due to the reactivity of the amine functional group. The major epoxy curing reaction, EC, would compete with the reaction between the epoxy group of resin and amine group of silane. Furthermore, anhydride curing agent is consumed by the reaction between the



**Figure 2.** Thermal degradation behavior for APS treated basalt fiber reinforced epoxy-anhydride composites with the fiber content of; (a) 0 %, (b) 3 %, (c) 5 %, and (d) 10 %.

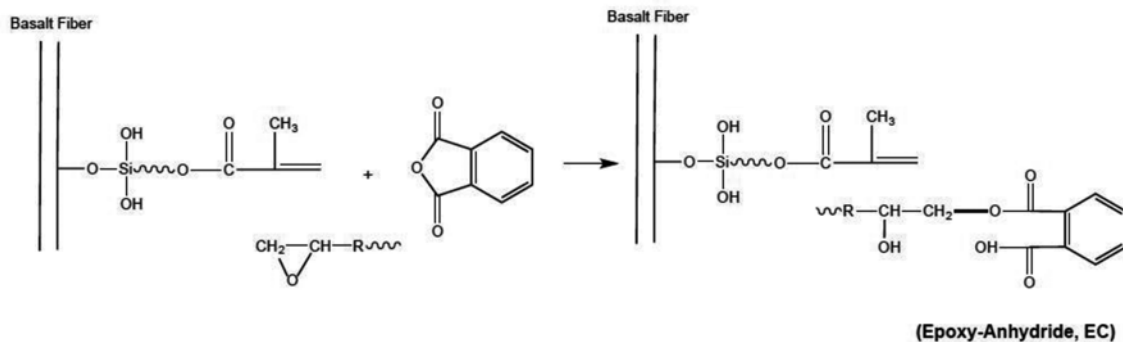


**Figure 3.** Thermal degradation behavior for MPS treated basalt fiber reinforced epoxy-anhydride composites with the fiber content of; (a) 0 %, (b) 3 %, (c) 5 %, and (d) 10 %.

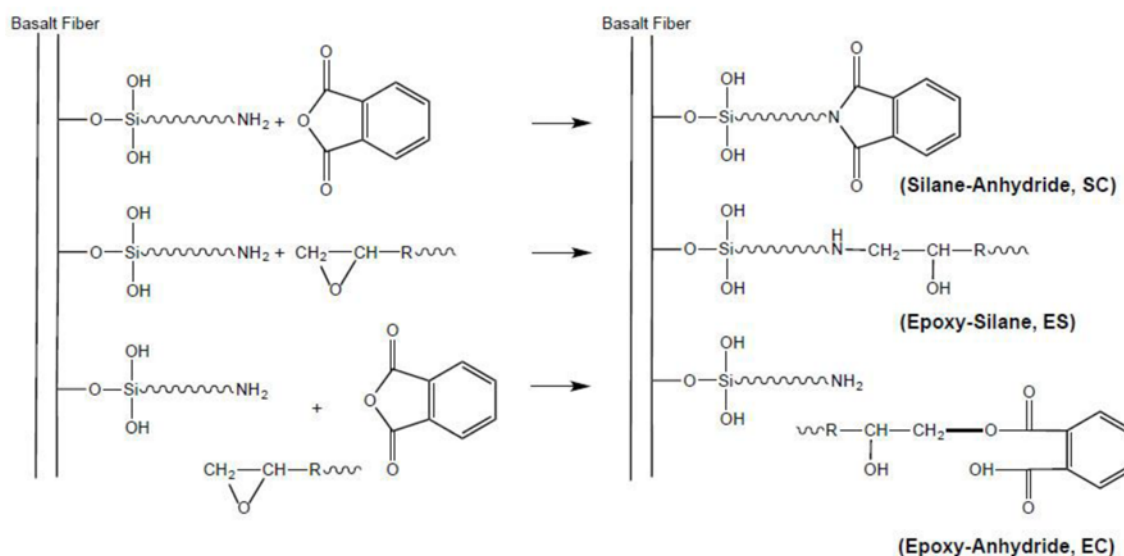
anhydride group and amine group of silane. Therefore, the physical and chemical interactions in the interface between basalt fiber and epoxy resin might be hindered. Also, the presence of APS coupling agent promotes ES and CS reactions which lead to the decrease of EC reactions and hinder the complete crosslinking reaction between epoxy and anhydride curing agent. The more silane coupling agent treated basalt fiber reinforcement is used, the more complex the environment around the interfacial area between basalt fiber and resin becomes. Although the physical enhancement around interfacial area could be obtained by these silane coupling agents, it is obvious that the existence of additional

interaction by the silane coupling agents make the thermal stability around 300 °C worsen. This will be further discussed in a later section with the behavior of the physical properties of the composite because they are closely related.

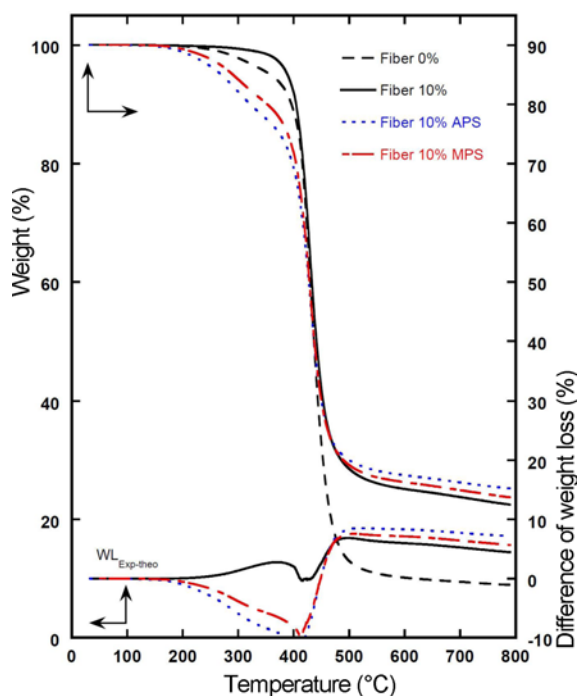
The other interesting feature is that the char yield at 800 °C is drastically increased with higher fiber contents. The formation of char is an important thermal property. The char yields of APS system are drastically increased from 9 % of bulk resin up to 25 % of the composite by the addition of basalt fiber in the case of the APS system. A very similar behavior is shown in the case of the MPS system, which increased from 9 % of bulk resin up to 24 %. These results



**Scheme 1.** Reaction between epoxy resin and anhydride curing agent with MPS treated basalt fiber.



**Scheme 2.** Reactions between epoxy resin and anhydride curing agent with APS treated basalt fiber.



**Figure 4.** Thermal degradation behavior and the net gain ( $WL_{Exp-Theo}$ ) by composite preparation for basalt fiber reinforced epoxy-anhydride composites using; (a) no basalt fiber, (b) 10 % of untreated basalt fiber, (c) 10 % of APS treated basalt fiber, and (d) 10 % of MPS treated basalt fiber.

are far exceeding the char yield of a simple rule of mixture since the inorganic basalt fiber content is just 10 %.

This behavior can be further analyzed by  $WL_{Exp-Theo}$ , which is shown in Figure 4. In order to interpret whether this

favorable improvement is from the simple addition of non-degradable inorganic basalt fiber or not, the difference ( $WL_{Exp-Theo}$ ) between the experimental and theoretical curves is obtained through the following equations (2) and (3) [14,16,17]:

$$WL_{theo} = rWL_{resin} + (1 - r) WL_{bf} \quad (2)$$

$$WL_{Exp-Theo} = WL_{exp} - WL_{theo} \quad (3)$$

$WL_{resin}$ : Weight loss in TGA thermograms of a used resin

$WL_{bf}$ : Weight loss in TGA thermograms of a pure basalt fiber

$r$ : Resin fraction of a composite

$WL_{theo}$ : Theoretical weight loss of a composite

$WL_{exp}$ : Experimental weight loss in TGA thermograms of a composite

$WL_{Exp-Theo}$ : Net gain of weight loss of a composite

If  $WL_{Exp-Theo} > 0$ , we can assume the presence of positive interactions between the resin and the basalt fiber that allow a relatively good thermal stability of the composite. In contrast, if  $WL_{Exp-Theo} < 0$ , negative interactions between the components are observed, which indicates a lower thermal stability.

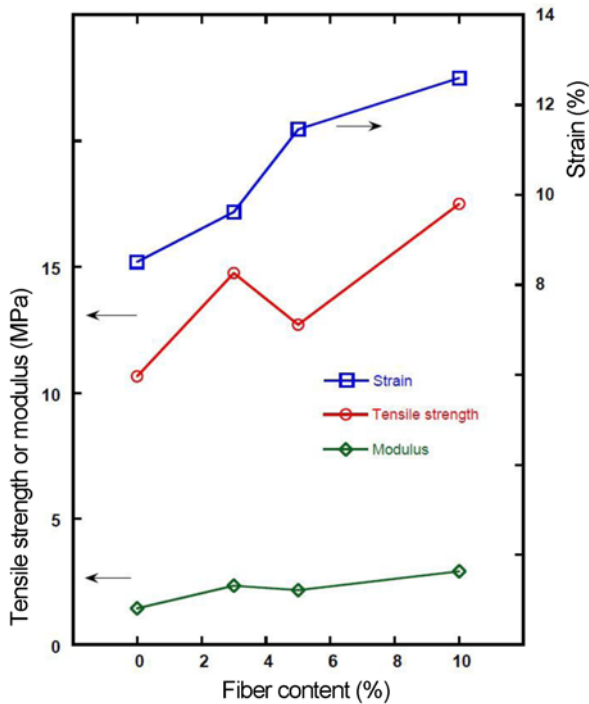
The effectiveness of this analysis is well shown in Figure 4 for the epoxy-anhydride composites with different fiber content. The  $WL_{Exp-Theo}$  for the composite with 10 % of untreated basalt chopped fiber shows almost 5 % starting from 400 °C, which implies the synergic interaction between the resin and the basalt fiber as reported in the previous study [14]. When the silane treated basalt fiber is incorporated, the  $WL_{Exp-Theo}$  for APS system and MPS system are increased to 7 % and 6 %, respectively. Although the increase of  $WL_{Exp-Theo}$

for silane system is marginal, it is obvious that the various interactions due to silane coupling agent are promoting a favorable synergy effect at high temperature.

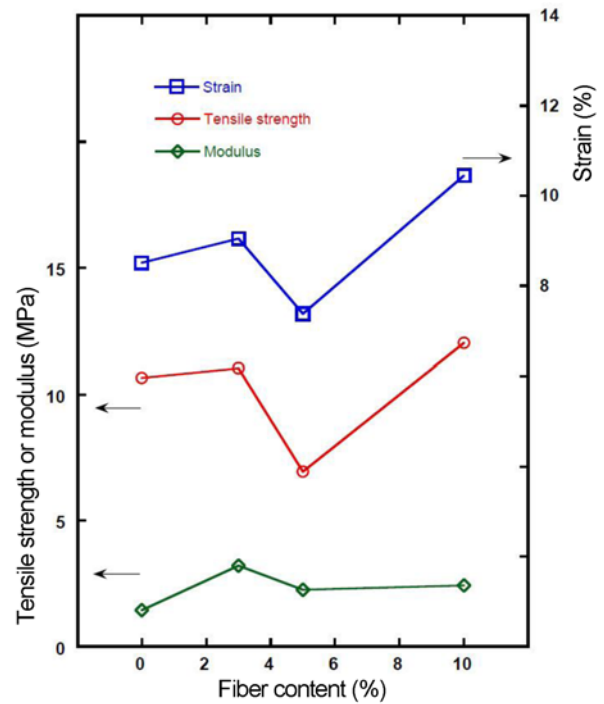
**Physical Properties of the Composites**

The tensile properties of epoxy-anhydride composites for the 2 silane system are shown in Figure 5 and 6 respectively. It seems that the effect of the silane coupling agent on the improvement of tensile strain is evident in both cases when they are compared with tensile properties of composite without silane modification shown in Figure 7. However, although the APS system shows much better improvement, the influence of silane modification to tensile strength is not significant. This means that the silane modification layer of basalt fiber is more influential for chemical and thermal properties than physical property. As shown in Figure 8, this can be observed from the fact that the difference of the physical interaction in interfacial area is difficult to find the changes in the fracture surfaces of the composites.

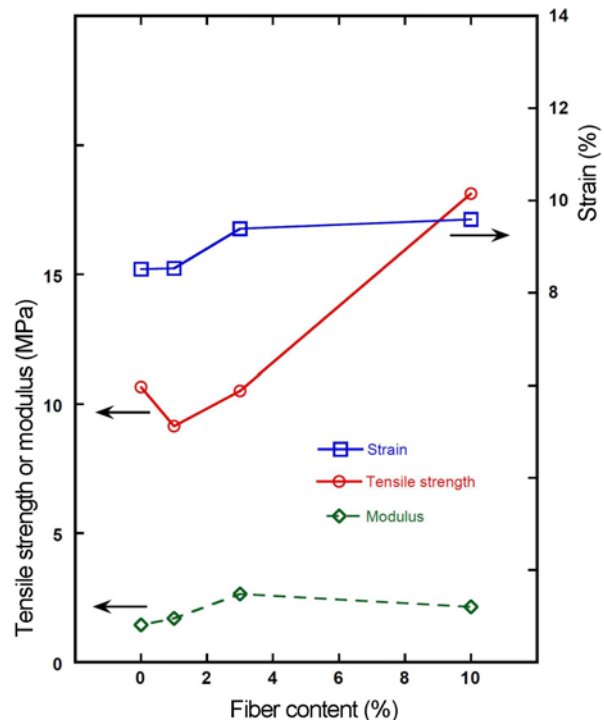
On the other hand, it is hard to conclude that tensile modulus improvement was observed in both systems. This is well known behavior for the composite of silane coupling agent treated fiber. Since the physical and chemical interactions between fiber and matrix in the interfacial area are improved, the physical properties, which is dominated by the stress distribution in the interfacial area, could be improved by the effective role of a silane coupling agent. The better improvement of the APS system over the MPS system is



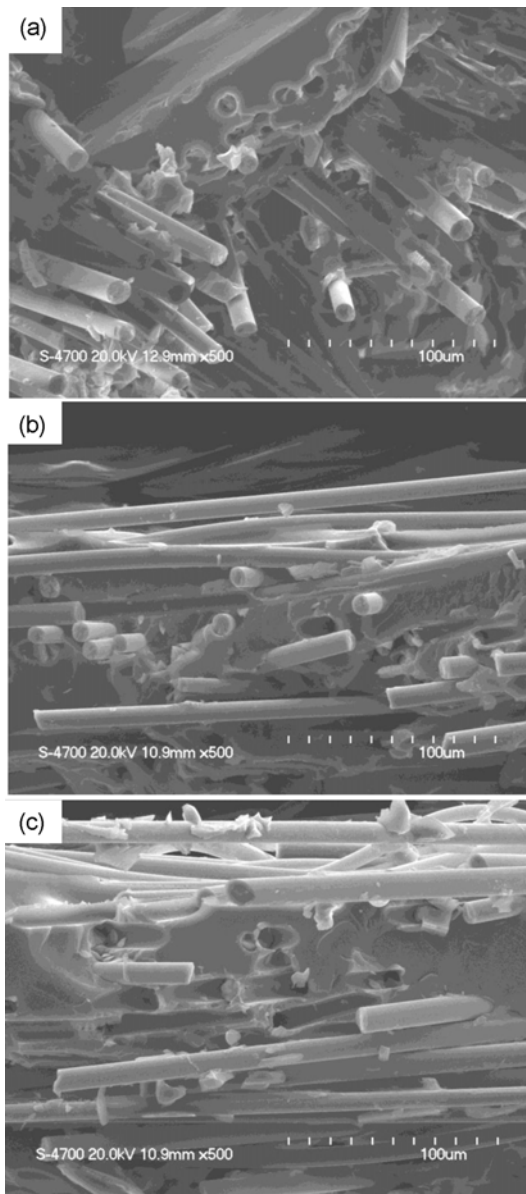
**Figure 5.** Comparison of tensile properties for APS treated basalt fiber reinforced epoxy-anhydride composites.



**Figure 6.** Comparison of tensile properties for MPS treated basalt fiber reinforced epoxy-anhydride composites.



**Figure 7.** Comparison of tensile properties for basalt fiber reinforced epoxy-anhydride composites (Redrawn from the previous study [14]).



**Figure 8.** Comparison of the fracture surface of composites using: (a) 10% of untreated basalt fiber, (b) 10% of APS treated basalt fiber, and (c) 10% of MPS treated basalt fiber.

closely related to the chemical interaction environment as discussed in Scheme 2. However, the tensile modulus is not affected by the increase of fiber contents. This could be attributed to the fact that the tensile modulus of composites is not influenced much by the interfacial modification but is dominated by a bulk property of matrix resin.

### Conclusion

In order to investigate the influence of silane coupling agents on the physical and thermal properties of epoxy-

anhydride composite, two different types of silane coupling agents, APS and MPS, were utilized to modify the basalt fiber surface. The interaction of epoxy resin, anhydride curing agent and silane curing agent was carefully evaluated through the means of  $T_g$ , thermal degradation behavior, char yield, and tensile properties.

Through the evaluation of  $T_g$  by DSC and thermal degradation behavior by TGA, it could be clearly concluded that the incorporation of silane treated basalt fiber in epoxy-anhydride resin has a great role and advantage in preparing high performance composites. Although the addition of basalt fiber makes the  $T_g$  of composites ca. 15 °C higher than bulk resin, there is no significant difference between non-treated basalt fiber and silane treated basalt fibers. However, based on the systematical evaluation of apparent char yield and net char yield gain of the composites, it is evident that the char yields at 800 °C for both silane systems are synergistically improved more than a rule of simple mixture. It is also observed that the tensile properties of the epoxy-anhydride composite with APS treated basalt fiber are effectively improved with the increase of fiber content due to the additional interaction between the amino silane, anhydride and epoxy.

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