

SELECTED PROPERTIES OF HAND-LAID AND COMPRESSION MOLDED VINYL ESTER AND PINEAPPLE LEAF FIBER (PALF)-REINFORCED VINYL ESTER COMPOSITES

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ABSTRACT

Pineapple leaf fibers (PALF) are of little use in Malaysia despite being mechanically and environmentally sound. Untreated and bleached PALF were used to reinforce vinyl ester (VE) utilizing hand lay-up (HLU) and liquid compression molding (LCM). Mechanical properties, water absorption and thermal stability were compared to neat resin and glass fiber-reinforced VE. Adding PALF reduced machinability dramatically while generally enhancing VE mechanical properties. Bleached PALF improved fiber-matrix adhesion compared to untreated PALF. Molding resin and composites with pressure enhanced water resistance by 2 – 3 times. Water absorption increased with increasing PALF while bleached PALF somewhat decreased water absorption due to improved wetting. PALF slightly reduced VE thermal stability although enhancement is expected upon using bleached PALF. Molding pressure has no effect on thermal stability of VE and PALF-reinforced VE. This study indicated that PALF may be used to reinforce VE to produce composites utilizing LCM and inexpensive bleach pretreatment.

Keywords: Natural fibers, PALF, liquid compression molding, vinyl ester, mechanical properties

1. INTRODUCTION

Recently, natural plant fibers have been used in scientific researches as potential alternatives to glass fibers (GF) in fiber-reinforced plastics (FRP). Relative to glass fibers, these lignocellulosic fibers have lower densities, cost relatively lower, consume lesser energies during production, pose no abrasion to machines and have no health risk when inhaled. Furthermore, natural fibers are also widely available, renewable, recyclable, biodegradable and are carbon dioxide (CO₂) neutral (Mallick, 1993). From a large selection of plant fibers, pineapple leaf fibers (PALF) obtained from the leaves of pineapple plants, *ananas comosus*, from *Bromeliaceae* family have among the highest cellulose contents which make the fibers mechanically sound (Mohnaty *et al*, 2005]. According to numerous literature (Mohanty *et al*, 2005; Arib *et al*, 2004; Taj *et al*, 2007; John and Anandjiwala, 2008) however, PALF seem to be among the least studied fibers especially for reinforcing plastics although this application is now becoming an important

research area (Mishra *et al*, 2004. Pineapple is one of the most important tropical fruits in Malaysia and the industry importance and plantation areas are increasing (MPIB, 2009). Focusing on the fruits and related foodstuffs, the industry treats pineapple leaves as agricultural wastes composted or burned by farmers after the fruits are harvested (Abdul Khalil *et al*, 2006). It is high time that value-added applications such as polymer composites utilizing excellent fibers from these pineapple leaves be developed. Despite numerous advantages, PALF possess inherent problems such as poor interfacial fiber-matrix adhesion and great affinity to water which hinder their use as reinforcement in composites. As the quality of fiber-matrix interface is significant in composites, there has been a large amount of research conducted during the past two decades on optimizing the interfacial adhesion between natural fibers and polymer matrices (John and Anandjiwala, 2008). However, no report has been found on the use of common household bleach containing sodium hypochlorite (NaOCl) typically used to bleach cellulosic fabrics and textiles to treat natural fibers like PALF prior to being used as composite reinforcements. Literature and bibliographic search also indicated that there has been no works reported on PALF-vinyl ester composites. Vinyl esters are expected to be tough, resilient and less susceptible to water degradation by hydrolysis (Li, 1998). Furthermore, the fiber-matrix adhesion measured by interfacial shear stress (IFSS) has been reported to be higher for natural fiber-vinyl ester compared to those of other matrices (Joffe *et al*, 2003). Furthermore, as highlighted by (Arib *et al*, 2004), most works on PALF-reinforced thermoset composites used hand lay-up method in sample preparation and very few if any reported the use of liquid compression molding process.

In this study, neat vinyl ester sheets and composites reinforced with PALF and glass fibers were fabricated using hand lay-up and liquid compression molding techniques. Both untreated and bleached PALF in the form of random and unidirectional PALF mats were used to reinforce the matrix. Mechanical properties, water absorption and thermal stability of various vinyl ester sheets and composites were measured in order to evaluate the viability of PALF-vinyl ester eco-composites and to better understand the effects of molding pressure and fiber pretreatment on these composite properties.

2. EXPERIMENTAL

2.1 Materials

Leaves from Josapine (Spanish) cultivar chosen for this study as justified in (Mohamed *et al*, 2009) were obtained from a plantation in Sepang, Selangor, Malaysia. Leaves were taken from plants recently harvested and PALF fiber bundles were carefully separated and manual cleaning was done to remove epidermal tissues as much as possible. The resin used in this experiment was epoxy vinyl ester, Hetron 922, supplied by Act (UK) Ltd. Antonox-90 methyl ethyl ketone peroxide (MEKP) supplied by the same supplier was used as the catalyst.

2.2 Composite preparation

PALF bundles chopped into 50 mm long fibers were used to form wet-laid random non-woven mats. Fiber mat was laid in the cavity of a three-piece stainless steel mold before pouring the resin-catalyst mixture. A unidirectional fiber mat was formed by manually placing 150 mm long PALF in the mold. Hetron 922 vinyl ester resin was catalyzed with 1.5 phr of MEKP and the mixture stirred for one minute before pouring on the fiber mat. A hydraulic compression molding machine, Technopress 40HC-B (Technovation), was used in liquid compression molding of the composite sheets. The resin and fibers were preheated for five minutes at 50 °C on the mold before they were pressed under 5.6 MPa for ten minutes at 50 °C. The composite sheet was heated at the same temperature without pressure for another 10 minutes before been cooled down at 20 °C without pressure for 10 minutes. In addition to PALF-reinforced VER, composite samples reinforced with glass fiber chopped strand mats (CSM) as well as neat VER were similarly molded as comparison. All samples were left to cure at ambient temperature for a minimum of 72 hours. Test specimens were end-milled with a TiN-coated 3 mm end-mill cutter into required dimensions using a Pro-light machining center (Light Machines Corp.). Other neat resin and composite samples were also fabricated using hand lay-up method for further comparison. Table 1 gives the details of various neat resin and composite samples produced.

Table 1 Details of test samples

Sample	Fiber Wt%	Fiber Configuration	S.G
HLU neat VER	0		1.20
HLU PALF-VER	15.0	Unidirectional	1.19
LCM neat VER	0		1.20
LCM PALF-VER A	14.6	Random	1.22
LCM PALF-VER B	24.8	Random	1.20
LCM PALF-VER C	28.5	Unidirectional	1.21
LCM GF-VER	40.0	Random	1.52

2.3 Testing

The Archimedes principle was used to determine the specific densities of the prepared polymer and composite sheets. An Alpha Mirage Electronic Densimeter MD-300S with a density resolution of 0.001 g/cm³ was used in this test. Ethyl alcohol with a specific gravity of 0.975 was used as the medium.

Tensile tests were carried out according to ASTM D638 using an Instron 3365 tensile testing machine fitted with a 10 kN load cell and operated at a cross-head speed of 20 mm/min. Specimens measuring 90 mm long, 10 mm wide and 3 mm thick were tested with a gage length of 50 mm. Flexural properties of the sheets were measured using a similar Instron 3365 with a 5 kN load cell utilizing specimens 63 mm long, 10 mm wide and 3 mm thick and ASTM D790 as a reference. A span to thickness ratio of 16 and a crosshead speed of 2 mm/min were used. Un-notched Charpy impact tests were carried out on specimens having 63 mm length, 10 mm width and 3 mm thickness using an Advanced Pendulum Impact tester (Dynisco Polymer Test) and ASTM D256 was used as a reference. In all the above tests five specimens were tested.

Square specimens 10 mm by 10 mm and 3 mm thickness were cut from the neat resin sheets and composites for studying the kinetics of water absorption as per ASTM D570. These samples were dried for 24 hours at 50 °C in an air oven until constant weights were obtained. Conditioned samples were then immersed in distilled water at a temperature of 33 °C in an oven. Samples were periodically taken out of the water and surface water wiped with tissue paper before weighing to the nearest 0.1 mg using a Sartorius CP224S balance. The samples were re-immersed in distilled water immediately. Weight readings of the samples were taken until the weight of each sample reached the equilibrium value.

The neat resin and composite samples were also tested for their thermophysical properties using a Perkin Elmer Diamond TG/DTA analyzer. Specimens were scanned from 30 – 600 °C at a heating rate of 10 °C min⁻¹ in a nitrogen flow of 200 ml/min.

Fractured specimens were examined under scanning electron microscope, JEOL JSM – 5600 after undergoing carbon coating using a Polaron SC7640 sputter coater. Samples were mounted on carbon tape before sputter coated and observed under SEM operated at 5 - 15 kV.

3. RESULTS AND DISCUSSION

The specific gravities of various neat resin and composite samples given in Table 1 indicated that compression-molded samples were denser than hand-laid ones. The use of hand lay-up method resulted in large amount of voids leading to

lower specific gravities. This was made worse by the addition of PALF. The densities of various PALF-reinforced composites were varying rather than increasing with increasing PALF weight fraction due to difficulty in properly distributing the fibers within the matrix. Estimates however gave an average PALF specific gravity of 1.283, an intermediate value between those reported in (Arib *et al*, 2004; George *et al*, 1997).

The mechanical properties of various neat resin and composites samples are given in Table 2. Generally, the mechanical properties of PALF-reinforced vinyl ester composites were very low due to the inability to end-mill the test specimens satisfactorily. Even though no efforts were spared to optimize the composite cure, the results obtained were significant and may be used for comparison purpose. Furthermore, some of the results may be used to highlight important findings of this study. It must therefore be noted that adding tough natural fibers into vinyl ester reduced the composite machinability dramatically as clearly illustrated by Figure 1 (a-e). Composites reinforced with random mats (Figure 1c and d) had worse machinability than that with unidirectional PALF (Figure 1e). To increase usage of natural fibers as viable replacement of glass fibers in polymer composites, the machinability of natural fiber-reinforced composites must be investigated and subsequently improved. This shall allow machining processes such as computer-controlled milling to be carried out without composite de-lamination while ensuring part dimensional accuracy and consistency.

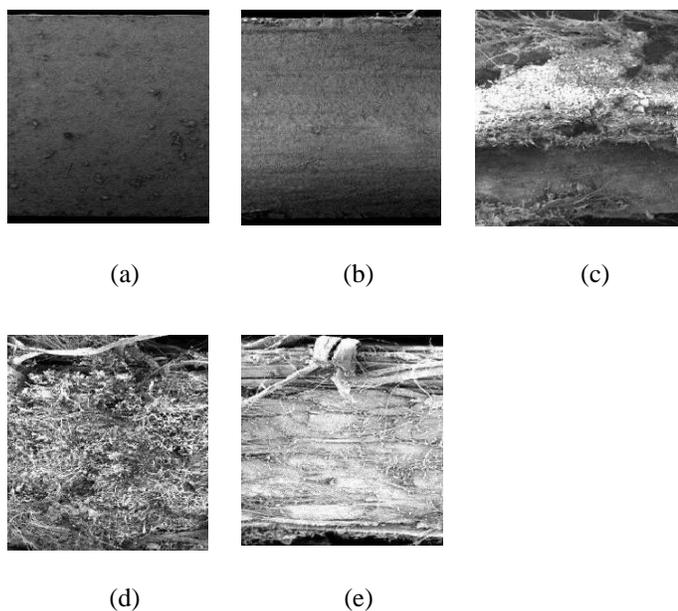


Figure 1 End-milling results of various LCM composite samples; a) neat VER, b) GF-VER, c) PALF-VER A, d) PALF-VER B and e) PALF-VER C.

Due to the inability to machine the specimens satisfactorily, the mechanical properties obtained for PALF-reinforced vinyl ester composites must be taken as absolute lower bounds. The values may however serve as indicators of the potentiality of PALF as efficient reinforcement to vinyl ester resin thus necessitating further investigations. It cannot be confirmed that adding low amount of PALF jeopardized the mechanical properties of vinyl ester due to the fibers serving mainly as defects attributed to poor specimen preparation. As an example, some values of tensile modulus of PALF-VER A improved as much as 26% at 14.6 wt% PALF.

Using rule of mixture (ROM) and mean values of tensile strength of neat VER and PALF-VER C, the mean effective PALF fiber strength was calculated to be only approximately 110 MPa; nearly half the mean fiber strength obtained in (Mohamed *et al*, 2009). Taking the mean PALF fiber strength value to be 198.2 MPa and the other relevant values as they were, a much higher tensile strength of 85.9 MPa was obtained at 28.5 wt% PALF. Assuming linear relationship as indicated by ROM, normalizing PALF-VER C at 40 wt% would generate composites as strong as those reinforced with 40wt% GF CSM. Comparing the same increment in PALF content, the increase in tensile strength was similar or higher than those achieved in the case of PALF-reinforced unsaturated polyester reported in (Mishra *et al*, 2001).

Pull-out lengths of PALF and glass fibers in broken composite samples were observed visually and under SEM. Figure 2 (a – c) gives a small selection of SEM micrographs obtained. For bleached PALF, the matrix adhered excellently and the fibers were defibrillated and torn apart. The lengths of PALF pulled out were almost non-existent. In contrast, untreated PALF had poor fiber-matrix adhesion indicated by long PALF pull out lengths clearly shown in Figure 2b. This behavior was somewhat similar to that of glass fiber-reinforced vinyl ester illustrated in Figure 2c.

Table 2 Mechanical properties of vinyl ester sheet and composites.

Sample	Tensile		EAB (%)	Flexural		Impact ST (kJ/m ²)
	ST (MPa)	MD		ST (MPa)	MD	
LCM neat VER	47.3	2.2	3.7	112.0	2.1	10.6
LCM PALF A	20.5	2.6	1.0	66.1	2.1	7.1
LCM PALF B	23.3	1.6	2.4	24.8	0.5	9.5
LCM PALF UD	64.9	3.9	4.2	82.4	2.6	13.8
LCM GF CSM	113.8	5.2	4.8	167.5	5.5	50.0

ST – strength, MD – modulus

Though there were no data available to give any comparison between properties of composites reinforced with bleached PALF and untreated PALF, this morphological study indicated clearly that the possible improvement in fiber-matrix adhesion as a result of pretreating PALF with dilute aqueous NaOCl solution. In terms of composite toughness, adding a certain content of PALF to VER may improve this property. Impact testing yielded reasonable results as exemplified by the impact strength of GF-VER of 50.0 kJ/m^2 at volume fraction (v_f) of 0.225% as compared to 50.0 kJ/m^2 for glass sheet molding compound (SMC) at v_f of 15% (Marsh, 2003). In addition to random chopped fibers, SMC is known to comprise of other constituents such as calcium carbonate (CaCO_3) that change the composite impact property. Lower impact strength of PALF-VER A may serve as an indication of improved fiber-matrix adhesion resulting in lower energy dissipation through fiber de-bonding and pull-outs. Some high toughness values were recorded for composites reinforced with chopped untreated PALF ($v_f = 0.22$) and unidirectional PALF ($v_f = 0.23$) in the range reported for flax SMC with comparable v_f (Marsh, 2003).

Water absorption tests of various samples yielded results of reasonable values and variations. The use of liquid compression molding was advantageous in reducing water absorption significantly for neat resin and composites. Without consolidating pressure water absorptions of neat resin and composites were between 2 – 3 times higher than those molded with pressure. Figure 3 shows a reduction in water absorption of compression-molded GF-VER composite compared to that of molded vinyl ester. Wetting of glass fibers by vinyl ester was perfect and water absorption was only possible via the voids and cracks in the neat resin as glass fibers are impervious. The reduction in water absorbed was due to the reduction in resin volume. As shown in Figure 4(a & b), consolidating pressure clearly reduces the networks of cracks present in compression-molded sample compared to those in hand-laid sample.

Adding lignocellulosic PALF dramatically increased composite water absorption and it increased with fiber content as found by others (George *et al*, 1997). Assuming linear relationship between water absorption and fiber content, bleached PALF had somewhat lower water absorption indicating the potentiality of this inexpensive method to enhance PALF and the resultant PALF-reinforced vinyl ester composites in terms of lower water absorption. This may be due to closer packing of the cellulose molecules and the increase in PALF crystallinity caused by the dilute NaOCl aqueous solution (Mohamed *et al*, 2009). Water was absorbed through relatively constricted lumens in the PALF fibers in addition to diffusing through voids and cracks in the matrix. The lack of PALF wetting by vinyl ester resin is not thought to play an important role due to the use of pressure as previously explained and due to excellent vinyl ester-natural fiber wetting (Komus *et al*, 2008). Without consolidating pressure however, the matrix may not have

penetrated the gaps between the individual fibers resulting in the increase in water absorption relative to that of the molded composite of similar fiber weight fraction.

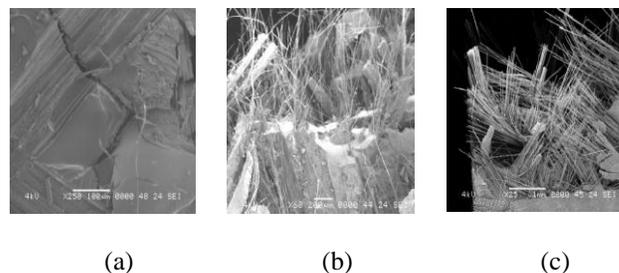


Figure 2 Micrographs of broken vinyl ester composites reinforced by a) bleached PALF, b) untreated PALF and c) glass fibers.

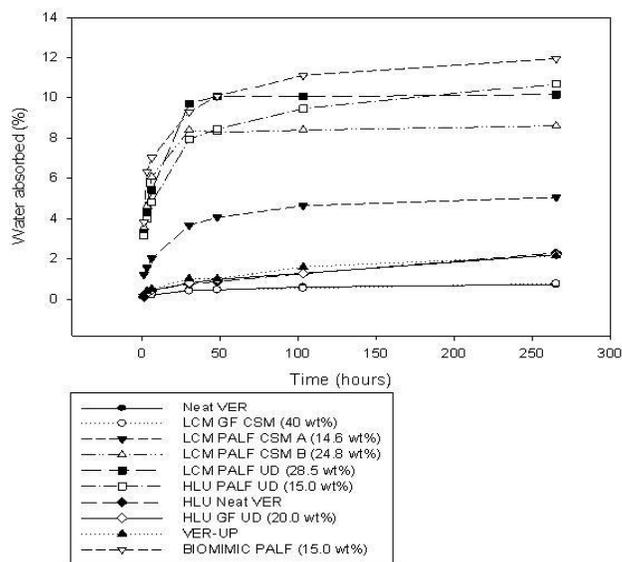


Figure 3 Water absorption of various polymer sheets and composites produced by HLU and LCM

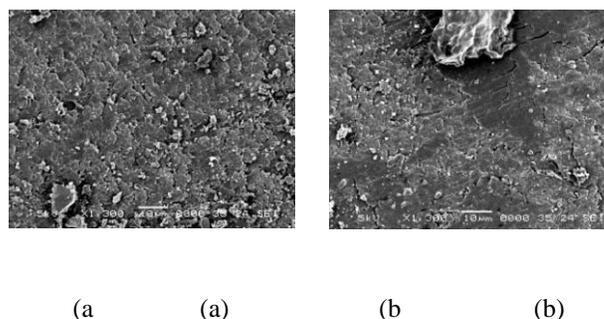


Figure 4. SEM micrographs of voids and cracks in (a) LCM neat VER and (b) HLU neat VER specimens.

Figure 5 shows the thermogravimetric curves for various molded resin and composite samples. The thermal stabilities of vinyl ester and PALF-reinforced vinyl ester (curves b-e) are higher than that of PALF due to lower PALF thermal stability and rapid fiber degradation at 230 °C. Adding about 15 wt% of PALF to vinyl ester caused slight decrease in the thermal stability of vinyl ester while molding pressure had no noticeable effects. The PALF used in this study were pretreated with 1% aqueous sodium hypochlorite for 2 hours while in [Mohamed *et al*, 2009] a 2% bleach solution was used for 4 hours which resulted in a shift in second PALF degradation phase by almost 20 °C. It is therefore expected that using PALF bleached with a higher concentration aqueous NaOCl solution would lead to improved composite thermal stability. This means that aqueous sodium hypochlorite solution may still be beneficial in the effort to produce vinyl ester composites with enhanced thermal stability.

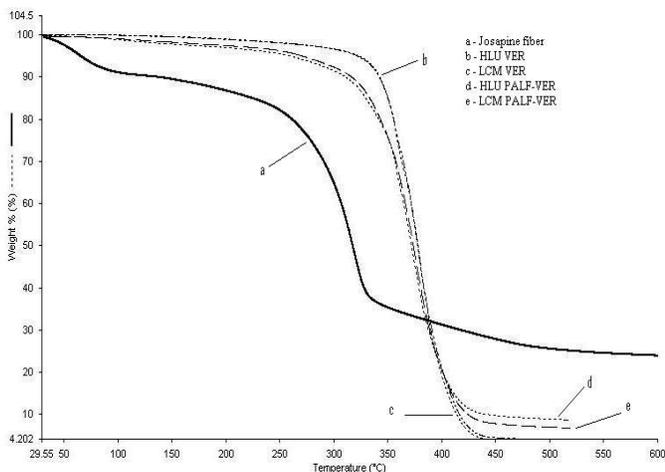


Figure 5 TG curves for various neat resins and composite samples.

4. CONCLUSION

It may be concluded from the present study that it is viable to use untreated PALF to reinforce vinyl ester resin to produce real composites. There is a real need to investigate the machinability of PALF-reinforced polymer composites in order to promote the use of PALF as an alternative to glass fibers. The use of liquid compression molding is clearly advantageous in enhancing PALF-reinforced vinyl ester composite properties especially their water resistance. Cost-effective pretreatment using dilute aqueous solution of sodium hypochlorite can be used to treat PALF resulting in enhanced mechanical properties, reduced water absorption and enhanced thermal stability of PALF-reinforced vinyl ester eco-composites.

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