Mechanical, moisture absorption, biodegradation and physical properties of nanoclay-reinforced wood/plant oil composites

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Abstract

Composite materials were prepared via a compression molding process utilizing modified soybean oil, wood flour, and rosin derivative. Montmorillonite (MMT) was used as a nano-filler to increase the properties of composites prepared from methacrylic anhydride based epoxidized soybean oil co-polymerized with divinyl acrylicpimaric acid. The synthesized composites were characterized by Fourier transform infrared spectroscopy and X-ray diffractometry. The MMT filled composites showed enhanced mechanical properties compared to MMT free composites. The thermal stability of MMT filled composites was higher compared to those of unfilled composites due to the development of a protective residue. The morphological study by scanning electron microscope showed that the nano-clay particles were well dispersed throughout the matrix. The effects of MMT on biodegradability of the wood composites was analyzed by UV-spectrophotometry. In addition to that, the mechanical properties of the composite were evaluated after exposure to microorganism attack.

Keywords Wood composites · Rosin derivatives · Thermal properties · Bio-degradation · Mechanical properties

1 Introduction

In the past few decades, current environmental guidelines and societal distress have provoked the necessity to develop bio-based materials and other innovative processes that can emancipate worldwide dependency on fossil fuels. These bio-based materials are used as replacement for various traditional materials (i.e. metals), due to their intrinsic properties such as ease of construction, structural control, productivity, abundance, less laborious process, and low cost [1]. Composites made from synthetic reinforcements and polymer matrices are losing popularity owing to their serious environmental issues and high cost [2]. Bio-based composites are witnessing numerous applications due to their enhanced properties and the various advantages they have over petroleum based resources in terms of renewability, availability, and biodegradability [3]. One crucial effort has been the preparation and utilization of bio-based materials from environmentally favorable

starting materials, such as starch, cellulose, straw, wood fibers, plant oils, proteins etc.

Wood is an important natural resource that addresses various survival and developmental needs of human society. However, solid wood has some disadvantages like dimensional instability which restrict its application in diverse sectors. The reason for such defects is due to the abundance of hydroxyl groups in the wood cell walls, which swell the fibres in the presence of moisture or water. As a consequence, the physical, mechanical, and chemical features of wood are negatively influenced [4]. Hence, the properties of wood can be enriched by the fabrication of wood polymer composites (WPCs) [5]. WPCs are known to have greater longevity and lower maintenance cost, desirable dimensional stability, better screening to moisture and biological degradation, low price compared to composites prepared with other fibers, and preferable recyclability [6]. Conventional chemical processing has turned out to be productive in enhancing composite's mechanical

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properties, dimensional stability, and stiffness. Apart from that, fire retardation, UV screening, and biological resistance can be considerably enhanced by the incorporation of nanomaterials within the wood composites [7]. Wood polymer nanocomposites (WPNCs) are materials in which nano-sized inorganic particles having at least one dimension in the nanometer range are dispersed in an organic polymeric matrix [8]. WPNCs have superior properties compared to the conventional composites due to their nano level characteristic which maximizes the interfacial adhesion [9]. Its improved barrier properties, chemical hindrance, and the exterior finish make it a worthy material for various applications such as automotive, constructions, marines, consumer products, packaging, electronic, and aerospace industries, etc. [10, 11].

Vegetable oils such as soybean and linseed oil are found to be suitable for the synthesis of resins to substitute the conventional petrochemical based polymers [12, 13]. Vegetable oil has the advantage of being one of the most affordable and eco-rich products available in large quantities. Soybean oil is an unsaturated triglyceride, which mainly consists of linolenic acid, linoleic acid, oleic acid, palmitic acid, and stearic acid. Triglycerides are composed of three fatty acid chains joined by a glycerol center. Soybean oil contains active functional groups such as double bonds which can be altered chemically to fabricate polymers having desirable properties [14, 15]. The motive for functionalization is to increase the molecular weight and the crosslinking density in order to provide stiffness in the polymeric chains, which leads to elevated mechanical properties [16]. The triglyceride molecules in soybean oil are modified through epoxidation reaction that results in the formation of epoxidized soybean oil (ESO). Epoxidized soybean oil is not reactive enough. One of the ways to make it reactive is to introduce the double bond which can be further utilized for polymerization reaction [17]. Thus ESO is modified further with methacrylic acid and methacrylic anhydride to produce methacrylic anhydride modified epoxidized soybean oil (MAESO). Reactive diluent like styrene (St) or divinylbenzene (DVB) having low molecular weight, which can be utilized as co-monomers to make the thermo-physical and mechanical properties of plant oil based resins acceptable for structural applications. However, both St and DVB are volatile organic compounds, and hence, efforts have been made to substitute all or part of St or DVB with environmentally favorable co-monomers [18, 19].

Rosin is a solid form of resin obtained from pines containing isomeric abietic acids (40–60%) and pimaric acids (9–27%). Rosin is abundant in nature, low cost, and

biodegradable it can be functionalized further to convert it into a promising renewable feedstock in polymer synthesis. Rosin acids are similar to cycloaliphatic or aromatic compounds in terms of molecular rigidity, owing to their huge hydrogenated phenanthrene ring composition. These derivatives are reported to be used as a replacement to various petroleum-derived rigid monomers in the synthesis of polymers [20, 21]. Rosin derivatives can be co-polymerized with soybean oil based polymers to develop thermosetting resins that are entirely bio-based [22].

Nano-fillers at a lower level are used to minimize the processing difficulties and also to increase the mechanical, chemical and thermal properties. The incorporation of nanomaterials such as TiO_2 , SiO_2 , nano-clay, CNTs, ZnO, etc. to the polymeric matrix shows an improvement in the properties of WPCs. Nanoclays are fine-grained particles regarded as hydrous silicates with a sheet-like structure stacked above one another. Nanoclay reinforced polymer composites have received immense attention in the area of nano-composites due to their exceptional capability of enhancing the mechanical, thermal and barrier properties even at a low level of addition [23, 24]. The enhanced performance of the nanocomposites could only be perceived at nanoscale diffusion and are achieved by the exfoliation of nanofiller [25, 26]. The petroleum-derived polymers are incompatible with clay minerals due to the dissimilarity in their surface energies, and hence the exfoliation of clay platelets is one of the major challenges experienced during the preparation of nanocomposites. This can be overcome by surface modification where surfactants having compatibility with the organic polymers are exchanged with exchangeable cations present in the nanoclay which increases the spacing between the layers (d-spacing) [27].

In our earlier work, wood composites were developed by using a derivative of rosin acid, i.e. divinyl acrylicpimaric acid (DAPA) containing two reactive divinyl functionalities and MAESO resin to form a strong network structure [28]. The improvement in various properties of the composite was also reported due to the presence of hydrophenanthrene moiety of rosin derivative. The current work aims to study the properties of wood polymer composites prepared by using wood, MAESO resin, DAPA, and MMT. A tiny part of the probable cross-linked structure of WPC is shown in Scheme 1. The properties of composites with different percentages of nano-clay were investigated and reported. Furthermore, surface morphology, mechanical properties, thermal stability, flame retardancy, biodegradability, dimensional stability and chemical resistance of the WPCs were investigated both with and without nano-clay.

Scheme 1 A plausible cross-linked structure of wood polymer composite reinforced with nanoclay

2 Experimental procedure

2.1 Raw materials

Epoxidized soybean oil (ESO) was bought from Agarwal organics, Indore (India). The physicochemical properties of ESO were reported in our previous paper [29]. Nanoclay (montmorillonite clay surface modified with 15–35 wt% octadecylamine and 0.5–5 wt% aminopropyltriethoxysilane), Methacrylic anhydride, Cobalt(II)2-ethylhexanoate were purchased from Sigma Aldrich, USA. Methacrylic acid, Methyl ethyl ketone peroxide (MEKP), *N*-methylimidazole and Diethyl ether were purchased from Merck India Limited, Mumbai (India). Sodium Hydroxide and Acrylic acid were procured from Sisco Research Laboratories Pvt. Ltd, India. Hydroquinone was purchased from G.S. Chemical testing laboratory and allied industries (India). Rosin acid was bought from Alfa Aesar, USA. Petroleum ether was obtained from

Ranbaxy Chemicals, India. Allyl Bromide was obtained from Loba Chemie, Mumbai, India. All other solvents were used as received.

Softwood, Krishnachura (*Delonix regia*) was gathered from the local forest of Tezpur, Assam (India). The collected wood specimens were chopped into small pieces ($\approx 2\text{--}3\text{ cm}$), washed with water and soap solution. It was treated with 1% NaOH solution to enhance the surface roughness and remove the lignin. It was then dried in an oven, grounded and sieved using 70 mesh sized sieve to obtain the wood powder [29].

2.2 Synthesis of acrylicpimaric acid (APA)

The synthesis of APA was carried out according to the procedure reported in the literature [28].

2.3 Synthesis of divinyl acrylicpimaric acid (DAPA)

To synthesize divinyl acrylicpimaric acid (DAPA), 5 g of APA, 3.5 g of potassium carbonate with 4.33 mL of acetone were placed in a round-bottom flask. 7 g of allyl bromide (0.6 mol) solution with 2 mL of acetone was added to the flask drop wise at 50 °C. The mixture was refluxed for 12 h at 70 °C after which it was cooled to room temperature and then cleansed with dichloromethane (DCM). The collection of the organic phase was done by an extraction process and again cleansed several times with distilled water and then the solvent was separated in a rotary evaporator. Finally, a yellow colored product was obtained, weighing 4.2 g with a yield of 81%. The characterization of the structure was done by FTIR and ¹H-NMR spectroscopy [28].

2.4 Synthesis of methacrylic anhydride epoxidized soybean oil (MAESO)

The preparation of MAESO was described in our previous paper [29]. Briefly, MAESO was prepared by the reaction of epoxidized soybean oil (ESO) with methacrylic acid to form methacrylated epoxidized soybean oil (MESO), which was further functionalized with methacrylic anhydride to form methacrylic anhydride modified epoxidized soybean oil (MAESO).

2.5 Development of wood polymer composite sheets reinforced with nanoclay

In a 3-necked round bottom flask, DAPA and nanoclay were added to MAESO resins with the predetermined ratio as shown in Table 1. After extensive stirring, cobalt (II) 2-ethylhexanoate solution (promoter) and methyl ethyl ketone peroxide (catalyst) were added with vigorous stirring to get a homogeneous mixture. To this mixture wood powder was added and again stirred intensely with a mechanical stirrer. Finally, the whole mixture was poured in a tray, dried and then composite sheets were prepared. The nano-clay reinforced composite sheets were prepared

with the help of a compression molding press (S.C. Dey Co. Kolkata). The temperature, pressure, and time for molding were kept at 140 °C, 50 MPa, and 30 min respectively.

2.6 Bacterial media

Mineral salt medium having the following composition was prepared for bacterial growth: 4.75 g of KH₂PO₄, 2.0 g of Na₂HPO₄, 2.0 g of (NH₄)₂SO₄, 1.2 g of MgSO₄·7H₂O, 100 mg of MnSO₄·5H₂O, 100 mg of CuSO₄·7H₂O, 70 mg of ZnSO₄·7H₂O, 10 mg of H₃BO₃·5H₂O, 10 mg of MoO₃, 1 mg of FeSO₄·7H₂O, and 0.5 mg of CaCl₂·2H₂O were dissolved in 1000 mL of distilled water. 100 mL of this liquid culture medium was then poured into a 250 mL conical flask and sterilized in an autoclave at 121 °C, 15 lb per inches² square pressure for 15 min. The autoclaved media was then allowed to cool to room temperature, and composite samples were added into the media under sterile condition inside a laminar air flow hood. Media containing only polymer samples without bacteria was also cultured as the control.

2.7 Bacterial strain

Pseudomonas aeruginosa MTCC 2297 was grown on nutrient broth at 37 °C for 18 h. 1 mL of bacterial culture was centrifuged at 6000 rpm for 20 min at room temperature, and the pellets were washed with 0.9% NaCl and re-suspended in 1 mL of mineral salt medium. Thereafter, 0.5 mL of the culture medium (0.4 O. D 660 nm) was inoculated in 50 mL centrifuge tube containing 10 mL of media for each test. The test tubes were then incubated at 37 °C, 120 rpm for the degradation study. The absorbance at 660 nm was recorded every month.

3 Characterization

3.1 Fourier transform infrared (FTIR) spectroscopy

FTIR study was performed in transmission mode over the wavenumber range of 4000–500 cm⁻¹ by a Nicolet

Table 1 Formulations of various wood polymer composites

Sample code	Ingredients					
	MAESO (resin)	DAPA (wt%)	Pro-moter (wt%)	MEKP (wt%)	Wood flour (WF)	Nanoclay (NC) (wt%)
MAESO/DAPA/WF/NC0	42	16.5	0.5	1	40	0
MAESO/DAPA/WF/NC1	42	16.5	0.5	1	39	1
MAESO/DAPA/WF/NC3	42	16.5	0.5	1	37	3
MAESO/DAPA/WF/NC5	42	16.5	0.5	1	35	5

MAESO, methacrylic anhydride epoxidized soybean oil; DAPA, divinyl acrylicpimaric acid; WF, wood flour; NC, nano-clay

(Madison, WI) FTIR impact 410 spectrophotometer using KBr pellets. The samples were prepared by keeping the ratio of thoroughly grounded composite sample to KBr as 1:20 approximately. Both the powder sample and KBr were homogeneously grounded in a mortar. Around 5 mg of the sample mixture was taken and pressed in hydraulic press in order to make the pellets.

3.2 Powder X-ray diffraction (XRD) study

The powder X-ray diffraction measurements were performed at room temperature on a D8 FOCUS X-ray diffractometer (Bruker Axs, Germany) using Cu K α ($\lambda = 0.154$ nm) radiation over the range of $2\theta = 3^\circ - 50^\circ$ at a scanning rate of $1^\circ/\text{min}$.

3.3 Transmission electron microscopy (TEM)

The distribution of nano-clay in the composite samples was studied by using a transmission electron microscope (JEM-2100, Japan) at an accelerating voltage of 60–200 kV. The samples were embedded with epoxy resin for the preparation of ultra-thin as well as polished sections. An ultramicrotome fitted with a diamond knife was used for ultrathin sectioning of the surfaces. The sections were then stained with 1 wt% of uranyl acetate for sufficient contrast, mounted on grids and examined.

3.4 Mechanical properties

The tensile and flexural tests for both with and without nano-clay reinforced composites were analyzed by Universal Testing Machine (Zwick, model Z010, Germany) according to ASTM D-638 and D-790 respectively. For this test, three specimens of each category were analyzed to calculate the average value of their tensile and flexural strength. The dimensions of the samples taken were (10 cm $\times$ 0.5 cm $\times$ 2 cm) and (1 cm $\times$ 1 cm $\times$ 10 cm).

3.5 Statistical analysis

Data were expressed as mean $\pm$ standard deviation (SD). The mechanical property results were analyzed statistically using one-way analysis of variance (ANOVA).

3.6 Hardness test

The hardness of the samples was measured with a durometer (model RR12) according to ASTM D-2240. It was

expressed as shore D. For this test, three specimens of each category were analyzed.

3.7 Thermogravimetric analysis (TGA)

It was performed on a thermogravimetric analyzer (TGA-50, Shimadzu, Japan) by using high purity nitrogen as the purge gas at a scanning rate of 5°C min^{-1} from 25 to 600 $^\circ\text{C}$. The nitrogen flow rate was maintained at 30 mL min^{-1} .

3.8 Limiting Oxygen Index (LOI) Test

LOI values were measured on a flammability tester (S.C. Dey Co., Kolkata) according to the ASTM D-2863 method. The sample was placed vertically in the sample holder of the LOI apparatus. The ratio of nitrogen and oxygen at which the samples continued to burn for at least 30 s was recorded and examined further.

Limiting Oxygen Index

$$= \text{Volume of O}_2 / (\text{Volume of O}_2 + \text{Volume of N}_2)$$

3.9 Scanning electron microscope (SEM) study

Scanning electron microscopy was performed on a scanning electron microscope, (JEOL JSM-6390LV, Japan) at an accelerating voltage of 5–10 kV. The fractured surface of the composite sample was mounted on a sample holder and sputter-coated with platinum.

3.10 Water vapor uptake and dimensional stability test

All the test specimens were oven dried and conditioned at room temperature (30 $^\circ\text{C}$) with 30% relative humidity before the test. Three samples of each category were cut into pieces of (2.5 cm $\times$ 0.5 cm $\times$ 2.5 cm), and weights of the oven-dried samples were measured. The test was carried out by placing the samples at 65% relative humidity maintaining a temperature of 30 $^\circ\text{C}$. The excess water was removed and weights of the specimens were recorded after 6, 12, 24, 36, 48, 60, 72, 84, 96, 120 h. The water uptake or water adsorption (wt%) was then calculated based on the ratio of the weight difference between the conditioned and dried samples to the dried sample weight. Similarly, volumetric swelling was measured as a change in volume and is expressed as the percentage of volume increase compared to oven-dried samples.

$$\text{Water vapor uptake (\%)} = (W_t - W_o) / W_o \times 100$$

where “ W_t ” is the weight of the specimen after moisture absorption and “ W_o ” is the weight of oven dried specimen.

Volumetric swelling was considered as a change in volume and is expressed as the percentage of volume increase compared to oven-dried samples.

$$\% \text{ Volumetric swelling} = (V_f - V_o) / V_o \times 100$$

where “ V_f ” is the volume of the specimen after water absorption and “ V_o ” is the volume of the oven-dried specimen.

3.11 Chemical resistance test

All the specimens were cut into pieces of (2.5 cm × 0.5 cm × 2.5 cm) and were kept immersed in 4% NaOH solution and 4% acetic acid solution for 24 h and 7 days. The volumes of these samples were measured using Vernier callipers. The percentage of swelling was calculated by using the equation as given below,

$$\% \text{ Swelling} = (V_c - V_o) / V_o \times 100$$

where ‘ V_c ’ is the volume of the wood polymer composite after immersion in chemicals and ‘ V_o ’ is the volume of the composite before immersion in chemicals.

3.12 Biodegradation study

The composite samples treated with various percentage of MMT were exposed to cellulolytic bacterial strain in liquid broth culture medium for the biodegradation study. Two samples of each category were analyzed for the biodegradation study. The bacterial growth and biodegradation rate in the broth culture medium were studied using a UV visible spectrophotometer (Shimadzu Corporation UV2450 spectrophotometer, Kyoto, Japan) at 600 nm against blank culture media under sterile condition. The bacterial growth on the samples was plotted with respect to time.

4 Results and discussion

4.1 FTIR spectroscopy

FTIR spectra of nanoclay, wood flour, and composites loaded with different MMT percentages are shown in Fig. 1. The FTIR spectrum of nanoclay (curve a) showed a peak at 3424 cm⁻¹ corresponding to -OH stretching, 2930 cm⁻¹ and 2850 cm⁻¹ which were due to asymmetric and symmetric vibration of methylene group (CH₂) in the organic compound, 1628 cm⁻¹ due to -OH bending and

Fig. 1 The FTIR spectra of (a) nanoclay, (b) wood flour, (c) MAESO/DAPA/WF/NC0, (d) MAESO/DAPA/WF/NC1, (e) MAESO/DAPA/WF/NC3 and (f) MAESO/DAPA/WF/NC5

1053–460 cm⁻¹ for oxide bonds of metals like Si, Al, Mg, etc. Wood flour (curve b) shows the presence of bands at 3457 cm⁻¹ for -OH stretching, 2920 and 2840 cm⁻¹ due to -CH₂ asymmetric stretching in alkyl groups for cellulose and lignin, 1740 cm⁻¹ due to C=O stretching of hemicellulose, 1660 cm⁻¹ due to -OH bending, and 1058 cm⁻¹ and 1000–650 cm⁻¹ due to -CO stretching and out of the plane -CH bending vibration respectively.

Figure 1, curve (c–f) shows the spectra of composites loaded with different percentage of nano-clay. In MAESO/DAPA/WF/NC0 (curve c), the hydroxyl peak that appeared at 3457 cm⁻¹ for virgin wood was found to shift to 3432 cm⁻¹. Similarly, for MAESO/DAPA/WF/NC1 (curve d), MAESO/DAPA/WF/NC3 (curve e) and MAESO/DAPA/WF/NC5 (curve f), the hydroxyl peaks were found to shift to 3425 cm⁻¹, 3424 cm⁻¹ and 3430 cm⁻¹ respectively. The shifting of hydroxyl peak to lower wavenumber might be attributed to the crosslinking reaction caused by the participation of -OH group of clay and wood. However, at higher clay (5%) loading, the shifting of hydroxyl peak to lower wave number was almost similar to that of clay free composites. This might be due to decrease in interaction among the components caused by the agglomeration of nanoclay. Hazarika et al. reported the shifting of hydroxyl peak to lower wavenumber while studying the FTIR analysis of softwood polymer nanocomposites reinforced with ZnO nanoparticles and nanoclay [30]. In the composites containing 5 wt% nanoclay, the hydroxyl peak shifted to higher wave number (i.e. 3430 cm⁻¹) compared to composites having 3 wt% nanoclay. This might be due to the decrease in the interaction of MMT particles with the composite matrix. Again, the -OH

bending peak that appeared at 1628 cm^{-1} for MMT was found to shift to 1625 cm^{-1} for MAESO/DAPA/WF/NC0 (curve c), 1620 cm^{-1} for MAESO/DAPA/WF/NC1 (curve d), 1616 cm^{-1} for MAESO/DAPA/WF/NC3 (curve e) and 1615 cm^{-1} for MAESO/DAPA/WF/NC5 (curve f), respectively. This might be due to the participation of hydroxyl group of clay with wood, nanoclay, co-monomer DAPA and MAESO resin [29, 31].

4.2 X-ray diffraction studies

The XRD patterns for wood flour and MMT are shown in Fig. 2A and for composites reinforced with different percentages of MMT are illustrated in Fig. 2B. In Fig. 2A, the peak (curve a) that appeared at $2\theta = 22.90^\circ$ was due to the diffraction of (002) plane of wood cellulose. The XRD pattern for nanoclay in Fig. 2A (curve b), showed peaks at around $2\theta = 4.03^\circ$ and 27.20° . The intensity of peak due to wood cellulose decreased in all the composites with the inclusion of MMT inside the polymer matrix. The position of band appeared at $2\theta = 22.50^\circ$ in nanoclay free composites was found to shift to 21.42° for MAESO/DAPA/WF/NC1 (curve b), 20.68° for MAESO/DAPA/WF/NC3 (curve c) and 20.74° for MAESO/DAPA/WF/NC5 (curve d) from 22.90° as shown in Fig. 2A (curve a). The decrease in peak intensity and shifting of broad peak indicated that the crystallinity in the wood decreased and some nano-clay laminae were incorporated into the amorphous area of wood cellulose. Comparing the diffraction patterns of the clay-reinforced composite samples, the peak for nanoclay at $2\theta = 4.03^\circ$ was found to shift towards lower angle (3.90° – 3.98°), indicating

occurrence of significant intercalation of polymer chains between the galleries of the clay [8].

4.3 Transmission electron microscopy (TEM)

The distribution of the nano-clay into the polymer matrix was inspected by a transmission electron microscope that is shown in Fig. 3. The silicate layers were visible as dark grey lines in the TEM images of 3 wt% nano-clay containing composite (i.e. MAESO/DAPA/WF/NC3). This suggested that the clay layers were delaminated and distributed into the polymer matrix of the composites. However, the clay particles were found to agglomerate in 5 wt% nano-clay containing composite (i.e. MAESO/DAPA/WF/NC5). Therefore, it could be said that the clay layers were not sufficiently delaminated and either very less polymers would intrude into the gallery spacing. It could be concluded that the dispersion of clay particles in 3 wt% MMT loading composite was better than that of 5 wt% MMT containing composites [32].

4.4 Scanning electron microscope (SEM)

The SEM micrographs of composites loaded with various percentage of clay are shown in Fig. 4. The rough surface observed for MAESO/DAPA/WF/NC0 (Fig. 4a) and MAESO/DAPA/WF/NC1 (Fig. 4b) composites indicated a poor interaction among wood, MAESO resin, and DAPA. With the increase in clay content, the surface roughness decreased up to a certain extent. For MAESO/DAPA/

Fig. 2 XRD patterns for **A**—(a) wood flour, (b) MMT, **(B)**—(a) MAESO/DAPA/WF/NC0, (b) MAESO/DAPA/WF/NC1, (c) MAESO/DAPA/WF/NC3 and (d) MAESO/DAPA/WF/NC5

Fig. 3 TEM images of **a** MAESO/DAPA/WF/NC3 and **b** MAESO/DAPA/WF/NC5

Fig. 4 SEM images of **a** MAESO/DAPA/WF/NC0, **b** MAESO/DAPA/WF/NC1, **c** MAESO/DAPA/WF/NC3 and **d** MAESO/DAPA/WF/NC5

WF/NC3 (Fig. 4c) composite, the clay particles were dispersed properly into the polymer matrix due to which a smooth surface was observed. This indicated a better interaction between MAESO, wood flour, and rosin derivative. However, when the clay content was increased to

5 wt%, the surface roughness increased, which might be due to less compatibility between various components of wood composites. In MAESO/DAPA/WF/NC5 (Fig. 4d), the clay particles might have agglomerated due to which

Table 2 Flexural, tensile, hardness and LOI values of the WPCs both with and without nano-clay

Sample	Flexural strength (MPa)	Tensile strength (MPa)	Hardness shore D	LOI (%)
MAESO/DAPA/WF/NC0	65.05 (± 0.38)	31.62 (± 0.68)	70.46 (± 0.97)	55
MAESO/DAPA/WF/NC1	67.13 (± 0.29)	32.02 (± 1.30)	70.89 (± 0.84)	57
MAESO/DAPA/WF/NC3	70.64 (± 0.64)	35.54 (± 0.60)	74.12 (± 0.08)	60
MAESO/DAPA/WF/NC5	68.95 (± 0.32)	33.47 (± 0.54)	71.09 (± 0.71)	58

an increase in surface roughness was observed [33]. This was further supported by the FTIR and TEM studies.

4.5 Mechanical properties

The flexural, tensile and hardness values of wood polymer composites loaded with various nanoclay percentages is shown in Table 2. The mechanical properties of the composites were dependent on the interactions between wood flour and the polymer matrix. For the composites, both the tensile and flexural strength increased with increasing nanoclay content up to 3 wt%. The improvement in properties at 3 wt% clay loading could be attributed to the development of strong interactions between the polymer matrix and silicate layers. Also, the presence of bulky hydrogenated phenanthrene ring of DAPA contributed to the improvement of mechanical properties. The decrease in tensile and flexural strength at 5 wt% of clay loading in the polymer matrix might be due to the formation of agglomerated clay tactoids. FTIR study of composites containing 5 wt% nanoclay also supported the decrease

in interactions between clay and other ingredients in the composites.

From Table 2, it was also observed that the LOI value increased with the increase in the percentage of nano-clay up to 3 wt%, but beyond that, it decreased. Nano-clay particles produced silicate char on the surface of the composites which provided a thermal barrier to the oxygen and heat leading to an improvement in the flame retardant property. At higher MMT loading, the agglomeration of nanoclay resulted in the decrease in interactions and barrier property.

4.6 Chemical resistance test

The chemical resistance study for both with and without nanoclay reinforced composites is shown in Fig. 5. The specimens were kept immersed in 4% acetic acid and 4% NaOH solution for the chemical resistance test. From the figure, it was observed that swelling was least in the case of composites treated with 3 wt% nanoclay. This was due to the formation of a compact structure that arose due to the increase in interfacial adhesion among the resin, cross-linker, wood, and nanoclay. The chemical resistance test

Fig. 5 Chemical resistance of (a) MAESO/DAPA/WF/NC0, (b) MAESO/DAPA/WF/NC1, (c) MAESO/DAPA/WF/NC3 and (d) MAESO/DAPA/WF/NC5

Fig. 6 Water vapor uptake and dimensional stability of (a) MAESO/DAPA/WF/NC0, (b) MAESO/DAPA/WF/NC1, (c) MAESO/DAPA/WF/NC3 and (d) MAESO/DAPA/WF/NC5

indicated that nano-reinforced composite was more resistant towards acid than alkali solution. The lower resistance observed in alkali solution might be due to the increase in interaction by sodium hydroxide with wood cellulose and clay layers [34].

4.7 Water vapor uptake and dimensional stability test

The water vapor uptake and dimensional stability of both with and without nanoclay reinforced composites versus time are shown in Fig. 6. The composites loaded with MMT absorbed less moisture than the composite without MMT. The silicate layers of clay provided a barrier to water vapor

uptake. The water vapour uptake capacity was least for 3 wt% of clay loading composite, which might be due to the formation of a compact structure and as a result the accessibility of moisture is restricted. At a higher percentage of clay loading (5 wt%), agglomeration of clay particles might have occurred. This facilitated the absorption of water vapor resulting in an increase of volumetric swelling.

4.8 Thermal properties

The results of thermogravimetric analysis (TGA/DTG) for different composites samples are shown in Fig. 7. The initial decomposition temperature (T_i), maximum pyrolysis temperature (T_m), decomposition temperature (T_D) at

Fig. 7 TGA/DTG curves of (a) MAESO/DAPA/WF/NC3, (b) MAESO/DAPA/WF/NC5, (c) MAESO/DAPA/WF/NC1 and (d) MAESO/DAPA/WF/NC0

Table 3 Thermal analysis of WPCs both with and without nano-clay

Sample	T_i	T_m^a	T_m^b	Temperature of decomposition (T_D) in °C at different weight loss (%)			RW% at 600 °C
				20%	40%	60%	
MAESO/DAPA/WF/NC0	210	282	377	280	345	389	22.70
MAESO/DAPA/WF/NC1	225	287	361	283	347	405	26.79
MAESO/DAPA/WF/NC3	240	307	382	315	377	427	30.82
MAESO/DAPA/WF/NC5	230	295	379	290	355	415	30.56

RW, residual weight; T_i , value for initial degradation; T_m^a value for the first step; T_m^b value for the second step

different weight loss (%) and residual weight (RW, %) for composites with and without nanoclay is summarized in Table 3. It can be seen that T_i , T_m , and T_D values improve after the incorporation of nanoclay into the polymer composites. All the composites display a loss in weight within the temperature range from 100 to 600 °C. For 20% weight loss, the decomposition temperature for composite without nanoclay was 280 °C, whereas for 1 wt% of nanoclay loaded composite, the decomposition temperature was 283 °C. It was observed that the thermal stability of the composite increased to some extent, due to the incorporation of 1 wt% of nanoclay. The temperature at which 60% weight loss occurred for the composite without nanoclay was 389 °C, whereas for the composites with different amount of nanoclay (1, 3, 5 wt%) the decomposition temperature was 405, 427 and 415 °C, respectively. The appreciable improvement of thermal resistance due to the incorporation of 3 wt% of nanoclay could be attributed to the development of a confined structure in the composites reinforced with nanoclay. The motion of the polymer chain was restricted by the silica domains, upon the introduction of clay particles into the polymer matrix. This improvement in the thermal stability was also attributed to the existence of the MMT nano-layers, which functions as a barricade to reduce the permeability of volatile degradation products out of the material. Therefore, MAESO/DAPA/WF/NC3 showed relatively high thermal stability. However, the composite containing 5 wt% of clay (i.e. MAESO/DAPA/WF/NC5) showed a reduction in thermal stability. The lower thermal resistance was due to clay aggregates present in the 5 wt% of clay loaded composites. The residual weight (%) of nanoclay loaded composites was more than the unloaded one, which might be due to the formation of more char on the surface of the composite when subjected to heat. The char protected the bulk of the composite from temperature and decreased the rate of mass loss throughout the thermal dissipation of the composites. Formation of intensive char in clay loaded composites was an indication for improvement in thermal resistance [35].

Fig. 8 Bacterial growth on (a) MAESO/DAPA/WF/NC3, (b) MAESO/DAPA/WF/NC5, (c) MAESO/DAPA/WF/NC1 and (d) MAESO/DAPA/WF/NC0

4.9 Biodegradation study

The composite samples treated with 0, 1, 3, 5 wt% of MMT were treated with cellulolytic bacterial strain in liquid broth culture medium for the study of biodegradation [36]. The production of bacteria and the rate of biodegradation in the broth culture medium were detectable after 1 month of incubation. During the biodegradation of composites, the bacterial OD increased specifying the usage of the carbon source with the increases in time of incubation. The growth of bacteria (absorbance at 660 nm) in the samples is represented in Fig. 8, with respect to the time. The increase in microbial growth was prominent in the case of the composite without MMT in comparison to the composite filled one. The inclusion of nano-clay declines the collapse of wood composites owing to its antimicrobial activity. Firstly, the development of the bacterial strain rises slowly with the time of exposure. However, after

Fig. 9 SEM micrographs of bio-degradable samples **a** MAESO/DAPA/WF/NC0, **b** MAESO/DAPA/WF/NC1, **c** MAESO/DAPA/WF/NC3 and **d** MAESO/DAPA/WF/NC5

3 months of incubation, it started decreasing in the composites. The bacterial growth was enhanced by the effectual ability of the bacterium *Pseudomonas* that degraded the lignin present in the wood [37]. Furthermore, the *Pseudomonas* sp. can produce cellulase and pectinase enzymes that could degrade the cellulose and pectin component present in the wood [38]. The decrease in bacterial growth after 3 months of incubation was because of the generation of inhibitory metabolites through the microbes.

The decomposition of the wood composites due to the bacterial growth was studied by SEM. The SEM images of the biodegraded samples are shown in Fig. 9. The physical breakdown of composites on exposure to microbes suggested that they were inclined to bacterial degradation. The images clearly revealed that the surface was

biodegraded and the degradation was prominent in unfilled composites (Fig. 9a) compared to MMT filled composites. The decrease in biodegradation might be due to the strongly interconnected network in the MMT loaded composite which diminished the accessibility and reactivity of microorganisms. Also, the composites treated with nanoclay showed low water absorption capacity thereby inhibiting the penetration of microorganism within the composite. The bio-degradation process of the composite depends on water absorption. Therefore, the composites with greater moisture absorption capacity showed higher biodegradation. The amount of MMT present in the composites highly influenced the biodegradation process. With the increase of MMT up to 3 wt%, the composite showed a decreased rate of biodegradation which was evident

Table 4 Mechanical properties of various WPCs after bio-degradation study

Sample	Flexural strength (MPa)	Tensile strength (MPa)	Hardness shore D
MAESO/DAPA/WF/NC0	43.38 (± 0.29)	19.36 (± 0.31)	42.14 (± 0.08)
MAESO/DAPA/WF/NC1	46.31 (± 0.30)	20.65 (± 0.22)	42.37 (± 0.35)
MAESO/DAPA/WF/NC3	50.60 (± 0.23)	24.67 (± 0.11)	45.15 (± 0.08)
MAESO/DAPA/WF/NC5	48.50 (± 0.43)	22.31 (± 0.25)	42.55 (± 0.41)

Table 5 Decreasing level (%) of the mechanical property before and after bio-degradation study for various WPCs

Sample	Flexural strength (%)	Tensile strength (%)	Hardness (%)
MAESO/DAPA/WF/NC0	33.31	38.77	40.19
MAESO/DAPA/WF/NC1	31.01	35.50	40.23
MAESO/DAPA/WF/NC3	28.37	30.58	39.08
MAESO/DAPA/WF/NC5	29.66	33.34	40.14

Decreasing level (%)=(Mechanical property before biodegradation – Mechanical property after biodegradation/Mechanical property before biodegradation) *100

from the changes in its hardness and mechanical property results (Table 4). The SEM of the 3 wt% nanoclay containing composite showed less irregularity compared to 1 wt% of nanoclay based composites, which revealed that the degradation rate was highly affected by the amount of the nano-filler. However, surface unevenness was prominent again in composites reinforced with 5 wt% of nanoclay, due to the accumulation of the nanoclay particles that increased the biodegradation process [39].

After exposure to the microorganism, there was a decrease in the mechanical properties and hardness values of composites loaded with different percentage of MMT (Table 4). The deterioration of both mechanical and hardness values of composites having 3 wt% nano clay was least compared to either neat/or other nano composites. This might be due to the higher resistance shown by the composite towards microbial attack. The retention in mechanical properties after the microbial attack was due to better interaction between the wood, DAPA, MMT and MAESO resin that hindered the absorption of moisture eventually decreasing the bacterial attack. However, as they are sensitive to moisture, the 5 wt% of MMT loading composites showed a decrease in strength retention after the microbial attack. This was due to the agglomeration of MMT particles. The percentage of decrease in mechanical properties (%) before and after biodegradation for wood polymer composites is shown in Table 5.

5 Conclusion

The wood polymer composites cross-linked with rosin derivatives and MMT have been prepared by a compression molding technique. SEM and FTIR results showed that MMT was dispersed uniformly into the polymer matrix. The composites loaded with MMT showed enhanced mechanical, thermal, flame retardance and other properties compared to the neat composites. Also, the MMT loaded composites showed higher resistance

to moisture absorption due to the compact structure formed by the interaction among the components of the composites. The mechanical properties of the composite decreased extensively upon exposure to the microorganism. However, the wood composites containing MMT showed higher retention in mechanical properties compared to neat composites due to greater resistance to the microorganism. This renders the wood polymer composites favorable in terms of environmental protection. There was a significant improvement in the thermal, mechanical, and flame retardant properties for the composite with 3 wt% of nanoclay. MAESO/DAPA/WF/NC3, displayed minimal water vapour uptake, microbial growth, and maximal chemical resistance. The incorporation of nanoclay improves the overall properties up to the addition of 3 wt% nanoclay beyond that further addition decreases the properties.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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