Synthesis and Characterization of New Unsaturated Polyesters for Composite Applications

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ABSTRACT

Bis-(2-hydroxyethyl) fumarate (III) and Bis-(6-hydroxyhexyl) fumarate (IV) were synthesized from ethylene glycol and 1, 6-hexanediol with fumaric acid in the presence of p-toluene sulfonic acid as catalyst. The chemical structures were confirmed by CHN analysis, FT-IR and ^{1}H-NMR spectroscopy. The new unsaturated polyesters were carried out by the condensation reaction between terepthaloyl chloride and monomer III and IV. The chemical structures of these polymers were confirmed by CHN analyses, FT-IR, ^{1}H-NMR, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). New oil palm empty fruit bunches reinforced polyester composite derived from the new unsaturated polyester resins containing bis-(2-hydroxyethyl) fumarate and bis-(6-hydroxyhexyl) fumarate were prepared. The mechanical (tensile, flexural and impact properties) and physical properties (water absorption) of oil palm empty fruit bunches reinforced polyester composite were also studied.

Keywords: *bis-(2-hydroxyethyl) fumarate, bis-(6-hydroxyhexyl) fumarate, composite, synthesis, oil palm empty fruit bunches, new unsaturated polyester*

Introduction

Unsaturated polyesters have been recently known as an important class of high performance and engineering polymers (Martin, 1999; Han & Bhowmik, 1997). Unsaturated polyesters are extremely versatile in properties and applications and have been a popular thermoset used as the matrix in polymer composites such as fibre-reinforced plastics and polymer concretes. They are widely produced industrially as they possess many advantages compared to other thermosetting resins including good balance of properties, room temperature cure capability and are relatively inexpensive (Seymour & Kirshenbaum, 1986; Sharifah et al., 2005). However, they are generally difficult to process because of their high temperature melting temperature or high glass-transition temperature by virtue their rigid structure (Bahman et al., 2004). As a result, flexible aliphatic units, methylene ($-CH_2-$) units were introduced in the backbone of the polymer. The presence of methylene groups in the repeat units also enhanced the processing and fabricating polyesters (Lagowski, 2004). In this paper, we report the synthesis of new unsaturated polyesters resin containing methylene groups as a matrix in reinforced composites.

The reinforcement of polyesters with oil palm empty fruit bunch fibres have been widely reported (Abdul Khalil et al., 2001; Mohamad et al., 2005). In this study, oil palm empty fruit bunches (EFB) has been chosen as a fibre material because of low cost, abundant in nature, low density and biodegradility (Hill & Abdul Khalil, 2000; Hill & Abdul Khalil, 2000a). It has been found to be an important source of fibre for composites and other industrial applications. Oil palm also is a native commercial crop in Malaysia. Over 30 million tones of its residues were generated annually (Mohamad et al., 2005). The properties of the composites were then compared with conventional resin composites.

Materials and Methods

Materials

Fumaric acid, 1, 6-hexanediol and terepthaloyl chloride were purchased from Fluka Co. and used without further purification. Ethylene glycol, Ethanol, Methylene Chloride, Toluene and Tetrahydrofuran (THF) were purchased from Aldrich Co. and purified by distillation under reduced pressure. Triethylamine (TEA) was purchased from Fisher Co. and distilled over calcium hydride (CaH_2) and stored in a septum sealed bottle until use.

Characterization

FTIR spectrophotometer measured in a Nicolet Avatar Model 360 instrument using KBr pellet for polymers and monomers ranged from 4000 to 400 cm^{-1}. Using Bruker 400 MHz NMR spectrometer in DMSO–d_6 as the solvent and Tetramethylsilane (TMS) as the internal reference ^{1}H–NMR spectra were obtained. Thermogravimetric analysis (TGA) was carried out in nitrogen with Perkin–Elmer TGA7 series at 10 $^\circ$C min^{-1}. Differential scanning calorimetry (DSC) measurements were carried out with a Perkin–Elmer DSC7 series at heating rate of 10 $^\circ$C min^{-1} in nitrogen. Inherent viscosities of polymer solutions (0.1g/dL in DMSO) were determined at 30 $^\circ$C in an Ubbelohde capillary viscometer.

Preparation of Bis (2-hydroxyethyl) fumarate (III)

Fumaric acid (0.25 mol) was added to ethylene glycol (1.5 mol) in the presence of *p*-toluene sulfonic acid as catalyst. The mixture was refluxed for 24 h at 120 $^\circ$C with stirring in 500 ml round bottom flask during the reaction, precipitated, filtered, washed several times with aqueous hydrogen carbonate and dried. Final purification was carried out by re–crystallization from Tetrahydrofuran (THF) to give white crystals. Yield was 70 %. Elemental analysis: Found: C, 58.09; H, 4.40; $C_{16}H_{14}O_8$ Calc.: C, 57.93; H, 4.19.

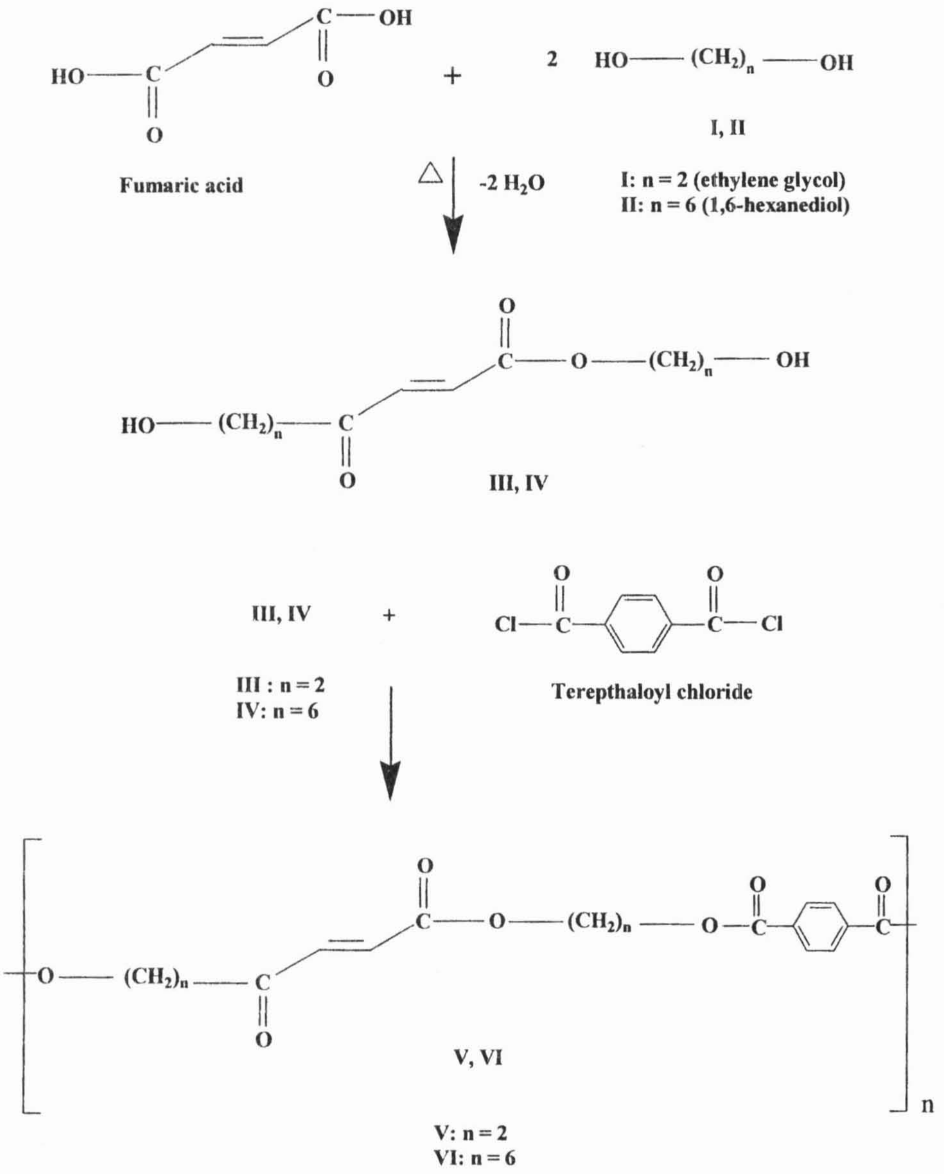
Preparation of Bis (6-hydroxyhexyl) fumarate (IV)

This compound was prepared by following the procedure of the preparation of bis (2-hdroxyethyl) fumarate except that 1, 6-hexanediol was substituted for ethylene glycol. The percent yield was 68 %. Elemental analysis: Found: C, 47.38; H, 6.12; $C_{24}H_{30}O_8$ Calc.: C, 47.06; H, 6.19.

Preparation of Polymers (V, VI)

The general polymerization equation and the structures are given in Scheme 1. Trietylamine (0.01 mol) in 25 ml of dichloromethane was added drop wise to a mixture of monomer III and IV (0.005 mol) in terephthaloyl chloride (0.005 mol) in 25 ml of dichloromethane at 20 $^\circ$C for 5 minutes. Subsequently, the temperature of the reaction mixture was maintained and continued stirring for 3 hours. The unsaturated polyesters V and VI were precipitated in absolute ethanol, filtered, and washed several times with ethanol then dried for 24 hours in a vacuum oven at 75 ° C. The results are summarised in Table 1.

Scheme I



Scheme 1. Schematic Diagram of monomers and Polymers of Unsaturated Polyester Resin

Table 1. Yield, Elemental Analysis and Thermal Properties of Unsaturated Polyesters

Polymer	Yield %	C%	H%	$^{(a)}T_g$	$^{(b)}T_m$
V	70	(57.49) 56.30	(4.19) 3.97	210 ^{0}C	255 ^{0}C
VI	68	(47.06) 46.38	(5.88) 5.55	190 ^{0}C	225 ^{0}C

* The data in the bracket were calculated; (a) Glass transition temperature, (b) Melting point temperature

Preparation of Composites (A, B and C)

Oil palm empty fruit bunches (OPEFB) fibres were washed, cut and chipped before fibre processing and mat preparation. Fibre mats were prepared by using the equipment for Manual Hand Sheet Paper Making. Fibre mats were then dried in an oven at 105 °C for 6 hours. The unsaturated polyester resin was mixed well with the initiator, methyl ethyl ketone peroxide (MEKP), in required amounts. Then, resin was poured onto the fibre mat about 10 minutes under vacuum impregnation to ensure good delivery of the resin. The wetted fibres mat in the mould was then placed between the electrically heated platens of a hot press at 100 °C. The mould was heated for 25 minutes at a moulding pressure 8 MPa. The composites were post-cured at 80 °C overnight in an oven. The composite was then ready for characterization by using different types of unsaturated polyesters matrix. Types A based on new unsaturated polyester resin V with EFB, types B based on new unsaturated polyester resin VI with EFB, while types C based on commercial unsaturated polyester resin produced by Euro Chemo-Pharma Sdn. Bhd with EFB. The formulation used consisted 100 parts resin by weight to 1.5 parts catalyst (MEKP) from Euro Chemo-Pharma Sdn. Bhd (Catalyst M).

Mechanical Tests

The tensile, flexural and impact tests of unsaturated polyester composites were studied. The tensile tests were performed using an Instron Universal Testing Machine Model 1114. The tensile test was carried out by using rectangular strips of 150mm x 20mm x 10 mm. The width and thickness of the specimens were measured and recorded. Specimens were tested at a cross-head speed of 3 mm/min and gauge length of 60 mm. The tests were carried out accordance with ASTM D 638 (ASTM, 2000). Tensile strength, tensile modulus and elongation at break were calculated from this test.

Flexural tests were performed according to ASTM D 790 by using the same machine (ASTM, 2000). The width and thickness of the specimens were measured and recorded. Specimens were tested at a crosshead speed of 3 mm/min. Rectangular strips of 160mm x 20mm x 10mm were carefully sanded using a fine graded sandpaper to remove small cracks. The flexural strength and flexural modulus were calculated from this test.

Charpy impact tests were performed using the Impact Pendulum Tester (Zwick) Model CS-1370. The width and thickness of the unnotched specimen were measured and recorded. The tests were carried out in accordance with ASTM D 256 (ASTM, 2000). The impact test was carried out on polished samples with dimensions of 70mm x 15mm x 10mm. The samples were rigidly mounted on a vertical position and were stricken struck using a pendulum with a force of 10 Joule at the center of the samples. The works of fracture values were calculated. All the specimens were conditioned at ambient temperature (25± 3 °C) and relative humidity (30% ± 2) before testing.

Physical Properties

The physical properties basically measure the bulk properties of the composite. Water absorption tests were carried out according to ASTM D570 at ambient temperature (25± 3 °C) by using Mettler balance type AJ150. The water absorption was determined by weighing the samples at weekly intervals time period up to 8 weeks (ASTM, 2000). The samples were weighed and immersed in water. They were removed at specified intervals, being gently blotted with tissue paper to remove the excess water on the surface, and then the weight was recorded. The water absorption was calculated according to the equation:

$$\text{Water absorption, WA (\%)} = \frac{M_2 - M_1}{M_1} \text{ X } 100$$

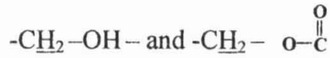
where M_2 is the mass of the sample after immersion (in grams) and M_1 is the mass of the same sample before immersion (in grams).

Results and Discussions

Structural Elucidation

The monomers showed bands centered at 3400-3439 cm^{-1} characteristic of the hydroxyl groups (-OH) and at 1704-1717 cm^{-1} due to the carbonyl stretching ($C = O$). In addition to the absorption bands due to the CH alkene (–HC=CH–) at 3069-3210 cm^{-1}.

The ^{1}H-NMR spectra of the monomers exhibit characteristic singlet peaks for protons of hydroxyl group in the range 4-5 ppm. Two characteristic triplet peaks in the range of 3.6-3.9 ppm and 3.5-4.1 ppm were due to the protons in the



$$\text{-C}\underline{\text{H}}_2\text{–OH – and -C}\underline{\text{H}}_2\text{– O–}\overset{\overset{\text{O}}{\|}}{\text{C}}$$

for monomer III and IV, respectively. The results of elemental and spectroscopic analysis confirmed the structure of the monomer III and IV.

The identity and purity of unsaturated polyesters were confirmed by elemental analysis, FTIR and ^{1}H–NMR spectroscopy. The FTIR spectrum of polymer V in Figure 1 showed the characteristic absorption bands of the carbonyl groups at 1791 cm^{-1} and 1722 cm^{-1}, respectively. This apparently confirmed the ester linkage. Apart from these absorption bands, the presence of the -C=C- aromatic and CH alkene (-CH=CH-) are also observed at 1469 cm^1 and at 2937 cm^{-1}, respectively.

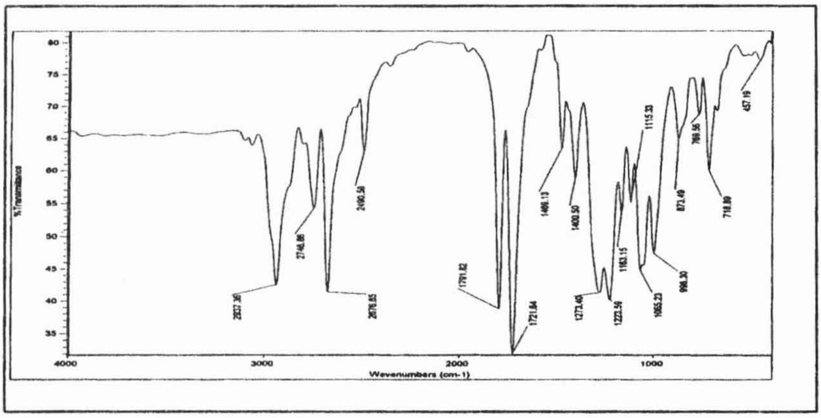


Figure 1. FT-IR Spectrum of Polymer V

The ^{1}H–NMR spectrum of the polymer VI was showed in Figure 2. A multiplet peak at δ = 1.3 and 1.6 ppm were due to the protons of $C\underline{H_2}–C\underline{H_2}$ and $C\underline{H_2}–CH_2O$, respectively. The spectrum also showed a characteristic triplet peak at 3.35 ppm due to the protons in the ester –$C\underline{H_2}$–COO linkages. In addition, two characteristics duplet peaks centre at 6.2 ppm and 7.3 ppm were due to the proton in the p-substitute ring from terepthaloyl chloride.

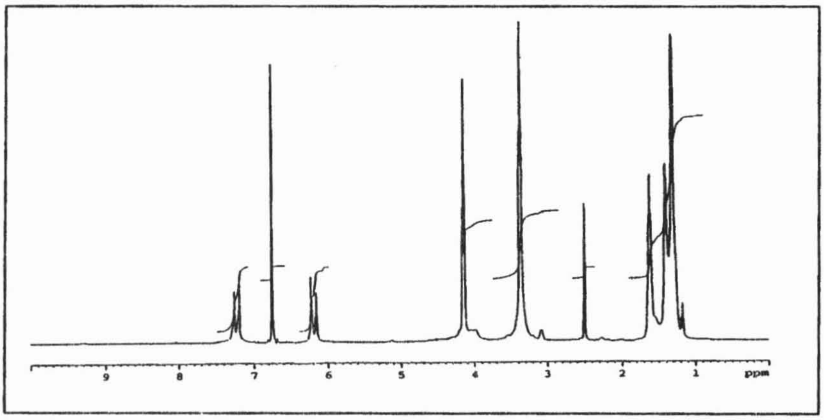


Figure 2. ^{1}H-NMR Spectroscopy of Polymer VI

Thermal stability and degradation of unsaturated polyesters V and VI were analyzed based on thermograms obtained from TGA at constant heating rate of 10 °C min^{-1} in the temperature range of 40 to 800 °C under nitrogen. Equal weights were used in all experiments to eliminate the mass effect. From the thermogram data, one step at 380 °C for 10% degradation (T_{10}) was observed in polymer V as shown in Figure 3. It was due to the degradation of methylene $(-CH_2)_n$ - and ester groups. The char yield was about 8 %. While for polymer VI, two steps were observed at 250 °C and 380 °C due to the cleavage of aliphatic group and ester group degradation, respectively. The char yield was about 8%.

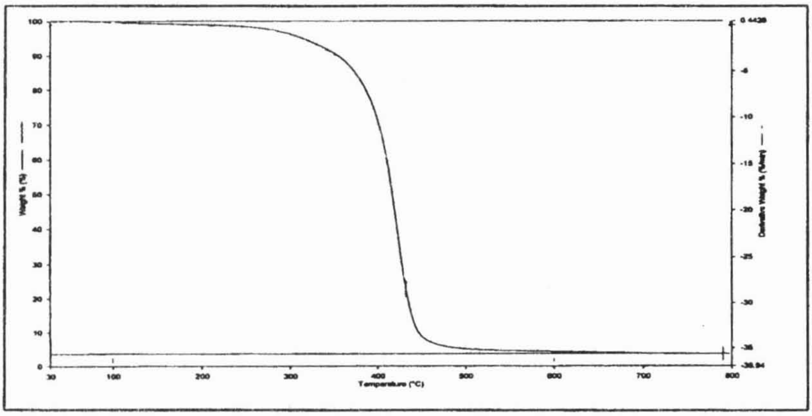


Figure 3. Thermogravimetric Analysis of Polymer V

The results imply that the presence of methylene spacers in the backbone of unsaturated polyester decrease the melting point thus make it easy to process. This is similar to what has been reported by earlier study (Abdul Khalil et al., 2001) on the effect of these groups conferring thermal stability in aromatic polyester.

From DSC data, single endothermic peak was observed during first heating in the polymer V and VI. No transition is observed during cooling or second heating. For polymer V, the glass transition temperature, T_g was 210 °C and melting point temperature, T_m was 255 °C. While for polymer VI, T_g was 190 °C and T_m was 225 °C.

The unsaturated polyester V and VI were soluble in petroleum ether and dimethyl sulfoxide (DMSO), whereas insoluble in common solvents such as methanol, benzene, chloroform, toluene and diethyl ether.

Mechanical Properties of Composites

OPEFB was selected for this work because abundant are available in Malaysia and good fibre alignment during composite manufacture (Mohamad et al., 2005). Types A was new unsaturated polyester resin based on monomer III, types B was new unsaturated polyester resin based on monomer IV, while types C was commercial unsaturated polyester resin produced by Euro Chemo-Pharma Sdn. Bhd. The formulation was used consisted 100 parts of resin by weight to 1.5 parts of catalyst (MEKP) from Euro Chemo-Pharma Sdn. Bhd (Catalyst M).

The effect on mechanical properties of reinforced composites containing different types of polyesters matrix were studied and summarized in Table 2. It can be observed that the mechanical properties of composites increased with the presence of methylene spacers units in polyester matrix.

From the histograms of the tensile modulus (Figure 4) it may be observed that polyester A gave superior values as compared to the polyester B and C. Polyester matrix A shows the highest tensile properties as compared to polyester matrix B and C. This phenomenon was due to the structures of polyester matrix (A) that had two methylene units as compared to polyesters B (six methylene units) and C. The presence of methylene units affected the tensile properties of the composites by increasing flexibility of the main structures of polyesters (Abdul Khalil, 2001). Hence, the compatibility in the interfacial region between the OPEFB fibre and polyester matrix were observed. This phenomenon was due to the increased dipole-interaction in the matrix with the presence of methylene units in the main chain. This may lead to good bonding quality between functional groups in the matrix. This resulted in good mechanical properties of Polyester A as compared to Polyester B and C.

Table 2. Mechanical Properties of Reinforced Composites.

Composite	Tensile Strength (MPa) ± SD	Tensile Modulus (GPa) ± SD	Elongation at Break (%) ± SD	Flexural Strength (MPa) ± SD	Flexural Modulus (GPa) ± SD	Impact Strength (KJ/m^2) ± SD
Polyester A	43 ± 1.1	3.6 ± 0.7	4.0 ± 0.8	50.29 ± 1.3	4.1± 0.7	11.5 ± 0.8
Polyester B	39 ± 0.9	3.2 ± 0.5	3.2 ± 0.7	46.72± 1.1	3.8 ± 0.8	10.2 ± 0.9
Polyester C	35 ± 1.2	2.8 ± 0.6	2.7 ± 0.5	38.86 ± 1.0	3.4 ± 0.5	9.1 ± 0.6

*** SD = Standard derivation**

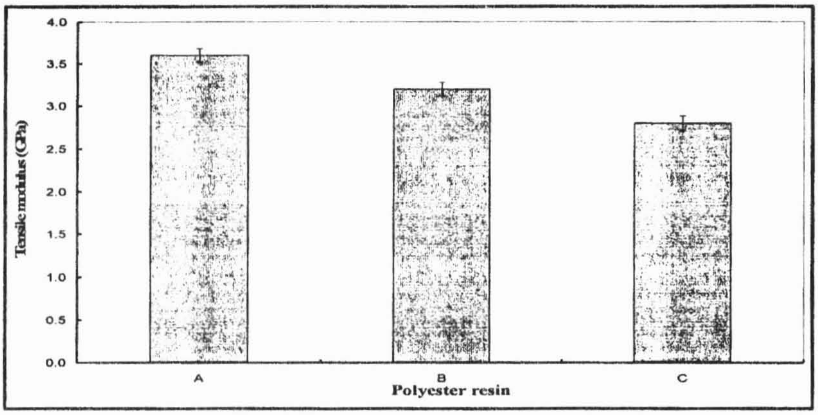


Figure 4. Tensile Modulus of the Reinforced Composites

Table 2 shows that all the mechanical properties follow the same trend as tensile modulus. The improvement in the flexural properties of the modified unsaturated polyester composite is attributed to the modifications at the molecular level of the matrix, which lead to fibre-matrix bonds, increased adhesion and more effective stress transfer. Hence, the compatibility in the interfacial region between the EFB fibre and polyester matrix were increased. This resulted in good mechanical properties of Polyester A as compared to Polyester B and C composite.

Polyester A composite gave the highest work of fracture values as compared to the polyester B and C composites. It has been reported by Oever et al. (in Bahman, 2004), that the Charpy impact strength decreased with enhanced fibre-matrix adhesion. Table 2 clearly shows that the impact strength of reinforced composites is significantly improved by the presence of methylene units. Composite fracture toughness is influenced by interlaminar and interfacial strength parameters. The fibres play a very important role in the impact resistance of the composite as they interact with the crack formation in the matrix and act as stress transferring medium. In this study, the impact strength increases because of the flexibility of the interface molecular chains. There is greater energy absorption in the composite. When the cracks moves forward, the chains motions change due to their flexibility and create a barrier to the crack growth. This resulted in good mechanical properties of Polyester A and B as compared to Polyester C.

The differences between the mechanical properties of polyester A when compared to the polyester B and C were also quite significant. From the overall results of tensile, flexural and impact properties, it can be concluded that the modification of the polymer structure and the additional monomer added to Polyester A and B made higher impact on the strength of the composite.

Physical Properties of Composites

The water absorption behaviour of the polyester A, B and C composites are depicted in the Figure 5. The water absorption curves of the composites displayed a typical Fickian behaviour where the mass of water absorbed by the composites increased linearly with square root of time and then gradually slow down until equilibrium plateau or complete saturation was reached.

Figure 5 showed that polyester C composite gave the highest values of water absorption as compared to the polyester A and B composite. It had been reported by fellow researchers (Lagowski, 2004) that the water absorption characteristic of a composite material is influenced by many factors such as temperature, fibre volume fraction, orientation of reinforcement, fibre and matrix characteristic such as polarity, extent of crosslinking and crystallinity of the matrix and presence of residual hardeners, area of exposed surface, duration of immersion in water, processing techniques and surface protection. For polyester A and B composite, the present of methylene units decreased the water absorption as compared to the polyester C.

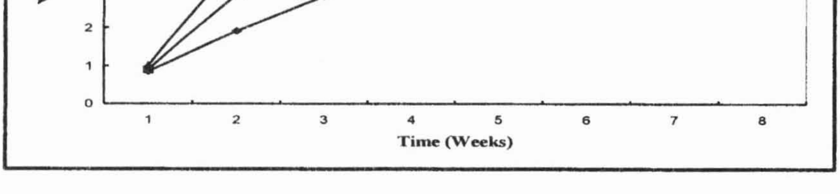


Figure 5. Water Absorption of the Reinforced Composites

The high water absorption behaviour of the oil palm fibre reinforced composite was mainly due to the highly hydrophilic nature of the oil palm fibres. The hydrophilic nature of the oil palm fibres was caused by the presence of polar groups such as hydroxyl, acetal and ether linkages in the cellulose structure of the fibres. The free hydroxyl groups from the cellulose and lignin structure of the oil palm fibre were able to interact with the water molecules by forming a hydrogen bond (Hill & Abdul Khalil, 2000). Porous surface structure of the oil palm fibre surface also facilitated the penetration of water into the fibre by capillary action especially when the fibre was exposed to water (Hill & Abdul Khalil, 2000a).

High water absorption behaviour of the oil palm fibre composites may be attributed by the swelling of the oil palm fibres (when exposed to water) leading to crack formation in the composite. Micro-crack formation created pathways for the water molecules to diffuse into the composite material hence enhancing the water absorption mechanism in the composite.

Conclusion

New unsaturated polyesters have been successfully synthesized and characterized by CHN elemental analysis, FTIR and ^{1}H–NMR techniques. Three formulations of composites comprised oil palm empty fruit bunches (EFB) in a matrix of one of three types of unsaturated polyester resin matrix, labeled A, B and C. Types A was new unsaturated polyester resin based on monomer III, types B was new unsaturated polyester resin based on monomer IV, while types C was commercial unsaturated polyester resin produced by Euro Chemo-Pharma Sdn. Bhd. Polyester A matrix composite possesses the highest mechanical properties as compared to the polyester B and C matrix composite. However, Polyester C matrix composite shows the highest water absorption as compared to polyester A and B. It demonstrated that bonding and interfacial adhesion between the fibre and matrix superior for the polyester A and B as compared to polyester C. From the overall results of mechanical and physical tests, it can be concluded that the modification of the polymer structure and additional monomer added to polyester A and B made a higher impact on the strength of the composites.

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