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Effect of Fibre/Matrix Modification on Tensile Properties and Water Absorption Behaviour of Hybridized Kenaf/PALF Reinforced HDPE Composite.

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ABSTRACT

This paper compared the effect of modification on hybridized kenaf/pineapple leaf fibre (PALF) and high-density polyethylene (HDPE) composite on their composite's tensile properties and water absorption behaviour. Modification was carried out on the fibre's surface using Vinyltri (2-methoxy ethoxy) silane (silane AH172), while the HDPE matrix was modified with Poly(methylene) poly(phenil) isocyanate (PMPPIC). The influence of water uptake on the absorption behaviour of the composites was studied by immersion in distilled water for 24 hrs at 27°C. The effects of modification on both water sorption and tensile properties were evaluated. The results showed that the properties of unmodified hybrid improved after its immersion in water, unlike modified ones. Modifying the matrix and combining it with treated fibres did not give better results as expected. Combining PMPPIC with silane induced toughness in the composite as observed in the test results. In addition, PMPPIC reduced the hydrophilicity of the composite considerably. Thus, regardless of either fibre surface modification or matrix modification, reinforcement with respect to treatment depends on the type of modifier used and not where it is applied in composite formulation.

INTRODUCTION

Work on natural fibre has been of great interest because of great potential application areas. However, the need to make them hydrophobic or at least reduce their rate of water absorption has proven to be difficult. This is because grafting techniques have not been able to help very well, especially at higher fibre loading of composites. The higher the loading, the more hydrophilic the composite becomes because of increased cellulose content in the composite. Natural fibres present some well-known advantages such as lower density and cost. They are less abrasive to the processing equipment, reasonably harmless,

biodegradable, renewable, and their mechanical properties can be comparable to those of inorganic fibres. Furthermore, they are recyclable, easily available in most countries, the surface is easily modified, and are relatively nonabrasive [1,2]. It is well known that the performance of composite depends on the properties of the individual components and their interfacial compatibility. Plant fibres have to be prepared or modified for numerous applications [3,4]. Properties like homogenization of the properties of the fibres, degree of elementarization and degumming, degree of polymerization and crystallization, good adhesion between fibre and matrix, moisture repellence and flame-retardation, which are factors considered in using natural fibres, can be partly influenced by different separation processes, but subsequent treatment process is more influential [5].

Earlier work by the authors [6] reviewed some of the achievements so far recorded in enhancing the effectiveness of interfacial adhesion between cellulose-based fillers and thermoplastics and discovered that many of these studies have been carried out on wood fibers. Several techniques have been reported that range from grafting of short-chain molecules and polymers onto the surface to using coupling agents and radical induced adhesion promoters to improve interfacial bonding [7,8,9,10,11]. Grafting improves wetting of the fiber with matrix by hydrophobizing the fiber surface, which then promotes interfacial bonding by diffusion of the chain segments of the grafted molecules into the matrix. Similarly, other researchers reported several strategies of surface modification aiming at improving the compatibility between cellulose fibers and polymer matrices. Coupling agents bearing two reactive groups can be used to chemically modify the interacting surfaces of fibers and of polymeric materials, i.e. the interaction between the OH functional group at the surface and the copolymerization of the other reactive group with that of the matrix material [10,12]. Edeerozey et al. [13] investigated the chemical modification of kenaf fiber using NaOH at different concentrations and discovered that the alkalization treatment of kenaf can improve the mechanical properties significantly through several morphological and structural changes, when compared to untreated kenaf. They noted that chemical treatment of the fiber could clean the fiber surface, chemically modify the surface, stop the moisture absorption process, and increase the surface roughness if 6% optimum concentration of the alkaline is used.

Combining kenaf with PALF, can help achieve high loading in the composite with potentially higher mechanical properties [14]. In addition, flexural and torsional rigidity of PALF is very much similar to that of jute fibres [15]. Hybridizing these two fibres can offer interesting synergistic behaviour in the resulting composite without sacrificing their optimal properties when combined with polymeric materials, such as HDPE.

This paper is targeted at comparing the tensile properties of unmodified hybridized composite with matrix and/or fibre modified ones, in addition to how tensile properties can be affected after immersion in water for 24 hrs.

EXPERIMENTAL

Materials

Pineapple leaf (*Ananas comosus*) was bought from Kraftangan, Malaysia with Johor pineapple plantation as the source. It was manually decorticated from the variety "Josephine". Kenaf (*Hibiscus cannabinus*) of variety V36, purchased from KEFI Malaysia Sdn. Bhd. was utilized in this research. These fibres were reinforced with HDPE also purchased from KEFI Malaysia. Poly(methylene) poly(phenil) isocyanate (PMPPIC) was used to modify the matrix while silane AH172, with chemical name vinyltri (2-methoxy ethoxy) silane, was used to modify the fibres. The tensile properties of HDPE used in this paper as earlier tested by the authors were 29.44 MPa and 287.70 MPa for strength and modulus respectively. However, additional properties provided by the supplier are shown in (Table 1).

Table 1: Supplier-provided properties of HDPE used

Density	Melt Mass Flow rate	Dart Drop Impact	Tensile Elongation	Forms	Melt Temp.°C	Sec. Mod (MPa)
0.95 g/cm ³	190°C/2.16 kg	17 µm, Blown film	TD : Break 17 µm, Blown film	Pellets	180-240	1% Sec, TD 17 µm, Blown film
	0.10 g/10 min	140 g	700%			1270

TD means polymer orientation in transverse direction.

Treatment

The cellulose fibres were immersed in distilled water containing 3 wt% of silane for 2.5hrs. One gram of fibre per 20 ml of water was utilized in the treatment. Fibres in silane were only squeezed to remove excess solution from it after the stated time. They were then put in an oven at 100°C for about 21 hrs to dry.

Preparation of Hybrid Composites

Short fibres of Kenaf and PALF at a ratio of 1:1 and length of 0.25 mm and below, with an average diameter of 76 µm and 130 µm, respectively, were utilized for this formulation. A Brabender plastograph was preheated and set at 190°C, and 40 rpm processing speed and the fibres were mixed with the matrix at a fibre loading of 50 wt%. The HDPE in the form of pellets were mixed with matrix modifier (i.e. PMPPIC) before introducing them into the brabender and then allowed to stabilize (fully melt). Fibres were then introduced to complete the final mixing of composite in the Brabender. The total time used to mix the hybrid composite was 25 minutes [16]. The mixed composite obtained from the Brabender was cut into pellets for compression moulding operation. The following samples were prepared for the experiment as described in Table 2.

Table 2: Hybrid composites formulation

Formulation	Matrix modification		Fibre Treatment	
	MaPE (%wt of matrix)	PMPPIC (%wt of matrix)	NaOH (%wt of water)	Silane (%wt of water)
HA1	-	-	-	-
HA3	-	-	-	3
HA4	-	3	-	-
HB2	-	3	-	3

Mechanical Property Testing of Composites

Sheets for tensile and water absorption sample of 150 mm X 150 mm X 1 mm and 150 mm X 150 mm X 3 mm, respectively, were produced in the compression-molding machine that was set at 170°C with 7 min preheat, 5 min full press, 6 times venting process, and 5 minutes cooling. Tensile specimen of dimension 10 mm X 1.5 mm X 1 mm and water absorption specimen of 150 mm X 15 mm X 3 mm were cut out from the composite sheets produced. Tensile tests was carried out in accordance with ASTM D-638 (type V) using a 5 kN Bluehill INSTRON universal testing machine. A 2 mm/min crosshead speed was used for the tensile specimen. At least five samples were tested and the mean value taken.

Water Immersion Test

Water absorption test using ASTM D570 (modified) was conducted on specimens produced. Specimen were conditioned in an oven at 50°C for 24 hrs and then 100°C for 2 hrs to ensure that they were completely dry. They were then allowed to cool in an environment devoid of humidity. After cooling, their initial weight (w_1) was taken and they were then immediately immersed in water at 27°C for 24 hrs. Thereafter, the specimens were quickly removed and their weight (w_2) taken. The difference between the mass after 24 hr immersion and the initial mass, compared to the initial mass led to the determination of the composite water absorption.

RESULTS AND DISCUSSION

Reinforcement of Hybridized Composite with Treatment

Figure 1(a and b) shows the results obtained from the composites produced with compatibilizer and coupling agent used and the subsequent improvements in tensile properties of composites before and after immersion in water. It can be observed that hybrid composites experienced an increase in tensile strength of about 21 and 22% in the case of HA3 and HA4, respectively, at the application of treatment; this is in agreement with other authors' results [17,18]. Similarly, modulus results of hybrid composites showed significant improvement in property with all the modifications carried out. In hybrid composites formulated using vinyltri (2-methoxy ethoxy) silane treated fibres, the alkoxy groups of silane hydrolyzed to

form silanols (-OH). This -OH group interacts with the -OH groups of lignocellulosic fibres, forming hydrogen bonds, while the vinyl group reacted with the polyester. This caused the matrix to become less interconnected, providing higher elongation of the silane-treated composites. PMPPIC matrix modification displayed the most significant improvement, having about a 56% increment in modulus. The enhanced bonding in PMPPIC modified composites could be attributed to the formation of strong covalent bonds between the -OH groups of the cellulose present in the fibres and the -NCO groups of PMPPIC. This highly reactive group in PMPPIC could have interacted with the -OH group of cellulose and a possible urethane linkage formed[19]. Subsequently, the long chain molecules interacted with polyethylene leading to a Van der Waals' type of linkages and because of the very high interfacial interactions achieved, higher tensile properties were obtained. The high tensile modulus observed in this result means that the material is rigid and more stress was required to produce a given amount of strain, which made it able to resist deformation or stretch. Even though the silane-treated composite presented mechanical properties that are nearly at par with that of PMPPIC modified composite in terms of mechanical properties obtained, silane made the composite brittle as observed during the test.

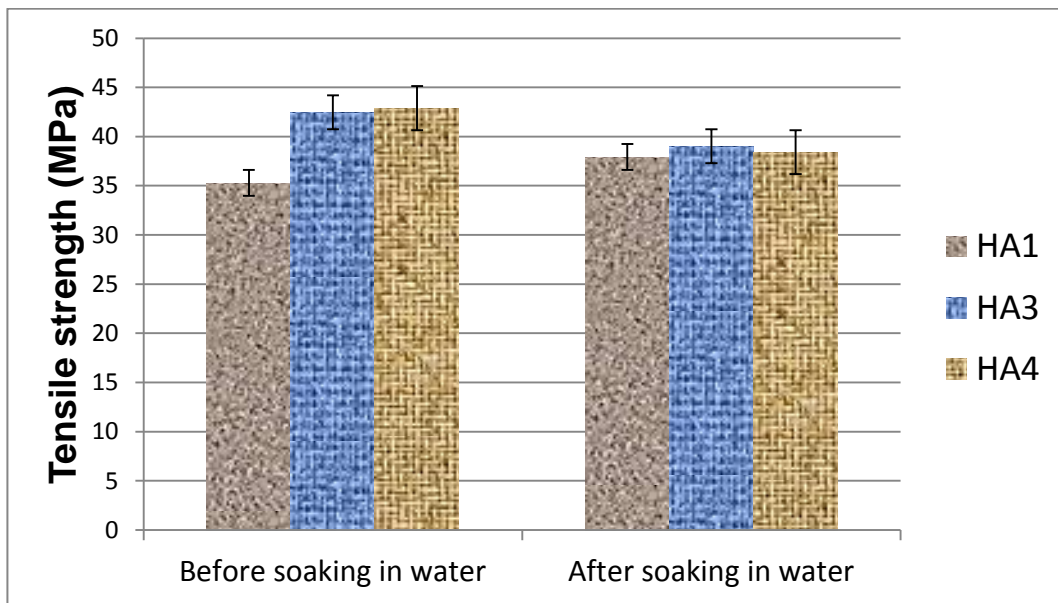


Figure 1a: Tensile strength of composites before and after immersion in water

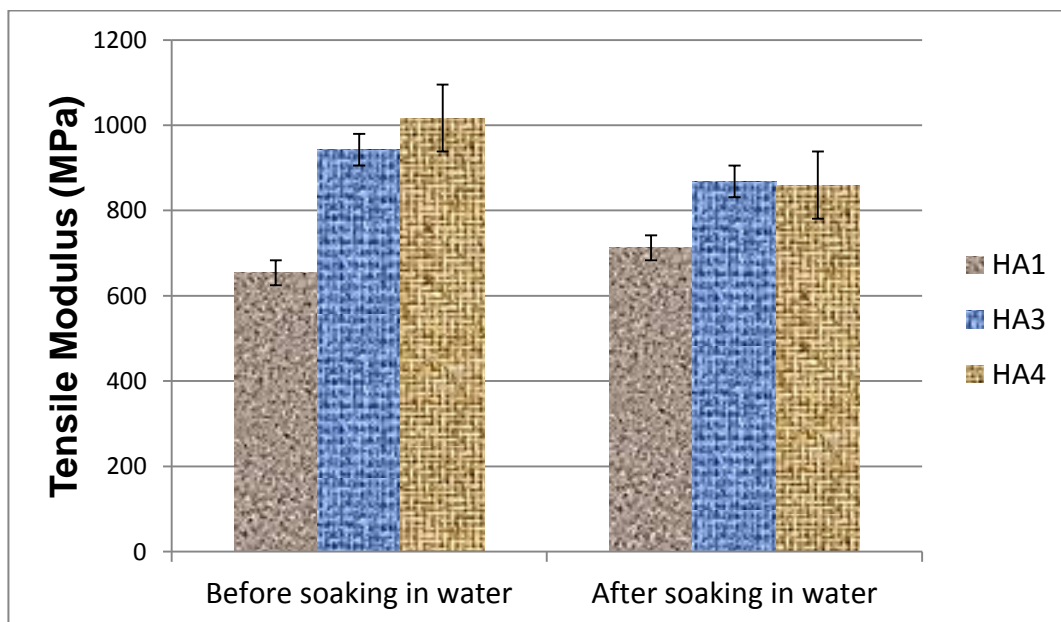


Figure 1b: Tensile modulus of composites before and after immersion in water

In addition to the results obtained from hybrids HA1, HA3 and HA4, an additional hybrid was formulated to observe the effect of combining treated fibre with a modified matrix. This is also to ascertain if such a combination could further improve the tensile properties and further reduce the water absorption of the composite especially in comparison with the hybrid that showed the best results in Figure 1. This hybrid was tagged HB2 (i.e. 3% silane treatment of fibres + 3% PMPPIC treated matrix).

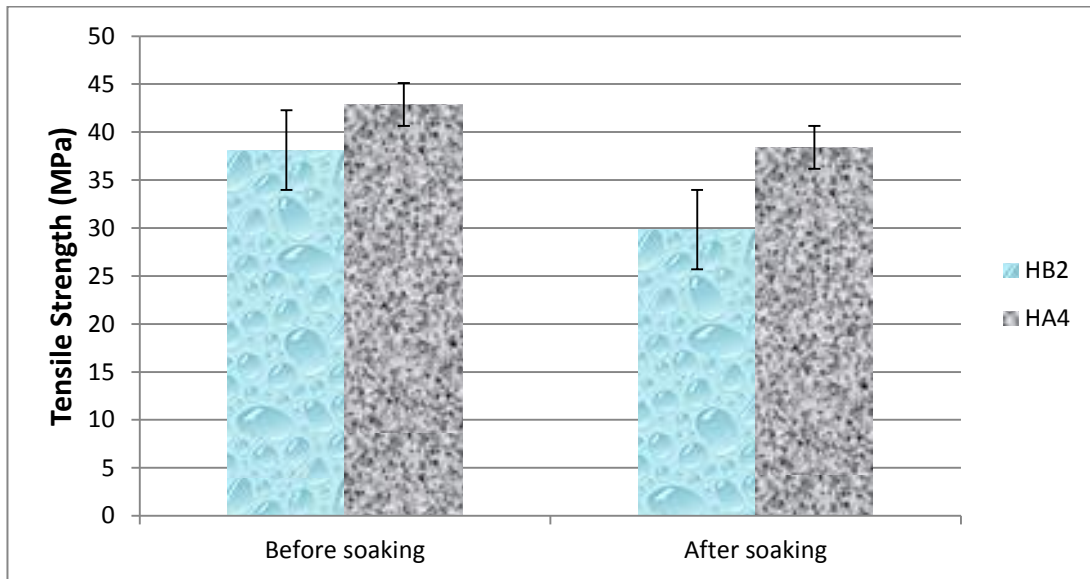


Figure 2a: Tensile strength of composites (with fibre and matrix modification) before and after immersion in water

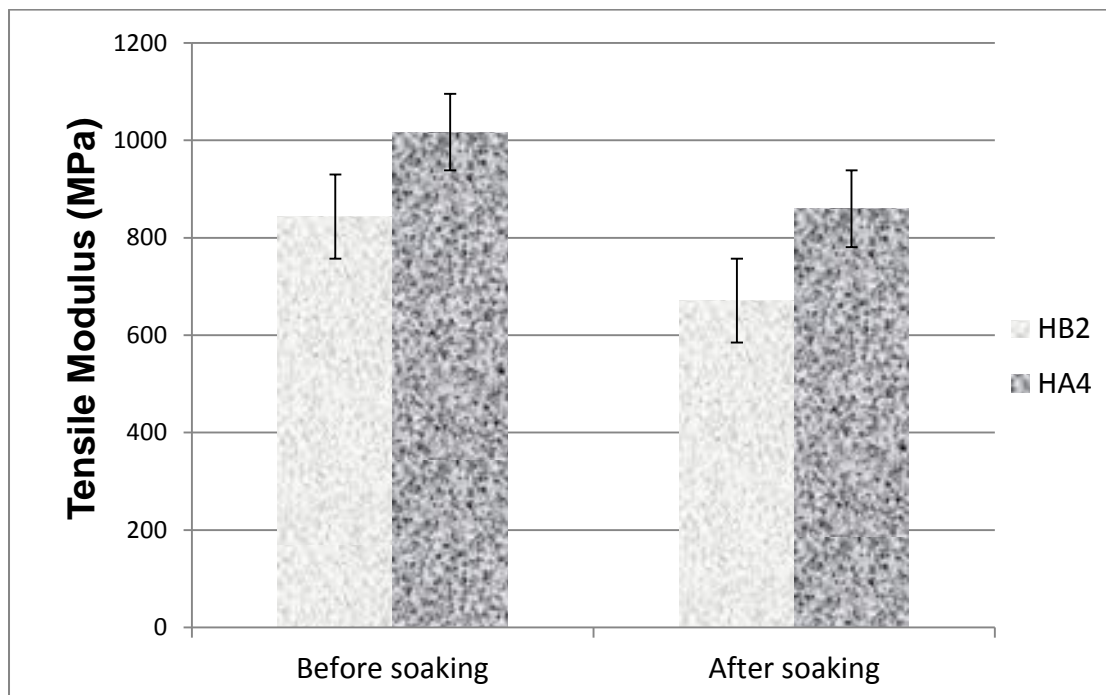


Figure 2b: Tensile Modulus of composite (with fibre and matrix modification) before and after immersion in water

Since the composite formulated with matrix modified with PMPPIC gave the best tensile result, it was used as the basis for comparison with HB2 for the same properties in question. It is clear from the tensile result in Figure 2 that combining PMPPIC-modified matrix with silanized fibre did not yield better results when compared to HA4. This is because further interaction between fibre and matrix was not achieved.

Expectation of interaction between silane and PMPPIC which could have further enhance compatibility between fibre and matrix could not take place.

Water Absorption

It is well known that increase in fibre loading in the formulation of composite means an increase in the quantity of water that will be lured by the cellulose, consequently drastic reduction in strength during service could be experienced. It has been reported that water uptake in natural lignocellulosic fibres greatly depends on their morphology, physical, and chemical structures [20]. The need to eradicate the hydrophilic phenomenon of natural fibre composite has continue to be difficult. It is therefore interesting to see the formulation without any form of treatment presenting some level of increase in strength after immersion in water for 24 hrs, even though it absorbed the most water. The thermal shrinkage of the matrix resulted in voids surrounding the fibres. The fibre can swell to fill this gap and may even produce some radial pressure. Partly, water molecules are bound to the hydroxyl groups of the cellulose. This may result in high tensile strength. Abdelmouleh et al. [11] observed a similar trend, where untreated composite absorbed more water than treated composite. Adequate hybridization can build and strengthen covalent bond between fibres and matrix, which can invariably reduce water absorption by composite[21]. There is a minimum quantity of water that can be absorbed by fibres, which will bring about its slight swelling. If achieved, it will develop a strong mechanical interlocking between fibre and the matrix and as a result, an improvement in mechanical properties may be experienced [11]. Figure 1(a and b) present this very interesting result. Considering the high loading (50wt%) employed in this experiment, it is interesting to see that weight increase after 24 hr immersion in water was about 3% for unmodified composite. The uptake could have been less if the cut edges of the immersed specimen were sealed with an epoxy or any other material that could abate the flow of water into the composite. Cut edges normally provide less resistance to water uptake because cutting generally expose fibres to their environment, which can increase its rate of water uptake.

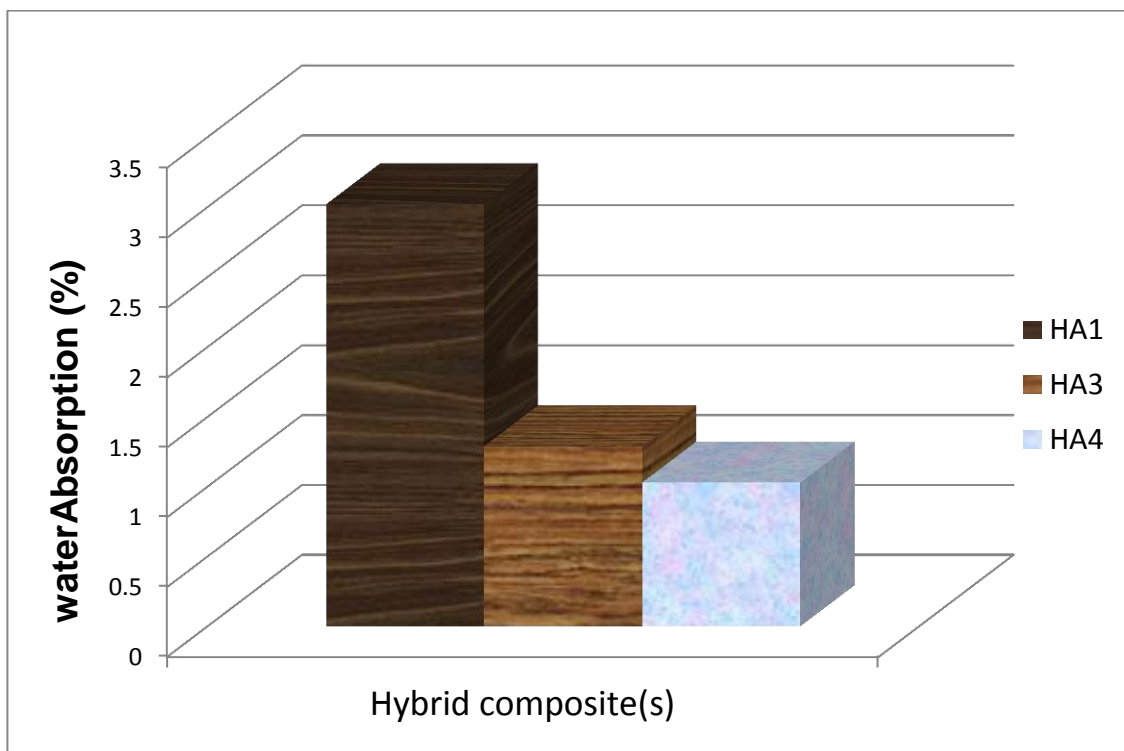


Figure 3a: Percentage water absorption of Partially Modified Composite

Water immersion test has also shown that while unmodified hybrid (HA1) experienced increased in tensile strength and modulus of 7.5 and 9%, respectively, the modified composites (HA3 and HA4), experienced reduction in both properties as shown in Figure 1. Modifying matrix and combining it with treated fibres did not give appreciable results as shown in Figure 2. It is clear from Figure 3 that PMPPIC helped to reduce the quantity of water uptake in composite. Treatment of fibres with silane, helped to polymerise vinyl groups. Individual molecules of the silane coupling agent, which are supposed to attach to

cellulose must have formed a continuous link. The long hydrophobic polymer chains of polymerised silane adhere to HDPE as a result of van der Waals' forces. Consequently, a strong interaction was induced at the fibre/matrix interface, which reduced water uptake. PMPPIC-modified composites showed the lowest water uptake because of enhanced bonding achieved. As explained earlier, formation of long chain molecules, which interacted with polyethylene led to the formation of Van der Waals' type of linkages and because of the very high interfacial interactions achieved between PMPPIC and PE, permeation of water molecules into the composite was slowed down.

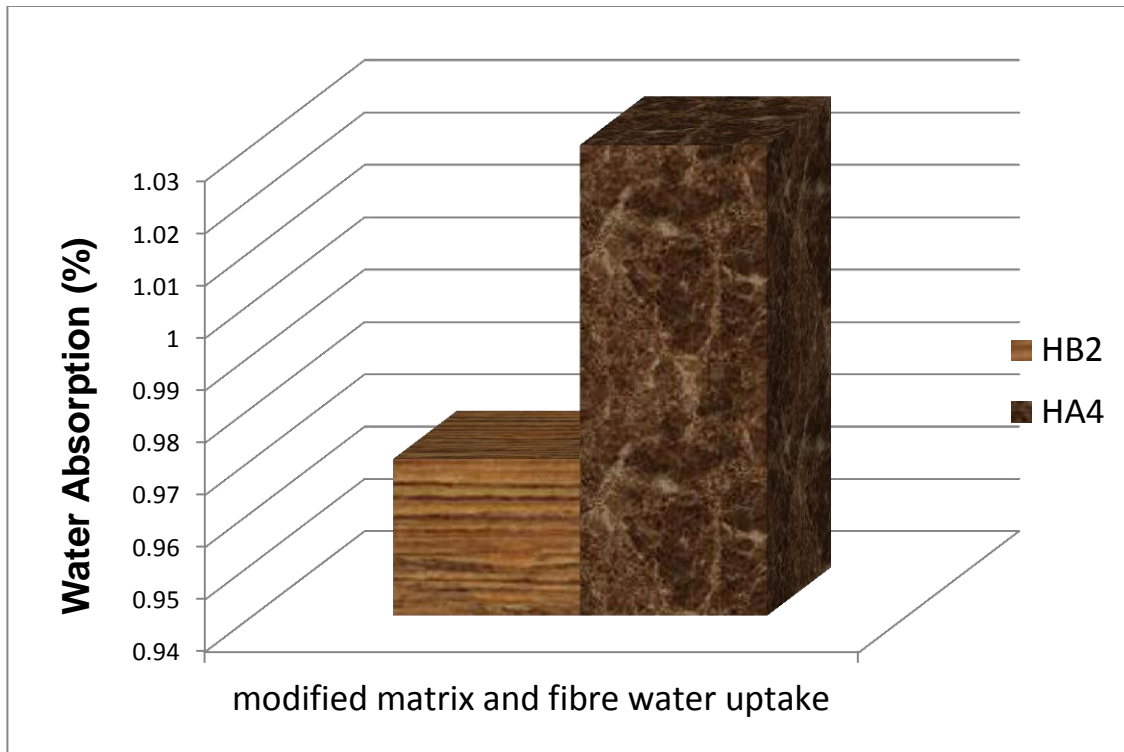


Figure 3b: Percentage water uptake by a fully modified Composite in relation to a partially modified one

CONCLUSION

Hybridized composite at 50wt% fibre loading was prepared and tested. The effects of minimum matrix modification on one hand and minimum fibre modification on the other were compared. Modification fully enhanced reinforcement in tensile properties of composites, especially in the case of matrix modified with PMPPIC. Even though silane-treated fibres showed similar results with that of PMPPIC especially after immersion in water, it made the composite brittle as observed during testing of specimen. Interestingly, hybrid formulated in this work presented some level of increase in strength after immersion in water through the strengthening of bonds between fibres and matrix, which invariably reduced water absorption. Modifying matrix and combining it with treated fibres did not give better result when compared partial treatment of the composite. Hence, irrespective of either fibre surface modification or matrix modification, reinforcement with respect to treatment depends on the type of modifier used and not where it was applied in composite formulation.

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