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## Performance Evaluation of PLA Based Biocomposites Reinforced with Photografted PALF

*Ocena učinkovitosti biokompozitov na osnovi polimlečne kisline, ojačenih s fotoinducirano cepljenimi ananasovimi listnimi vlakni*

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### Abstract

In this study, biocomposites were fabricated through a compression moulding technique that used untreated and grafted pineapple leaf fibre separately with polylactic acid (PLA) as a matrix. For grafting, pineapple leaf fibre (PALF) was chemically modified using two different monomers, i.e. 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA) solutions, in the presence of methanol (MeOH) and photoinitiator (Darocur-1664) under ultraviolet (UV) radiation with the aim of improving thermo-mechanical characteristics. Based on grafting efficiency and mechanical attributes, the intensity of UV radiation and monomer concentration were maximized. A series of solutions, created by varying the concentrations (10–60%) of monomers in MeOH along with 2% photoinitiator, were prepared. Experimental results revealed that composites made of PALF grafted with 30% HEMA at the 15<sup>th</sup> pass and 40% MMA at the 20<sup>th</sup> pass of UV radiation achieved the optimum mechanical properties compared with an untreated PALF/PLA composite. The optimized solutions were further enhanced by adding various concentrations (0.5–1.5%) of urea, with the best mechanical features achieved using a 1% concentration of urea. The chemical bonds formed due to photografting were viewed using Fourier transform infrared spectroscopy (FTIR). Degradation behaviour under heat was determined through thermogravimetric analysis, which found that photografted PALF/PLA showed significantly better thermal stability than the untreated composite sample. A water uptake test showed that grafting reduced the water retention capacity of the treated composite significantly. Crystallization characteristics were inspected using a differential scanning calorimeter, which showed that grafted PALF had a substantial effect on the degree of crystallization of PLA. In addition, scanning electron microscopy was used to monitor the interfacial bond, and revealed that interfacial adhesion was enhanced by the incorporation of photografted PALF into the matrix.

Keywords: photografting, PALF, thermo-mechanical properties, PLA, UV radiation

## Izvleček

V tej raziskavi so bili iz neobdelanih oziroma površinsko aktiviranih listnih ananasovih vlaken in polimlečne kisline (PLA) kot matrice po postopku oblikovanja z vlečenjem izdelani biokompoziti. Za izboljšanje termomehanskih lastnosti so bila ananasova listna vlakna (PALF) kemično modificirana s pomočjo dveh različnih monomerov, in sicer raztopine 2-hidroksietil metakrilata (HEMA) in raztopine metil metakrilata (MMA) v prisotnosti metanola (MeOH) in fotoiniciatorja (Darocur-1664) ter uporabe ultravijoličnega sevanja (UV). Intenziteta sevanja UV-žarkov in koncentracija monomera sta bila optimizirana glede na učinkovitost cepljenja in mehanske lastnosti kompozitov. Pripravljena je bila serija 10–60-odstotnih raztopin monomera v metanolu z dodatkom 2-odstotnega fotoiniciatorja. Eksperimentalni rezultati so pokazali, da so optimalne mehanske lastnosti dosegli kompoziti, ojačeni s predhodno cepljenimi vlakni PALF s 30-odstotnimi HEMA in 15 cikli osvetljevanja z UV-žarki, medtem ko so kompoziti iz predhodno cepljenih vlaken s 40-odstotno raztopino MMA dosegli optimalne lastnosti po 20 ciklih osvetljevanja z UV-žarki. Optimiziranim raztopinam je bila dodana sečnina v 0,5–1,5-odstotnih koncentracijah, pri čemer so bile najboljše mehanske lastnosti kompozitov dosežene z uporabo enoodstotne koncentracije sečnine. Kemične vezi, ki so nastale zaradi cepljenja vlaken, so bile dokazane s pomočjo infrardeče spektroskopije s Fourierjevo transformacijo (FTIR). Termogravimetrična analiza je pokazala, da je kompozit PALF/PLA s cepljenimi vlakni imel bistveno boljšo toplotno stabilnost kot kompozit PALF/PLA z neobdelanimi vlakni. Prav tako je cepljenje vlaken znatno zmanjšalo sposobnost zadrževanja vode v kompozitu. Z diferencialno termično kalorimetrijo je bilo ugotovljeno znatno zvišanje stopnje kristaliničnosti PLA v kompozitu PALF/PLA, ki je vseboval cepljena vlakna. Poleg tega je bila za spremljanje medfazne adhezije v kompozitu uporabljena tudi rastrska elektronska mikroskopija, ki je pokazala povečanje adhezije z vključitvijo fotoinduciranih cepljenih vlaken PALF v matrico. Ključne besede: fotoinducirano cepljenje, PALF, termomehanske lastnosti, PLA, UV-sevanje

## 1 Introduction

Interest in plant extracted lignocellulosic fibres as a reinforcing filler in composites has risen significantly during the last few decades for environmental reasons. However, research carried out in this area has determined that the integration of lignocellulosic fibres enhances the qualities of plastics. Plant-based fibres showed some notable benefits when compared to artificial fibres. For instance, they have comparable physico-mechanical properties, are inexpensive, cause no skin irritation, consume a small amount of energy during production and supply more  $O_2$  to the environment, and emit lower amounts of  $CO_2$  and toxic fumes during heat treatment, while the most prominent property is that they are renewable and decomposable. Due to their eco-friendly nature, these natural fibres are used in engineering applications in numerous sectors, such as the textile, automotive, aeronautic and construction industries, and in biomedical sectors [1–9], and thus encourage scientists to search for more and new classes of green and sustainable materials. In this regard, polylactic acid (PLA) is preferred for accelerating biodegradation in composites as a matrix because it is a biopolymer sourced from renewable products, it facilitates processing and has high thermo-mechanical properties compared to other thermoplastics, in combination with reduced manufacturing costs. PLA-based com-

posites reinforced with plant-sourced bast fibres have already been studied, although much variation has been found in their properties. To establish suitable applications of composites made with PLA, further enhancement is required through reinforcement, where natural fibres are preferred for that purpose [10, 11].

This study focuses on lingo-cellulosic pineapple fibre, which can serve as a favourable reinforcement, as it is abundantly available in tropical countries. Pineapple fibre is collected from the leaves of the pineapple plant, which are often discarded after the collecting of fruits. Currently, pineapple leaf fibre (PALF) holds no commercial value except for the nutritional purpose of its fruit, and is considered agro-waste. It is thus necessary to develop the standard of PALF by enhancing the physico-chemical and thermo-mechanical properties that might exaggerate the demand for consumption of the fibre. A study of PALF showed that it possesses outstanding thermal and mechanical characteristics that are equivalent to common lignocellulose fibres, such as jute, ramie and hemp, which are already established and extensively used as reinforcements in composite materials [12]. The fibre contains 67–82% cellulose, 18.8% hemicellulose, 4–15% lignin, 1–3% pectin, 4% waxing material, and a small amount of ash (3%). The density and diameter range is 1.07–1.52 g/cm<sup>3</sup> and 20–80  $\mu$ m respectively, together with a tensile strength (TS) of 413–1627

MPa, a Young's modulus (YM) of 34.5–82.51 GPa and elongation at break (Eb) of 1.6–3% [13, 14]. Thus, cellulose is the main component of PALF constituting anhydro-glucose units (1, 4- $\beta$  conformation). These units comprise –OH groups that are mainly responsible for the higher moisture take up of PALF as the main drawback relative to other plant-extracted natural fibres. Consequently, chemical treatment is crucial for enhancing the characteristic properties of the fibre, so that physical, mechanical and thermal properties, as well as sustainability, will be superior while at the same time preserving its environment-friendly property [15, 16].

For overcoming the problems associated with natural fibres, many researchers have attempted to develop existing properties using different chemical treatments, such as change of functionality, graft copolymerization and acetylation, with the aim of improving its quality and genetically enhancing end products for diversified applications in numerous fields [17]. One of the most successful methods for developing the physico-mechanical behaviour of natural fibres is grafting with vinyl monomers under a radiation-induced method [18]. Radiation processing technology is a convenient way for grafting and modifications due to the introduction of stronger cross-linking through the rapid free radical propagation reaction of the multifunctional vinyl monomer, along with the reduction of the hydrophilic nature of cellulose fibre [19]. Over the decades, the impact of radiation on polymeric substrates, predominantly UV and  $\gamma$  (gamma), has been examined comprehensively. These radiations create ionization through the production of electrons, ions and free radicals [20]. Photo cross-linkable polymers contain functional groups that can directly form a cross-linked polymer through light-induced reactions. Photoinitiators have numerous applications in photo-induced polymerization. The benefits of photocuring treatment in polymers include improved monomer stability, a

significant reduction in reaction time, low energy consumption, etc. [21, 22]. Numerous studies have already been performed on monomer-based grafting with cellulosic fibres [23–25] to enhance potentialities under certain environmental conditions, particularly on jute, which has already gained considerable interest from many researchers. However, fewer reports can be found on radiation and photocured grafting. Nevertheless, sounder study, noticeably skilful efforts and cautious experimental techniques are required to achieve the full commercial benefits in this area. The present study involves the modification of PALF to optimize the fibre's attributes with the aim of broadening its future use in industrial applications. For this purpose, PALFs were treated with two types of acrylic monomers under various intensities of UV radiation, and the resulting treated fibres were further set to produce PALF/PLA composites. A brief examination was carried out on thermo-mechanical properties of the treated composites and further proved that the composites can be used for diversified applications with better serviceability.

## 2 Experimental

### 2.1 Materials

PLA pellets and PALF were supplied from DS fibres, Belgium and Madhupur, Bangladesh respectively. The molecular weight and density of PLA was 209 kDa and 1.273 g/cm<sup>3</sup> respectively. Two types of monomer 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) and the swelling agent methanol (MeOH) were acquired from the German Company E. Merck. Darocur-1664, whose function was as photoinitiator, was purchased from Ciba-Geigy. The structures of the used monomers are shown in Figure 1. Urea, which was used as an additive and acetone (CH<sub>3</sub>COCH<sub>3</sub>), was purchased from British Drug House, UK.

#### Monomer

2-hydroxyethyl methacrylate (HEMA)

Methyl methacrylate (MMA)

#### Chemical structure

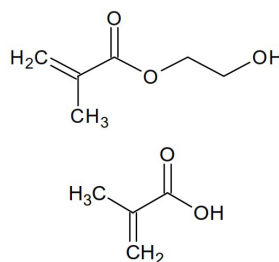


Figure 1: Chemical structure of the monomers used in this study

## 2.2 Evaluation of fibre properties

Fibre density was measured using the simplest method established by Archimedes where no equipment is required. At first, an open air-dried sample is weighed and weighed again after being dipped in a degassed fluid whose density was predetermined. The change in mass is referred to as buoyant force, which is then converted to specimen volume by dividing the fluid density. Finally, sample density was calculated by dividing the open air-dried sample weight by volume. This type of calculation is covered by the ASTM D3800 standard [26].

The ISO 1973:1996 standard was used to determine the linear density of the fibres. Ten fibre tufts with a mass of several milligrams were taken from the sample and the fibres of each tuft were brought into parallel arrangement according to the relevant method. The middle part of each combed tuft was 50 mm in length. Five fibres were taken from each of ten bundles in turn, so as to form a bundle of 50 fibres. Ten such bundles were made. These bundles were weighed individually using a scale, to an accuracy of 0.1 mg. The following equation was used to determine the mean linear density of fibre in each bundle.

$$L = \frac{m}{n \times l} \times 10^4 \quad (1)$$

where,  $L$  represents the mean linear density of the fibre in each bundle (dtex),  $m$  represents the mass of fibre bundle (mg),  $n$  represents the number of fibres in the bundle and  $l$  represents the length of the individual fibres in the bundle (mm).

Firstly, single fibres were separated manually from the bundle of pineapple fibres. The mechanical properties of individual fibres were determined according to the ASTM D3822 standard. The tests were done using universal Titan SN1410 series (James Heal) testing equipment. During testing, a load cell of 20 N and a gauge length of 10 mm were maintained. The test speed was 2 mm/minute. Five specimens were tested for each type of test. The data presented in Table 1 are the average values of the five tests for each case. Some properties of the used fibre are presented in Table 1.

## 2.3 Grafting of PALF with monomers

PALFs were first cut into the desired length (20–25 mm). To eliminate foreign components and dirt, the fibres were washed with acetone followed by drying at 105 °C in an oven and then weighed. The monomers (HEMA, and MMA) were used independently in various concentrations (10–60%) in the formulation.

Table 1: Physico-mechanical features of used PALF in the study

Properties	PALF fibre
Density (g/cm <sup>3</sup> )	1.523 ± 0.35
Linear density (dtex)	6.8 ± 0.78
Tensile strength (MPa)	182.7 ± 7.6
Young's modulus (GPa)	6.347 ± 0.87
Elongation at break (%)	2.75 ± 0.45

A 2% photoinitiator (Darocur-1664) and methanol (MeOH) were incorporated into the final composition. For swelling the cellulose backbone with the aim of improving impregnation, the monomers were appropriately mixed individually with methanol and the formulated solutions were stirred continuously for 1 hour to eliminate bubble formation. The resulting compositions are shown in Table 2. The dried virgin PALFs were immersed for 10 minutes in these resulting solutions. The soaked fibres were then subjected to irradiation with UV light. A UV radiation source (Minicure-200, IST Technik, Germany) was used for the irradiation of the fibres at the wavelengths of 254–313 nm, together with 50A current operated at 2kW power. A conveyor belt (length of 1 m) present in the UV irradiator rotates at a speed of 4 m/minutes around a mercury lamp. One movement towards the light is considered one pass. Specimens were kept on the conveyor and allowed to pass continuously through the UV source, and the number of passes was recorded. Before testing, the irradiated samples were kept in a relaxed state for 24 hours. Grafting percentage was calculated from the weight gain basis principle:

$$\text{Grafting (\%)} = \frac{A - B}{B} \times 100 \quad (2)$$

where, A and B represent weight of the sample after and before treatment respectively.

## 2.4 Composite manufacturing process

### 2.4.1 Fabrication of PLA sheets

The PLA and PALF were dried properly at 80 °C for 10 hours in vacuum conditions to remove moisture and avoid the creation of voids during the manufacturing process. First, PLA films of 1 mm thickness were prepared from pre-weighed pellets using a compression moulding machine (Carver Inc. model 3856, USA) at a temperature of 190 °C for 10 minutes, applying

Table 2: Composition of different formulations (w/w %)

Materials	H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>
HEMA	10	20	30	40	50	60
MeOH	88	78	68	58	48	38
Darocur-1664	2	2	2	2	2	2
Materials	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>4</sub>	M <sub>5</sub>	M <sub>6</sub>
MMA	10	20	30	40	50	60
MeOH	88	78	68	58	48	38
Darocur-1664	2	2	2	2	2	2

a pressure of 50 bar. Cooling was done for 5–7 minutes at the same pressure using a different moulding machine. The PLA films were cut to the required size (18 cm × 18 cm) and weighed.

#### 2.4.2 Fabrication of composite laminates

Prior to fabricating PALF/PLA composites, PALF fibre was cut to a length of 20–25 mm. Composites having 3 mm thickness were prepared by sandwiching three layers of PALF between four pre-weighed PLA sheets. The dimension of the mould was 18 cm × 18 cm × 3 mm for the preparation of composites. The sandwiched PLA sheets were then placed between two steel moulds with randomly oriented PALF and heated

at 190 °C at a pressure of 50 bar for 10 minutes in a Carver heat press (shown in Figure 2). They were then allowed to cool by passing water from an inlet pipe over both upper and lower plates for 10 minutes. The composite sheet was then removed from the mould plate to undergo natural cooling for 30 minutes at room temperature. Composites were manufactured using untreated and monomer treated fibres separately by maintaining the formulations shown in Table 3. The composite samples of the required dimensions were then cut carefully with a grinding machine from a large composite sheet for the purpose of determining different physical and mechanical properties.

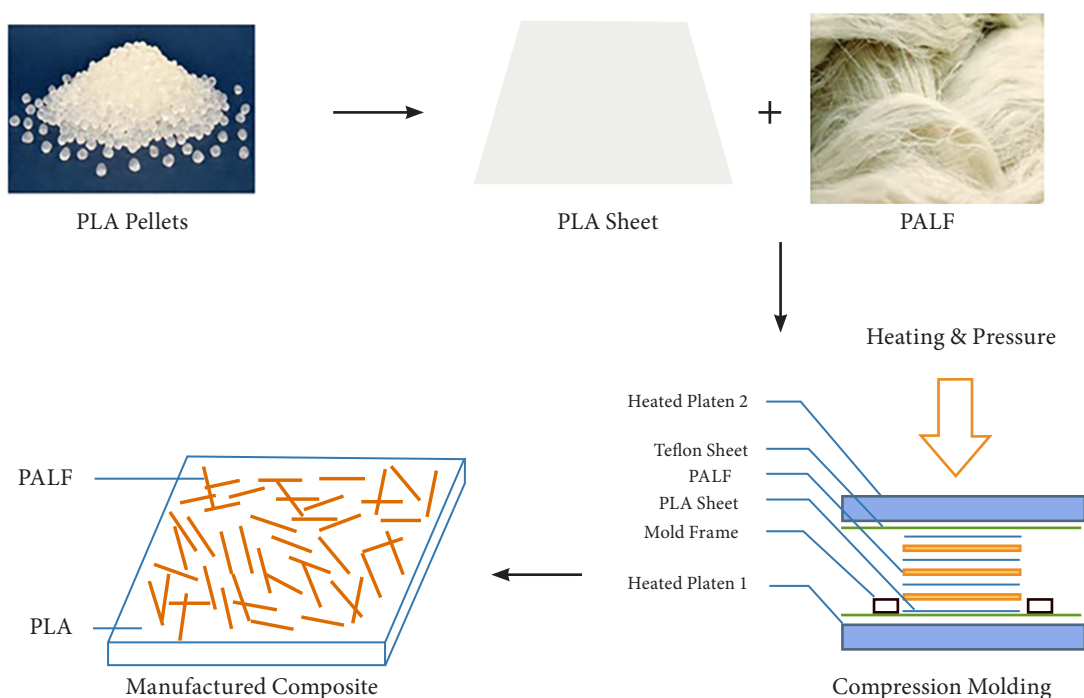


Figure 2: Fabrication model of PALF/PLA composites by compression moulding



Table 3: Composite formulations

Composite termed as	Type of treatment on fibre	Composition (PALF: PLA)
UC	Untreated	40:60
HC	30% HEMA treated (H3 sample)	40:60
MC	40% MMA treated (M4 sample)	40:60

### 2.5 Mechanical testing of composites

The mechanical properties of composites were determined in accordance with the ISO 527-4:1997 standard using a universal testing machine (Instron 5569). The load was 10 kN with an extension rate of 2 mm/minutes using a 25 mm gauge length. The flexural properties were measured in accordance with the ISO 14125:1998 method with a different Instron (type 4411) machine using a load cell of 5 kN and a speed of 2 mm/minute. The Izod test method (BS EN ISO 180: 2000+A2:2013) was used to determine the impact property, followed by the use of an Avery pendulum impact tester with a specimen size of 80 mm × 15 mm × 3 mm. For tensile and bending tests, a sample size of 60 mm × 25 mm × 3 mm was maintained. To determine the final result, the mean value of 10 specimens was calculated at an accuracy of ± 0.5%. All of the experiments were performed under standard atmospheric conditions (25 °C ± 2 °C and 65% ± 2% RH). Table 4 shows the properties of PLA and virgin PALF/PLA composite.

Table 4: Mechanical behaviours of pure PLA and untreated PALF/PLA (UC) composite

Properties	Neat PLA	PALF/PLA
PALF fibre content (wt.%)	0.0	40
Tensile strength (MPa)	62.0 ± 2.5	111.7 ± 4.5
Young's modulus (GPa)	5.8 ± 0.5	10.8 ± 1.1
Flexural strength (MPa)	87.5 ± 3.5	175.0 ± 6.0
Flexural modulus (GPa)	6.3 ± 0.4	13.6 ± 0.7
Impact strength (kJ/m <sup>2</sup> )	6.9 ± 0.7	15.3 ± 1.5

### 2.6 Thermogravimetric analysis (TGA)

To investigate the thermal stability and decomposition configuration of PALF/PLA composites, thermogravimetry (TG) and derivative thermogravimetry (DTG) were carried out using a TA Instrument Q500 under nitrogen atmospheric conditions. For testing, small pieces of samples were prepared (10–20 mg wt.)

and positioned into crucibles. The experiment was performed at temperature ranging from 0–600 °C with 5 °C/minute scan rate, and the corresponding weight loss (%) was recorded.

### 2.7 Differential scanning calorimetry (DSC)

Thermal behaviour and melting features of PLA and PALF/PLA composites were examined using a differential scanning calorimeter (model TA instrument DSC Q100) under nitrogen atmospheric conditions. The specimens were scanned from –20 to 220 °C at a heating rate of 10 °C/minute. The cooling rate was same as the heating rate. The following calculation was used to determine the degree of crystallinity:

$$X_c(\%) = 100 \times \frac{\Delta H_m}{\Delta H_f} \quad (3)$$

where  $\Delta H_m$  represents the melting enthalpy of pure PLA and PALF/PLA composites and  $\Delta H_f$  represents the melting enthalpy of 100% crystalline PLA (93.7 J/g).

### 2.8 Water retention test

To study the swelling behaviour of composites, a water retention test was performed to simulate the soaking phenomena of fibres. To determine the water retention capacity, a 5 g sample was immersed in a beaker holding 200 ml of deionized water. The samples were withdrawn periodically, wiped carefully and weighed. The water retention (%) was determined by means of the following weight gain formula:

$$W_z(\%) = [(W_x - W_y)/W_y] \times 100 \quad (3)$$

where  $W_z$  represents the water absorption quantity and  $W_x$  and  $W_y$  represent the mass of the specimens before and after immersion.

### 2.9 Morphological studies

To observe the interfacial bonding of composites, fractured surface images were viewed using a scanning electron microscope (Philips XL30) with an acceleration of 5.0 kV.

### 3 Results and discussion

In this work, two types of acrylic monomers were selected to achieve enhanced features of PALFs by means of a radiation-induced graft copolymerization technique. A brief study was made of the impact of UV radiation and monomer concentration (%) on grafting and mechanical properties, the effect of additives on mechanical properties, and the water absorption of grafted PALF/PLA composites. The variation in thermal properties and morphological changes due to grafting and radiation were also studied.

#### 3.1 Grafting ( $G_f$ )

PALFs were dipped for 10 minutes in solutions produced according to a predetermined formula at various concentrations (10–60%) of MMA and HEMA, followed by UV irradiation at different intensities (5–30 UV passes). The results are depicted in Figures 3 and 4, where grafting is shown against UV intensities with regard to monomer concentrations. The grafting percentage indicates the amount of cross-linkage produced between monomer and fibre. The grafting values were comparatively low at minor concentrations of monomer, and increased to a certain level of concentration before decreasing. The grafting (%) upsurge with the increase in UV dose reaches an extreme level at a definite intensity of UV and then declines as UV intensity is increased. However, the optimum grafting in most of the experiments was seen at the 15<sup>th</sup> UV pass for HEMA and the 20<sup>th</sup> pass for MMA treated fibre. After 20

passes, the amount of grafting decreases, possibly due to the degradation of the polymer under radiation. Nevertheless, the maximum grafting value (17.8%) was observed for 30% HEMA cured with 15 passes of UV radiation ( $H_3$  sample). The optimum grafting occurs at the 15<sup>th</sup> pass ( $G_f = 15.7\%$ ) of UV radiation for MMA with a 40% concentration ( $M_4$  sample), after which the grafting value falls, as seen in Figures 3 and 4 respectively. Hereafter, all tests were performed under these optimized conditions. Among the three monomers, HEMA treated fibres showed more grafting (%) than the MMA monomer, possibly due to its bulkier functional group with a long polymer chain. At a lower level of monomer concentration, free radicals form very quickly through propagation reactions. The photoinitiator strongly supports acrylic monomers to accelerate these reactions. Therefore, branched structures are produced by using double bonds during graft copolymerization. With an increase in monomer concentration, the residual unsaturation amount also rises, resulting in the quicker formation of 3-D network structures, which restricts mobility [27, 28]. After the achievement of the highest  $G_f$  (%), the amount of grafting was reduced with an increase in monomer concentration, which experimental data indicated might be the result of two main factors. At the upper level of concentration, the radical-radical formation reaction can be the result of recombination methods and additional homopolymers may instead generate the creation of monomer, together with cellulose. An additional factor may be the inadequate soaking of MeOH with the backbone

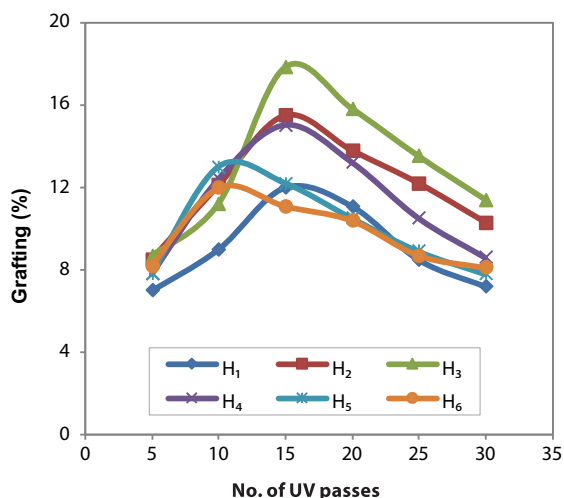


Figure 3: Grafting (%) of HEMA treated PALF against UV intensities as a function of various monomer concentrations

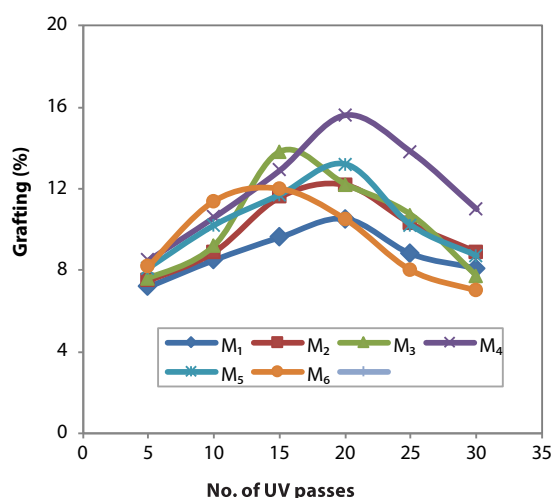


Figure 4: Grafting (%) of MMA treated PALF against UV intensities as a function of various monomer concentrations

of cellulose due to a lower quantity of solvent, which inhibits the monomer molecules' ability to penetrate the cellulose molecules, resulting in fewer sites that are actively involved in the reaction at the backbone of cellulose, and thus continuously decreases the number of reacting sites with a lower level of MeOH present in the case of upper monomer concentration. It is evident that the rate of cross-linking formation was proportional when radiation was initially applied. However, the termination of radical-radical reaction was enhanced greatly by an increase in the monomer concentration and consequently reduced the degree of scission reaction and oxidation [29, 30].

### 3.2 Effect of UV radiation on the mechanical performance of the composites

Strength is a vital physical property of any textile material, since every change in physical or chemical composition always results in a variation in strength. That also happened in our case. The evaluation of the tensile strength (TS), Young's modulus (YM), flexural strength (FS), flexural modulus (FM) and impact strength (IS) of virgin PALF/PLA composites were expressed by taking the mean values that were determined to be  $111.7 \pm 3.5$  MPa,  $10.8 \pm 1.1$  GPa,  $175 \pm 6$  MPa,  $13.6 \pm 0.7$  GPa, and  $15.3 \pm 0.8$  KJ/m<sup>2</sup> respectively (according to Table 4). It is evident from the table that the tensile and flexural properties of the biocomposite are higher than neat PLA after the

incorporation of PALF, as anticipated. The graphical presentation of the TS, YM, FS, FM and IS of monomer (HEMA, and MMA) treated PALF composites are seen in Figures 5-7 against the intensities of UV with regard to monomer concentration. The highest TS of  $156.3 \pm 3$  MPa, YM of  $15.4 \pm 0.15$  GPa, FS of  $243 \pm 5$  MPa, FM of  $18.7 \pm 0.8$  GPa, and IS of  $21.6 \pm 0.9$  KJ/m<sup>2</sup> were achieved by the HC sample (30% HEMA) while the optimum TS of  $149.4 \pm 4$  MPa, YM of  $14.9 \pm 0.3$  GPa, FS of  $237.3 \pm 5.5$  MPa, FM of  $18.5 \pm 0.7$  GPa and IS of  $20.9 \pm 0.6$  KJ/m<sup>2</sup> were achieved by the M<sub>4</sub> (40% MMA) sample respectively. Analysed data showed that TS, YM, FS, FM, and IS improved to 40, 42.6, 38.9, 37.5 and 41.7% respectively for the HC composite, while the results for the MC composite were 33.7, 38.4, 35.6, 36.2 and 37.2% respectively compared to the UC sample. The values indicate that the amount of grafting directly influences mechanical properties. The higher the grafting, the better the mechanical behaviours of the composites. Experimental results also showed that TS, YM, FS, FM and IS rise with an increase in UV intensity up to a certain dose and then declined as UV intensity rose. It was reported that maximum TS, YM, FS, FM and IS were exhibited by the HC sample at the 15<sup>th</sup> UV pass, and at the 20<sup>th</sup> UV pass for the MC sample. The reason for the improvement in mechanical properties with an increase in UV doses may be attributed to intercross-linking formation among adjacent

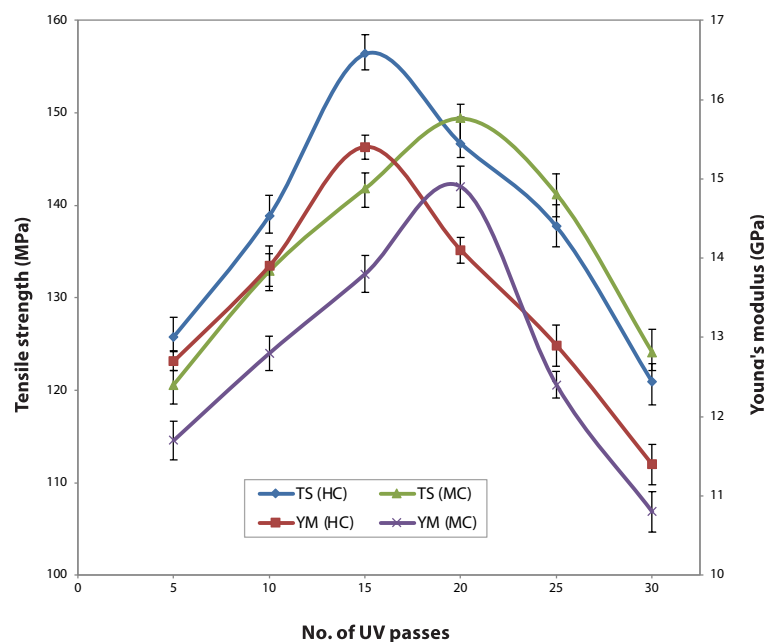


Figure 5: Tensile strength and Young's modulus of monomer treated optimized PALF/PLA composites with regard to UV intensities



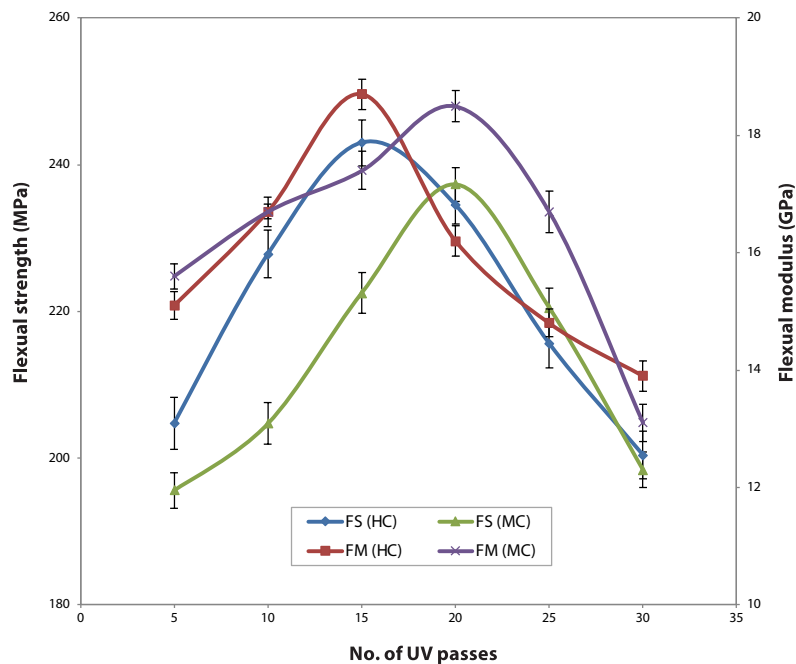


Figure 6: Flexural strength and Flexural modulus of monomer treated optimized PALF/PLA composites with regard to UV intensities

cellulose elements. During the application of UV light, free radicals were created by the photoinitiator (Darocur-1664) and are responsible for starting the free radical reaction. Originally, free radical reactions take place among –OH groups existing in cellulose and monomers and consequently develop properties. During the reaction process, inter reaction between –OH groups may also occur. In the case of HEMA,

the reaction mechanism comprises two stages: first, the formation of poly(HEMA) and second, the acrylic groups present in HEMA react with the –OH group of PALF, as illustrated in Figure 8 (a) and 8 (b) respectively. Similar mechanisms also occurred between MMA and PALF during UV curing.

Fundamentally, initiators assist in the initiation of the reaction of the monomer, through which free radical oxygen is formed, but does not actually impart in the reaction. At this time, a homo-polymerization reaction may occur. The treatment of cellulosic fibres with monomers reduces the hydrophilic property, which also imparts developed tensile properties. The experimental data showed that under UV radiation, the mechanical properties improve to a guaranteed value, after which declines may be attributed to two contrasting and simultaneous occurrences referred to as photo-crosslinking, which is responsible for the development of fibre properties and photo-degradation, for which reason fibre characteristics deteriorated. In the case of lower intensities, photo-crosslinking takes place due to the stabilization of free radicals by combination reaction. The grafting efficiency is higher if a higher number of active sites is created on the polymer. At higher intensities of radiation, however, polymer degrade into fragments due to the breaking of the main chain, resulting poor mechanical properties [31, 32].

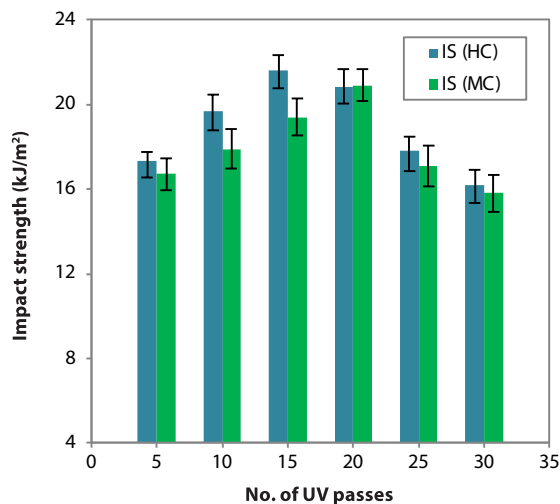


Figure 7: Impact strength of monomer treated optimized PALF/PLA composites with regard to UV intensities

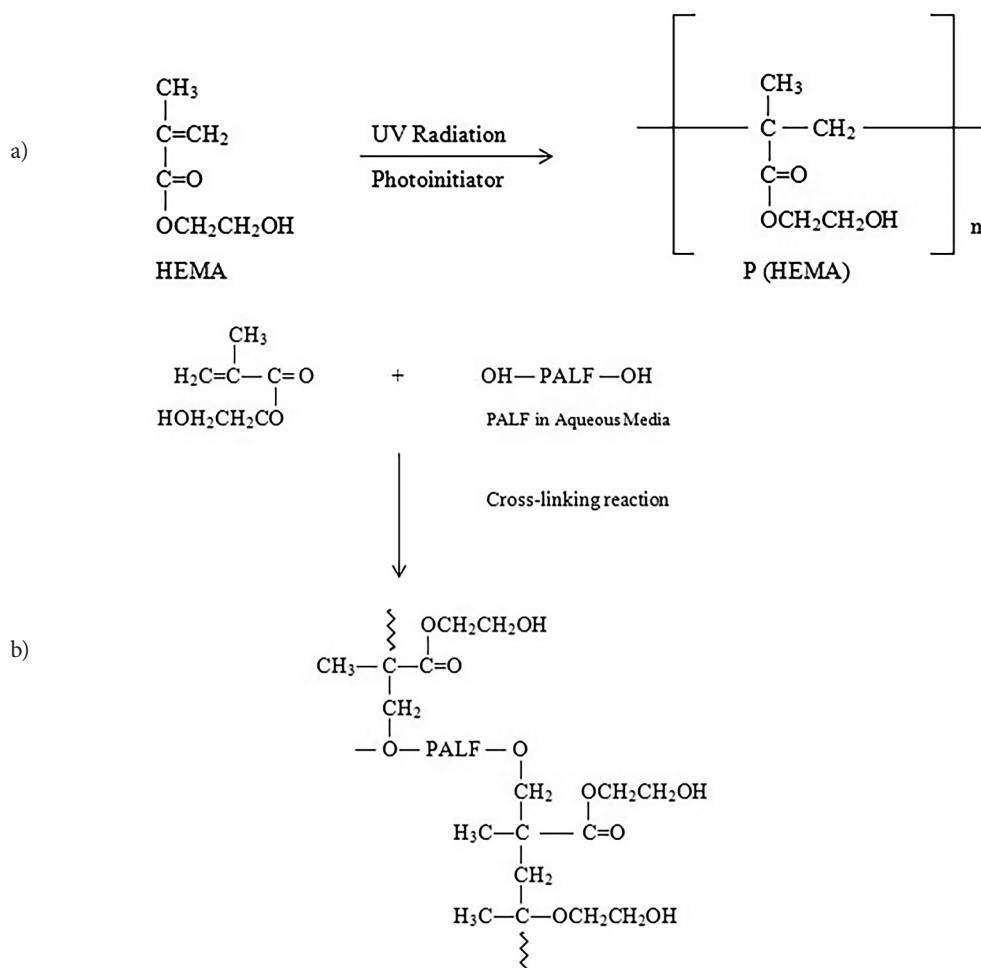


Figure 8: a) Formation of poly(HEMA) during applying UV radiation;  
b) Cross-linking mechanism between PALF and HEMA

The improvement in the mechanical properties of composites due to the incorporation of photografted PALF is also evident from the stress-strain curve. Typical tensile stress-strain curves of the neat PLA matrix, and the untreated PALF/PLA and monomer treated PALF/PLA composites are shown in Figure 9. In the figure, neat PLA shows a more linear behaviour, while the composites behave more nonlinearly as the strain increases. The linear phase corresponds to the linear deformation of the fibre and matrix, while the nonlinear deformation of the composites has been explained as a three-phase mechanism. First, a microcrack initiates at the fibre-end/matrix interface and propagates along the fibre lengths. Second, the matrix undergoes plastic deformation. Finally, the microcracks in the matrix open and propagate through the deformed matrix. Due to the pulling out of fibres from the matrix,

catastrophic crack propagation also takes place through the matrix.

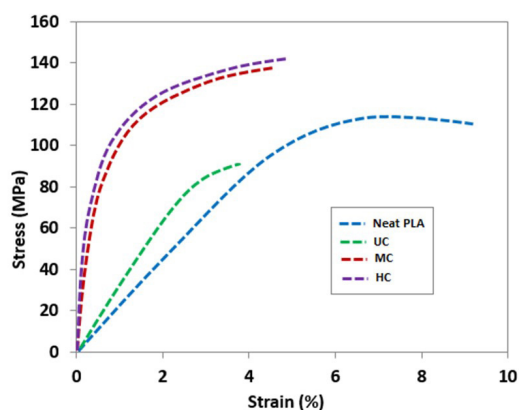


Figure 9: Tensile stress-strain curve of neat PLA and PALF/PLA composites

### 3.3 Analysis of the mechanical behaviours of composites following the integration of an additive

Experimental data revealed that the H<sub>3</sub> (30% HEMA) and M<sub>4</sub> (40% MMA) solutions provided improved properties of the treated PALFs. During treatment, various concentrations (0.5–1.5%) of urea were incorporated into the augmented formulations. Tables 5 and 6 show the achieved results of TS, YM, FS, FM and IS with G<sub>f</sub> (%). The G<sub>f</sub> and mechanical behaviours improved due to the addition of urea into the H<sub>3</sub> and M<sub>4</sub> solutions at optimal radiation intensity. The best enhanced mechanical properties were achieved through the addition of 1% urea. It was reported that HC sample (30% HEMA treated + 1% urea) showed an increase of 51% in TS, 49.5% in YM, 45.7% in FS, 46.3% in FM and 47.4% in IS compared to the UC sample. A similar increase was also observed for other monomer treated composites by adding urea. The presence of >C=O groups neighbouring the nitrogen atom in urea has an elongated pair of electrons; by activating them during reaction through an additive, a bridge is formed between cellulose and monomer. Oxygen existing in >C=O groups has a great affinity to electrons. As a result, electrons are closely populous around it, thus drawing additional electrons from the nitrogen atom of urea, and generating certain advantageous situations for the expansion of the monomer molecules and the backbone of cellulose through additives. Urea possesses some properties that when added would stimulate segregation by complex compound formation with monomer molecules, which might lead to

an increase in the concentration of monomer at the grafting position and thus accelerate the reaction mechanism at that point [33].

### 3.4 Thermogravimetric analysis (TGA)

One of the restrictive features in using plant-based lignocellulosic fibres in composite materials is lower thermal stability. In this study, an attempt was made to increase the thermal stability of PALF/PLA composites through photografting. The thermal stability of the UC, HC, and MC samples were studied using TG and DTG curves, as illustrated in Figures 10 and 11 respectively. Both untreated and treated fibre composites lost weight in three steps, although decomposition actually occurs in two main phases that are similar to other lignocellulosic fibre composites, as shown in TG curves. For the UC (virgin PALF/PLA) composite, initial weight loss (of 9.9%) was recorded at between 30–105 °C due to the removal of moisture from the fibres. At temperatures above 200 °C (onset temperature), however, thermal stability was reduced and fibre degradation occurred. In brief, stage I (200–285 °C) corresponds to the cleavage of glycosidic linkages of cellulose with the thermal degradation of hemicellulose and pectin (18.6% weight loss), while stage II (275–382 °C), where maximum weight loss (53.5%) was seen, corresponds to  $\alpha$ -cellulose degradation. As lignin consists of aromatic rings that make it complex, its structure decomposed slowly over the entire range of temperatures [34]. Table 7 shows the weight loss (%) of untreated and monomer grafted PALF/PLA composites at different temperature intervals.

Table 5: Grafting and tensile properties of photografted PALF/PLA composites treated with urea

Composites	Concentration of urea								
	0.5%			1%			1.5%		
	G <sub>f</sub>	TS (MPa)	YM (GPa)	G <sub>f</sub>	TS (MPa)	YM (GPa)	G <sub>f</sub>	TS (MPa)	YM (GPa)
HC	18.6	162.4 ± 3.2	15.8 ± 0.14	19.7	168.6 ± 3	16.1 ± 0.57	18.9	163.1 ± 2.8	15.9 ± 0.16
MC	16.5	155.3 ± 2.8	15.3 ± 0.25	17.4	161.2 ± 2.4	15.7 ± 0.22	16.3	154.8 ± 2.5	15.2 ± 0.27

Table 6: Flexural and impact properties of photografted PALF/PLA composites treated with urea

Composites	Concentration of urea								
	0.5%			1%			1.5%		
	FS (MPa)	FM (GPa)	IS (kJ/m <sup>2</sup> )	FS (MPa)	FM (GPa)	IS (kJ/m <sup>2</sup> )	FS (MPa)	TS (MPa)	IS (kJ/m <sup>2</sup> )
HC	249.3 ± 5	19.3 ± 3.2	21.4 ± 0.7	255.1 ± 6	19.8 ± 3	22.5 ± 0.3	250.2 ± 4	19.4 ± 1.8	21.6 ± 0.5
MC	243.8 ± 4	18.9 ± 2.8	20.6 ± 0.3	251.4 ± 5	19.3 ± 2.4	21.7 ± 0.2	245.3 ± 6	18.8 ± 1.7	20.7 ± 0.27

Table 7: TG data of untreated and grafted PALF/PLA composites

Composites	Temperature (°C)			Weight loss (%)		
	Initial stage	Stage I	Stage II	Initial stage	Stage I	Stage II
UC	30-105	200-285	285-398	9.9	18.6	66.7
HC	90-198	251-343	343-492	4.6	8.7	58.8
MC	82-192	245-332	332-479	4.5	9.1	59.6

It can be clearly seen from the graphs that grafting increased the thermal stability of PALF/PLA composites. All the monomer treated grafted fibre composites showed improved thermal stability compared to that of untreated samples, as presented in Figure 10. In the initial stage, treated fibre composites (both HC and MC) demonstrated very low weight loss (5.3 and 5.8% for the HC and MC sample respectively), which actually depends on the amount of grafting, as well as the small amount moisture present in the grafted fibre. Grafted composite samples also exhibited a significantly lower amount of weight loss in stage I (8.7-9.1% between 245-343 °C) and stage II (58.8-59.6% between 332-492°C) than the untreated samples. Among the treated samples, 30% HEMA treated PALF/PLA (HC) we more resistant to heat than other samples, probably due to their stronger cross-linkage formation than the other samples. The reaction between the chemical components of monomers and -OH of PALF changes the structure by forming cross-linkage, resulting in the improved

strength of the mechanical bond between PALF and the monomer. The complex structure of cross-linkage prevents further degradation, which in turn increases the degradation temperature in stages I and II, and is also responsible for the low weight loss in these two stages. Moreover, free radicals formed due to UV radiation also react with the cellulose and alter its chemical nature, thus creating more hydrophobic and stronger covalent bonds, and increased thermal stability [35]. The degradation of PALF is primarily dependent on the degradation of cellulose, which is the leading constituent of the fibre. However, the chemical structure of cellulose is altered due to photografting, which influences the degradation reaction of cellulose and thus the degradation temperature. Together, this contributes to the enhanced thermal stability of photocured PALF/PLA composites. DTG curves (Figure 11) also provide evidence of the three-stage degradation of modified fibre composites, with weight loss profiles that confirm the developed thermal properties of the monomer treated PALF/PLA.

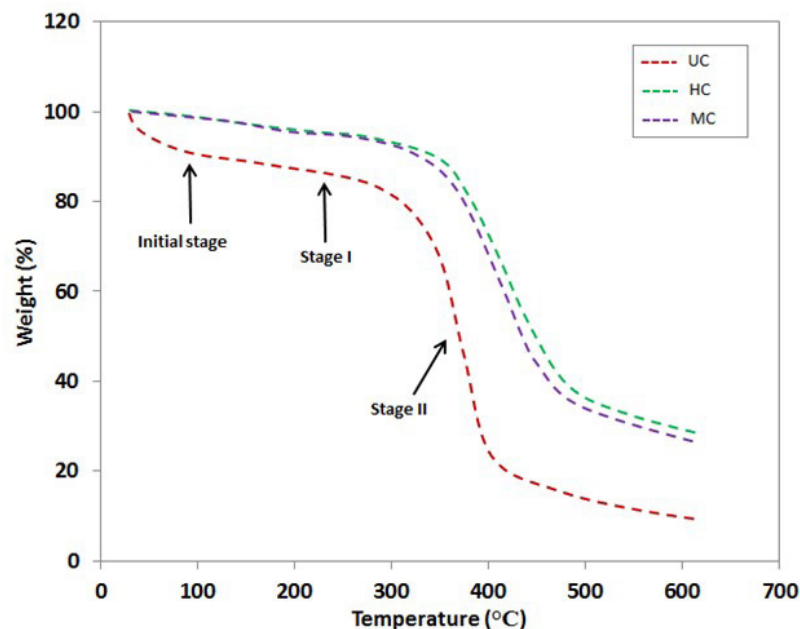


Figure 10: TG curves for untreated and photografted optimized PALF/PLA composites

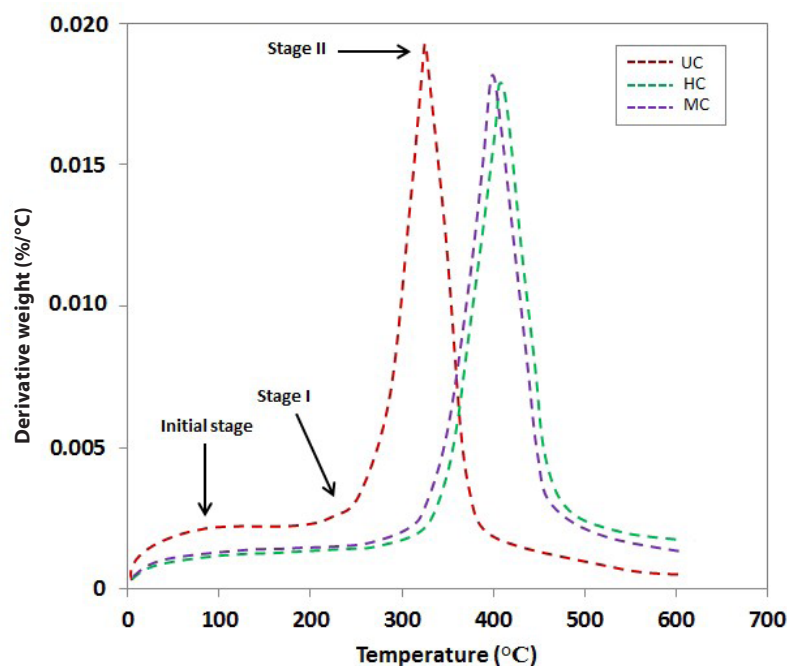


Figure 11: DTG curves for untreated and photografted optimized PALF/PLA composites

### 3.5 Differential scanning calorimetry

The melting behaviour and degree of crystallinity of neat PLA and PALF/PLA composites were examined using DSC. Figure 12 shows the DSC curves of the UC, HC and MC samples, together with pure PLA, and a summary of results is presented in Table 8. It is evident from the graphs that the addition of PALF fibre into the PLA matrix changed the glass transition and melting temperature of the composites. Observations reveal that the untreated fibre composite exhibited improved  $T_g$  relative to neat PLA, which indicates the changing properties from flexible to hard [11]. It is evident that the melting temperature (onset) and melting enthalpy decreased marginally due to the incorporation of PALF into PLA, which may be attributed to the role of PALF as a diluent, resulting in the smaller amount of heat required to melt the UC and the resulting lower  $T_m$ . Another rea-

son may be that the polymer chains in PLA might be diffused and weakened due to the presence of PALF [10]. Due to radiation induced grafting, the hydrophilic characteristic of PALF is greatly reduced, which further develops adhesion between PALF and PLA resulting in the higher melting temperature of photocured PALF composites (HC and MC) than the untreated sample (UC).

It is evident from Table 8 that crystallinity (%) decreases when PALF is added to the matrix PLA, which is due to the amorphousness of PALF. Nevertheless, (monomer + UV) treated composites demonstrated an increased degree of crystallinity because, during grafting under radiation treatment, both fibre and monomer have active points and produce a complex structure by forming cross-linkage, which ultimately reduces amorphousness and increases crystallinity (%).

Table 8: Thermal properties of neat PLA and grafted PALF/PLA composites

Material	Glass transition temperature, $T_g$ (°C)	Melting temperature, $T_m$ (°C)		Melting enthalpy, $\Delta H_m$ (J/g)	Degree of crystallinity, $X_c$ (%)
		Onset melting temperature	Peak melting temperature		
Neat PLA	61	167	175	46	49
UC	63	151	162	32	34
HC	65	161	169	37	39
MC	64	157	166	36	38



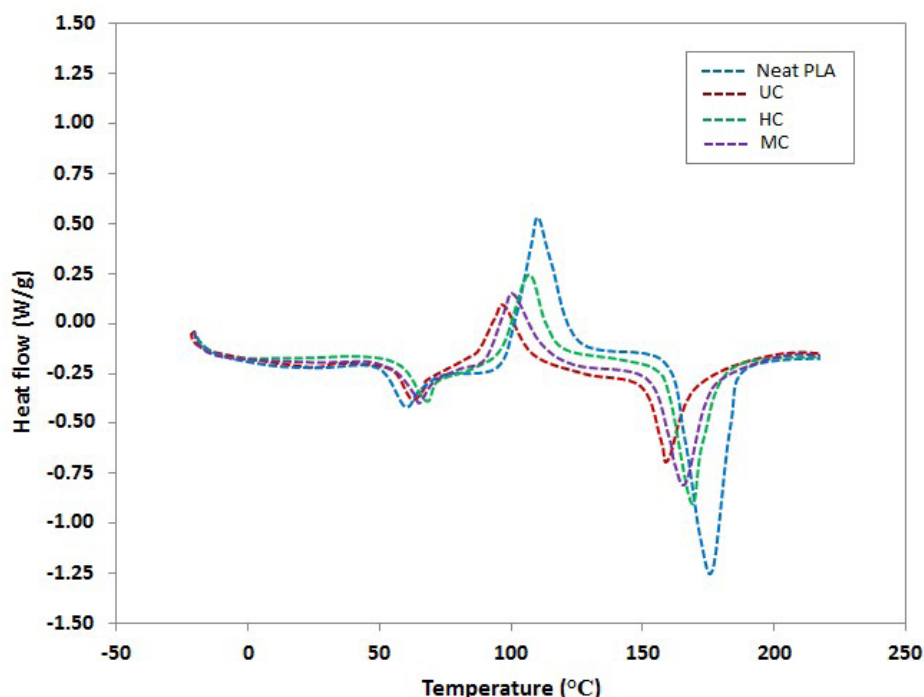


Figure 12: DSC curves for untreated and photografted optimized PALF/PLA composites

### 3.6 Swelling behaviour

Water absorption indicates the soaking performance of fibres, which is deemed to be a barrier property. Figure 13 shows water absorption (%) with respect to swelling time (days). For this test, neat PLA, UC (composite without treatment of PALF), HC (30% HEMA treated at the 15<sup>th</sup> UV pass) and MC (40% MMA treated at the 20<sup>th</sup> UV pass) samples were selected. Observations reveal that the UC sample soaks water in a distinctive way, while the monomer treated samples absorb water at very high rate during the initial 10–15 days. After that time, the absorption rate declined in an almost static manner, while the untreated fibre composite demonstrated continuous water soaking with the progression of time. After 30 days, neat PLA and UC sample absorbed water up to 2.5, and 75.8% respectively, while that rate was 38 and 40.6% for the HC and MC samples respectively, which is actually determined by their grafting values. Because of grafting, void space in the fibre was filled by polymers, and several hydroxyl groups present in the cell wall polymer were replaced during the bond formation of chemical groups, thus reducing the hygroscopicity of treated fibre. The degree of crystallinity of the composites is also responsible for their water retention behaviours, as pure PLA demonstrated a degree of crystallinity of 49%, which decreased to 39, 38 and 34% for the HC, MC and UC composites

respectively. It was thus established that water absorption primarily occurred in amorphous regions. For this reason, grafted fibre composites exhibited lower water absorption than untreated composites. Thus, from the above result, it can be stated that an increase in grafting values significantly reduced the water retention capacity of photografted fibre reinforced composites.

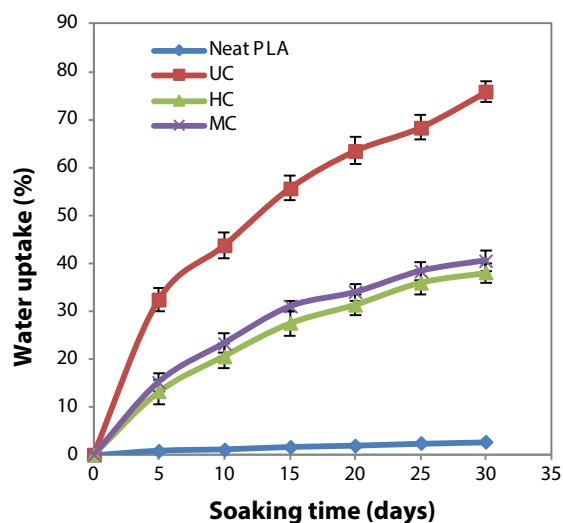


Figure 13: Water uptake (%) of untreated and monomer treated optimized PALF/PLA composites with regard to soaking time

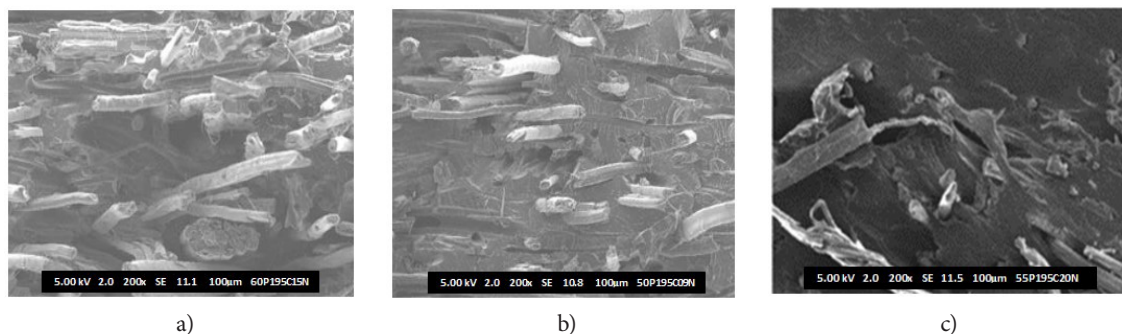


Figure 14: SEM micrograph of: a) untreated PALF/PLA composite, b) and c) 30% HEMA treated PALF/PLA composite

### 3.7 SEM analysis

To understand fibre matrix adhesion, SEM micrographs of the composites were studied. The tensile fracture surface of untreated and monomer treated PALF/PLA composites are shown in Figures 14 (a), and 14 (b) and (c) respectively. The untreated PALF partially adhered to the matrix PLA, indicating weak adhesion. More voids and debonding were found on untreated the PALF/PLA composite. A high degree of fibre agglomeration and wider gaps at interfaces result in poor mechanical and thermal properties. An improved fibre-matrix bonding in grafted PALF/PLA was seen, as PALF was entirely surrounded with PLA, while good dispersion can be seen in Figure 14 (c). Also evident is a lower number of voids with improved fibre distribution, indicating a better interface between fibre and matrix, which in turn led to enhanced mechanical and thermal properties, which supports the achieved experimental results.

## 4 Conclusion

A photografting technique was used to modify PALF fibres with two types of vinyl monomers, i.e. HEMA and MMA, while the mechanical properties of produced composites were successfully assessed. Based on grafting and mechanical properties, the concentration of monomers and radiation intensity were augmented. Taking into account the relevant parameters, the achieved results illustrated that composites made of PALF grafted with 30% HEMA at the 15<sup>th</sup> UV pass and 40% MMA at the 20<sup>th</sup> UV pass of UV radiation resulted in optimized mechanical properties. Moreover, the addition of urea (1%) into the optimized solution significantly enhanced the mechanical properties of the composites. Optimized mechanical properties were achieved by fragmenting

(glucosidic + weaker) bonds and forming a stronger cross-linkage. The water uptake behaviour of the grafted sample showed a more hydrophobic nature than the virgin sample. Thermogravimetric studies demonstrated that photografting improved the thermal stability of the composites, as well as their resistance to degradation under heat. Although various surface pretreatments can improve the mechanical properties of cellulosic fibre, it can be concluded with a high degree of certainty from this experimental study that photografting is an effective, safe and pollution-free process for the development of the thermo-mechanical behaviours of PALF/PLA composites, which can lead to prospects for the commercial and industrial application of PALF fibres.

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