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Fabrication of polymethyl methacrylate reinforced wood lumbers for outdoor environment

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Polymethyl methacrylate (PMMA) reinforced wood lumbers (PWLs) with improved mechanical properties, thermal stability and resistance against degrading environment were fabricated and investigated for their feasibility under outdoor environment. The process of fabrication of PWLs was executed through swelling of mango wood lumbers (MWLs) into a polymerizing composition in methanol followed by thermal curing n anaerobic environment. A representative procedure of fabrication of PWLs involves swelling of MWLs into a polymerizing composition involving 2, 2-azobisisobutyronitrile (1.0% w/v) and methyl methacrylate in methanol (20 and 40%, v/v) for 24h followed by curing at 75±1ºC for additional 6h. This has afforded the PWLs with PMMA loading (wt %) up to 25 wt%. The reinforcement of PMMA into PWLs was reveled through UV, visible, Fourier transform infrared spectra and atomic force microscopy. Diverse analytical procedures revealed the formation of PWLs with improved thermal stability, mechanical properties, resistance against moisture, chemicals and biodegradation. The study reveals a feasible method for producing PWLs for potential use as a high-performance construction material that may sustain outdoor environment.

Keywords: Polymethyl methacrylate, reinforcement, mango wood lumbers, fabrication, performance evaluation

INTRODUCTION

Wood has drawn a great deal of attention since the dawn of civilization as a renewable material for construction of building components, furniture, transport, tools and weapons [1-4]. Commercially, wood has been considered as lumber or timber particles, compressed and plies boards over decades leading to circular economy [2]. This is despite the fact that the construction industry relies on concrete and alloys as substitute possibilities [1]. Preservation of wood through biocides and their polymer-assisted modification has been of great academic and industrial interest over decades due to affordable cost of manufacture and ease of operations [2-4]. Leo H. Arthur Baekeland from North America, credited as inventor of polymer reinforced wood materials, called wood plastic composites by the early 20th century. This has been accomplished during his exploratory attempt to combine wood flour with phenolic resins.The process was based on Italian extrusion technology in which wood floors were extruded at equal weight of thermoplastic materials to afford the products that have been deployed as floorings for ships and panels for automobiles [5].

Mango wood tree (*Mangifera Indica*) is a hard wood with dense grains and is primary grown for its fruit in the tropical Asian regions and other parts of Oceania. Mango tree produces a soft wood with sufficient strength for construction of furniture and building components. Mango wood suffers from periodic expansions and contractions under humid environment and is prone to dehydration in sun, heat and dry outdoor conditions [6, 7].

PMMA as such and in combination of copolymers has been employed as reinforcement for modification of a series of low-grade woods [8-10]. However, to the best of the literature survey, no reports are available on development of PWLs through reinforcing PMMA into MWLs and their onward investigation for outdoor applications sustained outdoor applications.

In order to have an insight into the scope of mango wood as a sustainable construction material for outdoor environment, investigations are still persistent to improve their mechanical properties, dimensional stability, resistance against chemicals, moisture, and microorganisms. The current study aims to develop a facile method of fabrication of PWLs through reactive reinforcement of polymethyl methacrylate (PMMA) into MWLs for possible outdoor applications. PWLs with selected PMMA loading were investigated for mechanical properties, thermal stability, resistance against solvents, water, chemicals and biodegradation in presence of a decay fungus *Gleophyllum Striatum* (brown rot).

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EXPERIMENTAL

Starting materials

MMA and AIBN were procured from Ms Sigma Aldrich. Rest of the chemicals and solvents were locally purchased (purity > 99% and used without further purification) . Inhibitor content of MMA was removed through extraction in aqueous sodium hydroxide solution (10%), followed by washing with distilled water. Fraction of MMA collected at 101±1ºC/10mm Hg (density 0.98 g/cc) was used for polymerization reactions [8].

Mango wood (*Mangifera Indica*) was arranged from nearby forest area and seasoned under relative humidity of 40% at 27± 1ºC for 3 months. The oil and wax components of seasoned wood were leached through submerging into toluene: methanol mixture (1:1, v/v) over 36h.Leached wood (density, 0.56 g/cc) was fabricated as per recommendations of IS 1708 66 for mechanical testing [5].

Fabrication of PWLs

A series of PWLs was fabricated through slight modification in traditional Bethel process, conducted in a custom designed stainless-steel chamber with provision of an evacuator and volume regulated hoper. The fabricated MWLs (IS 1708 66) were evacuated at 50±1ºC400 mmHg over 24h, thereafter submerged into a composition of MMA in methanol (20 to 60 %, v/v) supplemented with AIBN (5 wt %) at 30 ± 1ºC for 24h.The treated MWLs were placed in a furnace maintained in anaerobic environment through circulation of carbon dioxide @ 0.1 mL/min and cured at 60±1ºC for additional 12h to afford the PWLs. The loading of PMMA into PWLS was quantified through differential weighing procedure. PMMA was also synthesized under identical reaction conditions to serve as control for spectral measurements [11].

Characterization

UV spectra were recorded on a Genesis10 Thermospectronic spectrophotometer. The stock solutions (0.025M) of MMA and AIBN were prepared in dichloromethane and used for scanning of their UV spectra. Clear solutions of MWLs and PWLs were separately prepared through ultrasonic treatment of their suspensions (1.0 wt %) of saw dust in dichloromethane at 500W over 1 min followed by filtration. The FTIR spectra were recorded on a Bruker Alpha-2 spectrophotometer in KBr. AFM images were recorded over NTEGRA Prima AFM in tapping mode using ultra sharp Si cantilevers having force constant of 48 N/m at room temperature. Compressive test was conducted on ENKAY-UT-40 Universal Testing Machine of capacity of 40 tons and a precision of 80 kg. Impact tests were conducted at a domestically developed swinging pendulum machine. Simultaneous TG-DTA-DTG was conducted on a Stanton Red-Croft model STA-781@ 10ºC/min up to 500ºC with reference to alumina in a nitrogen flow of (@ 50 mL/min). Effect of PMMA reinforcement on lignin content, moisture content and solubility of PWLs in water, NaOH (1%), methanol/benzene, and ether were investigated with reference to MWLs according to standard procedures (Table 1).

Biodegradation

Biodegradation of PWLs (mesh size 60) was investigated at 25°C for 10 days under the invasion of a decay fungus *Gleophyllum Striatum (*brown rot) through food poison technique in minimal salt media (MSM) with reference to streptomycin according to early reported procedure [12]. The inhibition of fungal growth by PWLs was compared with solvents, wood flour, MMA, PMMA and AIBN. The MSM consisting of $Na_2HPO_4{\cdot}2H_2O$, KH_2PO_4, $MgSO_4$, $NH_4Fe\ (CH_3COO)_3$, and $Ca\ (NO_3)_2{\cdot}4H_2O$ was inoculated with fungus pellets and incubated at 30±1°C. The culture collected at different times was centrifuged and their supernatants were analyzed for protein, reducing sugar content and enzyme activities. A mixture containing Na_2CO_3 (2.0%), NaOH (0.1N, 50mL), $CuSO_4$ (0.5g), sodium potassium tartrate (1.0%, 5mL), and Folin Ciocalteu reagent (0.50 mL) was incubated at 25±1ºC for 30 min and measured at a wavelength of 660 nm. Standard curve was drawn using bovine serum albumin (0.5 mL, 20-200 mg/mL). Protein and reducing sugar contents were estimated (mg/mL) with reference to incubation time. CMCase assay [5,8] was made in citrate buffer (pH 4.8, 0.05M) supplemented with carboxymethyl cellulose (2%). The pre-incubated enzyme (0.5 mL) was mixed with the substrate (0.5 mL) and incubated at 50±1ºC for 30 minutes. The xylanase assay was made through monitoring the liberated reducing sugar from oat spelled xylem. A reaction mixture comprising enzyme (0.9mL) supplemented with birch xylem (0.1mL) was incubated at 50±1ºC for 10 minutes. The reducing sugar was liberated within 10 min and onward estimated at 540 nm with reference to xylose as positive control. FPase assay was made in presence of enzyme (0.5 mL), citrate buffer (pH 4.8, 1.0 mL,0.05M) and Whatman filter paper (No.1, 1×6 cm = 50±0.025 mg) under incubation at 50±1ºC for 60 min [5, 8].

RESULTS AND DISCUSSION

Spectra

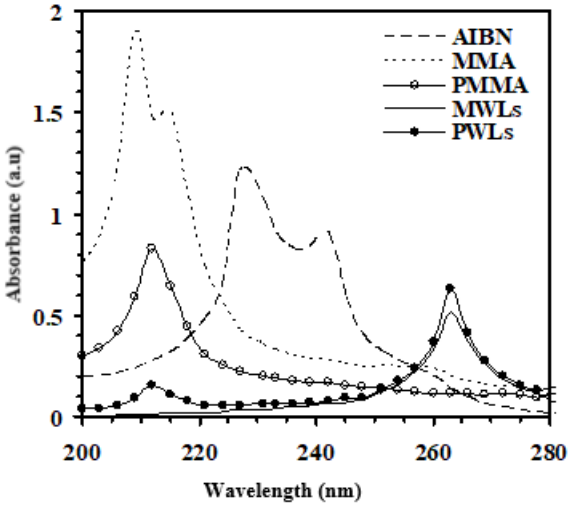

Figure 1. UV spectra

Formation of PWLs was ascertained through UV (Figure1), FTIR spectra (Figure2) and AFM (Figure3). AIBN [13], MMA [9] and PMMA [9] reveal characteristic wavelength maxima (λ_{max}, nm) at 227,245 [13],209 [9], and 212 [R], respectively. Red shift in λ_{max} of MMA from 209 to 212 nm reveals the n-π transition of the carbonyl linkage within the ester group [9]. MWLs reveal characteristic λ_{max} corresponding to lignin at 263 nm [14]. The pair of λ_{max} common to PMMA (212) and lignin (263) reveals the formation of PWLs [9, 13-14].

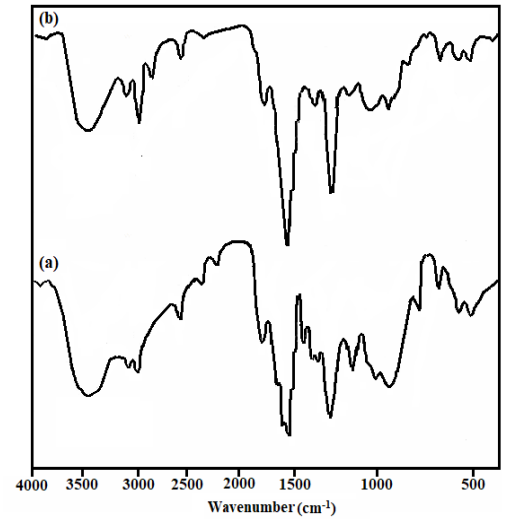

Figure 2. FTIR spectra of the saw dust of MWLs (a) and PWLs (b)

Figure 2 reveals the comparative FTIR spectra of the flours derived from MWLs and PWLs. Both MWLs and PWLs exhibit common wave numbers (cm^{-1}) corresponding to stretching vibrations of –OH (3371.5), C-H (2939.5), C=O (1738.7), bending vibrations of CH_2 (1460.2), and skeletal vibrations corresponding to C-C and C-O (1245.2 cm^{-1}). MWLs and PWLs display lignin-related absorptions at 1594.9 cm^{-1} and 1508.1, respectively. The reinforcement of PMMA has rendered a shift in wave number corresponding to lignin at 1592.7 cm^{-1}, eliminating the absorption at 1508 cm^{-1} in MWLs. In both MWLs and PWLs the wave numbers at 1629.5 and 1364.0 attribute to the bending mode of absorbed water and stretching vibrations of $–CH_3$. Due to PMMA reinforcement, the C-O-C pyranose ring skeletal vibration associated with hemicelluloses, observed at 1053.6 cm^{-1} in MWLS was shifted to 1143.7 cm^{-1} in PWLs [14, 15].

Microstructure

Absorbance of PWLs was measured through AFM (Figure 3). (bottom). The AFM topo graphs of MWLs (bottom) and respective nano-indentation images (top) are presented at 10 µm scale. The bright and dark zones in AFM represent the cellular domains of the wood. AFM and respective nanoindentations reveal characteristic cellular morphology with occasional knots and voids into MWLs (Figure 3a). AFM of PWLs and the corresponding nanoindentations reveal the absence of knots and voids with random prominence of PMMA phase into the voids of MWLs (Figure 3b).

Thermal stability

Figure 4 illustrates the effect of PMMA loading on the thermal stability of PWLs in terms of TG(a), DTA(b), and DTG(c). MWLs have shown TG onset at 210^{0}C leaving 88.70 % Wr. Reinforcement of PMMA (15 wt %) has increased the TG onset for PWL-I to 240 ^{0}C leaving 90.70 %Wr. Further increase in PMMA loading to 35 wt% has raised the TG onset of PWL-II to 320 ^{0}C with a marginal reduction in the %Wr to 86.22. Prior to TG onset temperature the residual weight loss associated with MWLs and respective PWLs attributes to their moisture content. In the present investigation the moisture content based on TG was in close agreement with (ASTM D1037 72a 79) (Table 1). MWLs have shown 6wt% moisture content. Increase in loading of PMMA has gradually reduced the moisture content of PWLs-I and PWL-II to 3.02 and 1.5 wt%, respectively [9].

TG reveals a two-step thermal decomposition by MWLs and respective PWLs. With PMMA loading the first step decomposition range for PWLs was shifted to higher temperatures. For instance, PWL-I and PWL-II have shown their respective first step decomposition temperatures ranging from 210 to 320^{0}C and 320-372 ^{0}C leaving 55 to 54.5%Wr.

Accordingly, the second step decomposition for MWLs appeared in the range of 343-450^{0}C leaving 2wt% of char residue. PWL-1 has shown second step decomposition in the higher range of 372 to 450^{0}C leaving 3.75% of char residue. The second step decomposition of PWL-II appeared in the range of390 to 480 ^{0}C leaving 2wt% of char residue (Figure3a).

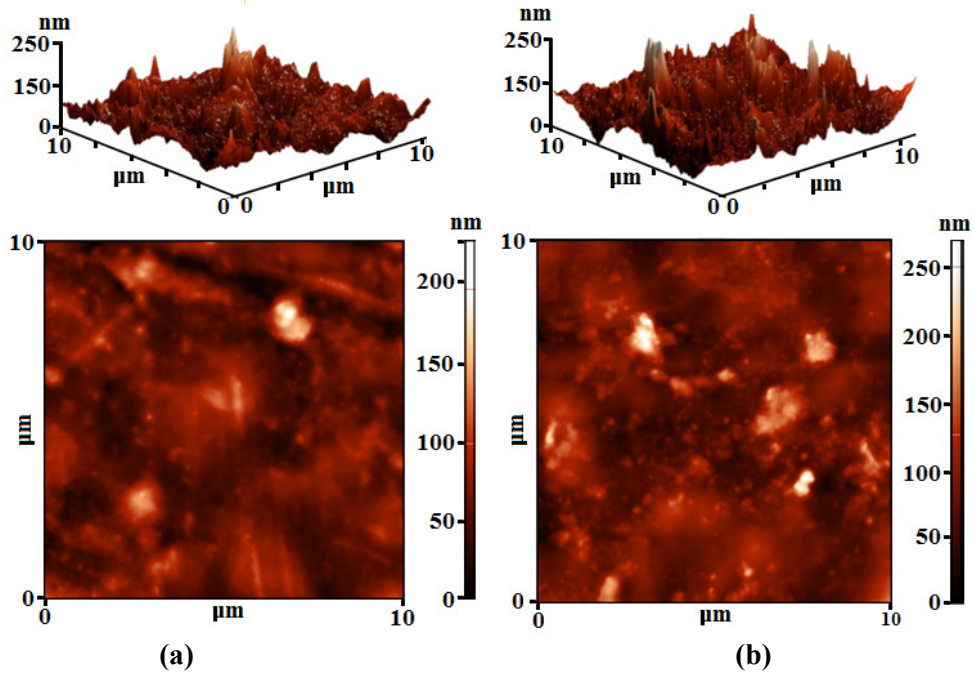

Figure 3.AFM topographs of MWLs (a) and PWL-II (b)

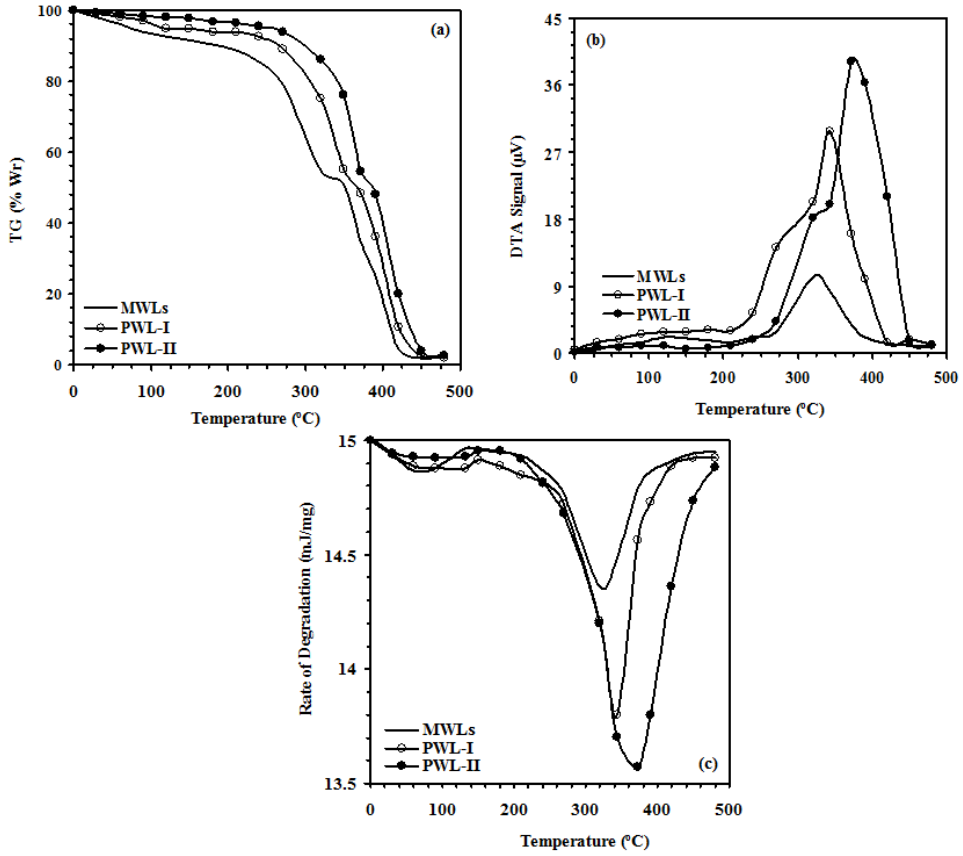

Figure 4. Effect of PMMA loading on thermal stability of PWLs

In order to have further insight into the effect of PMMA loading on thermal stability of PWLs, their respective DTA and DTG were investigated. With PMMA loading, the peak temperatures corresponding to DTA and DTG gradually increased with simultaneous reduction in the rate of degradation of PWLs. With PMMA loading, the DTA and DTG peak temperatures of PWLs were found in ascending order ranging from 320 to 372 ^{0}C (Figure4b). This was followed by simultaneous reduction in their thermal degradation (mg/min) ranging from 14.36 to 13.49 (Figure 4c). Thermal data revealed that thermal stability of PWLs increased with quantitative loading of PMMA [8, 9].

Mechanical properties

Mechanical properties of PWLs were found in increasing order with PMMA loading (Table1). MWLs have rendered 16.56 Nm of Charpy impact. With PMMA loading, the Charpy impact of PWLs gradually increased to 18.96 Nm, Similarly, the Izod impact for MWLs (8.85 Nm) increased to 13.57 Nm for PWLs-II. The compressive strength ($\times 10^7$, N/m^2) of MWLs was 3.23 that marginally increased to 4.36 for PWL-II. The experimental data pertaining to mechanical properties in association with findings through AFM revealed modification in dimensional stability of PWLs due to grafting of PMMA into the cell walls of MWLs [9,17].

Biodegradation

Figure 5a demonstrates the production of protein and reducing sugar release (mg/mL) by MWLs and respective PWLs in presence of *Gleophyllum Striatum as* a model test fungus under incubation as a function of incubation time (h). MMA and AIBN each at 250 ppm showed100% and 38% respective inhibitions in the growth of *Gleophyllum Striatum as* a model test fungus under incubation over 10 days [5].

PMMA and MWLs at ≤ 50 ppm showed remarkable fungal growth under incubation within 12 days. Whereas, under the similar experimental conditions no fungal growth was noticed over PWLs till 12 h. Production of protein (mg/mL) was initiated (0.14) in presence of MWLs and PWL-I at 12h of incubation and reached the maximum level (0.31) at 96h of incubation. However, PWL-II rendered a remarkable reduction in the production of protein from 0.09 to 0.16 in 12h.

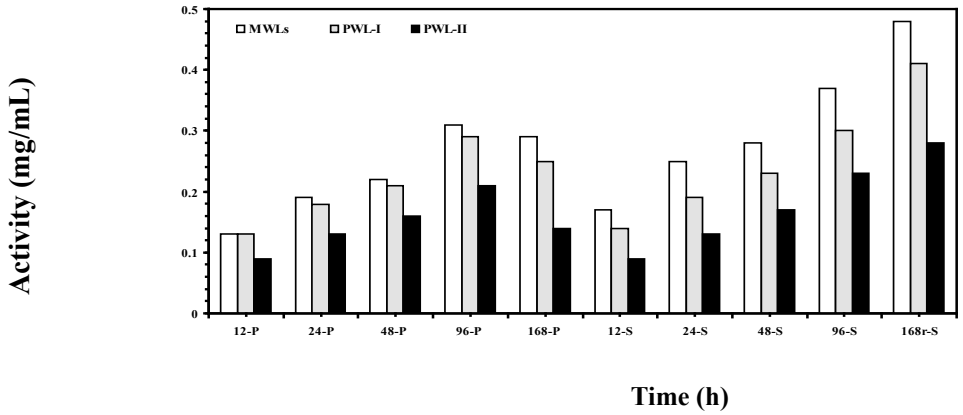

Figure 5a. Effect of PMMA loading on protein and reducing sugar activity of PWLs

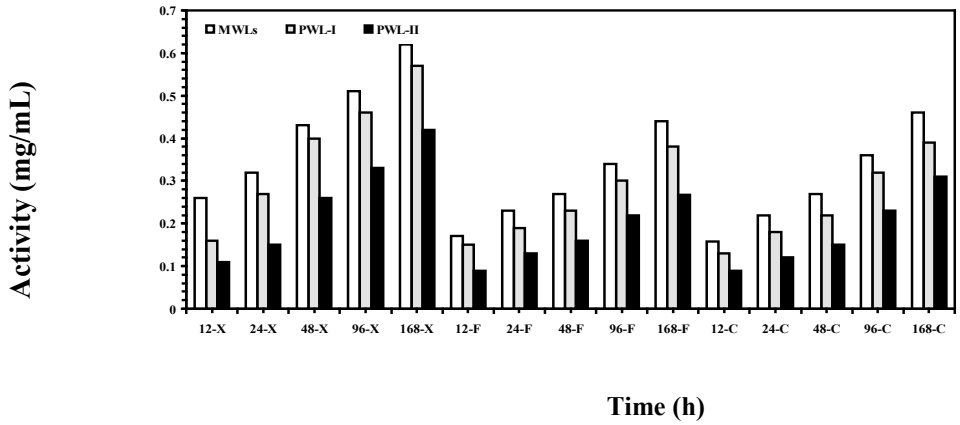

Figure 5b. Effect of PMMA loading on enzyme activity of PWLs

Table 1. Effect of PMMA reinforcement on physical characteristics of PWLs

Properties	MWLs	PWLs	
		PWL-I	PWL-II
[MMA] (v/v% in methanol)	0.00	20.00	40.00
PMMA Loading (%)	0.00	15.00	25.00
Charpy impact (Nm)[A]	16.56	17.71	18.96
Izod impact (Nm)[B]	8.85	11.65	13.57
Compression strength (n/ M^2) [C]	3.23	4.43	4.36
Moisture content (%) [D] ASTM D1037 72a 79	7.12	3.90	2.05
Lignin content (%) [E] ASTM D 1106-56	34.14	28.00	14.12
Solubility in NaOH (1%) [D]	21.11	20.50	18.35
Solubility in methanol/benzene [D]	84.80	80.12	74.36
Solubility in ether [D]	93.80	92.70	90.50
Solubility in hot water [D]	37.50	11.28	8.32
Solubility in cold water [D]	18.80	9.63	5.95

A:10 × 10 × 55 mm with V notch at the center with 2 mm depth and 45° included angle;
B: 10 × 10 × 75 mm with V notch at 28 mm with 2 mm depth and 45° included angle;
C: 50 × 50 × 75 mm;
D: ASTM D 1109 56 72.

The decline in production of protein after 96 h attributes to the utilization of available substrate in the medium by fungus. The reducing sugar content of MWLs reached maximum after 168h of incubation. PWLs-II showed reduction in reducing sugar content by 46.56% up to 24 h, followed by 25.22% for PWL-I and PWL-II. Such increase in the production of reducing sugar attributes to the availability of substrate for *Gleophyllum Striatum.*

MWLs and respective PWLs rendered a collective progress in Cellulolytic (FPase, CMCase) and xylanolytic enzymes production, that reached a maximum after 168 h of incubation in presence of *Gleophyllum Striatum.* PWLs rendered a remarkable reduction in enzyme activity due to PMMA loading. Relatively, MWLs rendered higher production of Xylanase (IU/mL) over cellulytic (IU/mL) enzyme in comparison to PWLs. In presence of MWLs, Xylanase enzyme activity (0.22) was initiated after 12 h of incubation and reached maximum (0.62) at 168h. PWLs-II rendered a reduction (50.80%) in the Xylanase activity within 24 h [5,9].

Figure 5b demonstrates the enzyme activity (IU/mL) by MWLs and respective PWLs in presence of *Gleophyllum Striatum* under incubation as a function of incubation time (h). FPase activity (0.15) was started after 12h of incubation and reached maximum (0.44) at 168 h of incubation in PWLs. The sequential reduction (45.6%) in the FPase activity was noticed for PWLs-II followed by PWLs at 12h. CMCase activity (0.16) started after 12 h of incubation and reached maximum (0.47) at 168 h for MWLs. PMMA loading reduced the CMCase activity for PWL-II (43.69%) followed by PWL-I (39.25%) in 12h of incubation in presence of the test fungus. The reduction in production of protein, reducing sugar contents in coherence with enzyme activities attributes to resistance of PWLs towards biodegradation due to restricted transport of moisture across their cell walls due to the loading of PMMA [5,9,18].

Solubility behavior

Treatment of thermosetting [5, 8-10] and thermoplastic polymers [19] with wood substrates offers an amicable way to achieve the biocomposites with improve resistance against water and organic media. The present study demonstrates the impact of PMMA reinforcement on solubility behavior of PWLs in water, alkaline solutions and organic solvents. The solubility of PWLs in various solvating media has been gradually reduced with their PMMA content [8]. PWLs has rendered decreasing order of their solubility over MWLs in alcohol benzene mixture, followed by hexane, hot water, aqueous sodium hydroxide (1%), and cold water. The low solubility of PWLs in the alcohol benzene mixture attributes to the loss of waxes, fats, resins, and oil contents associated with MWLs [5]. The reduction in solubility in a sodium hydroxide (1%) solution attributes to the qualitative reduction in the fraction of lignin content with quantitative reinforcement of PMMA into PWLs [9,20]. (Table 1).

CONCLUSION

Polymethyl methacrylate (PMMA)-reinforced mango wood lumbers (MWLs) with improved mechanical properties, thermal stability, resistance to chemicals, solvents, and biodegradation were fabricated and designated as PWLs. Progressive loading of PMMA led to enhancement in mechanical characteristics, encompassing impact strength and compressive strength. The biodegradation studies through monitoring the changes in protein and reducing sugar contents (mg/mL), as well as cellulolytic *(FPase, CMCase)* and *xylanolytic* enzyme activities (IU/mL) at various incubation times up to 168 hours unveiled the significant resistance of PWLs to the *Gleophyllum Striatum* decay fungus. The study yielded valuable insights into the potential of PWLs as high-performance construction materials for future outdoor applications.

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