Thermal Characterisation of Bio Fibre Composites

Mariana D. Banea, Jorge S. S. Neto, and Henrique F. M. Queiroz

Abstract The bio fibre composites thermal stability is an essential factor to consider, as the processing temperature plays a critical role in the manufacturing process of composites. At higher temperatures, the natural fibre components (i.e., cellulose, hemicellulose, and lignin), start to degrade and their properties change. Different methods are used in the literature to determine the thermal properties of bio fibre composite materials as well as to help to understand and determine their suitability for a particular application. The thermal stability of composites is investigated using TGA, DSC and DMA. The most frequent thermal properties evaluated by these methods are the weight loss percentage, the degradation temperature, T_g and viscoelastic properties. This chapter presents the main techniques used for thermal analysis of bio fibre composites. The main factors that affect the thermal properties of bio fibre composite materials (fibre and matrix type, the presence of additive fillers, fibre content, and fibre orientation, the chemical treatment of the fibres, manufacture process, and type of loading) are briefly discussed.

Keywords Natural fibre reinforced composite material · Thermal analysis · Thermogravimetric analysis (TGA) · Differential scanning calorimetry (DSC) · Differential Mechanical Thermal Analysis (DMA)

1 Introduction

Composites are increasingly being used in various industries, particularly in aerospace industries [1]. Nowadays, the industry is seeking new desirable characteristics of composite materials, eco-friendliness and low cost. Consequently, there has been significant interest in research and innovation in bio fibre composites, owing to

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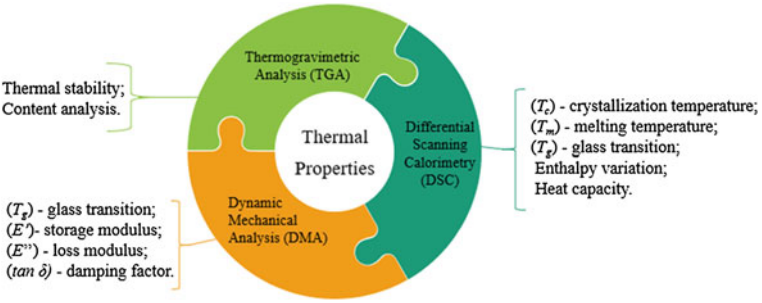

Fig. 1 The main methods for determining the thermal characteristics of composites are depicted in this diagram

the advantages of these materials compared to their synthetic fibre counterparts (i.e., lower environmental impact and low cost), supporting their potential across a wide choice of applications in several industrial sectors [2–7].

The methods used in the literature for thermal analysis of bio fibre composites are as follows: TGA, DSC, DMA. Figure 1 summarises the main methods used in the literature to determine the thermal properties of bio fibre composite materials.

Different methods are used to determine the thermal properties of bio fibre composites and also helps to understand and determine the suitability of bio fiber composites for a particular application. This chapter presents an overview of the main techniques used for the thermal analysis of bio fibre thermoset composites. The main factors that affect the thermal properties of bio fibre composite materials (fibre and matrix type, fibre content and arrangements, the treatment of the bio fibres) are briefly discussed.

2 Thermogravimetric Analysis (TGA)

TGA analysis measures the weighted temperature sample in specific controlled atmosphere (e.g. nitrogen, helium, air, or other gases) [8, 9]. Different temperatures and measurement times are applied in accordance with the matrix type of the bio fibre composite sample [10]. The TGA analysis's thermal data depends on several parameters, sample mass, sample form, atmosphere, flow rate, heating rate, and the treatment applied [10].

The thermal behaviour of biocomposites depends on the composite's principal constituents (bio fibres and matrix type). In general, the derivative thermogravimetric test (DTG) curve of bio fibres shows the elimination of water and the thermal decomposition of cellulose components of the fibres. The DTG curve and peaks in each degradation range indicate fibre constituents. For instance, the lignocellulose [11–15].

Several authors used thermogravimetric analysis to determine the thermal properties of bio fibre composites [16–23]. For example, Arulmuruganet al. [23], studied the

effect of barium sulfate (BaSO4) on the thermal properties of an aloe vera/flax hybrid composite. The fibres were subjected to chemical pretreatment (sodium hydroxide and potassium permanganate) with 10% and 5% for one h, respectively. Then they were treated with sodium laurel sulphate with 2% for 30 min. The configurations studied were: 4 layers of aloe verafibre (HNRP1), four layers of flax fibre (HNRP2), two layers of flax fibre + 2 layers of aloe verafibre (HNRP3), four layers of aloe verafibre + 5% of BaSO4 (HNRP4), four layers of flax fibre + 5% of BaSO4 (HNRP5), two layers of flax fibre + 2 layers of aloe verafibre + 5% of BaSO4 (HNRP6). The authors report that the increase in BaSO4 in pure and hybrid composite increased the thermal resistance of HNRP. Moreover, the maximum peak for the treated composites shows an increment with the addition of BaSO4 in its structure.

Hidalgo–Salazar et al. [24], studied the thermal properties of Fique fibre reinforced bio composites. The bio fibre composite were manufactured with two types of resin: Linear Low-Density Polyethylene (LLDP) and Epoxy resin (EP). The fabrication method used was thermo compression and resin film infusion processes. Figure 1 shows TG (Fig. 1a) and DTG (Fig. 1b) curves of the Fique fibre, which reveal that degradation occurred at 296 °C, whereas decomposition of the neat EP begins at 96 °C. As a result, the EP/Fique samples decomposed after the neat resin in both degradation phases. This has previously been observed in the literature for EP/Phormium Tenax leaf fibre composites and was explained due to an improved fibre/matrix interface [25]. After final degradation, the residual char for epoxy resin was 6.1 per cent and 11.1 per cent for epoxy-Fique bio fibre composite. According to the authors, the Fique fibre insertion on the epoxy resin increased the residual char of the composite.

Figure 2 shows TG and DTG curves of LLDPE and LLDPE/Fique bio-composites, whereas Fig. 3 shows thermal curves for EP and EP/Fique bio-composites, respectively. For the neat LLDPE sample, a single step degradation was observed with T_o (onset) at 439 ºC and T_{max} and 478 ºC, correspondingly (see Fig. 2a). The char residue

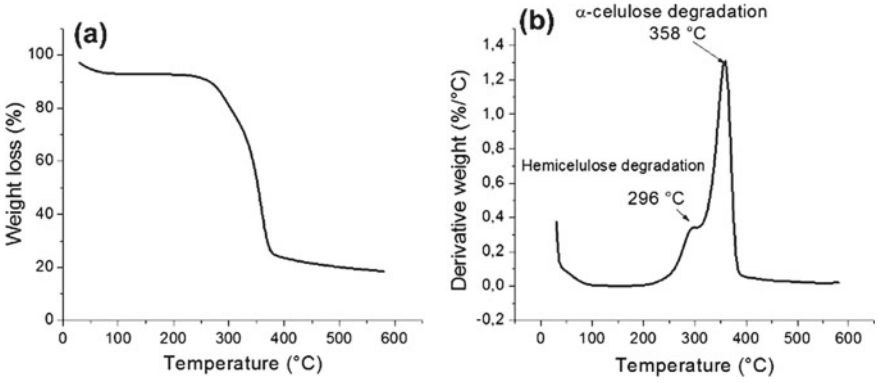

Fig. 2 **a** TG and **b** DTG curves of Fique fibres at heating rates of 10 °C/min. Reproduced with permission from [24]

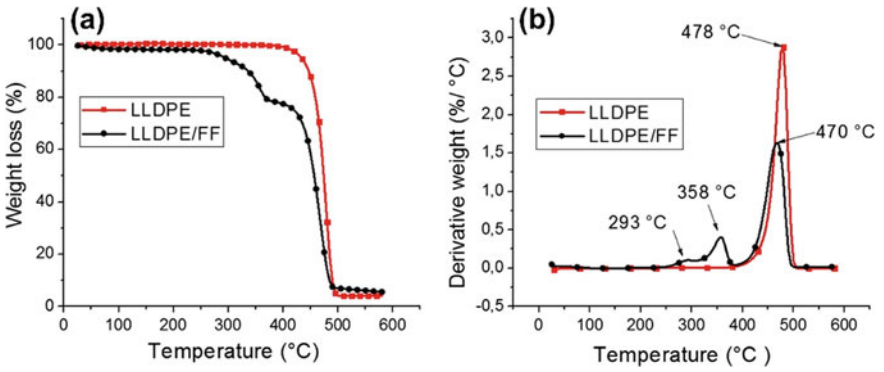

Fig. 3 **a** TG curve of neat Linear Low-Density Polyethylene (LLDPE) and **b** DTG curve of Linear Low-Density Polyethylene nonwoven Fique Fibre biocomposite (LLDPE/FF). Reproduced with permission from [24]

at the end of degradation was 4.1%. For the PE/Fique case, a two-step degradation process was observed. The authors state that the first degradation step is linked to the fibre constituent degradation (T_0 at 266 °C), presenting a mass loss of 21%. A slight decrease in the polymeric matrix's thermal stability was detected, connected to fibre breakdown 170 °C thermos-compression. Due to the addition of Fique fibre, the residual weight increased to 5.6 per cent. From Fig. 2b it can be seen that the DTG curve presented two T_{max} peaks at 293 °C and 358 °C, which can be linked to hemicellulose and α-cellulose degradation. The second degradation step is related to LLDPE matrix decomposition. The process starts at 437 °C and presents a T_{max} of 470 °C. On the other hand, a two-stage weight loss process was reported composites, indicating a similar thermal degradation behaviour (see Fig. 3). In addition, the disintegration of the significant polymeric chain is demonstrated in the second degrading step (250 °C–500 °C). For EP and EP-Fique, the observed T_o were 344 °C and 352 °C, respectively, while T_{max} was 365 °C and 373 °C.

Chin et al. [16] investigated bamboo fibre reinforced composites' mechanical and thermal characteristics in three types of thermoset matrices (epoxy, polyester, and vinyl ester). The fibres underwent two types of treatment: chemical (10% de NaOHbest case) and physical (milling method). The authors analyzed the following volumetric variations: 0%, 10%, 20%, 30% and 40%, whereas the manufacturing method used in the study was hand-lay-up. TGA was used to measure the effect of treatment of the decomposition of bamboo fibres as a function of the type of resins. Figure 4a shows an example of TGA curves of untreated and treated bamboo fibres with different chemical concentrations and times. It was found that the best case was 10% NaOH because of the hydrophilic reduction of the fibre when compared to the untreated fibre.

Furthermore, the concentration of chemical treatment eliminates several constituents, such as hemicellulose. Figure 5b–d shows the degradation of bamboo fibre as a function of temperature for three types of resin.

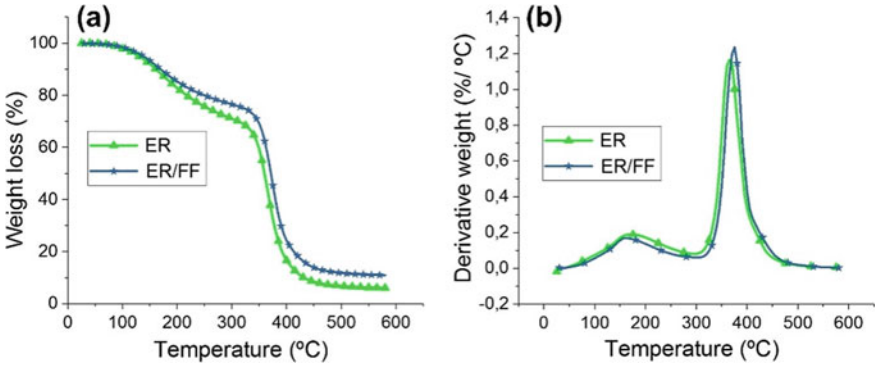

Fig. 4 **a** TG and **b** DTG curves of neat Epoxy resin (EP) and Fique biocomposite based Epoxy (EP/FF). Reproduced with permission from [24]

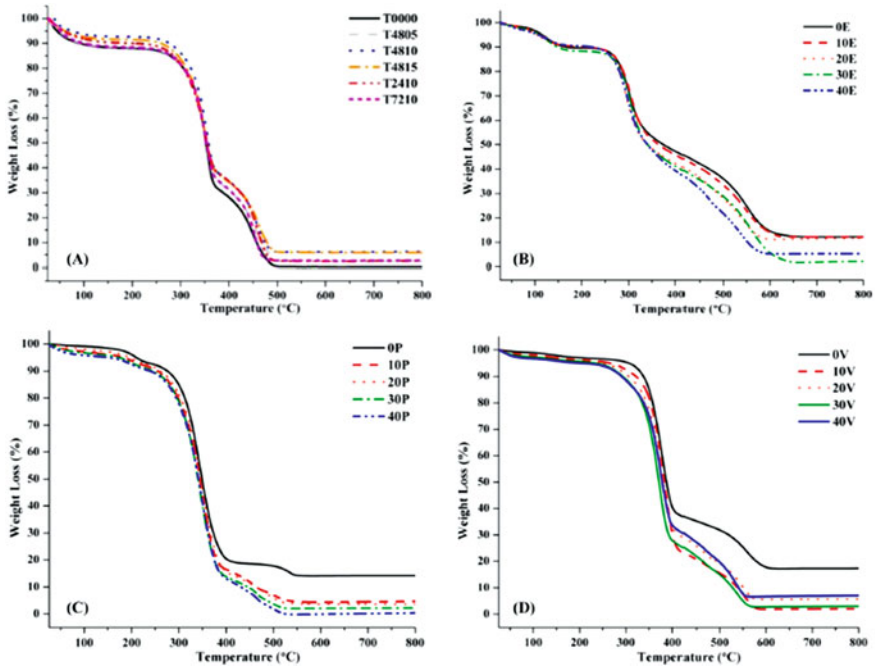

Fig. 5 TGA curves of bamboo fibre and its composites: and different types of resins: **a** bamboo fibre treated at different NaOH concentrations and soaking time **b** bamboo fibre reinforced epoxy composites, **c** bamboo fibre reinforced polyester and **d** bamboo fibre reinforced vinyl ester composites. Reproduced with permission from [16]

Rashid et al. [19], studied the effect of treatments on the mechanical and thermal properties of the sugar reinforced composite based on phenolic resin. The natural fibres underwent two types of treatment: the first was alkalization (0.5% of NaOH) for four h, the second was the washing of the fibres with distilled water. The manufacturing method used was compression moulding using a hot press. The results obtained showed that the first peak was lower for the case treated by mercerization when compared to the other cases: washed and untreated. The authors report that the chemical treatment applied reduced the hydrophilicity of natural fibre in composites. The best case was found for the untreated composite with a value of 430.97 °C, while for the treated and washed case, the maximum peak was 426.99 °C and 423.61 °C, respectively.

Lavoratti et al. [18] analyzed the thermal characteristics of composites reinforced with buriti and ramie fibre. The natural fibres were washed in distilled water and treated with NaOH (2.5 and 10%). The composites were produced by resin transfer moulding (RTM). The authors report that the buriti fibre starts to degrade at 217 °C, while for the ramie fibre, the degradation starts at 247 °C. The maximum degradation temperature obtained after washing with distilled water showed an enhancement in the thermal stability of the biocomposites. However, the alkalization treatment of these fibres negatively affected their thermal properties compared to natural and washed cases.

Nimanpure et al. [22], investigated the effect of hybridization between sisal (S) and kenaf (K) bio-fibre in polyester (P) based composites. The mechanical, electrical, and thermal properties were analyzed. The natural fibres were treated by alkalization with 5% NaOH for 48 h at room temperature. The configurations studied were: SK10P90 (Sisal-5% + Kenaf-5%), SK20P80 (Sisal-10% + Kenaf-10%), SK30P70 (Sisal-15% + Kenaf-15%), SK40P60 (Sisal-20% + Kenaf- 20%), S40P60 (Sisal-40%) and K40P60 (Kenaf- 40 compared to the composite samples reinforced by pure fibres (K40P60 and S40P60).

Cavalcanti et al. [21] used the TGA analysis to study the thermal proeprties of bio fibre composite based on polyester and epoxy resins. The jute + curauá and pure jute fibre composites did not undergo any chemical treatment, whereas the jute + sisal fibre composite was submitted to chemical alkalization treatment. They found that the thermal stability of epoxy-based composites was greater compared to the polyester-based composites. The epoxy-based composite presented a degradation onset temperatures of 318 °C and 317 °C for the jute and jute + curauá cases, while the polyester-based jute and jute + curauá cas-es presented onset temperatures of 310 °C and 312 °C, respectively.

Asim et al. [20], used TGA to analyse the effect of silane treatment on the thermal properties of pineapple (PALF) and Kenaf (K) fibre composites based on phenolic resin. The natural fibre were treated in distilled water with silane (2% for 3 h). The studied cases were 70(PALF):30(Kenaf) – (7P3K), 50P:50 K (1P1K), 30P:70 K(3P:7 K), treated (T-7P3K), (T-1P1K) and (T-3P7K). They found that the T-3P7K and T-7P3K composites were the cases with the highest thermal stability. Moreover, the treated composite presented a higher onset temperature than the untreated composites. Table 1 summarizes the thermal properties of bio fibre composites.

Table 1 TGA research revealed the thermal characteristics of bio fibre composites

Fibre	Matrix	Thermal Properties	References
Bamboo	Epoxy, Polyester and Vinyl ester	The inclusion of bamboo fibre to the composites did not result in a substantial reduction in the composites' initial onset degradation temperature (T_{onset}) of the composites	[16]
Buriti and ramie	Polyester	The maximum peak of degradation temperature (T_d) for the ramie fibre reinforced composite was 372 °C while for the buriti compositea value of 346 °C was reported	[18]
Sisal, sisal + curauá and sisal + ramie	Epoxy	The hybridization increased the thermal stability of the composites when compared to the pure sisal composites	[17]
Sugar Palm	Phenolic	The chemical treatment negatively affected the thermal stability of the composite	[19]
Sisal fibril + kenaf	Polyester	The thermal stability of hybrid composites was superior to pure fibres	[22]
Jute, jute + sisal and jute + curauá	Epoxy and Polyester	The onset temperature (T_{onset}) was higher for the jute, jute + curauá based on epoxy composite compared to polyester composites. For jute + sisal there was no significant change in$T_{onset}$for both matrices	[21]
Kenaf + pineapple	Phenolic	The treated hybrid composites decreased the amount of water and increased the maximum degradation temperature (T_d) when compared to the untreated cases	[20]
Flax + aloevera	Epoxy	The chemical treatment of $BaSO_4$ increased the thermal stability of the composites	[23]

(continued)

Table 1 (continued)

Fibre	Matrix	Thermal Properties	References
Curauá	Polyester	The addition of the fibre and chemical treatment of fibres with NaOH improved the thermal stability of the composites	[26]
Mulberry	Polyester	The thermal stability of the composites increased by increasing the NaOH concentration	[27]
Jute + Oil palm	Epoxy	The hybridization of the composites increased the maximum degradation temperature when compared to the pure Oil palm composite	[13]

3 Differential Scanning Calorimetry (DSC)

The DSC determines the material transitions. The thermal phase change of the composites is shown [28, 29].

The T_g is a vital material property when considering the biocomposites for a particular end-use application. It is well known that the "normal" state of most thermoset polymers at room temperature is rigid (amorphous solid). Below the T_g, the molecular chains of the thermoset resins do not present enough energy to let them move around (the molecules are frozen in place as a rigid structure because of the short-chain length, molecular groups separating off the chain and interlocking with each other). Moreover, when the polymer resin is heated, the molecules of the polymer resin gain energy and they can start to move around. The amorphous rigid structure of the thermoset polymer resin is transformed to a flexible structure (rubbery state) when a certain heat energy level is attained, and the polymer molecules are allowed to move freely around each other.

To conclude, the service temperature of polymer resins should always be below the T_g. If the composites are used above their T_g, they will quickly lose their mechanical properties (strength and stiffness), and they will continue to maintain some mechanical properties until the temperature reaches T_m. The crystallization temperature (T_c) is associated with the point where polymer chain alignment modification is possible. Upon reaching the T_c, ordered crystalline chain regions appear, called lamellae. However, amorphous regions remain in the structure.

It should be noted that the crystallization is an exothermic peak in a DSC curve. T_c temperature is higher than T_g but still lower than the melting temperature (T_m). Finally, the melting temperature (T_m) is when the polymeric chains lose their bonds and turn into a liquid. This process is called endothermic transition. In general, T_m for a thermoset polymer is higher than its T_g. At temperature above T_g but below T_m,

the polymer resin is in a rubbery state, and the material can exhibit large deformation under a relatively low load.

The DSC technique was utilised by several researchers to test the thermal stability of bio composites. [17, 26, 30–35]. Teixeira et al. [26], used the DSC method to investigate the effect of several chemical treatments on the thermal characteristics of curauá fibre polyester based composites. Different types of chemical treatments were used: 10% of barium hydroxide Ba(OH)2 for 48 h at 25 °C, 14% of calcium hydroxide Ca(OH)2 for four h at 70 °C, 10% of potassium hydroxide (KOH) for one h at 25 °C, 5% of sodium hydroxide (NaOH) for two h at 70 °C and 5% of silane (Trimethoxy(propyl) for four h at 25 °C. It was found that the chemical treatment increased the T_g of the treated composite when compared to untreated. Furthermore, the study reports that the chemical treatment of calcium hydroxide (Ca (OH)2) provide a T_g of 141.2 °C for the treated composites, compared to the 133.69 °C obtained for the untreated composite. The authors state that this increase in T_g was due to an improvement in the interaction.

Souza et al. [30] studied the percentage of fibre on the thermal characteristics of biocomposites reinforced with caranan fibre. The studied variation of fibre/matrix percentage was 0 to 30%. The authors show that the increase of the caranan fibre increases the T_g of the composites. The fibre content with 20% and 30% had a Tg value of 96 °C and 113 °C, respectively.

Bhoopathi et al. [32] studied the effect of eggshell nanoparticles on the thermal properties of hemp reinforced composites. The natural fibres were treated by mercerization (5% of NaOH for five h at room temperature). The studied cases were: Hemp without eggshell (0%ESP), hemp + 7% eggshell (7%ESP), hemp + 14% eggshell (14%ESP), hemp + 21% eggshell(21%ESP). When compared to unmodified composite samples, the authors found that raising the nanoparticle proportion boosted the thermal properties of composites. The best-case found was the 14%ESP, where the maximum exothermic peak value of degradation temperature onset was 411.6 °C, while for the unfilled case, it was 326.2 °C.

Gupta et al. [31] used the DSC technique to study the thermal properties of jute/sisal fibres in epoxy-based composites. The studied cases were: jute (J1), sisal (S1), 50% of jute + 50% of sisal (H1), 25% of jute + 75% of sisal (H2) and 75% of jute + 25% of sisal (H3). The composites were manufactured using the hand-lay-up technique and total fibre loading of 30%wt. The values of T_g found for H1 samples was 73.86 °C, for the H2 case was 72.86 °C, while for H3, the T_g value found was 68.36 °C when compared with the T_g of the matrix (65.16 °C).

Pereira et al. [17], used DSC to investigate the influence of hybridisation on the thermal properties of pure sisal and epoxy hybrid composites. Figure 6 shows the DSC curves for the composites studied. It can be seen that two events predominate, endothermic and exothermic, around 100 °C and 375 °C, respectively. Sisal + curauá was the sample that absorbed the most heat in the endothermic event and the least released heat in the exothermic event.

Sumesh et al. [33] investigated the thermal properties of pineapple (P)/Flax(F) reinforced epoxy-based composite. The microfilters were extracted by peanut oil cake. The percentages of CMF were 1 to 3% and treated by mercerization (4% of

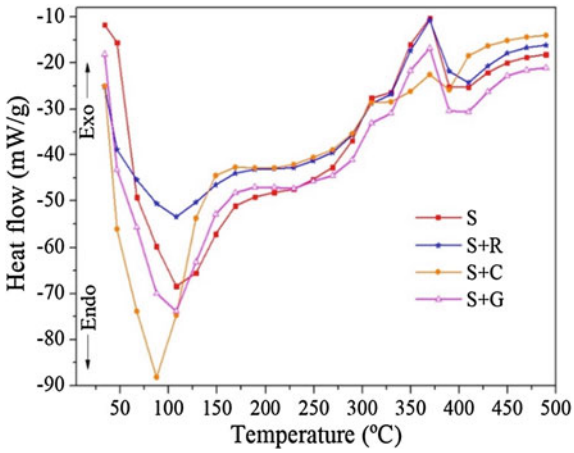

Fig. 6 DSC curves of epoxy sisal-based composites function as a hybridization (S-Sisal; S + R- Sisal + ramie; S + C-Sisal + curauá and S + G- sisal + glass fibre). Reproduced with permission from authors of Pereira et al. [17]

NaOH with 80 °C for 1.5 h). The natural fibres of pineapple and flax were treated using the mercerization treatment (5% NaOH for three h), and 30 and 35% wt of reinforcement were used in the hybrid composites. The manufacturing process used was compression moulding. The studied cases were: 30 wt% PF/0%CMF, 30 wt% PF/1%CMF, 30 wt% PF/2%CMF, 30 wt% PF/3%CMF and 35 wt% PF/0%CMF, 35 wt% PF/1%CMF, 35 wt% PF/2%CMF, 35 wt% PF/3%CMF. In addition to untreated cases, the untreated 30 wt% PF/2%CMF and untreated 35 wt% PF/3%CMF were studied. The results found indicate that for the case of 30%wt, the percentage of 2% CMF shows the higher endothermic peak with a value of 114.94 °C and enthalpy of 499.39 Jg^{-1}. For the case of 35%wt, the percentage of 3%CMF had an endothermic peak value of 120.39 °C and enthalpy of 504.21 Jg^{-1}. The authors indicated that untreated composite presented lower thermal properties when compared to the treated composite cases. Table 2 summarizes the results from numerous modern researches on the thermal properties of bio fibre.

4 Dynamic Mechanical Analysis (DMA)

DMA determines the following thermal data: storage modulus (*E*'), loss modulus (*E*"), glass transition temperature (T_g) [39], and damping factor ($tan\ \delta = E''/E'$). The storage modulus (*E*') is associated with the energy storage of the elastic characteristics of the material [34, 40, 41]. It has also been linked to the composites sample's "stiffness" [40, 41]. The loss modulus (*E*) is linked to the energy dissipation promoted by the viscous part of the composite sample. This dissipation is related to the internal molecular friction of the molecular chain for the following reasons: morphological transformation and relaxation, morphological and system heterogeneity [10, 41]. Damping factor It is calculated by dividing the storage modulus and loss modulus ($tan\ \delta$=*E*"/*E*'), and is related to the internal mobility of polymer molecular chains,

Table 2 Bio fibre composites: Thermal properties by DSC analysis

Fibre	Matrix	Thermal Properties	References
Curauá	Polyester	The chemical treatments used increased the T_g of the composites. The best treatment was Ca $(OH)_2$ with a T_g value of 141.92 °C	[26]
Jute + ZrO_2	Polyester	The presence of the nano filler increased the T_g of the composite	[35]
Jute + ramie	Epoxy	Alkalization and mixed (alkalization + silane) treatment increased the thermal properties	[34]
Caranan	Epoxy	The endothermic peak shows a large amount of water retained in the fibre	[30]
Jute + sisal	Epoxy	The addition of natural fibre produced an increase of thermal properties (T_g and T_c)	[31]
Hemp + eggshell	Epoxy	The incorporation of filler reduced the exothermic peak of the composite	[32]
Flax + Pineapple + Micro Cellulose (CMF)	Epoxy	The addition of CMF improved the endothermic peak and enthalpy when compared to the unmodified composite	[33]
Kenaf + Sisal	Bio-Epoxy	UV aging increased the T_g of hybrid composites and pure fibres	[36]
Jute + coir	Epoxy	The endothermic peak showed water loss between 60–120 °C	[37]
Flax + TiO_2	Epoxy	The addition of 0.7% of nano filler increased the T_g by 5 °C when compared to the unfilled composite	[38]

indicating the influence of fiber/matrix interaction [34, 41, 42]. Due to the quality of the fiber/matrix interaction, a high *tan δ* value means that the system consumes more energy than it stores. On the other hand, a low *tan δ* value indicates that the polymer chain is less fluid, indicating that the fiber/matrix interface contact is appropriate.

Several different test technique setups are possible in the DMA analysis. However, the three-point bending mode is the most popular test method for composite materials because it eliminates the mixed loading seen in single and double cantilever modes and generates quantifiable stresses in reasonably rigid materials. Depending on the methodology used, the glass transition temperature variation for a given material may be reported via the DMA analysis (up to 25 °C). The calculation method may also be more or less conservative, taking the T_g via first inflexion point/modulus drop onset or the *tan δ* peak, respectively [43].

The presence of fillers, fibre content and orientation, and chemical treatment of the fibres have all been proven to alter the dynamic mechanical properties of composite materials in the literature [41, 44, 45]. The testing mode also influences the DMA test results.

The DMA analysis was used by several researchers to determine the thermal properties of bio fibre composites [20, 27, 31, 34, 36, 46, 47]. For example, Yorseng et al. [36] analyzed the effect of natural kenaf/sisal hybrid composites' accelerated weathering on bio-epoxy resins. The configurations studied were: Kenaf (KKK), Sisal (SSS) and Kenaf + Sisal (KSK and SKS). The exposure time was 555 h with interleaved UV and water spray cycles. They state that the degradation process showed an increase in thermal properties for all cases studied. The incorporation of fibres (sisal and Kenaf) did not affect the glass transition (T_g) of the composites. Moreover, the hybridization of natural fibres increased the storage modulus values (E') compared to pure resin.

Shanmugasundaram et al. [27], estimated the effect of alkalinization treatment on the mechanical and thermal properties of mulberry reinforced polyester-based composites. The studied composites were: untreated mulberry fibre composite (UTMF) and Akali treated mulberry fibre composite. It was found that the 10% ATMFC samples presented higher values of storage modulus and loss modulus compared to the other cases studied.

Kumar et al. [46], used the DMA analysis to investigate the thermal properties of bio fibre composites. The studied cases were: Flax (F), Ramie (R) and Flax + Ramie (F + R). The value of E' found for the hybrid composite was 9.03GPa, whereas, for the pure resin, the value of the storage modulus (E') was 1.84 GPa, showing that the hybridization increased the viscoelastic properties of the composite. The highest T_g value was reported for the hybrid composite (110 ℃), while for the flax, ramie and bio epoxy cases, the reported values were 91 °C, 95 °C and 80 °C, respectively. It was found that the hybridization technique resulted in a higher number of polymer chains, increasing the dissipation of energy of the composite, positively affecting the glass transition temperature.

Chee et al. [48] used the Thermomechanical analysis (TMA) and DMA analysis to investigate the effect of hybridization of bamboo (B) and kenaf (K) fibres on the thermal properties of various configurations in epoxy resin-based hybrid composites. The authors reported that the composite with 100% Bamboo obtained a value of storage modulus (E') of 979 MPa, while the epoxy resin and 100% Kenaf had 449 and 775 MPa, respectively. Figure 7a shows that the storage modulus values of hybrid composites were between the values of composites reinforced by kenaf and bamboo fibres. The loss modulus (E'') curves showed that the hybrid composite Kenaf (50%) + Bamboo (50%) presented a T_g of 74.24 °C, while for the 100% Kenaf composite, the T_g value was70.85 °C (see Fig. 7b). It was also shown that fibre incorporation increases the peak width of the loss modulus (E''). The weight ratio of 50:50 of the bamboo fibre to kenaf fibre was the ideal mixing ratio which presented improved thermomechanical and dynamic mechanical properties. The authors state that this indicates effective stress transfer and improved interfacial interaction between fibre and matrix. Figure 7c shows that the neat epoxy resin had the highest $tan\ \delta$ peak

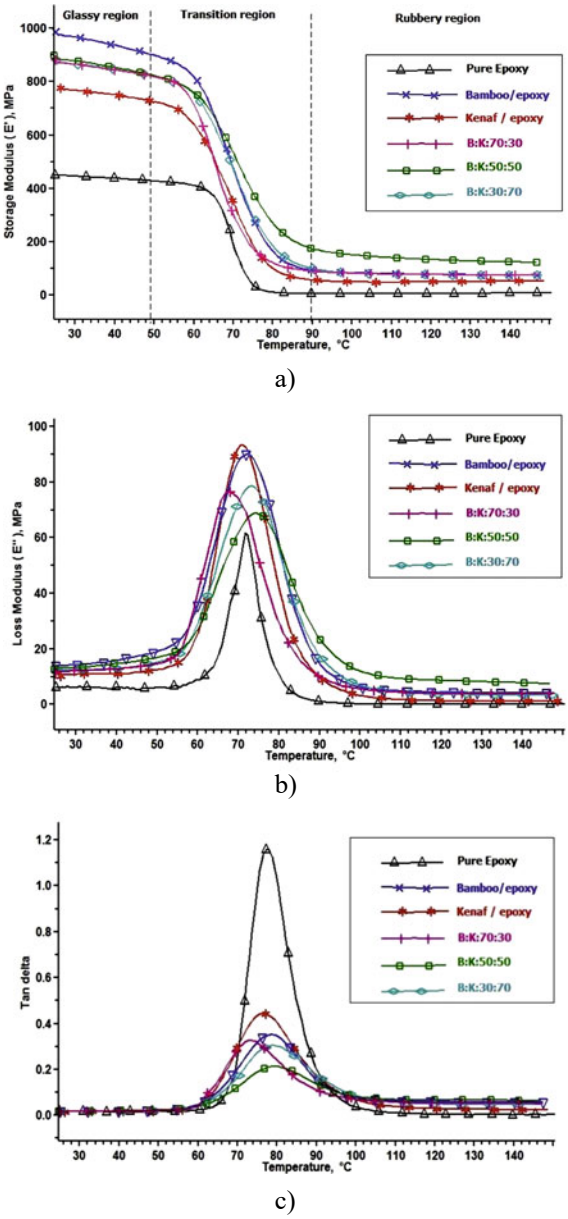

Fig. 7 Representative curves for the DMA test results of epoxy resin and hybrid epoxy composites **a** Storage modulus (*E*') and **b** Loss modulus (*E*"), **c** Tan delta versus temperature. Reproduced with permission from [48]

value (1.15), indicating that the system presented increased molecular mobility with more energy dissipation and other vicious behaviour. Lower molecular mobility was linked to the interlocking among fibres and the polymer matrix once fibres were added, which lowered the *tan δ* peak.

Ramakrishnan et al. [47] analyzed the effect of the chemical treatment and incorporating nano-clay in jute reinforced epoxy-based composite. The thermal properties were analyzed using the DMA. The natural fibres were treated with 2.5%, 5% and 7.5% de NaOH. The composites were modified with different percentages of nano-clay: 1, 3, 5 and 7% wt. The studied cases were: untreated jute: 2.5% NaOH treated jute composite, 5% NaOH treated jute composite, and 7.5% NaOH treated jute composite. It was found that the nano-clay modified jute composites presented higher E', E" and *tan* δ values. The composites modified with 5 wt.% of nano-clay had improved viscoelastic properties. 5% treated jute fibres composites presented highest E' and E'' value but the lowest *tan* δ value. This was explained by the improved interfacial bonding provided by the chemical treatment of the bio fibres.

Table 3 summarizes the results from researches on the thermal properties of bio fibre composites obtained through DMA analysis.

Table 3 DMA study revealed the thermal characteristics of biocomposites

Fibre	Matrix	Thermal Properties	Ref
Jute + sisal	Epoxy	The storage modulus (E') of composites was raised through hybridization. Furthermore, when compared to pure jute composite, the T_g of hybrid composites was lower	[31]
Pineapple + kenaf	Phenolic	The treated pineapple fibre increased the T_g of the composites	[20]
Mulberry	Polyester	Treatment with 10% of NaOH increased the storage modulus (E') of the composite. The fibres decreased the T_g (values of 69 °C was found the neat resin and 63 °C was found for the untreated composites, respectively	[27]
Aloevera /Hemp/Flax	Epoxy	The hybridization and chemical treatment ($BaSO_4$) increased the storage modulus (E') and T_g of composites	[49]
Kenaf + Nanofiller	Epoxy	The incorporation of nanofiller improved the T_g of the composites	[50]
Kenaf + Sisal	Bio-Epoxy	The storage modulus decreased as a function of temperature	[36]
Flax + ramie	Bio-Epoxy	Hybrid composites at 30% weight fraction of fibresprovided best results with maximum storage (9.03 GPa), loss modulus (1.45 GPa), and maximum T_g (110 °C)	[46]

(continued)

Table 3 (continued)

Fibre	Matrix	Thermal Properties	Ref
Jute + Nanoclay	Epoxy	The nano-clay modified jute composites presented higher E', E'' and *tan* δ values. The composites modified with 5 wt.% of nano-clay had improved viscoelastic properties 5% treated jute fibres composites presented highest E' and E'' value but the lowest *tan* δ value. Chemical treatment with 5% NaOH + 5wt% nanoclay provided higher storage modulus and T_g	[47]
Bamboo + Kenaf + Nanoclay	Epoxy	The addition of the nanofiller improved the storage modulus, loss modulus and *tan* $\delta$when compared to the other hybrid composite	[51]
Ramie + Buriti	Polyester	The ramie reinforced composite treated with 2% de NaOH presented higher storage modulus and loss modulus compared to the other treated cases	[18]
Jute + Oil palm	Epoxy	High oil palm to jute fibre ratio lowered the storage modulus. Loss modulus presented an increasing trend as a function of increasing jute fibre content	[13]
Bamboo + Kenaf	Epoxy	The complex and storage modulus of bamboo composite are higher compared to kenaf composite. Hybrid composites value lie between bamboo and kenaf composites	[48]

5 Conclusions

Thermal analysis can provide helpful information for developing new materials and optimising the selection process of these materials for new applications. The weight loss %, the deprivation of temperature, T_g, and viscoelastic properties are the literature's most commonly researched thermal properties. The thermal properties of bio fibre composites are influenced by a number of factors. For example, the kind of fibre and matrix, the presence of additives and fillers, fibre content, fibre origination, chemical treatment of the fibres, manufacturing process, and loading type. It is critical to make sure the bio fibres used in composites can resist the heat generated during the fabrication process and preserve their properties after that. Different approaches were used in the literature to enhance the thermal properties of bio fibres based composite materials. Using natural fibres with low lignin content, for example, improves the thermal performance of composites. Another approach is removing lignin through

fibres treatment. Finally, adding synthetic fibres or fillers to natural fibre reinforced composites improves their thermal stability.

References

1. Banea MD, Da Silva LFM (2009) Adhesively bonded joints in composite materials: An overview. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications 223(1):1–18. https://doi.org/10.1243/14644207JMDA219
2. Budhe S, de Barros S, Banea MD (2019) Theoretical assessment of the elastic modulus of natural fiber-based intra-ply hybrid composites. Journal of the Brazilian Society of Mechanical Sciences and Engineering 41 (6). doi:https://doi.org/10.1007/s40430-019-1766-z
3. Banea MD, Neto JSS, Cavalcanti DKK (2021) Recent Trends in Surface Modification of Natural Fibres for Their Use in Green Composites. In: Thomas S, Balakrishnan P (eds) Green Composites. Springer Singapore, Singapore, pp 329–350. doi:https://doi.org/10.1007/978-981-15-9643-8_12
4. Wambua P, Ivens J, Verpoest I (2003) Natural fibres: can they replace glass in fibre reinforced plastics? Compos Sci Technol 63(9):1259–1264
5. de Queiroz HFM, Banea MD, Cavalcanti DKK (2021) Adhesively bonded joints of jute, glass and hybrid jute/glass fibre-reinforced polymer composites for automotive industry. Applied Adhesion Science 9 (1). doi:https://doi.org/10.1186/s40563-020-00131-6
6. Pereira AL, Banea MD, Pereira AB (2020) Effect of intralaminar hybridization on mode I fracture toughness of natural fiber-reinforced composites. Journal of the Brazilian Society of Mechanical Sciences and Engineering 42 (9). doi:https://doi.org/10.1007/s40430-020-02525-w
7. de Queiroz HFM, Banea MD, Cavalcanti DKK (2020) Experimental analysis of adhesively bonded joints in synthetic- and natural fibre-reinforced polymer composites. J Compos Mater 54(9):1245–1255. https://doi.org/10.1177/0021998319876979
8. Asim M, Jawaid M, Paridah MT, Saba N, Nasir M, Shahroze RM (2019) Dynamic and thermo-mechanical properties of hybridized kenaf/PALF reinforced phenolic composites. Polym Compos 40(10):3814–3822
9. Krishnasamy S, Thiagamani SMK, Kumar CM, Nagarajan R, Shahroze R, Siengchin S, Ismail SO, MP ID, (2019) Recent advances in thermal properties of hybrid cellulosic fiber reinforced polymer composites. Int J Biol Macromol 141:1–13
10. Asim M, Paridah MT, Chandrasekar M, Shahroze RM, Jawaid M, Nasir M, Siakeng R (2020) Thermal stability of natural fibers and their polymer composites. Cellulose 174:175
11. Guo Y, Zhu S, Chen Y, Li D (2019) Thermal properties of wood-plastic composites with different compositions. Materials 12(6):881
12. Członka S, Strąkowska A, Kairytė A (2020) Effect of walnut shells and silanized walnut shells on the mechanical and thermal properties of rigid polyurethane foams. Polymer Testing:106534
13. Jawaid M, Khalil HA, Bakar AA, Hassan A, Dungani R (2013) Effect of jute fibre loading on the mechanical and thermal properties of oil palm–epoxy composites. J Compos Mater 47(13):1633–1641
14. Dalla Libera Junior V, Leão RM, Franco Steier V, da Luz SM (2020) Influence of cure agent, treatment and fibre content on the thermal behaviour of a curaua/epoxy prepreg. Plast, Rubber Compos 49(5):214–221
15. El Boustani M, Lebrun G, Brouillette F, Belfkira A (2017) Effect of a solvent-free acetylation treatment on reinforcements permeability and tensile behaviour of flax/epoxy and flax/wood fibre/epoxy composites. The Canadian Journal of Chemical Engineering 95(6):1082–1092
16. Chin SC, Tee KF, Tong FS, Ong HR, Gimbun J (2020) Thermal and mechanical properties of bamboo fiber reinforced composites. Materials Today Communications 23:100876. doi:https://doi.org/10.1016/j.mtcomm.2019.100876

17. Pereira AL, Banea MD, Neto JS, Cavalcanti DK (2020) Mechanical and Thermal Characterization of Natural Intralaminar Hybrid Composites Based on Sisal. Polymers 12(4):866
18. Lavoratti A, Romanzini D, Amico SC, Zattera AJ (2017) Influence of Fibre Treatment on the Characteristics of Buriti and Ramie Polyester Composites. Polym Polym Compos 25(4):247–256. https://doi.org/10.1177/096739111702500401
19. Rashid B, Leman Z, Jawaid M, Ghazali MJ, Ishak MR (2017) Influence of Treatments on the Mechanical and Thermal Properties of Sugar Palm Fibre Reinforced Phenolic Composites. 2017 12 (1):16
20. Asim M, Paridah MT, Saba N, Jawaid M, Alothman OY, Nasir M, Almutairi Z (2018) Thermal, physical properties and flammability of silane treated kenaf/pineapple leaf fibres phenolic hybrid composites. Compos Struct 202:1330–1338
21. Cavalcanti DKK, Banea MD, Neto JSS, Lima RAA (2020) Comparative analysis of the mechanical and thermal properties of polyester and epoxy natural fibre-reinforced hybrid composites. J Compos Mater 55(12):1683–1692
22. Nimanpure S, Hashmi SAR, Kumar R, Bhargaw HN, Kumar R, Nair P, Naik A (2019) Mechanical, electrical, and thermal analysis of sisal fibril/kenaf fiber hybrid polyester composites. Polym Compos 40(2):664–676. https://doi.org/10.1002/pc.24706
23. Arulmurugan M, Selvakumar AS, Prabu K, Rajamurugan G (2020) Effect of barium sulphate on mechanical, DMA and thermal behaviour of woven aloevera/flax hybrid composites. Bull Mater Sci 43(1):58. https://doi.org/10.1007/s12034-019-2018-7
24. Hidalgo-Salazar MA, Correa JP (2018) Mechanical and thermal properties of biocomposites from nonwoven industrial Fique fiber mats with Epoxy Resin and Linear Low Density Polyethylene. Results in Physics 8:461–467. https://doi.org/10.1016/j.rinp.2017.12.025
25. De Rosa IM, Santulli C, Sarasini F (2010) Mechanical and thermal characterization of epoxy composites reinforced with random and quasi-unidirectional untreated Phormium tenax leaf fibers. Materials & Design (1980–2015) 31 (5):2397–2405. doi:https://doi.org/10.1016/j.matdes.2009.11.059
26. Teixeira LA, Vilson Dalla Junior L, Luz SM (2020) Chemical treatment of curaua fibres and its effect on the mechanical performance of fibre/polyester composites. Plast, Rubber Compos 50(4):189–199. https://doi.org/10.1080/14658011.2020.1862978
27. Shanmugasundaram N, Rajendran I, Ramkumar T (2018) Static, dynamic mechanical and thermal properties of untreated and alkali treated mulberry fiber reinforced polyester composites. Polym Compos 39(S3):E1908–E1919. https://doi.org/10.1002/pc.24890
28. Jesuarockiam N, Jawaid M, Zainudin ES, Thariq Hameed Sultan M, Yahaya R (2019) Enhanced Thermal and Dynamic Mechanical Properties of Synthetic/Natural Hybrid Composites with Graphene Nanoplateletes. Polymers 11(7):1085
29. Veerasimman A, Shanmugam V, Rajendran S, Johnson DJ, Subbiah A, Koilpichai J, Marimuthu U (2021) Thermal Properties of Natural Fiber Sisal Based Hybrid Composites – A Brief Review. Journal of Natural Fibers:1–11. doi:https://doi.org/10.1080/15440478.2020.1870619
30. Souza AT, Pereira Junio RF, Neuba LdM, Candido VS, da Silva ACR, de Azevedo ARG, Monteiro SN, Nascimento LFC (2020) Caranan Fiber from Mauritiella armata Palm Tree as Novel Reinforcement for Epoxy Composites. Polymers 12(9):2037
31. Gupta MK (2016) Thermal and dynamic mechanical analysis of hybrid jute/sisal fibre reinforced epoxy composite. Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications 232(9):743–748. https://doi.org/10.1177/1464420716646398
32. Bhoopathi R, Ramesh M (2020) Influence of eggshell nanoparticles and effect of alkalization on characterization of industrial hemp fibre reinforced epoxy composites. J Polym Environ 28:2178–2190
33. Sumesh KR, Kanthavel K, Kavimani V (2020) Peanut oil cake-derived cellulose fiber: Extraction, application of mechanical and thermal properties in pineapple/flax natural fiber composites. Int J Biol Macromol 150:775–785. https://doi.org/10.1016/j.ijbiomac.2020.02.118
34. Neto J, Lima R, Cavalcanti D, Souza J, Aguiar R, Banea M (2019) Effect of chemical treatment on the thermal properties of hybrid natural fiber-reinforced composites. J Appl Polym Sci 136(10):47154

35. Biswas B, Sawai P, Santra A, Gain A, Saha P, Mitra BC, Bandyopadhyay NR, Sinha A (2019) Thermal stability, swelling and degradation behaviour of natural fibre based hybrid polymer composites. Cellulose 26(7):4445–4461. https://doi.org/10.1007/s10570-019-02383-3
36. Yorseng K, Rangappa SM, Pulikkalparambil H, Siengchin S, Parameswaranpillai J (2020) Accelerated weathering studies of kenaf/sisal fiber fabric reinforced fully biobased hybrid bioepoxy composites for semi-structural applications: Morphology, thermo-mechanical, water absorption behavior and surface hydrophobicity. Construction and Building Materials 235:117464. doi:https://doi.org/10.1016/j.conbuildmat.2019.117464
37. Saw SK, Sarkhel G, Choudhury A (2012) Preparation and characterization of chemically modified Jute-Coir hybrid fiber reinforced epoxy novolac composites. J Appl Polym Sci 125(4):3038–3049. https://doi.org/10.1002/app.36610
38. Prasad V, Joseph MA, Sekar K (2018) Investigation of mechanical, thermal and water absorption properties of flax fibre reinforced epoxy composite with nano TiO2 addition. Compos A Appl Sci Manuf 115:360–370. https://doi.org/10.1016/j.compositesa.2018.09.031
39. Chandrasekar M, Ishak M, Sapuan S, Leman Z, Jawaid M (2017) A review on the characterisation of natural fibres and their composites after alkali treatment and water absorption. Plast, Rubber Compos 46(3):119–136
40. Lu N, Oza S (2013) A comparative study of the mechanical properties of hemp fiber with virgin and recycled high density polyethylene matrix. Compos B Eng 45(1):1651–1656
41. Saba N, Jawaid M, Alothman OY, Paridah M (2016) A review on dynamic mechanical properties of natural fibre reinforced polymer composites. Constr Build Mater 106:149–159
42. Jawaid M, Khalil HA, Hassan A, Dungani R, Hadiyane A (2013) Effect of jute fibre loading on tensile and dynamic mechanical properties of oil palm epoxy composites. Compos B Eng 45(1):619–624
43. Akay M (1993) Aspects of dynamic mechanical analysis in polymeric composites. Compos Sci Technol 47(4):419–423
44. Ashok R, Srinivasa C, Basavaraju B (2019) Dynamic mechanical properties of natural fiber composites—a review. Advanced Composites and Hybrid Materials:1–22
45. Członka S, Strąkowska A, Kairytė A (2021) Coir Fibers Treated with Henna as a Potential Reinforcing Filler in the Synthesis of Polyurethane Composites. Materials 14(5):1128
46. Kumar S, Zindani D, Bhowmik S (2020) Investigation of mechanical and viscoelastic properties of flax-and ramie-reinforced green composites for orthopedic implants. J Mater Eng Perform 29:3161–3171
47. Ramakrishnan S, Krishnamurthy K, Rajeshkumar G, Asim M (2020) Dynamic Mechanical Properties and Free Vibration Characteristics of Surface Modified Jute Fiber/Nano-Clay Reinforced Epoxy Composites. J Polym Environ 29(4):1076–1088. https://doi.org/10.1007/s10924-020-01945-y
48. Chee SS, Jawaid M, Sultan MTH, Alothman OY, Abdullah LC (2019) Thermomechanical and dynamic mechanical properties of bamboo/woven kenaf mat reinforced epoxy hybrid composites. Compos B Eng 163:165–174. https://doi.org/10.1016/j.compositesb.2018.11.039
49. Arulmurugan M, Prabu K, Rajamurugan G, Selvakumar AS (2019) Viscoelastic behavior of aloevera/hemp/flax sandwich laminate composite reinforced with BaSO4: Dynamic mechanical analysis. J Ind Text 50(7):1040–1064. https://doi.org/10.1177/1528083719852312
50. Khan A, Asiri AM, Jawaid M, Saba N, Inamuddin (2020) Effect of cellulose nano fibers and nano clays on the mechanical, morphological, thermal and dynamic mechanical performance of kenaf/epoxy composites. Carbohydrate Polymers 239:116248. doi:https://doi.org/10.1016/j.carbpol.2020.116248
51. Chee SS, Jawaid M, Alothman OY, Fouad H (2021) Effects of Nanoclay on Mechanical and Dynamic Mechanical Properties of Bamboo/Kenaf Reinforced Epoxy Hybrid Composites. Polymers 13 (3). doi:https://doi.org/10.3390/polym13030395