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ORIGINAL PAPER

Influence of Montmorillonite Clay Content on Thermal, Mechanical, Water Absorption and Biodegradability Properties of Treated Kenaf Fiber/ PLA-Hybrid Biocomposites

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Abstract
Nowadays, the starring attentions of the polylactic acid based composites are improved due to environmental awareness and diminution of petroleum oil. The bio-plastics were restricted to limited applications due to its higher cost. The bio-plastics filled fiber and or fillers lessen the cost with enhanced properties. In this research, the PLA- biocomposite and PLA-hybrid biocomposites were prepared with twin screw extruder, two-roll mill, and compression molding method. The PLA based bio and hybrid biocomposites are fabricated with 30 wt% of treated kenaf fiber and 0, 1, 2 and 3 wt% montmorillonite clay filler. The influence of MMT clay on thermal, mechanical, water absorption and biodegradable properties of PLA-biocomposite and PLA-hybrid biocomposites has been studied. The PLA-hybrid biocomposites thermal, mechanical and water resistance properties are increased with adding of MMT clay. However, 1 wt% MMT clay included PLA-hybrid biocomposite exhibits increased tensile, flexural and impact properties, and abrasion resistance than other PLA-hybrid biocomposites. The PLA-bio and hybrid biocomposites showed higher tensile and flexural modulus than pure- PLA. The results TGA analysis depicted that inclusion of MMT clay can improve the decomposition temperature of the biocomposite. SEM analysis discloses that, MMT clay it acts as a transfer mechanism. The water absorption and biodegradability properties results illustrates that water resistance of hybrid biocomposites improved and biodegradability decreased due to adding of MMT clay.

Keywords Polylactic acid · NaOH treated kenaf fiber · Montmorillonite clay · Thermal properties · Mechanical properties · Water absorption and biodegradable properties

1 Introduction

The improved utilization of plastics throughout the world has resulted in enhanced plastic waste. The recent developments in recyclable polymers play vital role as today there is an uncertainty of petroleum usage in the world [1]. At present, polylactic acid (PLA), PBS, PVA, PHB and PHA are most commonly used as matrix phase biopolymers [2–5]. Among the biodegradable polymers, the renewable resource based PLA has more attracted by researchers due to its properties, biodegradability, process ability and biocompatibility. It is derived from corn starch or sugar beets by fermentation [6–8]. However, it is expensive and it needs further alteration for many useful applications [9]. Hence, a right approach is to improve and make it more cost effective material is the addition of natural fibers, that have recently gained attention to replace convention fibers [10, 11] because of their low density, nonabrasive character, high specific strength, low cost and biocompatibility [12]. Various forms of cellulose have been explored as reinforcements into PLA composites. Therefore, it is necessary to use natural fibers and incorporate them into PLA in order to effectively reduce the production cost by partially replacing the expensive PLA by low cost natural fibers without destroying the biodegradation performance of the polymer matrix [12]. Among the natural fibers kenaf fiber (KF) is identified as most important one for biocomposites study because of its availability, acceptable specific strength, good biodegradability, low weight and low cost when

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compared to glass, kevlar and poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) fibers [13–16]. Among the huge amount of residues in the agriculture crop, some quantity of residues are applied in household for domestic and remaining foremost part of residues was burned in the fields; this causes the air-pollution on the environment. The essential alternative to resolve this dilemma is to apply the agriculture crop residues as reinforcement with polymers to improve the mechanical properties of the materials. In the various kinds of natural assets, kenaf plants have fast growth in past years due to their rapid progress with consequence of low price under the extensive range of climatic circumstances. KF has a prospective alternating medium to replace the conventional fibers as reinforcement in composites; it diminishes the waste, creates the jobs and contributes healthier atmosphere [17–23]. The foremost problem with natural fiber composites is incompatibility between hydrophobic polymer and hydrophilic natural fiber which leads to poor interfacial adhesion, thus reducing the thermal and mechanical properties of the composite. However, it can be overcome by chemical and physical treatments, or incorporating of additives and compatibilizers [24–28]. The various chemical modification methods such as alkaline, peroxide, acetylating, silane and benzoylation treatments have been studied in the past [29]. Among them, alkaline treatment (NaOH) is inexpensive, easy and effective method when compared to other methods [30]. The main drawback of PLA/kenaf fiber biocomposite is lower strength, poor thermal stability, poor water resistance [10, 31]. However, nano clay has significant effect to increase moisture absorption, flame retardancy, thermal and impact properties [32]. According to hybrid composite, the weaknesses of one component will be balanced by the strength of another. Therefore, the combination of PLA-TKF-MMT system will show much better properties than the individual system. Thus, it is necessary to investigate the both KF, MMT with PLA to get better properties. At present, nano particles or fillers such as organically modified montmorillonite (OMMT) and montmorillonite clay (MMT) getting higher consideration as they possess the potential tendency to modify extensively the thermal, mechanical and functional properties of both thermoplastic and thermoset polymers [33, 34]. The various nano clays are pyrophyllite, organo clay, hectorite, saponite and nontronite nanoclay, montmorillonite clay (MMT); among these MMT is the most commonly used layer silicate in polymer composites due to its high strength, low cost, high aspect ratio and high modulus [34, 35]. In the recent years, hybrid technology creates the new revolution in the area of material science showing the most high-tech advanced composites. The addition of nano particles demonstrates remarkable enhancement in the thermal, mechanical, physical and thermo-mechanical properties due to better distribution, high specific ratio and effective polymer filler interaction [12, 36]. Previously some scientists have achieved the preferred properties through hybridization method like addition of fillers and or natural fibers into the conventional polymers or plastics [37, 38]. Tang et al. [13] researched the glass fiber/spherical BN fillers/epoxy laminated composites with enhanced electrical insulation and thermal conductivity properties. Sinha ray et al. [39] has reported the effect of silicate on tensile strength and young's modulus of PLA/layered silicate nanocomposite. Jalalvandi et al. [40] studied the influence of MMT clay on mechanical, water absorption, biodegradability and physical barrier properties of starch/PLA hybrid biocomposites. Saba et al. [41] researched and compare the morphological and mechanical properties of OPEFB/kenaf/epoxy, OMMT/kenaf/epoxy and MMT/kenaf/epoxy hybrid composites. Azmi et al. [42] found the optimum concentration of MMT clay in kenaf/PP/PLA/MMT clay hybrid biocomposites. Meng et al. [43] experimented the effects of nanoclay on mechanical and thermal properties of PLA/clay/wood nanocomposites. Ramesh et al. [44] researched the influence of MMT clay content on mechanical, thermal, biodegradable and water resistance properties of PLA/TAF.

Every one of the above researchers have attempted to determine appropriate hybrid composites with preferred properties. So far investigators knowledge this is the first article on PLA based composites reinforced by both KF, MMT prepared via screw extruder, compression molding with a KF content of 30 wt%. The only other research dealing with PLA/kenaf/clay composites reported by Kaiser et al. [45] and Lutpi et al. [46] involved a low 20 wt% kenaf fiber loading. Note that economic viability requires an as large as possible KF content.

The main objective of this article is to investigate the effect of MMT content on mechanical, morphological, thermal, water absorption and biodegradability properties of PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites. The PLA/TKF and PLA/TKF/MMT composites having total 30 wt% of TKF loading by weight together with 1, 2 and 3 wt% MMT content in PLA/TKF/MMT hybrid biocomposites. The addition of TKF decreases the cost of the PLA. The addition of MMT improves the mechanical, thermal, water absorption properties of PLA/TKF composite. So the research scope of this work was to find out the optimum MMT content for better mechanical, thermal, biodegradability and water absorption properties of hybrid biocomposites. Besides these, the internal bonding behaviour is also obligatory to be investigated in order to synchronize properties. Finally, the fabricated hybrid biocomposites were compared with PLA/TKF biocomposite and virgin PLA in order to develop an environmental friendly (fully biodegradable) composite and as well to replace the conventional polymer in terms of cost, availability and property.

2 Experimental

2.1 Materials

In this research pellet formed 3052D PLA with 1.24 g/cm^3 at specific gravity, 145-160^o C of melting temperature and 55-

60^o C of glass transition temperature material was acquired from Nature Tech, Chennai. The KF supplied through Go-Green Products, Chennai, India. The NaOH was supplied by SR-Scientific Chemicals, Tirupati, AP in India. The 1–3 mm long chopped fibers was used. The 1.01 g/cm^3 density MMT (Nanomers® I.31PS) by modifying onium ion, powder formed with ≤20 μm sized was procured from Sigma-Aldrich at Bangalore, India. It contains 0.5–5 wt% aminopropyltriethoxysilane, and 15 to 35 wt% octadecylamine. The respective material properties with their respective sources are displayed in Table 1.

2.2 Methods

2.2.1 NaOH Treatment

The NaOH treatment method was applied for KF surface modification. The pellet formed sodium hydroxide (NaOH) was provided by S.R.S. Chemicals at Tirupati, India. KF was covered with water in 6% NaOH solution for 3 h at room temperature [44, 47]. The TKF were then washed with flowing distilled water. The pH value was kept 7 as constant [44]. Afterwards, the treated fibers were kept in an oven at 100^o C for a period of 8 h.

2.2.2 Preparation of PLA- Hybrid Biocomposites

The produced composites formations were tabulated in Table 1 Prior to fabrication of sample PLA, TKF and MMT were held in an oven at 110^o C for 1 h. The PLA, TKF and MMT are physically pre-mixed and then compounded through twin-screw extruder (ZV 20 model). Screw diameter and L/D ratio were 21 mm and 40, respectively. For compounding of all PLA-composites (Table 2), screw speed and temperature profile were set to 78 rpm and 155^o C to 190^o C, respectively. Then, compounded pellets are kept in an oven for dry at 80 °C for 4 h. After drying, the compound pellets were pre-melted at 185^o C in a counter rotating two roll mill internal mixer through a revolve speed of 50 rpm. Then, the compounded pellets are processed through compression molding machine. During the process, keep the temperature 185^o C and 30 ton force applied (up stroke) and then compacted at 165 bar pressure for 30 min followed by cool under pressure. When the mold temperature reached at 90^o C the platens are opened from press; then composite sheets (200 mm × 200 mm × 3 mm) are removed from platens and cut to desired form for tensile, flexural, impact, abrasion resistance, thermogravemetric analysis, water absorption and biodegradability evaluations. The same procedure is followed for preparation of bio and hybrid biocomposites. Pure- PLA sheet is produced through two roll mill- compression molding.

2.2.3 Mechanical Characterizations

Tensile test of PLA-biocomposite and PLA-hybrid biocomposites were carried out by Instron-3369 Universal Testing Machine-USA according to ASTM D638 at 25^o C. Speed of cross head is 10 mm/min. Flexural test of composites was also performed through the same UTM i.e.50KN load and 50 mm span length according to ASTM D790–03 at 18^o C. Impact test of composites were finding through Izod testing machine according to ASTM D256 at 18 J. Abrasion resistance test of composites were carried out by abrasion machine according to ASTM D1044 standards for 100 cycles.

Table 1 Material properties and sources

S.No	Raw Material	Properties	Source
1	PLA	Specific Gravity-1.24 g/cm^3 MFR, g/10 min (210 °C, 2.16 kg)- 14 Crystalline Melt Temperature (°C)- 144–160 Glass Transition Temperature (°C)- 55–60 Tensile Yield Strength, psi (MPa)- 9000 (62) Notched Izod Impact, ft-lb/in (J/m)- 0.3 (16.0) Flexural Strength (MPa)- 15,700 (108) Flexural Modulus (MPa)- 515,000 (3600) Heat Distortion Temperature (°C) 55	Nature Tech, Chennai, INDIA.
2	KF	Density- 1.34- 1.45 g/cm^3 Diameter- 150- 250 μm Length- 1-3 mm	Go Green Products, Nungambakkam, Chennai, Tamilnadu, INDIA
3	MMT	Density- 1.01 g/cm^3 Form- Powder Contains-0.5-5 wt. aminopropyltriethoxysilane 15–35 wt.% octadecylamine particle size – ≤20 μm	Sigma-Aldrich, Bangalore, INDIA.
4	NaOH	Highly soluble in water	SR-Scientific Chemicals, Tirupati, Andhra Pradesh, INDIA.

Table 2 Compositions and composite names

Denotation	Sample	PLA, wt%	TKF, wt%	MMT clay, wt%
P	PLA	100	0	0
S	PLA-30TKF	70	30	0
S1	PLA-30TKF-1MMT	69	30	1
S2	PLA-30TKF-2MMT	68	30	2
S3	PLA-30TKF-3MMT	67	30	3

2.2.4 Morphological Characterizations

JSM-IT500 scanning electron microscope (SEM) (Japan Electronics Optic Limited, USA) was used to examine the break surface of tensile fracture specimens. Before examination, the specimens were sputter coated with gold.

2.2.5 Thermal Characterizations

The PLA-biocomposite and PLA-hybrid biocomposites thermal stability were carried out through TGA (Thermogravemetry analysis) by Perkin Elmer instrument [12, 44]. The samples (5–30 mg) were heated from 30 to 800^o C with a heating rate of 10^o C/min under nitrogen gas flow. The $T_{Heat\ Resistance\ Index}$ values of composites were calculated through following eq. 1 [48].

$$T_{HRI} = 0.49*[T_5 + 0.6*(T_{30}–T_5)] \quad (1)$$

T_5 and T_{30} represents the corresponding decomposition temperature of 5% and 30% weight loss, respectively.

2.2.6 Water Absorption Test

Water absorption test was carried out through direct immersion of PLA-biocomposite and PLA-hybrid biocomposites in normal water at room temperature with dimension 10 mm × 10 mm × 3 mm for up to 30 days [44]. At regular intervals, each specimen removed and washed with tissue paper and then weighing through electronic balance. It was calculated through following eq. 2.

$$\text{Water Absorption } (\%) = \left(\frac{W2-W1}{W1}\right)x100 \quad (2)$$

Where, W_2 and W_1 are after and before immersion mass of sample.

2.2.7 Biodegradability Study

Biodegradability study of samples (1 cm × 1 cm) was performed through simple soil burial examination. Each sample weighed and buried in ordinary soil of garden at an average temperature of 30^o C and 80% humidity for 10, 30 and 90 days, respectively [12]. The 80% humidity was maintained constant by regular watering [44]. The mass loss of composted samples was calculated and evaluated using the following eq. 3.

$$\text{Weight loss } (\%) = \left(\frac{Wi-Wf}{Wi}\right)x100 \quad (3)$$

Where, W_i and W_f are before and after mass of sample.

3 Results and Discussions

3.1 Mechanical Characterization

The PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites acquired tensile strength is displayed in Fig. 1. It is marked that, the addition of MMT improved the tensile strength of the PLA/TKF/MMT hybrid biocomposite. The PLA/TKF/MMT hybrid biocomposites flexural and impact strength also pursued similar development. The attained flexural and impact strength has been presented in Figs. 2 and 3. The adding of 1 wt% MMT included PLA/TKF/MMT hybrid biocomposite flexural, impact and tensile strengths are improved 46.4, 10.6 and 5.7%, respectively than PLA/TKF biocomposites. As the MMT load beyond 1% (addition of 2 and 3 wt%) by weight flexural, impact and tensile strength are decreased. The impact, flexural and tensile strength results pursued similar development. These obtained results are confirmed with those obtained results by Alamri et al. [49] in their investigation they concluded that 1 wt% nano filler epoxy contained nanocomposites demonstrates superior mechanical properties than other (3 wt% and 5 wt% filler) nanocomposites. Kundan et al. [50] found that, bamboo /polyester with 1 wt% containing nano clay hybrid composites flexural and tensile strength are improved; beyond 1 wt% nano clay the properties are diminished. Yong lei and co-workers [51]

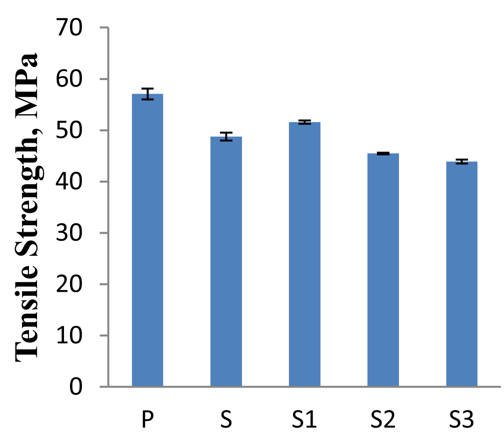

Fig. 1 Tensile strength of composites

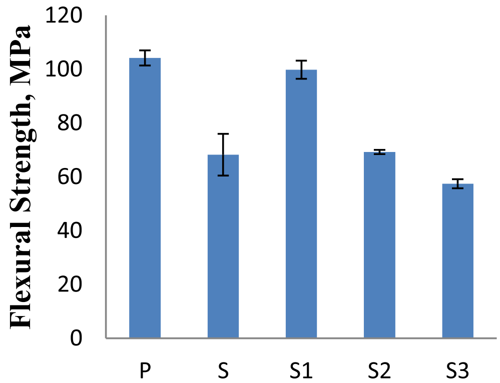

Fig. 2 Flexural strength of composites

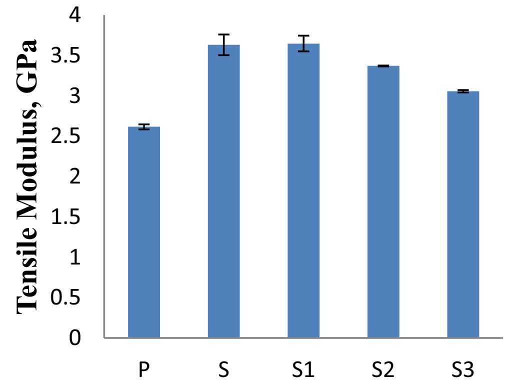

Fig. 4 Tensile modulus of composites

observed that the higher amount of clay (beyond 1 wt%) affects the tensile and flexural strength of the wood/HDPE composites. Chern et al. [52] reported that addition of 1 wt% MMT K10 – polylactic acid/polycaprolactone nanocomposites enhanced higher mechanical properties than 3 wt% MMT-PLA/ polycaprolactone, 5 wt% MMT-PLA/ polycaprolactone and 7 wt% MMT-PLA/ polycaprolactone nanocomposites. In addition, the advantage of manufactured composite is eco-friendly (fully biodegradable) when compared to wood/HDPE/MMT, Bamboo/polyester/MMT and Recycled cellulose fiber/clay/epoxy hybrid composites.

The PLA/TKF biocomposite, PLA/TKF/MMT hybrid biocomposites tensile and flexural modulus are plotted in Figs. 4 and 5. The PLA/TKF biocomposite flexural and tensile moduli are progressively increased with addition of TKF. The PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites have greater flexural and tensile moduli than virgin PLA. PLA/TKF biocomposites flexural and tensile moduli are improved 67.85 and 39.23%, respectively than clear PLA. Additionally, 1 wt% MMT included PLA/TKF/MMT hybrid biocomposite tensile and flexural moduli are improved 39.61% and 62.85%, respectively than neat PLA. The addition of TKF and MMT into neat PLA the tensile and flexural modulus was expected increment, since introduced stiffer materials or reinforcement into the polymers [53–55]. Similar trend was observed in the previous studies [56]. El-Shekeil et al. [57] studied that the treatment and fiber content influences the tensile and flexural modulus [1]. Adversely, as shown Figs. 1-3, tensile, flexural and impact strength were decreased by the addition of natural filler. As example, the PLA/TKF biocomposite impact strength was decreased from 56.69 to 49.34 kJ/m^2; the flexural strength was reduced from 104.16 to 68.24 MPa; the tensile strength was diminished from 57.06 to 48.75 MPa. According to Yang et al. [58] and Ismail et al. [59] this diminish is recognized due to the irregular shapes, fiber inability, stresses transferred (support from matrix), micro-voids and various processing procedures [60].

The addition of 1 wt% MMT is improved the tensile, impact and flexural strength of PLA/TKF/MMT hybrid biocomposites. The improvement was 5.7, 10.6 and 46.4%, respectively than PLA/TKF biocomposite (Near to P). This improvement is clearly indicated that clay fillings the micro pores, improved interface bonding among TKF and PLA in case of 1% MMT, as evident from its superior impact, flexural and tensile strength, abrasion resistance and SEM results.

Moreover, these finding results were agreement with those obtained results in our previous research [44]. The similar mechanical trend results were observed in our previous study, the 1 wt% included PLA/treated *Aloe vera* fiber/MMT hybrid

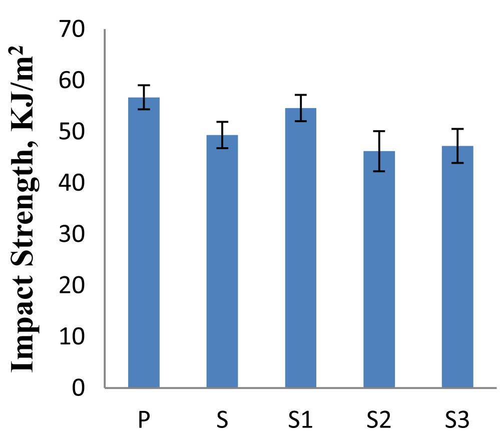

Fig. 3 Impact strength of composites

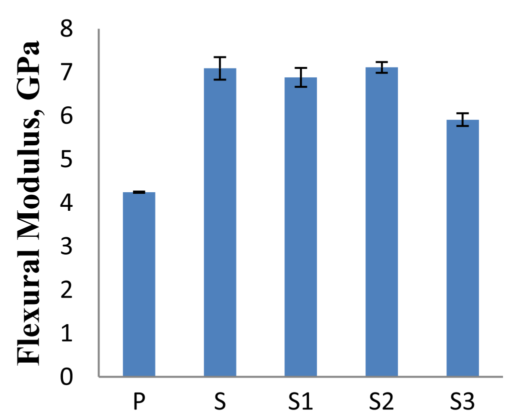

Fig. 5 Flexural modulus of composites

biocomposite exhibits superior tensile, impact and flexural properties than 2 and 3 wt% included hybrid biocomposites.

Better mechanical properties of PLA/TKF/1MMT hybrid biocomposite than PLA/TKF/2MMT and PLA/TKF/3MMT hybrid biocomposites were due to MMT homogeneous dispersion. The higher homogeneous dispersion helped a higher percentage of polymer chain and interlocking between the TKF and PLA, resulting better bonding between the fiber and matrix. Thus when the load or stress were applied, the stress concentration easily get transferred from matrix to fiber resulting delayed in crack or fracture initiation mechanisms. Thus it can be concluded that the lower amount MMT incorporations in the PLA/TKF composites enhances the physical adhesion at the interface and results effective stress transfer under load, leading ultimately the increase in impact, flexural and tensile properties. Similar mechanism was observed in previous study [61]. In other case, the addition of 2 and 3 wt% MMT included PLA/TKF/MMT hybrid biocomposites showed diminish mechanical properties by having voids and agglomerations formations; these were reduced both fiber-PLA bonding and load transfer capacity [61, 62]. There are numerous reasons for the addition of reinforcements, among them; the very important reason was the enhancement in properties. Though the tensile, impact and flexural strength weren't significantly improved, the flexural and modulus were improved significantly as shown in Figs. 4-5. Another key reason is to reduce the cost, which also supports the significance of reinforcement addition. PLA/TKF/1MMT hybrid biocomposite will be at least 30% cheaper than virgin PLA due to the easy availability and cost. The MMT clay content plays a vital role in improved performance of PLA-hybrid biocomposites, the lowered content enhanced higher mechanical properties.

3.1.1 Abrasion Resistance

Performed PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites abrasion resistance results are displayed in Fig. 6. It is understandable that 1 wt% MMT included PLA/TKF/MMT hybrid biocomposite shows higher abrasion resistance than other. The 1 wt% MMT improves the bonding between PLA and TKF; it is evident from mechanical and morphological results. After more than 1 wt% MMT affects the abrasion resistance of biocomposites. Previously the similar effect was observed in previous research [44, 63]. The mechanical result was also followed similar trend as shown in Figs. 1-3.

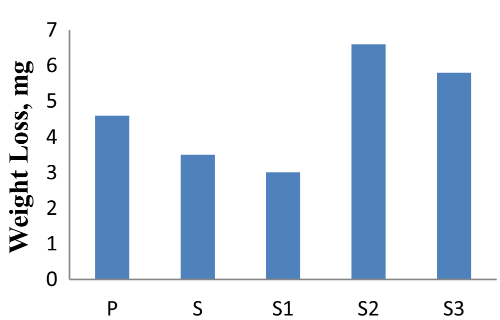

Fig. 6 Abrasion resistance of composites

3.2 Morphological Properties

Figure 7 (a-d) shows the PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites structures. Multiplicities of failure mechanisms such as fiber pullouts, fiber-matrix debonding, voids, agglomerations, matrix failure and fiber fracture are observed. The PLA/TKF biocomposite (Fig. 7a) shows some de-bonding between the fabrics and matrix, fiber bending, pullouts. The adding of 1 wt% MMT included PLA/TKF/MMT hybrid biocomposite (Fig. 7b) demonstrates fine bonding agent between fibers to matrix by the bonding of fiber-nano-matrix. In the same way the 2 wt% MMT included PLA/TKF/MMT clay hybrid biocomposite shows voids, agglomeration, fiber bending, fractured fibers and fiber pullouts (Fig. 7c). Addition of 3 wt% MMT included PLA/TKF/MMT hybrid biocomposite demonstrates a number of agglomerations, voids, fractured fibers, fiber bending and pullouts (Fig. 7d). The voids and agglomerations are formed due to higher load of MMT. These failure mechanisms of bio and hybrid biocomposites are confirmation for enhancement of mechanical properties. For example, the 1 wt% MMT including PLA/TKF/MMT hybrid biocomposite reveals superior mechanical properties (Figs. 1-3) which indicates better bonding agent among by the sequence of fiber-nano-matrix that leads to superior load transfer capacity (Fig. 7b).

3.3 Thermal Characterization

Thermal stability of PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites are investigated by thermo gravimetric analysis (TGA). Figure 8 shows the TGA curve of PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites. The hybridization improved thermal stability of composites as evidenced from thermo gravimetric curve. The 10 and 75% weight loss temperatures set as base line for analyzing thermal stability of PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites [12, 44]. The T_{10} and T_{75} of hybrid biocomposite improved 280 to 311^o C and 337 to 355^o C (Table 3). The decomposition takes place in three-stages. In the primary stage moisture evaporation occurred up to 150^o C and in second phase due to lignin, cellulose and hemi celluloses. Finally, degradation of PLA and MMT takes place. The virgin PLA thermal stability diminishes with adding of natural fiber.

Generally common trend is the polymer thermal stability decrement with adding of natural fiber [12, 64–66]. For PLA/

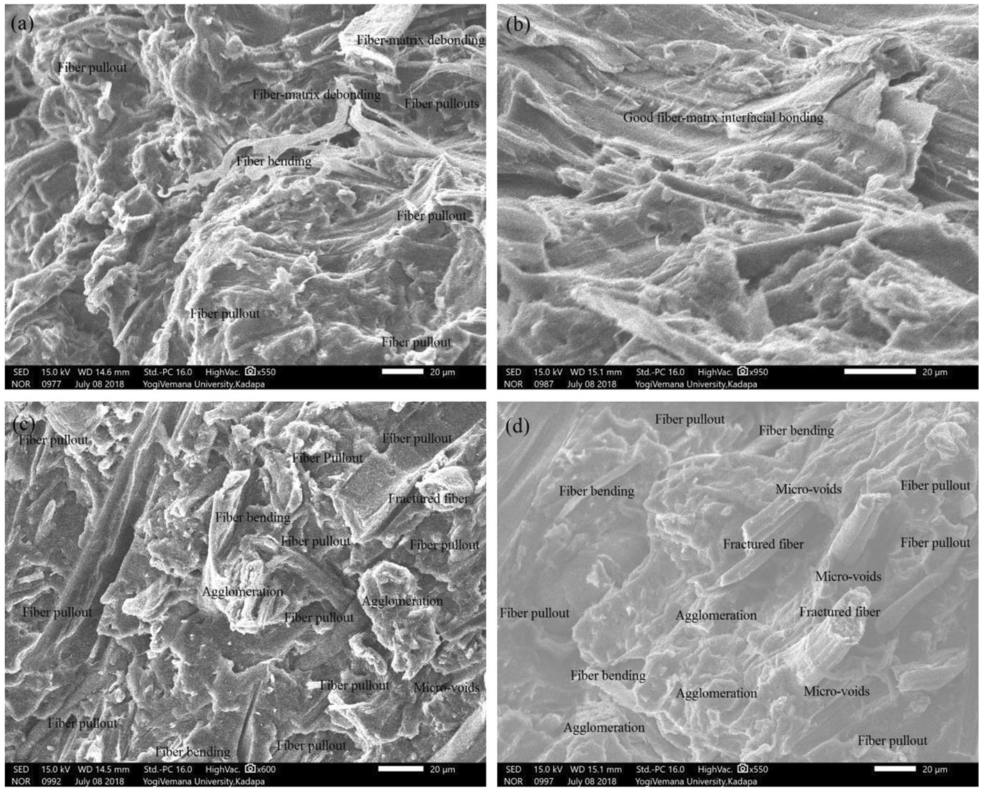

Fig. 7 SEM images of (tensile specimen) (a) S, (b) S1, (c) S2 and (d) S3 composites

TKF biocomposite and PLA/TKF/MMT hybrid biocomposites 10% mass loss are degraded at 280, 289, 300 and 311° C, respectively. About 75% weight loss at 337, 338, 346 and 355° C, respectively. For 10 and 75% weight loss the pure PLA degrades at 327 and 358° C, respectively. The 3 wt% contained PLA/TKF/MMT hybrid biocomposite exhibits highest decomposition temperature (311° C for 10% and 355° C for 75%) when compared to other. In addition to that, the $T_{Heat\ Resistance\ Index}$ (T_{HRI}) values are depicted in Table 4. The 3 wt% included PLA/TKF/MMT hybrid biocomposite present relatively higher T_{HRI} value than 1 and 2 wt% addition PLA/TKF/MMT hybrid biocomposites. The corresponding T_{HRI} value of the PLA/TKF biocomposite is increased from 140.04 to 153.95° C after addition of 3 wt% MMT. These improvements take place due to MMT; it is acted as barrier, constrained the mobility to chain and hinders decomposition process. Meantime, the relatively better compatibility between PLA matrix and MMT can further enhance the thermal stability of PLA/TKF/MMT hybrid biocomposites. The similar enhancement was observed in previous studies [48, 66–69].

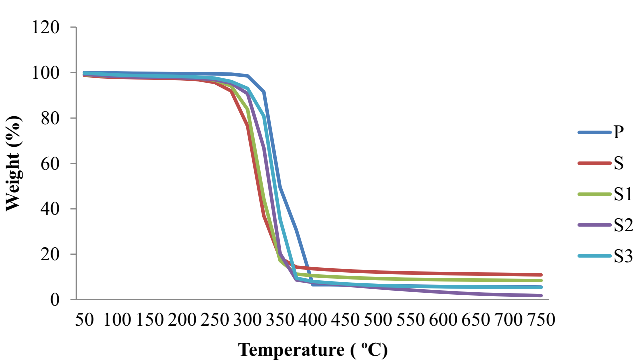

Fig. 8 TGA curve of P, S, S1, S2 and S3 composites

3.4 Water Absorption Test

The conducted water barrier properties of composites were displayed in Fig. 9. All samples absorption gain percentage were finding with respect to submerging period. At the beginning period, the water absorption for all samples are improved significantly and then reached to equilibrium. The Fig. 9 demonstrates for all specimens that, water gain percentage is

Table 3 TGA Characterization of biocomposites

Sample	Denotation	Weight loss, Decomposition Temperature (° C)	
		10%	75%
PLA	P	327	358
PLA-30TKF	S	280	337
PLA-30TKF-1MMT	S1	289	338
PLA-30TKF-2MMT	S2	300	346
PLA-30TKF-3MMT	S3	311	355

Table 4 Thermally characteristic data of composites

Sample	Denotation	Weight loss temperature (° C)		T_{HRI} / °C
		T_5	T_{30}	
PLA	P	318	341	162.58
PLA-30TKF	S	257	305	140.04
PLA-30TKF-1MMT	S1	269	311	144.15
PLA-30TKF-2MMT	S2	279	323	149.64
PLA-30TKF-3MMT	S3	286	333	153.95

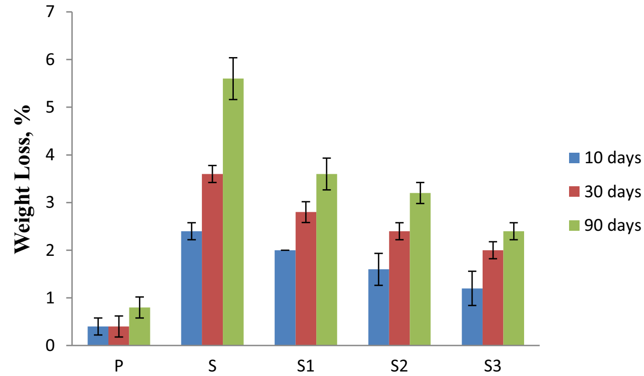

Fig. 10 Biodegradability test of P, S, S1, S2 and S3 composites

increased with increasing of submerging time. The neat PLA water barrier property decreased with adding of TKF.

However, the incorporation of MMT effectively raises the water resistance for MMT-filled TKF/PLA hybrid biocomposites. The water resistance increased maximum with continuous adding of MMT. Additionally 1 and 2 wt% MMT integrated PLA/TKF/MMT biocomposites decreased 2.18 to 2.18%, 1.81%, and 9.45 to 9.09%, 7.27% at 3 and 30 days, respectively when compared to PLA/TKF biocomposite. The 3 wt% MMT included PLA/TKF/MMT hybrid biocomposite decreased from 2.18 to 1.45% and 9.45 to 6.18% at 3 and 30 days, respectively when compared to PLA/TKF biocomposite. The addition of MMT content PLA/TKF biocomposite water gain is decreased.

This phenomenon attributed because of fiber treatment and MMT presence in PLA/ TKF biocomposite; the clay act as barrier medium and it restricts flow of water into biocomposite in all path way, thus resultant in lower water uptake as described in the literature [70–72]. Similar examination was made by Ramesh et al. [44], Alamri et al. [73] and Sajna et al. [74]. As consider the effect of MMT on water resistance of hybrid biocomposite, PLA/TKF/3MMT hybrid biocomposite exhibited tremendous water resistance property than other bio and hybrid biocomposites. This could be due to the barrier effects of the MMT decreasing the water absorption. The similar effect was determined in previous research [44, 73, 74].

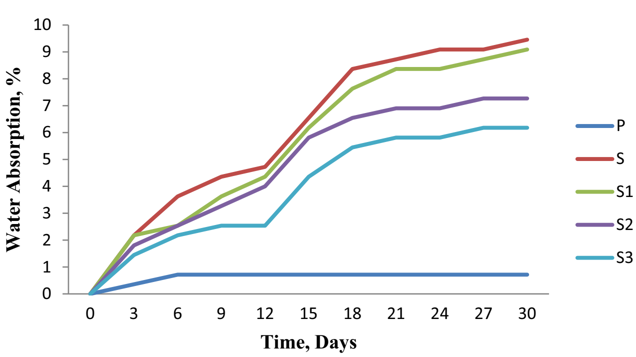

Fig. 9 Water absorption test of P, S, S1, S2 and S3 composites

3.5 Biodegradability Test

Biodegradability test of samples was performed without any composting and enzymatic material through simple soil burial (normal environment) investigation test [12, 44]. All samples weight loss percentages were finding with respect to burial period time. Biodegradability of the hybrid biocomposites are improved with burial test time. Figure 10 shows the rate of biodegradability of neat PLA, PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites with respect to time.

The biodegradability of 1 wt% MMT integrated PLA/TKF/MMT hybrid biocomposite decreased from 2.4 to 2%, 3.6 to 2.8% and 5.6 to 3.6%, respectively at 10, 30 and 90 days burial time. Additionally, the 2 wt% MMT integrated PLA/TKF/MMT hybrid biocomposite biodegradability decreased from 2.4 to 1.6%, 3.6 to 2.4% and 5.6 to 3.2%, respectively at 10, 30 and 90 days burial time. However, the 3 wt% MMT included PLA/TKF/MMT hybrid biocomposite shows lowest degradability than other; the degradability is 1.2, 2 and 2.4%, respectively at 10, 30 and 90 days burial time. It is observed from the obtained results that the MMT negative effect on the biodegradability of PLA/TKF biocomposite.

The virgin PLA biodegradability increased with adding of TKF. The PLA/TKF biocomposite demonstrates optimum biodegradability followed by clear PLA and other PLA/TKF/MMT hybrid biocomposites. However, 1 wt% MMT included PLA/TKF/MMT hybrid biocomposite biodegradability properties higher than unreinforced PLA. The higher amount of MMT content (2 and 3 wt%) leads to agglomeration; it is raised owing to attractive force between PLA and MMT. Similar examination was made by Ramesh et al. [44] and M.S. Islam et al. [75]. However, the PLA/TKF biocomposite and PLA/TKF/MMT hybrid biocomposites biodegradability increases with increases of composting time.

4 Conclusions

The effect of MMT content on mechanical, thermal, water absorption and biodegradability properties of PLA/TKF/MMT hybrid biocomposites has been reported. The TKF at 30 wt% reinforced biocomposites are developed with MMT loadings of 0, 1, 2 and 3 wt%. The pure PLA modulus and biodegradability drastically enhanced with adding of TKF; however, the impact, flexural and tensile strength, thermal stability, water absorption properties are declined. MMT shows outstanding effect in enhancing mechanical, thermal, water absorption and biodegradable properties. The optimum content of MMT is observed to be 1 wt% for mechanical properties. The 1 wt% MMT containing PLA/TKF/MMT hybrid composites impact, flexural and tensile strength are increased by 10.6%, 46.4% and 5.7%, respectively than PLA/TKF biocomposite; whereas the PLA/TKF biocomposite flexural and tensile moduli are increased by 67.8 and 39.2%, respectively compared to neat PLA. These remarkable improvements are due to well bonding among matrix-nano-fiber, which are confirmed through SEM analysis. The PLA/TKF/1MMT hybrid biocomposite demonstrates superior abrasion resistance than other biocomposites. However, the tensile, flexural and impact strengths of PLA/TKF/MMT hybrid biocomposites are negatively affected when the excess (2 and 3 wt%) MMT was added. The composites thermal stability significantly increased trend with increase of MMT content. The 3 wt% MMT included PLA/TKF/MMT hybrid biocomposite shows superior thermal stability and $T_{Heat\ Resistance\ Index}$ than other manufacturing composites. From water absorption and biodegradability results, higher content of MMT minimizes the biodegradability rate and maximizes the water resistance of hybrid biocomposites.

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