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Surface Modification and Characterisation of Industrial Hemp Preform with Fenton-Initiated Free Radical Methyl Methacrylate Graft Copolymerisation

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ABSTRACT
In this study, free radical graft copolymerization of methyl methacrylate (MMA) onto industrial hemp (Ihemp) preform was successfully performed using Fenton's reagent (hydrogen peroxide, H_2O_2, as initiator and ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, as co-catalyst) under an inert nitrogen atmosphere in aqueous medium. The homopolymer formed during the reaction was removed by acetone extraction. The grafting percentage and grafting efficiency obtained were 21.5 % and 44.2%, respectively. These values were achieved when 10g of Ihemp preform was copolymerized with 5mL of MMA monomer at 50°C for 90 minutes using 2g of ferrous ammonium sulfate dissolved in 250mL of distilled water. The grafted copolymers were characterised by Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis/differential thermogravimetry (TGA/DTG), and scanning electron microscopy (SEM). The appearance of a new absorption peak at 1724cm^{-1} in the FTIR spectrum and the SEM micrographs confirmed that the Ihemp preform surface was almost completely covered by poly(methyl methacrylate) after grafting.

Keywords: Free radical graft copolymerization, Industrial hemp, MMA monomer, 2D woven preform, surface modification

INTRODUCTION

The non-biodegradability, recycling challenges, and toxic by-products associated with petroleum-based synthetic fibre polymer composites are the primary drivers for the development of natural fibre composites.

Industrial hemp (*Cannabis sativa* L.) is a sustainable and versatile natural bast fibre derived from the plant stem. It possesses high cellulose content, low density, and excellent mechanical properties, including high specific strength and stiffness. These attributes, combined with growing environmental concerns and the demand for biodegradable materials, have increased interest in industrial hemp for industrial applications (Elfaleh *et al*., 2023).

Over the years, environmental regulations and sustainability demands have prompted researchers and industries to replace petroleum-based materials with agricultural resources to produce eco-friendly and economically viable products (Haghighatnia *et al*., 2017). Although synthetic fibres such as glass, carbon, and aramid are widely used in polymer composites due to their high strength and stiffness, they suffer from poor biodegradability, high processing costs, and high energy consumption (Kabir *et al*., 2012). In contrast, natural fibre reinforced composites (NFRCs) offer biodegradability, ease of processing, low cost, high toughness, and good specific properties (Sair *et al*., 2017). Their high specific strength and stiffness, corrosion resistance, energy absorption capacity, and long fatigue life have enabled their adoption in various markets (Abdel-Fattah *et al*., 2013).

Key growth drivers in this sector include the rising demand for lightweight materials in aerospace, defence, automotive, and construction industries (Lucintel, 2020).

Graft copolymerization is a well-established technique for modifying the chemical and physical properties of polymers. Grafting vinyl monomers onto an existing polymer backbone enables the development of new materials with enhanced performance and broader applications (Liu *et al*., 2006). This approach is particularly effective for improving the compatibility between hydrophobic thermoplastics and hydrophilic lignocellulosic fibres (Bledzki *et al*., 1996).

MATERIALS AND METHODS

Industrial hemp yarn was purchased from Hemp Affairs, India. Methyl methacrylate (MMA, density 0.94 g/mL), analytical-grade sodium hydroxide (NaOH), acetone, and ferrous ammonium sulfate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) were obtained from commercial suppliers. An ice bath, activated alumina, glass wool, conical flasks, reflux condensers, and nitrogen gas were used. A floor loom (AD-A-HARNESS, L.W. MACOMBER, Model B4D, Serial No. 1409) from the Department of Industrial Design, Ahmadu Bello University, Zaria, was used to weave the Ihemp yarn into 2D preforms.

2D Weaving of Ihemp Yarn into a Preform

Ihemp yarn was woven into a plain-weave preform using the floor loom. Plain weave was selected for its simplicity, tight and uniform structure, and suitability for composite reinforcement. Each repeat pattern required approximately 35 minutes, with consistent beating force maintained between levels 4 and 5 on a subjective scale (1 = light tap, 10 = heavy slam). For Ihemp performs, the weaving processes are shown in Figures 1(a) and (b).

Figure **1**a: 2D Ihemp yarn weaving process

Figure 1b: Ihemp plain woven preform

The Grafting Process

The method and procedure described by Kalia *et al*. (2008) and Thakur *et al*. (2014) were adopted for grafting.

A 2000 mL 3-neck round-bottom flask was used for the grafting process. The flask was purged for 15 minutes with nitrogen gas at a pressure gauge of 0.1 – 0.2 bar with a flow rate maintained slowly at 50 – 100 mL/min. The 3-neck 2000 mL round-bottom flask was fixed and coupled with a reflux condenser, glass stirring rod and aided by a retort stand and was adjusted to sit firmly on a water bath. Sodium hydroxide (NaOH) treated Ihemp (10g) by weight was introduced into a 2000 mL 3-neck round-bottom flask with the aid of a tong. Fenton's solution was added to the reaction medium, nitrogen gas was activated to purge any available oxygen in the combined mixture of pretreated Ihemp preform and Fenton's reagent for 10 minutes. 5mL Methyl methacrylate monomer was added to the reaction medium slowly and stirred with the aid of a glass rod to ensure an even mixture with Fenton's reagent and preform.

The water bath temperature was maintained at 50 °C for 1 hour and 30 minutes. The grafted Ihemp product was further treated by removing the PMMA homopolymer that was formed during the reaction. The grafting reaction was carried out using a Fenton's reagent system, with ferrous ion concentration [Fe^{2+}] of 6.8 mM (0.0068 M) and hydrogen peroxide concentration [H_2O_2] of 0.235 M (235 mM), corresponding to a molar ratio of Fe^{2+} to H_2O_2 of 1:35. The monomer to preform ratio was maintained at 0.5:1 during the graft copolymerization process. All grafting experiments were conducted in triplicate (n = 3), and the average values were reported.

The Stoichiometry of the reaction

The graft copolymerization was initiated by Fenton's reagent (Fe^{2+}/H_2O_2), which generates highly reactive hydroxyl radicals (•OH) capable of abstracting hydrogen atoms from the Ihemp preform (cellulose backbone) to create macro-radical sites. The reaction pH was 2.9

Primary reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$$

In the presence of excess H_2O_2, the ferric ion (Fe^{3+}) is partially reduced back to ferrous ion (Fe^{2+}), allowing a limited catalytic cycle: $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\bullet + H^+$ (where $HO_2\bullet$ is the hydroperoxyl radical, less reactive than •OH). Hydroxyl radical (•OH) is the main oxidant responsible for initiating grafting by abstracting a hydrogen atom from the cellulose chain:

$$Ihemp–H + \bullet OH \rightarrow Ihemp\bullet + H_2O$$

Generation of hydroxyl radicals (Fenton's reaction)

a. $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$

b. Formation of cellulose macro-radicals (Hydrogen abstraction)

$$Cellulose–H + \bullet OH \rightarrow Cellulose\bullet + H_2O$$

c. Initiation of grafting (Addition of MMA to cellulose radical)

$$Cellulose\bullet + CH_2=C(CH_3)COOCH_3 \rightarrow Cellulose–CH_2–C\bullet(CH_3)COOCH_3$$

d. Propagation (Growth of PMMA side chains)

$$Cellulose–CH_2–C\bullet(CH_3)COOCH_3 + n\ CH_2=C(CH_3)COOCH_3 \downarrow Cellulose–[CH_2–C(CH_3)(COOCH_3)]_n–CH_2–C\bullet(CH_3)COOCH_3$$

e. Termination

Combination:

$$Cellulose\ [CH_2–C(CH_3)(COOCH_3)]_n–CH_2–C\bullet(CH_3)COOCH_3 + \bullet R \downarrow Cellulose–g\text{-}PMMA$$

(where: •R is another radical, another growing chain)

Removal of homopolymer and determination of graft level

After completion of the graft copolymerization reaction, the Ihemp preforms were separated from the reaction mixture and subjected to thorough removal of poly (methyl methacrylate) (PMMA) and (PMA) homopolymer, unreacted monomer, and residual Fenton's reagent (Fe^{2+}/Fe^{3+} and H_2O_2).

The preforms were first rinsed repeatedly with distilled water to remove water-soluble residues. Subsequently, the homopolymer was removed by solvent extraction using acetone.

The extraction procedure was as follows: Each preform was immersed in 50 mL of fresh acetone and agitated (using a mechanical shaker at 150 rpm) for 30 minutes at room temperature. This is followed by washing repeatedly three times with fresh 50 mL portions of acetone at each interval to ensure complete removal of the homopolymer. After the final acetone wash, the preforms were rinsed once with distilled water to remove any trace acetone and then air-dried at room temperature (25 ± 2 °C) for 24 hours.

The preforms were subsequently dried at 60 °C to constant weight until no further weight loss was observed. The completeness of homopolymer removal was confirmed by the absence of further weight loss in an additional acetone wash of the final acetone extract. The weight of the dried grafted Ihemp preform (free of homopolymer) was then recorded.

The grafting percentage (% G) and grafting efficiency (% E) were calculated using the following equations (Abu Bakar *et al.,* 2008):

$$G\ (\%) = [(W_1 - W_0) / W_0] \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ 1$$

$$E\ (\%) = [(W_1 - W_0) / (W_1 - W_0 + W_2)] \times 100 \quad \ldots.2$$

where:

W_0 = initial dry weight of ungrafted Ihemp preform (g)

W_1 = dry weight of grafted Ihemp preform after homopolymer removal (g)

W_2 = weight of extracted PMMA homopolymer (determined by evaporation of combined acetone extracts to constant weight, where applicable)

FOURIER INFRARED SPECTROSCOPY

FTIR spectra of ungrafted Ihemp preform, pure PMMA, and Ihemp-g-PMMA were recorded on a Perkin Elmer Spectrum 2000 spectrometer using KBr pellets to identify functional groups.

Thermogravimetric Analysis

Thermogravimetric analysis was performed using a Perkin-Elmer thermal analyser under nitrogen atmosphere from 30 °C to 800 °C at a heating rate of 10 °C/min with a nitrogen flow rate of 50 mL/min. Thermograms were obtained by plotting residual weight percentage against temperature.

Scanning Electron Microscopy

Surface morphologies of ungrafted and grafted Ihemp preforms were examined using a Phenom Pro X (Model 800-07334) scanning electron microscope. Samples were mounted on stubs and sputter-coated with gold to prevent electrostatic charging.

4.0 RESULTS AND DISCUSSION

Free radical graft copolymerization reaction analysis

The grafting parameters were adapted from Yesmin *et al*. (2023) with modifications based on Kalia *et al*. (2008) and Thakur *et al*. (2014). The grafting percentage and grafting efficiency were 21.5 % and 44.2 %, respectively. These values confirm successful grafting of MMA onto the Ihemp preform surface under a nitrogen atmosphere. The postulated mechanism is shown in Figure 2.

Fourier transform infrared spectroscopy

Table 1: Summarized comparative FTIR Spectra of Ungrafted Ihemp and Ihemp-g-PMMA preform.

The FTIR spectra of ungrafted Ihemp, pure PMMA, and grafted Ihemp-g-PMMA in the range 4000–370 cm^{-1} show a broad absorption band at 3500–3100 cm^{-1} attributed to O–H stretching of cellulose and absorbed water. A new peak at approximately 1724–1730 cm^{-1} in the grafted sample corresponds to C=O stretching of the ester group in MMA. Additional peaks at 1150–1250 cm^{-1} (C–O stretching) and 2950–2850 cm^{-1} (C–H stretching) confirm the successful incorporation of PMMA side chains onto the Ihemp structure (Kalia *et al*., 2009).

The FTIR spectra of ungrafted and grafted Ihemp preform are presented in Figure 2 (a) and (b).

Table 1: Summarized comparative FTIR Spectra of Ungrafted Ihemp and Ihemp-g-PMMA preform

Wavenumber (cm^{-1})	Ungrafted Ihemp (A)	Ihemp-g-PMMA (B)	Assignment / Interpretation
3340–3400	Strong, broad peak (marked)	Present but slightly modified	O–H stretching (cellulose, hemicellulose)
2920–2930	Strong peak (marked)	Present	C–H stretching (aliphatic)
1730–1735	Absent or very weak	Very strong, sharp peak (marked at ~1730)	C=O stretching (ester carbonyl from grafted PMMA) – Key evidence of successful grafting
1645–1650	Strong peak	Reduced intensity or shifted	C=O stretching (lignin) or adsorbed water
1540–1550	Present	Absent or very weak	Aromatic C=C (lignin) partial removal or masking
1450–1460	Present	Present	C–H bending
1370–1380	Present	Present	C–H bending / O–H in-plane bending
1160–1165	Present	Present	C–O–C asymmetric stretching (cellulose)
1050–1070	Strong	Present	C–O stretching (cellulose)
1000–1030	Present	Present	C–O stretching
890–900	Present	Present	β-glycosidic linkage (cellulose)

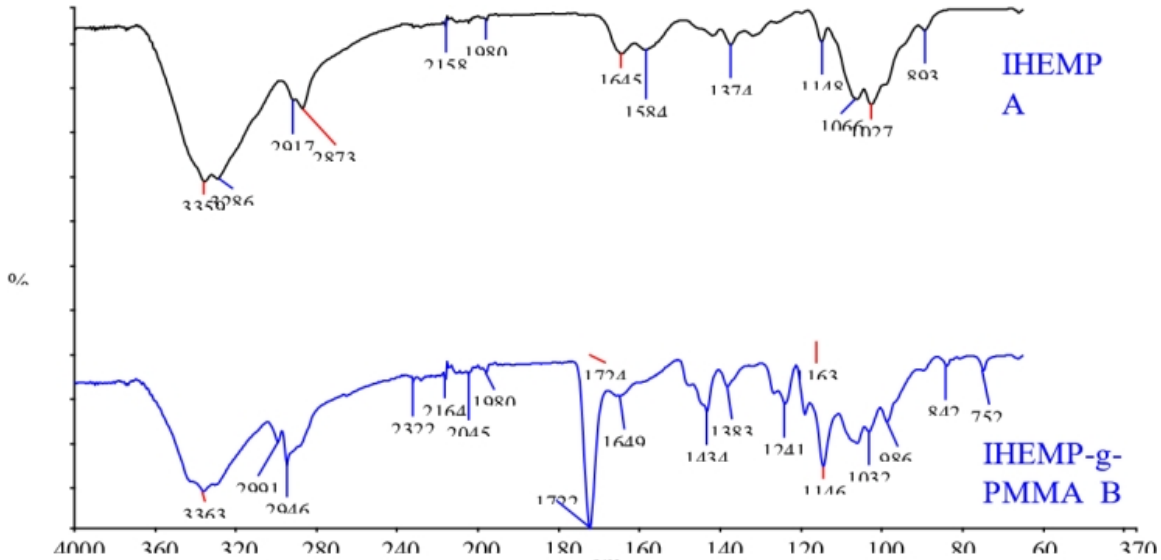

Figure 2: FTIR spectra of (a) ungrafted Ihemp preform and (b) Ihemp-g-PMMA.

Thermogravimetric Analysis

The ungrafted Ihemp preform exhibits typical lignocellulosic degradation behaviour: minor weight loss below 100 °C (moisture evaporation), major decomposition between 200–400 °C (hemicellulose and cellulose), and gradual lignin degradation above 500 °C, leaving 10–15 % char residue at 800 °C.

The grafted Ihemp-g-PMMA shows improved thermal stability. The main degradation peak shifts to approximately 400 °C, and higher char residue is observed at 800 °C. This enhancement is attributed to the grafted PMMA chains, which restrict cellulose and hemicellulose decomposition and increase cross-linking (Sanjay *et al*., 2016).

TGA thermographs of ungrafted and grafted Ihemp preform are shown in Figure 3 (a) and (b).

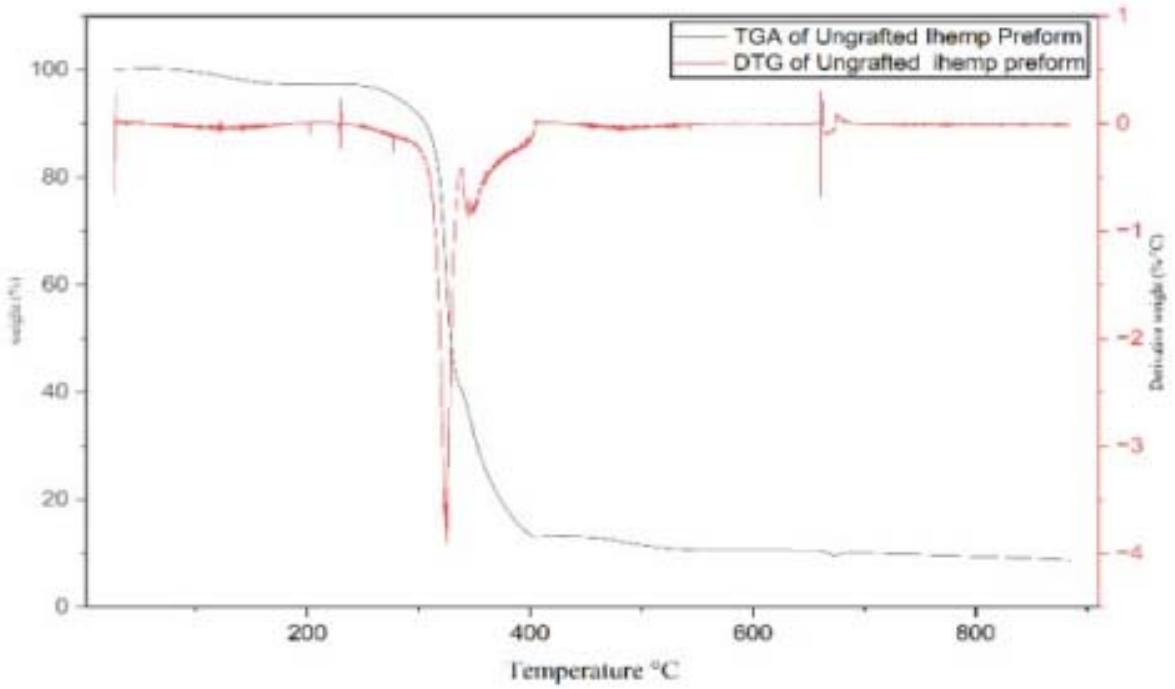

Figure 3a: TGA/DTG of Ungrafted Ihemp preform

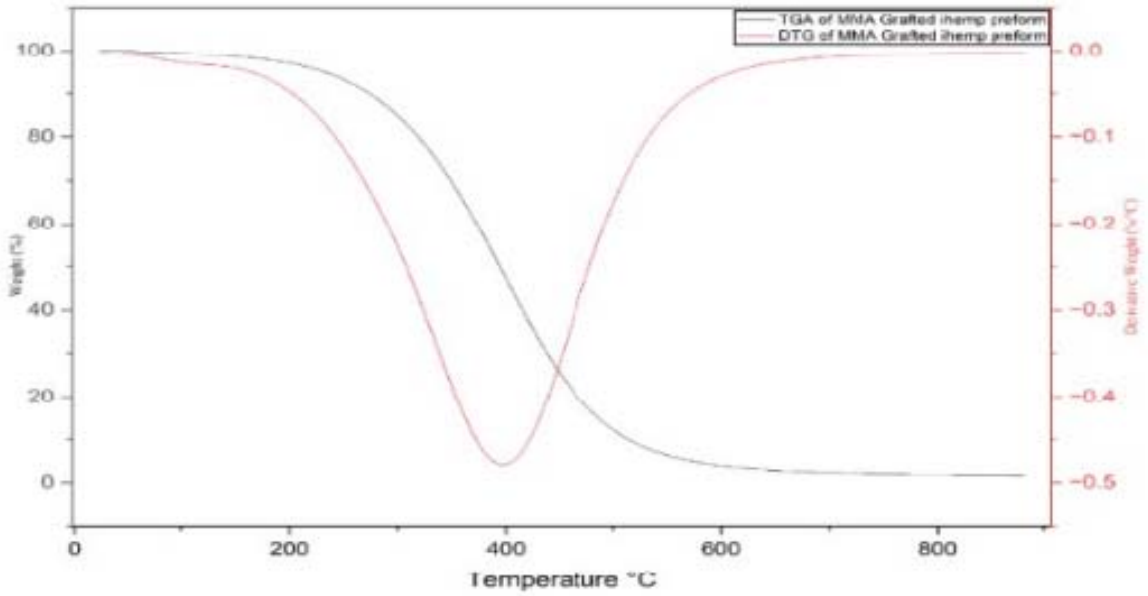

Figure 3b: TGA/DTG of grafted Ihemp preform with MMA

Scanning Electron Microscopy

The SEM micrographs reveal a clear difference between the samples. The surface of the grafted Ihemp preform (Figure 4b) is almost completely covered by a layer of poly(methyl methacrylate), indicating strong attachment of PMMA to the fibre surface.

The SEM results, which show almost complete surface coverage of the Ihemp preform with poly(methyl methacrylate) (PMMA) chains, indicate that this modification is expected to significantly enhance preform fibre-matrix interfacial adhesion when the grafted preform is incorporated into polymer composites. The grafted hydrophobic PMMA layer reduces the inherent hydrophilicity of the lignocellulosic fibre, minimises moisture absorption, and promotes better wettability and compatibility with hydrophobic polymer matrices such as vinyl ester and epoxy resins. This improved interfacial bonding facilitates efficient stress transfer from the matrix to the reinforcing preform, potentially leading to composites with superior mechanical properties, including higher tensile strength, flexural modulus, and impact resistance. Similar MMA grafting on bast fibres (e.g., kenaf and jute) has been reported to enhance fibre-matrix adhesion and overall composite performance through improved interfacial bonding (Bakar *et al*., 2014). The SEM micrographs of ungrafted and grafted Ihemp are shown in Figures 4 (a) and (b), respectively.

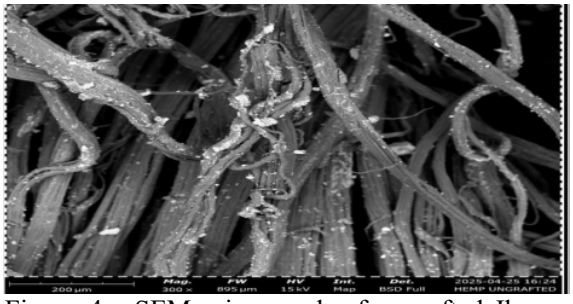

Figure 4a: SEM micrograph of ungrafted Ihemp preform

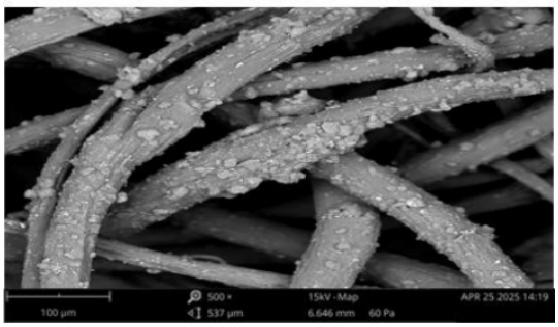

Figure 4b: SEM micrograph of grafted Ihemp preform

CONCLUSION

Free radical graft copolymerization of the hydrophobic monomer MMA onto Ihemp preform was successfully achieved using hydrogen peroxide and ferrous ammonium sulfate as the initiator system. The optimised conditions (10g Ihemp preform, 5mL MMA, 50°C, 90 minutes, 2g ferrous ammonium sulfate in 250 mL distilled water) yielded a grafting percentage of 21.5 % and grafting efficiency of 44.2%. The presence of PMMA on the Ihemp surface was confirmed by FTIR, TGA/DTG, and SEM analyses. The grafted Ihemp-g-PMMA exhibited significantly improved thermal stability compared with the ungrafted preform, making it a promising material for eco-friendly composite applications.

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