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Recent advances in thermal properties of hybrid cellulosic fiber reinforced polymer composites

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Abstract

Bio-composites are easy to manufacture and environmentally friendly, could reduce the overall cost and provide lightweight due to the low density of the natural fibers. In a bid to compete with the synthetic fiber reinforced composites, a single natural fiber composite may not be a good choice to obtain optimal properties. Hence, hybrid composites are produced by adding two or more natural fibers together to obtain improved properties, such as mechanical, physical, thermal, water absorption, acoustic and dynamic, among others. Regarding thermal stability, the

composites showed a significant change by varying the individual fiber compositions, fiber surface treatments, addition of fillers and coupling agents. The glass transition temperature and melting point obtained from the thermomechanical analysis and differential scanning calorimetry are not the same values for several hybrid composites, since the volume variation was not always parallel with the enthalpy change. However, the difference between the temperature calculated from the thermomechanical analysis and differential scanning calorimetry was lower. Significantly, this critical reviewed study has a potential of guiding all composite designers, manufacturers and users on right selection of composite materials for thermal applications, such as engine components (covers), heat shields and brake ducts, among others.

Keywords: Hybrid composite, natural fiber, thermomechanical analysis, dynamic mechanical analysis, thermogravimetric analysis, differential scanning calorimetry.

1. Introduction

Thermal analysis of materials is essential to industries that are producing or/and using inorganic and organic chemicals, pharmaceuticals, foods, petroleum, polymers, polymeric composites, to mention but a few. It is one of the main branches of material science, where the physical and chemical properties of the materials are investigated, as functions of temperature and time (Pleşa, Noţingher, Schlögl, Sumereder, & Muhr, 2016; Saba, Paridah, Abdan, & Ibrahim, 2016c). Thermal analytical methods have been in existence since the 18th century. The first thermal analytical measurement was made by Le Chatelier in 1887, by placing a thermocouple in a clay sample and heating it in a furnace. Then, the heating curves were recorded on a photographic plate using a mirror galvanometer (Fortunato, 2013). In 1899, a significant improvement was made by Roberts-Austen with the introduction of two differential thermocouples connected in opposition, to measure the temperature difference between the

sample and an inert reference (Kayser & Patterson, 1998). Till the invention of thermogravimetric measurements in 1915, the mass difference was measured only by back weighing (Wagner, 2017) . The development of the heat flow through differential scanning calorimetry (DSC) and the power compensated DSC was witnessed in the middle of 19th century (Boersma, 1955; Watson, O'neill, Justin, & Brenner, 1964). Furthermore, in recent years, the dynamic mechanical measurements came into reality with different selectable frequencies. The modern developments in the thermal analysis techniques and their phenomenal usage in material characterization could be attributed to the efforts of the scientists and the emergence of efficient computer hardware and software systems.

A broader analytical approach is required to understand the thermal behavior of the materials. The present-day thermal analysis techniques can provide information for new material development and selection process optimization, engineering design and the prediction of end-user performance. They can also be used to test materials for consistency against specifications and to troubleshoot processing problems (Pryde, 1990). Currently, a wide range of proven thermal analysis techniques such as thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermomechanical analysis (TMA) have been used. These analytical techniques are very much useful in the study of the structural changes (glass transition, melting/crystallization, crosslinking, volatilization and phase transitions in the solid and liquid states), mechanical properties (elastic behavior, damping), thermal properties (expansion/shrinkage, specific heat capacity, melting/crystallization temperature, coefficient of expansion and chemical reactions (decomposition and thermal stability in different gaseous environments, chemical reactions in

solutions or liquid phase, reactions with the purge gas and dehydration) (Saba, Jawaid, & Sultan, 2017; Liszkowska, Czupryński, & Paciorek-Sadowska, 2016).

Moreover, polymers and polymeric composites are used in a variety of applications, such as electronics, biomedical, energy, food packaging, construction and manufacturing industries for several decades. However, because of the inherent lower thermal conductivity and stability of these polymeric materials, their wide range of applications is restricted, especially where excellent heat dissipation and low thermal expansion are necessarily required (Yang et al., 2018). Furthermore, differences in the structural aspects, chemical nature and other processing parameters influenced the functional properties of the fiber reinforced polymeric composites (John & Thomas, 2008; Mohanty, Misra, & Hinrichsen, 2000). It is also vital to examine the thermal properties of fibers in the formulation of composites. Moreover, it is essential to ensure that the fibers used in the polymer composites can withstand the heat required during processing and retain their characteristics after exposed to heat. This will be useful in determining the thermomechanical and thermo-dielectric characteristics of the fiber (Yusriah, Sapuan, Zainudin, & Mariatti, 2014). Natural fibers are considered as potential feed stocks for large production of ecofriendly composite structures (Kumar et al., 2018). However, their poor physical properties, such as brittle structure, lower mechanical properties, inferior natural properties and low melt viscosity limit their effectiveness in many applications. Hence, in order to overcome these issues, it is inevitable to understand their rheological and thermal characteristics (Ilyas, Sapuan, Ishak, & Zainudin, 2019a; Ilyas, Sapuan, Ishak, & Zainudin, 2018b). The poor thermal properties of the fibers can also limit their applications, however formulation of composites could embrace different applications (Mishra, Mohanty, Drzal, Misra, & Hinrichsen, 2004; Bledzki & Gassan, 1999). The composition of the fibers can also influence their thermal properties (Ilyas, Sapuan,

Ishak, & Zainudin, 2017). It was reported that the chemical treatment of fibers can improve the thermal properties by removing their lignocellulosic components (Ilyas, Sapuan, & Ishak, 2018a; Ilyas et al., 2019b). Hence, possible strategies to overcome other several drawbacks have been implemented to produce various new materials for the ever-changing industrial needs. In the recent years, extensive researches are undertaken for the enhancement of thermal properties of composite materials. The inclusion of metallic, carbon and ceramic based fillers have improved the properties of the ensuing hybrid composites (Burger et al., 2016). The thermal and mechanical performances of a material play a significant role in determining its final application. To improve material properties, thermal analysis is an essential study on the new material development (Costa, Fonseca, Serra, & Coelho, 2016).

The existing review articles based on the thermal analysis of polymers and polymer composites with different fiber reinforcement techniques are inadequate and are less informative, especially on hybrid natural fiber reinforced polymer composites. Consequently, this review focuses on the application of thermal analysis techniques: TGA, TMA, DMA, and DSC to study thermal properties of various hybrid natural fiber reinforced polymer composites. This review also updates the research that have been performed in the recent years on the front of thermal behavior of advanced materials for different applications. Moreover, emphasis was given on the analysis of thermal properties associated with some factors, such as the type of matrix and fiber, fiber loading, layering sequences of fibers when two or more fibers are used, chemical modifications and addition of fillers.

2. TGA of hybrid composites with the natural fibers/thermoset polymers

2.1 Thermal decomposition temperature

Thermal stability of a composite, through TGA, is determined from the thermal degradation temperature and weight loss percentage obtained from the thermogram and the amount of char residue remaining in the chamber after heating to the maximum temperature range, respectively.

Figure 1 illustrates the typical graph of TGA and associated labels used in a TGA curve (Table 1).

Figure 1. A typical graph of TGA curve

Table 1. Terms used in a TGA curve

Natural fibers are lignocellulosic material with cellulosic and non-cellulosic constituents in their fiber structure. Non-cellulosic constituents include lignin, pectin, wax, moisture, to mention but a few. Degradation of these constituents in terms of weight loss at different temperature ranges occur during the TGA. The weight loss occurs in two or three stages depending on the fiber composition in the composite (Table 2).

Table 2. Weight loss in the hybrid composite at different temperatures

The initial weight loss that occurs in the first, second and final stages is attributed to the moisture absorption, hemicellulose and non-cellulosic constituents, followed by cellulose and de-polymerization of the matrix.

2.2 Char residue

The char residue and final degradation temperature for the hybrid composites reinforced with the two different natural fibers are shown in Table 3. It could be observed that both the char residue and final degradation temperature improved significantly on hybridized kenaf fiber (KF), empty fruit bunch (EPFB) and sal wood flour with the pineapple leaf fiber (PALF), jute and teak wood flour, respectively. The teak/sal wood flour/epoxy hybrid composite exhibited a better thermal

resistance than other two. Similarly, an improvement in thermal stability of the hybrid composites, due to the substitution of fiber with another superior thermal resistant fibers was reported by Saxena and Gapta (2018b), Boopalan et al. (2013) and Chee et al. (2019) on mango/sal wood/epoxy, banana/jute/epoxy and bamboo/kenaf/epoxy composites, respectively.

Table 3. Thermal properties for the pure and hybrid fiber-based composites from TGA

2.3 Fiber treatments

Previous studies have also indicated that thermal properties of natural fiber reinforced polymeric composites could be enhanced by the fiber treatment with chemicals and coupling agents. Some of the reported studies are tabulated in Table 4. For instance, sisal/jute/epoxy composite with NaOH treated fibers exhibited higher degradation temperature than the composites with untreated fibers (Gupta & Srivastava, 2016). The decomposition temperature of jute/*Sansevieria cylindrica*/epoxy hybrid composites increased from 355 ^{o}C to 358 ^{o}C, due to the fiber treatment with 5% NaOH for 1 hour (Kumar & Ramachandra Reddy, 2014a). The changes in the fiber composition owing to the removal of hemicellulose and other non-cellulosic constituents during the fiber treatment induced a positive effect on the thermal properties. In addition to the removal of these non-cellulosic components from the fibers, the coupling agents, such as silane and 2-hydroxyethyl acrylate (HEA) contributed to increase in initial and final degradation of the composites. Initial and final degradation temperatures shifted to higher values for the EPFB/jute/epoxy and PALF/kenaf/phenolic composites as a result of fiber treatment with 2-hydroxyethyl acrylate (Jawaid et al., 2015; Asim et al., 2018). However, it was observed that the composites with treated fibers have lower char residue and higher weight loss than the composites with untreated fibers.

Table 4. Reported studies on TGA properties of chemically treated natural fiber hybrid composites

2.4 Fillers

Other than the fiber treatments, thermal properties of the natural fiber reinforced hybrid composite could be enhanced by infusion of nano-fillers into the matrix. The results obtained by Vivek and Kanthavel (2019) indicated that 1 wt%, 3 wt% and 5 wt% bagasse ash produced higher char residue from banana/kenaf/epoxy and sisal/kenaf/epoxy. Infusion of bagasse ash into the hybrid composites shifted the initial and degradation final temperature, thereby influenced their thermal behavior. In another study, nanoclay incorporated into KF/epoxy composites yielded higher char residue than its counterpart without nanoclay. Nanoclay in the matrix was shielded against the heat, delayed the release of volatile constituents of the fiber and led to larger residue at higher temperatures (Saba et al., 2016c). Similar findings have been reported on the sugar palm/polyester and sisal/soil clay composites with the nanoclay fillers (Shahroze et al., 2018; Venkatram, Kailasanathan, Seenikannan, & Paramasamy, 2016). According to Sajna et al. (2017), the char residue increased from 6.93% to 9.55% with an addition of 3 wt% C30B nanoclay into the banana/closite composite. All these studies suggested that nanoclay fillers are compatible with thermoset and thermoplastic matrices. Therefore, introducing them into the composites can produce better thermal properties. The main advantage of fillers is that significant improvement in thermal properties is achieved by adding small quantity of fillers. Noticeably, a few studies are reported on TGA of nano-fillers incorporated into hybrid composites with the natural fibers.

3. TGA of hybrid composites with natural fibers/thermoplastic polymers

The thermal properties of composites with the thermoplastic matrix presented similar characteristic to that of thermoset based composites. Thermal properties depended on the fiber type, fiber composition and fiber loading. According to Aji et al. (2012), introducing PALF/KF to a high-density polyethylene (HDPE) matrix altered their thermal behavior in two ways: (a) degradation changed from 2-stage for pure HDPE to 3-stage after hybridization and (b) lower degradation temperature. PALF/betel nut husk/polypropylene (PP) composite showed weight loss at the maximum thermal degradation temperature at 10 wt% fiber loading. A further increase in the fiber loading led to weight loss at a lower temperature (Ramengmawii, Jawaid, Ariffin, & Sapuan, 2018). Sutradhar et al. (2018), Prasad et al. (2018) and Boujmal et al.,(2017) demonstrated that slightly higher degradation temperatures can be obtained by using equal amount of fibers in the hybrid banana/betel nut/PP, banana/coir/low-density polyethylene (LDPE) and alfa fiber/clay/PP composites. Additionally, these hybrid composites with uneven fiber ratio exhibited various inferior thermal properties. This limitation occurred especially in composites with a fiber constituent that has larger non-cellulosic content than their counterpart in the hybrid configuration; betel nut has higher hemicellulose than the banana fiber (Prasad et al., 2018).

Furthermore, hybrid composites have been developed by blending two different thermoplastic matrices with one type of fiber. There was a reduction in weight loss percentage (%) and higher degradation temperature was obtained by adding soil clay particles in the composite with pine cone/PP (Arrakhiz, Benmoussa, Bouhfid, & Qaiss, 2013) and oil palm fiber/HDPE (Essabir et al., 2016). The clay particles in the hybrid composite acted as a gas barrier and hence, improved their thermal degradation temperature during the pyrolysis. In a different study, an increment in char residue % was observed with an increase in zeolite content in the PP/pine wood flour hybrid

composite. The silicates present on the surface of zeolite enriched the thermal stability of the composite, thereby produced higher char residue (Kaymakci, Gulec, Hosseinihashemi, & Ayrilmis, 2017).

4. TGA of hybrid composites with natural fibers/biodegradable polymers

Thermoset resins, such as polyester, epoxy, among others and thermoplastic polymers include PP, HDPE, to mention but a view, have synthetic sources. Reinforcing them with the natural fibers only partially solves the biodegradability issues. Thus, completely biodegradable hybrid composites were developed with some matrices, such as polylactic acid (PLA) (Huda, Drzal, Mohanty, & Misra, 2007; Siakeng, Jawaid, Ariffin, & Sapuan, 2018), liquid rubber (Jacob, Jose, Thomas, & Varughese, 2006) and starch (Jumaidin, Sapuan, Jawaid, Ishak, & Sahari, 2017). According to Jumaidin et al. (2017), increasing the sugar palm fiber proportion in the seaweed/sugar palm/sugar palm starch composite provided maximum onset temperature and higher thermal degradation temperature, while increasing the seaweed provided greater char residue. This was attributed to the presence of carbonate content in seaweed, which left a larger residue on heating and sugar palm fiber, being a lignocellulosic material. Therefore, it improved the temperature due to the volatile components in their fiber structure. Siakeng et al. (2018) reported that an addition of PALF provided superior thermal properties than coir in coir/PALF/PLA composite. The difference in chemical composition of coir fiber and PALF was responsible for such variations in their thermal properties. However, using equal weight proportion of fibers produced optimum thermal properties in their hybrid composites. Huda et al. (2007) showed that different grades of talc (Silverline 002, Nicron 403 and Mistron CB) when used in PLA/recycled newspaper cellulose fiber (RNCF)/talc exhibited difference thermal properties, as follows: PLA/ RNCF (70/30) > PLA/RNCF / Silverline 002 (60/30/10) > PLA/

RNCF / Mistron CB (60/30/10). Introducing sisal/oil palm in the liquid rubber reduced the degradation temperature from 360.5 ^{o}C to 356.3 ^{o}C. The degradation temperature was improved due to the NaOH and silane treatment of the sisal/oil palm (Jacob et al., 2006).

5. Dynamic mechanical analysis

Polymers are viscoelastic materials that exhibit both solid and liquid characteristics in their mechanical behavior. DMA is the most popular method for characterizing viscoelastic properties. In DMA, a small cyclic stress is applied to a sample, and the resulting stress response is measured. Some critical applications of DMA are given thus.

- Distinguish transitions rising from molecular motions or relaxations
- Examine mechanical properties
- Develop structure-property relationships

Many researchers have investigated the effects of dynamic mechanical analysis of hybrid composites by (i) varying the layering sequences, (ii) varying the fiber loading or fiber weight percentage, (iii) adding fillers, (iv) chemical treatments of fiber and (v) using different types of resins, such as thermoplastics, thermosets and biodegradable. These factors are subsequently discussed. Moreover, Figure 2 shows the influential factors that affect the DMA measurements.

Figure 2. Influencing factors of the DMA measurement

5.1 Factors affecting the dynamic mechanical analysis of hybrid composites

5.1.1 Effect of layering pattern

The storage modulus of bamboo/kenaf epoxy hybrid composites followed 50:50 > 70:30 > 30:70 > kenaf/epoxy > pure epoxy. The loss modulus of pure fiber composites recorded highest, followed by 30:70 > 70:30 > 50:50 > epoxy. A damping factor of pure epoxy recorded highest

peak in plot m, followed by kenaf/epoxy and bamboo/epoxy composites. The kenaf fiber had a higher possibility of creating voids, which were helped to promote higher molecular movements. This led to higher damping, while lesser voids were observed in the bamboo composites due to the closely packed fiber arrangement and higher cellulose content of bamboo fiber (Chee, Jawaid, Sultan, Alothman, & Abdullah, 2019). Table 5 shows some of the reported works on DMA of natural fiber-based hybrid composites.

It is clear from Table 5 that the dynamic mechanical properties of hybrid natural fiber reinforced composites showed variation in peak loss modulus, peak storage modulus, glass transition temperature and peak tan delta according to the number of layers used, fiber stacking sequence, fiber weaving position (warp and weft directions) and fiber weaving patterns. Hybrid composites reinforced with three different natural fibers within the composite showed better storage and loss moduli of composites than the hybrid composite with two natural fibers in the stacking sequence. However, the latter outperformed the former in case of the glass transition temperature.

Table 5. Thermal properties of natural fiber hybrid composites

Damping factor was improved by adding a small amount of jute fiber with oil palm/epoxy composites in glass transition temperature regions (Jawaid & Khalil, 2011). Bagasse (B) and coir fibers (C) were used to fabricate bilayer, trilayer and intimate mix type of hybrid composites (Saw et al., 2011). The results obtained depicted that bagasse fiber as skin layer and coir fiber as the core layer showed maximum stiffness. The higher stiffness of BCB hybrid composite was further improved by a lower coefficient value of 0.170. However, the intimately mixed hybrid composite exhibited comparable results with the BCB hybrid composite. Theoretical modeling presented a good agreement with the experimental results obtained above the glass transition temperature. The bilayer hybrid composite showed maximum damping property. Composites

with intimately mixed and trilayers (BCB) had higher activation energies than composites with bilayers. Similarly, a study on combination of jute (J), hemp (H) and flax (F) fibers with the epoxy polymer composite has been conducted by Chaudhary et al. (Chaudhary et al., 2018). They fabricated different types of the composite, such as composites with the pure fiber, bilayer (JH and HF) and trilayer (JHF). The results showed that combination of natural fibers with the epoxy caused a reduction in the damping characteristic. Plant fibers reduced the brittleness of the epoxy matrix. Among the developed hybrid composites, the highest elastic nature occurred with JHF hybrid composite. It was evident from the lowest peak in tan delta plot. Furthermore, they reported that the damping characteristic, storage and loss moduli of composites were highly depended on the type of natural fibers used and its hybrid combinations.

The weaving pattern of hemp and polyethylene terephthalate (PET) along warp and weft directions influenced the storage modulus of the hemp/PET/epoxy composites (Ahmad et al., 2018). Interwoven hemp/PET/epoxy (HP) composites with hemp fibers oriented in the warp direction exhibited the highest storage modulus (E'), and the interwoven PET/hemp/epoxy (PH) composites with PET in the warp direction showed the lowest E'. HP composites yielded better glass transition temperature of 69 ^{o}C in loss modulus than PH 63 ^{o}C, owing to the lower mobility of matrix molecules within their composites. The effectiveness of fiber-matrix bonding of HP composites was significantly established by indicating a lesser value in damping factor than PH composites. Rajesh and Pitchaimani (2016) used different types of weave patterns such as plain, basket, stain, twill and huckaback in the jute/banana/polyester composites. Variations of warp and weft directions of each fiber were: (i) warp jute fiber, and weft banana fiber (WJWB) (ii) warp banana fiber, and weft jute fiber (WBWJ) and (iii) warp and weft banana and jute fiber (WAWBJ), called an intra-ply hybrid polyester composites. It was reported that the basket-type

woven had better dynamic mechanical properties. A higher glass transition temperature was recorded with both jute woven and banana woven composites. Likewise, the intra ply hybrid composites in which jute fibers oriented in warp direction from the basket type woven mat had higher dynamic mechanical properties compared to the other composites. Furthermore, it was reported that the natural fiber in the form of woven and intra-ply hybridization enhanced the storage and loss moduli of composites, when compared with the short and random fiber composites for a similar amount of fiber loading.

5.1.2 Effects of chemical treatment

Various studies on effects of chemical treatments such as alkali (Saw, Sarkhel, & Choudhury, 2012), silane (Asim et al., 2018), alkali+silane (mixed) (Neto et al., 2019) on the viscoelastic properties have been carried out, as shown in Table 6. Precisely, Saw et al. (2012) reported that hybrid jute/coir/epoxy composites with NaOH treated (jute fiber) and furfuryl alcohol (coir fiber) exhibited superior mechanical and dynamic mechanical properties than the pure jute and pure coir fiber composites. From the storage modulus plot, an increase in the amount of coir fibers caused a slight reduction in storage modulus, due to the fiber-fiber agglomeration. Moreover, the effectiveness of hybrids was indicated by the least value of 0.12 in tan delta for 1:1 fiber ratio. The flax/PLA/polycarbonate (PC) exhibited peak storage modulus and tan delta peak when 2% NaOH treated flax fiber was used, as a reinforcement (Karsli & Aytac, 2014).

Table 6. Thermal properties of chemically treated hybrid natural fiber reinforced composites

In addition, silane treated hybrid composites from PALF and KF possessed higher storage modulus than the untreated fiber composites in a room temperature, except for PALF: KF ratio of 30:70 (Asim et al., 2018), as presented in Table 6. In the rubbery region, the treated and

untreated hybrid composites of 70:30 ratio of PALF: KF presented the highest storage modulus values and maximum glass transition temperature, respectively. Hence, the fiber treatment facilitated the improvement of the stiffness as well provided good interfacial bonding with fibers/matrix. Therefore, the dissipation of energy within the composites was improved. The 1:1 ratio of PALF and KF showed the least value in the damping factor. This implied a good fiber-matrix bonding.

The bilayer composites, such as jute/sisal, jute/curaua and jute/ramie epoxy-based composites with fibers treated by alkali and alkali+silane (combined treatment) presented high energy dissipation at the interface of the material. This was confirmed by the peak loss modulus of the treated composites. The sisal/jute composites with combined treatment showed the least amplitude in damping factor, whereas the jute/curaua and jute/ramie (alkalized, combined treatment) composites exhibited higher amplitude, when compared to the untreated fiber reinforced composites. The combined treatment offered benefits to the composites by having higher values of storage and loss moduli. In the case of tan delta peaks, the alkali treated fiber composites provided maximum glass transition temperature (Neto et al., 2019). Similar study was carried out by Goriparthi et al. (2012) on jute/PLA/PCL with the silane treated jute fibers. When the content of PCL was increased in PLA/jute fiber composites, the storage modulus was significantly reduced, tan delta values were improved, whereas there was a drop in the glass transition temperature. Among the composites, there was a notable decrement in E' values, as observed at 35:15:50 (PLA/PCL/jute). The silane treated composites exhibited lower tan delta peaks, but a higher glass transition temperature. This behavior was due to an effective stress transfer between the treated fibers and matrix.

5.1.3 Effects of fillers

Mechanical, thermal and dynamic mechanical properties of a composite can be improved by the addition of a small amount of fillers. Examples of some fillers are silver oxide, iron oxide, magnesium hydroxide, magnesium oxide, nano-clay, among others. Some studies have reported concerning the addition of fillers to improve the DMA properties of natural fiber hybrid polymer composites, as presented in Table 7.

Table 7. Reported studies on the DMA effects of fillers addition in composites

The viscoelastic properties of hybrid composites have been studied by varying the weight of magnesium hydroxide (MH) from 10 to 25 wt% with kenaf fiber/epoxy composites (Saba et al., 2019). The results showed that the MH filler adequately compensated for the modulus incompatibility between fiber and matrix, and further improved their bonding, led to an enhanced storage modulus. Furthermore, an improvement in hydrogen bonding was observed between the fiber and the matrix. It was used to decrease the segmental chain movement in the material and caused remarkable enhancement in the storage modulus. Moreover, the MH had higher rigidity and stiffness when compared to the kenaf fiber; it reduced the movement of polymeric chains, led to an increase in the value of storage modulus. The tan delta of hybrid composites was lower in magnitude, when compared with the pure kenaf fiber composites. This result was attributed to good bonding and effectiveness of hybridization made by the MH fillers. The excellent bonding and lesser movements of epoxy chains were also confirmed by showing broader tan delta peaks of the hybrid composites. More also, oil palm empty fruit bunch (OPEFB), montmorillonite (MMT) and OMMT nano-fillers have been used with kenaf/epoxy composites (Saba et al., 2016a). Among the hybrid composites, the OPEFB filled kenaf/epoxy composites exhibited higher storage modulus, loss modulus and lower damping factor, owing to their higher hardness and stiffness. Addition of nano OPEFB enhanced the bonding between kenaf fiber and epoxy

matrix. Hence, there was a restriction in the free movement of the epoxy molecular chain of the composite.

In addition, Aloevera (A), Hemp (H) and flax (F) were used as fibers and their combination of a bilayer and trilayer composites of AH, AHB, FH and FHB were fabricated (Arulmurugan, Prabu, Rajamurugan, & Selvakumar, 2019). In addition to the hybridization with barium sulfate filler, the effect of DMA properties was also analyzed by changing frequencies: 0.2, 1.0 and 5.0 Hz. The results depicted that the AHB composite had higher storage modulus and glass transition temperature than the FHB composite. There were no significant changes observed from the storage modulus, due to the change in frequency. When the temperature was increased, the storage modulus of FHB composites recorded higher value, and the AHB went to a lower value. This was attributed to the nature of the hybrid composite and forcing frequency. The increase in temperature increased the molecular movement and broke the molecular chain. The further increase in temperature at the glassy region promoted the large molecular motion, led to a reduction of storage modulus of hybrid composites.

Moreover, Wang et al. (2019) experimented nanoclay grafted onto the flax fibers and examined the dynamic mechanical properties of flax fiber reinforced epoxy composites (FFRP). Silane coupling agent was used to graft nanoclay onto the flax fiber under the sonification approach. The aggregated nanoclay was found grafted onto the flax fiber surfaces by covalent bonds between the hydroxyl groups. The results depicted that the fibers grafted with nanoclay based FFRP exhibited the maximum glass transition temperature of 96.21 ^{o}C, which was consistent with the highest increase in the bonding strength. The fiber treatment with NaOH and the addition of clay particles were found to be efficient in achieving excellent fiber-matrix adhesion in the oil palm/clay particles/HDPE hybrid composites (Essabir et al., 2016). The best dynamic

and mechanical properties were obtained at 12.5:12.5 ratio. Moreover, the addition of clay particles enhanced the degradation temperature of composites to provide better thermal stability to the fiber reinforced composites.

An innovative method of developing hybrid composites, short jute fiber/stearic acid modified nanoclay/natural rubber has been introduced (Roy et al., 2018). Because of the effective dispersion of the short jute fiber with natural rubber in the presence of modified nanoclay, the hybrid composites exhibited the highest storage modulus in the whole range of measurement and lower tan delta. From the results obtained from the strain sweep analysis, the storage modulus of filled natural rubber composites decreased. It was attributed to the breaking of filler-filler networks at the higher strain.

Fly ash silica (FASi)/precipitated silica (PSi)/natural rubber (NR) composites have been experimentally studied by varying the total silica contents in FASi/PSi (Thongsang et al., 2012). It was observed that 40 phr of total silica loaded composites exhibited higher storage modulus than the 10 phr loaded composites. The behaviors of these composites were further pronounced at the rubbery region, due to the high stiffness of rubbers and good interaction between the silica-rubber molecules. A decrease in the tan delta curve indicated the effectiveness of rubber and filler in the silica hybrid composites. In addition, they reported that there was no significant variations observed from the glass transition temperatures of hybrid composites by increasing the silica content.

5.1.4 Effects of fiber loading/fiber length on dynamic mechanical properties of natural fiber hybrid composites

Several factors such as fiber length, fiber loading, fiber weave type, type of resin and blends are possibly influencing the properties of cellulose fiber-based composites. Table 8 shows the effects of fiber related parameters on the viscoelastic properties of composites.

Three different types of studies have been adopted on the kenaf/PALF/HDPE composites (Aji, Zainudin, Sapuan, Khalina, & Khairul, 2012). In the first phase, the total fiber loading of kenaf and PALF maintained at 40% with a fiber length of 0.25 mm. In the second phase, fiber loading varied from 10 to 60% (order of 10) with the fiber length of 0.25 mm. In the last phase, the fiber lengths of 0.25 mm, 0.50 mm, 0.75 mm and 2.00 mm with constant fiber loading of 50%. The results showed that the initial storage moduli of all the hybrid composites with varying fiber loading were significantly improved compared to the HDPE matrix. It was evident that the modulus depended on the cellulose content of natural fibers.

For hybridization with kenaf fiber, a lower percentage of PALF was needed to achieve a positive hybridization effect. When the temperature was increased up to nearly 130 ^{o}C, an increase in the storage modulus value was observed and was highest at higher fiber loading. Peak damping factor also increased with temperature, when fiber loading was increased. There was an increase in the storage modulus with an increase in the fiber length from room temperature to nearly 65 ^{o}C. Up to the less viscous point of the matrix, variation in fiber length became irrelevant above this temperature. There was also a marginal difference in the loss modulus with variation in fiber length and no difference in the tangent loss could be observed.

Table 8. Viscoelastic properties of hybrid composites based on fiber related parameters

DMA results obtained by Tajvidi (2004) showed that there was no detectable change in the glass-transition temperature by replacing wood flour with the kenaf fiber. The wood flour

composite had an identical glass transition intensity, as a hybrid composite. In the case of kenaf fibers, the coefficient of linear thermal expansion, α transition took place at a relatively higher temperature, and its intensity was also higher. It was described by the bulkier nature, therefore the higher volume fraction at a given weight content of kenaf fiber. From another study, the viscoelastic properties of Alfa fibers/clay/PP hybrid composites were analyzed by varying the fiber and clay loadings from 0% to 30% (Boujmal et al., 2017). To improve the bonding with the PP, Alfa fibers were treated with alkali solution, and the clay was purified and ground to fine particles. They reported that the complex shear modulus steadily increased by clay content over the Alfa fibers. The values of the tan delta of hybrid composites were lower than unity, and exhibited elastic behavior.

Among the sisal/banana reinforced polyester hybrid composite variants (Idicula, Malhotra, Joseph, & Thomas, 2005), the composites maintained with equal fiber ratio (1:1) presented significant enhancement in storage modulus and T_g values. Furthermore, these composites have shown an improved fiber-matrix bonding which was ascribed to the lowest tan delta values. A similar study was carried out to understand the effects of relative volume fraction of banana and sisal fibers. The total volume fraction was fixed at 0.4. When the fiber volume fraction was maintained at a 3:1 ratio, the E' and T_g values were higher than the pure fiber composites. It was attributed to good bonding of fibers within the matrix. Jute/sisal/polyester hybrid composites have been fabricated by Gupta et al. (2018). They maintained the overall fiber loading of 30 wt% with varying individual fibers from 0% to 100% (order of 25%). It was found that the jute/sisal at 25:75 fiber ratio exhibited an improved glass transition temperature of 94 ^{o}C, better storage modulus, loss modulus and least damping factor than the other configurations. Similarly, Gupta (2018) studied sisal/jute hybrid epoxy-based composites, with fiber weight maintained at 30 wt%

in all the composites. From his results, it was observed that the hybrid composites possessed superior storage modulus, loss modulus and glass transition temperature. Moreover, the percentage of jute fiber used in the composites influenced the improvements in the viscoelastic properties. Among the composites, the jute/sisal/epoxy in 75:25 fiber ratio exhibited better thermal stability compared to the pure and hybrid composites.

More also, Saxena and Gupta (2018a) reported that mango/shorea robusta/epoxy hybrid composites 50:50 exhibited the highest E' value. An excellent damping was observed for hybrid composite when the proportion of mango wood was used higher than the shorea robusta wood. They concluded that the lowest content of mango seed hybrid composites provided better thermal stability (least tan delta value and higher glass transition temperature) than the other type of configured hybrid composites. The same authors, Saxena and Gupta (2018b) carried out another study which showed that the 50:50 ratio of mango/sal wood/epoxy hybrid composite exhibited maximum glass transition temperature and the highest storage modulus in the glassy region, due to the strong bonding between the fibers and the matrix. By increasing the temperature, the storage modulus of all the composites decreased, due to the loss of stiffness. In the rubbery region, the lowest storage modulus was exhibited by the pure mango wood/epoxy composites, owing to its lower stiffness and strength. They further reported that the hybridization effect was not prominent in terms of peak storage modulus as minimal difference was observed between the various configurations.

An experimental study on epoxy-based hybrid composites made by teak/shorea robusta wood with 33% of wood flour in hybrid composites has been conducted (Jain & Gupta, 2018b). From their results, it was reported that 50:50 (teak wood/shorea robusta) type of hybrid composite showed the highest storage modulus. An increase in the content of teak wood to 75% within the

hybrid composites produced a highest value of the damping value. Conversely, a lower damping value was recorded when the shorea robusta fiber was increased to 100%. Similarly, Jain and Gupta (2018a) analyzed the DMA properties by varying the fiber loading of teak wood/sal wood/epoxy hybrid composites. The 50:50 ratio of fiber loaded hybrid composites showed the highest storage modulus in glassy and rubbery regions, due to strong woods-matrix bonding and followed by the pure teak wood composites. Further increase in the temperature led to a linear fall due to the loss of stiffness of the composites. A higher glass transition temperature (around 90 ^{o}C) was observed by the 25:75 ratio of teak wood/sal wood hybrid composites from the tan delta plot.

Furthermore, phenolic-based hybrid composites has been fabricated by varying the fiber loading of PALF and KF in hydraulic press machine (Asim et al., 2019). An addition of higher percentage of KF to the PALF resulted to a better storage modulus in both glassy and rubbery regions. There was an improvement in both T_g and loss modulus with 50:50 and 30:70 (PALF/KF) ratios of the composites, respectively. Hence, the addition of PALF and KF improved the thermal properties and increased the loss modulus, respectively. Good interfacial fiber-matrix bonding was evident from the lowest tan delta peaks of 50:50 and 30:70 fiber ratios of PALF/KF. PALF/coir/PLA hybrid composites has been similarly studied by varying the individual fiber contents (Ramengmawii et al., 2018). The composite stiffness was improved by addition of PALF, while the coir fiber showed a lesser improvement in the modulus. The results depicted that a higher storage modulus (glass region), higher glass transition temperature (loss modulus) and lowest tan delta peak were observed by the 50:50 ratio of hybrid composites. It has been reported that satin and basket weave types of hemp/PLA hybrid composites exhibited lesser

damping and better storage modulus of hemp/PLA hybrid composites (Baghaei, Skrifvars, & Berglin, 2015).

6. Thermomechanical analysis

Fabricated polymers, plastics, fibers and films are used in (i) kitchenware coatings, (ii) medical devices, (iii) food containers, (iv) materials for controlled drug delivery, (v) blood storage bags, and sutures as well as (vi) plastic devices, such as composite parts for aerospace devices and automobile. Polymers are viscoelastic, unlike metals and ceramics. Polymers contain both viscous and elastic elements, which regulate the mechanical response in terms of time and temperature. For the prediction of performance and service life, therefore, accurate characterization of polymeric material is fundamental. Figure 3 shows the influencing factors that affect the TMA measurements.

Figure 3. Factors that affect the TMA measurement

Thermomechanical analysis measures changes in sample length or volume as a function of temperature or time, under load at atmospheric pressure. Typically, the load is static or varying. This technique is also known as the Thermo-Dilatometry (TD), if measured at an insignificant load. TMA experiments under compression, tension or flexure are generally conducted under the static load. From TMA, the coefficient of linear thermal expansion (CLTE, α) and the glass transition temperature (T_g) of a polymer-based composite can be determined. Also, estimation of more measurements is possible by applying some special modes and various attachments. These include: (i) creep, (ii) stress relaxation, (iii) tensile properties (films and fibers), (iv) flexural properties, (v) dimensional stability (both of reversible and irreversible dimensional change), (vi) volume dilatometry and (vii) parallel plate rheometry. Nevertheless, TMA of the hybrid natural fiber reinforced polymer composites is scarce and rare.

Recently, thermal expansion coefficient (CTE) of hybridized composites made from PALF and KF incorporated in phenolic at the different weights of 30%, 50% and 70%, using hydraulic hot press technique was reported (Asim et al., 2018). They compared the CTE of hybridized composites with silane treated hybrid composites. It was concluded that the treated hybrid composites exhibited better thermal stability than the untreated counterparts. A better thermal stability of treated 30:70 and 70:30 fiber ratios of PALF/KF composites was observed. The increased thermal stability of the composites was attributed to the excellent compatibility of fiber and matrix, with enhanced mechanical properties than the untreated fiber hybridized composites.

A comparison study on the thermomechanical behavior of bamboo/kenaf/epoxy with varying ratios of hybrid composites has been conducted (Chee et al., 2019). They reported that improved dimensional stability was obtained by using a woven kenaf mat. Increasing the weight ratios of kenaf fiber attracted a positive hybridization effect at an optimum mixing ratio of 50:50 (bamboo: kenaf). A similar study on epoxy composites made by banana and kenaf has been reported (Sathish, Kesavan, Ramnath, & Vishal, 2017). They varied the fiber orientation (as vertical, horizontal and 45^{o}) and changed the stacking sequences, and maintained an overall fiber loading between 40 to 42%. The CTE was measured in an axial direction. The results showed that 45^{o} oriented fiber reinforced composites exhibited the highest CTE of 34.61×10^{-6} /^{o}C. Moreover, the overall range of CTE of the hybrid composites was observed between 31 to 35×10^{-6} /^{o}C. The CTE of kenaf/epoxy composites were compared with 3% loaded of oil palm nanofiller, MMT and OMMT composites, using TMA technique (Saba et al., 2016b). A reduction in the CTE was observed from the filled kenaf/epoxy composites concerning the pure kenaf/epoxy composites. Furthermore, they reported that comparable CTE was observed from

the oil palm nanofiller/epoxy with MMT/kenaf/epoxy, even though the CTE values were relatively smaller concerning OMMT.

In addition, KF and PALF have been incorporated into the phenolic matrix to develop hybrid composites (Asim et al., 2019). Among the hybrid composites produced, the 30% PALF/70% KF exhibited better thermal stability. However, the difference between the 70% PALF/30% KF and 30% PALF/70% KF hybrid composites were less. Furthermore, when an equal fiber proportions in the composites was maintained, the least thermal stability was obtained for the pure KF and pure PALF composites (Figure 4).

Figure 4. TMA graph of pure PALF, KF, and their hybrids (Asim et al., 2019)

Studied on the dimensional stability of coconut fiber (C)/PALF/ polylactic acid (PLA) hybrid composites has been reported (Ramengmawii et al., 2018). It was observed from the results obtained that an increase in the coconut fiber within the pineapple leaf composites (C70/PALF30) showed a lowest thermal expansion, followed by the C50/PALF50 hybrid composite. While the thermal stability of the C30/PALF70 was reduced compared to the pure fiber composites. This was attributed to the poor fiber dispersion and agglomeration, resulting in free space for the movement of the polymer chain.

7. Differential scanning calorimetry

Differential scanning calorimetry can be used to understand the behavior of polymers in heating condition. This can be further used to characterize the melting and crystallization temperatures of a polymer composite. In a typical DSC investigation, two containers are heated in a closed chamber. The empty container is used as a control or reference, while the sample to investigate is placed in the other one. The containers usually sit directly on the sensors which measure the heat

flow through the samples. To maintain similar temperatures in both containers, the heat provided to one of the containers changed, due to the change in constituents of these containers. Hence, a change in heat output of both heat sources are used to calculate and analyze the T_g, melting and crystallization temperatures of the samples. A typical plot to identify these properties is shown in Figure 5, where T_g, T_c and T_m are glass transition, crystallization and melting temperatures, respectively.

Figure 5. A typical plot to identify T_g, T_c and T_m

Within the scope of this review report, a combination of studies on various fibers and fillers reinforced polymer composites and their effects on the DSC parameters are extensively discussed. For instance, Biswal, Mohanty and Nayak (2009) incorporated PALF along with nanoclay in PP and observed that adding these reinforcements decreased the melting temperature. They linked this behavior to the existence of genuine interface. Also, the crystallization temperature was increased with the addition of reinforcements. They explained that these fillers acted as the nucleation agents. Also, they elaborated that the observed crystallinity behavior was attributed to the enhanced matrix-reinforcement interface. Table 9 shows some of the reported studies on thermal properties of chemically treated hybrid fiber composites.

Table 9. Reported works on DSC properties of chemically treated natural fiber hybrid composites

Neto et al. (2019) studied the hybridization behavior of various fibers (sisal, ramie and curauá) with jute fibers reinforced in epoxy resin. The DSC analysis depicted that both sisal and curauá hybridization with jute fibers increased the temperatures at the endothermic peaks of the composites. On the other hand, the temperatures at exothermic peaks were enhanced by all the

three hybridizing reinforcements (sisal, ramie and curauá). They also investigated the effect of chemical treatment of these reinforcements on the DSC parameters. They concluded that the alkaline treated jute reinforced composite showed the highest thermal stability, owing to the removal of impurities and low stability components on the fiber surface. An investigation into the effects of treatment on the endothermic and exothermic peaks of hybrid jute/*Sansevieria cylindrica* fibers composites has been reported (Kumar & Ramachandra Reddy, 2014b). They concluded that the treatment of the fibers in the hybrid composites increased the temperature of both the endothermic and exothermic peaks, as extracted from DSC analysis. In addition, the study revealed that treatment did not result in any significant change of the glass transition temperature of the hybrid composites. Gupta (2018) studied on hybrid composites with various weight fractions of jute and sisal reinforced in epoxy. He reported that hybridization of fibers increased the glass transition temperatures of the composites in comparison with the non-hybrid composites. Moreover, a slight enhancement in the crystallization and a slight reduction in the melting temperature were observed. Another study on investigation into the DSC properties of composite of sisal fibers hybridized with Kapok in polyester has been reported (Venkata, Venkata, Shobha, & Subha, 2009). Comparing these two studies (Gupta, 2018; Venkata et al., 2009), the T_g and T_m extracted from DSC plots showed a significant difference. This difference can be attributed to the matrix system, as higher values of T_g and T_m are expected in epoxy when compared with polyester.

Penultimately, addition of hybridized natural reinforcements (cork/wood) in PP did not result in a significant change in the crystallinity levels, when compared with unmodified PP (Andrzejewski, Szostak, Barczewski, & Łuczak, 2019). They further explained that during the cooling stage of DSC, there was a lack of visible changes in the crystalline structure of PP

composites with or without natural fillers. The results obtained and observation from this study were in agreement with other previous studies (Magalhães da Silva, Lima, & Oliveira, 2016; Fernandes, Correlo, Mano, & Reis, 2014). As observed in the above studies, having natural reinforcements in the polymeric matrix can alter the DSC characteristics of the composites. Moreover, it can be summarized that hybridization of different natural fillers can also further modify these characteristics; however, the degree of change may be negligible in some cases, depending on the nature of the reinforcements.

8. Concluding remarks

This paper has critically, extensively and comprehensively addressed the thermal properties of natural fiber-based hybrid composites. Based on the thermal properties characterized from TGA, DMA, TMA and DSC techniques, the following conclusions are drawn:

- The fiber compositions present in several hybrid composites influenced the weight loss of the composites.
- The char residue availability was subjected to the thermal resistivity of individual fibers in hybrid composites.
- Fiber surface treatments and the addition of coupling agents were also helped to improve the thermal properties. However, the treated fiber hybrid composites exhibited lower char residue and higher weight losses, when compared with the untreated fiber hybrid composites.
- The thermoset and thermoplastic-based hybrid composites exhibited a similar trend in thermal characteristics, as observed from the TGA technique.
- DMA properties of chemically treated fiber hybrid composites were improved by providing good fiber-matrix interfacial bonding and enhancing dissipation of energy

within the composites. Moreover, these properties could be enhanced by the addition of fillers such as silver oxide, iron oxide, magnesium hydroxide, magnesium oxide and nanoclay.

- The results obtained from TMA are applicable to materials used in the paints and dyes, plastics and elastomers, composite materials, ceramics, glass, films, fibers and adhesive films. Also, TMA was suitable for studying the chemical factors, such as (i) effects of pendant groups, (ii) crosslinking, (iii) tacticity and (iv) molecular mass that have the primary effect on the glass transition temperature and expansion of the polymer.
- The major applications of DSC include, but are not limited to, pharmaceutical fields, food technology, biotechnology, polymer, inorganic and organic chemistry. DSC can be used to determine: (i) glass transition temperature, (ii) heat capacity jump at the glass transition, (iii) melting and crystallization temperatures, (iv) heat of fusion, (v) heat of reactions, (vi) purity of the sample, (vii) measuring the heat capacity, (viii) thermoset characterization and (ix) measuring the liquid crystal transition.

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Table 1. Terms used in a TGA curve

A	Starting point	Intersection of extrapolated starting mass with the tangent applied to the maximum slope of the thermogravimetric curve.
B	End point	Intersection of extrapolated end mass after reaction with the tangent applied to the maximum slope of the thermogravimetric curve.
C	Midpoint	Intersection of the thermogravimetric curve with the line parallel to the abscissa, that is midway between A and B.
T_A/t_A	Starting point temperature/time	Temperature/time at the start.
T_B/t_B	End point temperature/time	Temperature/time at the end.
T_C/t_C	Midpoint temperature/time	Temperature/time at the midpoint.
m_s	Starting mass	Mass before heating.
m_f	End mass	Mass after end temperature attained.

Table 2. Weight loss in the hybrid composite at different temperatures

Composite	Weight loss at different temperature ranges			Reference
	First stage (ºC)	Second stage (ºC)	Third stage (ºC)	
Jute/bagasse/ epoxidized phenolic novolac.	70-80	250-400	600	(Saw & Datta, 2009)
Jute/sisal/epoxy, jute/curaua/epoxy, and jute/ramie/epoxy.	30-180	215-450	480 - 600	(Neto et al., 2019)
Kenaf/epoxy/ organically modified montmorillonite (OMMT)	100-150	300-400	700	(Saba et al., 2016b)
Teak/Sal/epoxy.	267-281	404-415	532-650	(Jain & Gupta, 2018a).
Empty fruity bunch/jute/epoxy.	268-271	441-452	-	(Jawaid et al., 2015)

Table 3. Thermal properties for the pure and hybrid fiber-based composites from TGA

Composite	Fiber ratio	Char residue (%)	Final degradation temperature (°C)	Reference
PALF/KF/phenolic	100:0	24.23	447.99	(Asim et al., 2019)
	0:100	29.22	391.38	
	70:30	32.91	394.58	
	30:70	29.42	401.36	
	50:50	30.60	397.66	
Jute/EPFB/epoxy	0:100	09.04	433	(Jawaid & Khalil, 2011)
	100:0	25.02	499	
	25:75	12.10	443	
	75:25	12.92	441	
Teak/sal wood flour/epoxy	0:100	-	578	(Jain & Gupta, 2018a)
	100:0	-	650	
	25:75	-	534	
	75:25	-	540	
	50:50	-	532	

Table 4. Reported studies on TGA properties of chemically treated natural fiber hybrid composites

Properties	Sisal/jute/epoxy (Gupta & Srivastava, 2016)			EPFB/jute/epoxy (Jawaid et al., 2015)			PALF/KF/phenolic (Asim et al., 2018)		
	untreated	alkali treated	Significant effect	untreated	2-HEA treated	Significant effect	untreated	silane treated	Significant effect
Initial weight loss at temperature (°C)	292	298	Alkali treated (5%, 30 min) hybrid composites improved the adhesion between the fiber and matrix. Hence the degradation temperature was found to be increased.	268 to 271	269 to 297	• The improved temperatures attributed to the complex reaction. • Owing to the cross linking between jute fiber and epoxy matrix, the molecular weight may be increased.	278 to 281	302 to 306	• Treated hybrid composites enhanced the weight losses (38-45%). It was ascribed by the removal of hemicellulose and lignin. • Since removal of lignin in treated fiber composites, the char residue was lowered.
Major weight loss at temperature (°C)	513	517		-	-		-	-	
Final weight loss at temperature (°C)	652	693		441 to 443	457 to 462		394 to 401	400 to 411	
Char residue (%)	-	-	-	12.1 to 12.9	7.8 to 10.3		29 to 33	23 to 31	

Table 5. Thermal properties of natural fiber hybrid composites

Properties	**Empty fruit bunch (EFB)/jute/epoxy** (Jawaid & Khalil, 2011)	**Short bagasse/coir/ epoxy novolac composites** (Saw, Sarkhel, & Choudhury, 2011)	**Interwoven hemp/polyethylene terephthalate (PET)/epoxy** (Ahmad, Abdul Majid, Ridzuan, Mazlee, & Gibson, 2018)	**Jute/hemp/flax/ epoxy** (Chaudhary, Bajpai, & Maheshwari, 2018)
Peak storage modulus (MPa)	Around 3.75; jute/epoxy	Around 4250; bagasse/coir/bagasse	Around 3600; interwoven hemp/PET hybrid along hemp direction	Around 1.6 e+9 GPa; flax/epoxy
Peak loss modulus (MPa)	Around 3; jute/epoxy	Around 225; epoxy phenolic novolac	Around 490; interwoven hemp/PET hybrid along hemp direction	Around 2.25e+9GPa; flax/epoxy
Peak tan delta	0.36; epoxy	Around 0.30; epoxy phenolic novolac	Around 0.425; interwoven PET/hemp hybrid along PET direction	Around 0.8; epoxy
Glass transition temperature (T_g) from loss modulus (^oC)	76.44; jute/epoxy	116.3 Intimate mix	69; interwoven hemp/PET hybrid along hemp direction	Around 79; Jute/hemp/flax/epoxy
T_g from tan delta (^oC)	85.37; EFB	113.1; intimate mix	75; interwoven hemp/PET hybrid along hemp direction	Around 83; Jute/hemp/flax/epoxy

Table 6. Thermal properties of chemically treated hybrid natural fiber reinforced composites

Properties and effects of chemical treatment	**Jute/coir/ epoxy** (Saw et al., 2012)	**KF/ PALF/ phenolic** (Asim et al., 2018)	**Jute/sisal/epoxy; jute/curaua/epoxy; jute/ramie/epoxy** (Neto et al., 2019)	**Flax/PLA/ Polycarbonate** (Karsli & Aytac, 2014)	**Jute/PLA/ polycaprolactone (PCL)** (Goriparthi, Suman, & Nalluri, 2012)
Peak storage modulus (MPa)	Around 4200; 50% Jute/50% coir/epoxy	Around 4750; 70% PALF/30% KF (silane treated)	9289.07; Jute/sisal/epoxy (mixed treatment)	Around 4000; Flax/PLA/PC (2% alkali treated)	Around 7900; 50% Jute/ 50% PLA (silane treated)
Peak loss modulus (MPa)	-	Around 190; 70% PALF/30% KF (silane treated)	1617; Jute/sisal/epoxy (mixed treatment)	-	-
Peak tan delta	Around 0.25; epoxy	-	0.817; epoxy	Around 2.3; Flax/PLA/PC (untreated)	Around 0.35; 45% 45% PLA/5% PCL/50% Jute (silane treated)
T_g from loss modulus (^oC)	-	101.68; 30%PALF/70%KF (untreated)	98.5; epoxy	-	-
T_g from tan delta (^oC)	Around 150; 50% Jute/50% coir/epoxy	134; 70% PALF/30% KF (silane treated)	110.4; epoxy	Around 63; Flax/PLA/PC (untreated)	Around 90; 45% PLA/5% PCL/ 50% Jute (silane treated)
Significant effects due to chemical treatment	• Treated fiber composites enhanced the stress transfer at the interface owing to strong interfacial bonding	• Silane treated PALF enhanced the interfacial bonding with the KF/phenolic (i.e., 70PALF:30KF: phenolic) and showed the highest storage modulus. In contrast, the untreated 70	• Untreated jute/curaua/epoxy and jute/ramie/epoxy composites outperformed than the alkali and combined treated composites in storage modulus. • untreated jute/sisal/epoxy	• Storage modulus increased in the order; PLA/PC<10%alkali treated flax<untreated flax<5% alkali treated flax <2% alkali treated flax	Silane treated 50:50 PLA/jute hybrid composites effectively transferred stresses from the PLA matrix to jute fiber owing to the good interfacial bonding. Therefore, the storage modulus of treated composites showed higher values than the untreated

	between the fiber and matrix. • Treated hybrid fiber composites outperformed than the treated non-hybrid composites.	PALF:30KF: phenolic composites showed the least value in storage modulus. • The silane treated 70 PALF:30KF: phenolic, improved the dissipation of energy within the composites, hence resulting increased loss modulus. • The damping factor of silane treated composites were found to be decreased.	composites outperformed in loss modulus than the alkali treated composites. • untreated jute/ramie/epoxy composites showed lesser in tan delta than the alkali and combined treated composites.	fiber composites. • Tan delta increased in the order; 2% alkali treated flax <5% alkali treated flax<10% alkali treated flax<untreated flax fiber composites.	fiber composites.

Table 7. Reported studies on the DMA effects of fillers addition in composites

Properties	**Kenaf/ Magnesium hydroxide (MH)/epoxy** (Saba, Alothman, Almutairi, & Jawaid, 2019)	**Kenaf /oil palm nanofiller /epoxy** (Saba, Paridah, Abdan, & Ibrahim, 2016a)	**Fly ash silica (FASi)/ precipitated silica (PSi)/natural rubber (NR)** (Thongsang, Vorakhan, Wimolmala, & Sombatsompop, 2012)	**Short jute fiber /nanoclay/natural rubber (NR)** (Roy, Chandra Debnath, Das, Heinrich, & Potiyaraj, 2018)
Peak storage modulus (MPa)	Around 4000; kenaf/20% MH /epoxy	Around 3990; OMMT/kenaf/epoxy	Around 4300; composites made by 40 phr of silica content	6.99MPa; Natural rubber/nanoclay/ jute
Peak loss modulus (MPa)	Around 450; kenaf/20% MH /epoxy	Around 375; OMMT/kenaf/ epoxy	Around 900; composites made by 40phr of silica content	-
Peak tan delta	Around 0.45; kenaf/epoxy	Around 0.45; Kenaf/epoxy	Around 2.03; composites made by 10phr of silica content	2.5; Natural rubber-gum
T_g from loss modulus (^oC)	-	Around 80; Nano OPEFB/ kenaf/epoxy	-	-
T_g from tan delta (^oC)	Around 100; kenaf/15% MH /epoxy	Around 90; MMT/kenaf/epoxy	-39.2; composites made by 40phr of silica content	Around -30; Natural rubber/nanoclay/ Jute

Table 8. Viscoelastic properties of hybrid composites based on fiber related parameters

Properties	**Kenaf /wood flour/PP** (Tajvidi, 2004)	**Jute/sisal/ polyester** (Gupta, Choudhary, & Agrawal, 2018)	**Mango wood/ shorea robusta wood/epoxy** (Saxena & Gupta, 2018a)	**KF/PALF/ phenolic** (Asim et al., 2019)	**PALF/ coconut fiber/PLA** (Ramengmawii et al., 2018)
Peak storage modulus (MPa)	Around 5900; 25% kenaf fiber/PP	Around 3900; Jute 25%/sisal 75%/polyester	Around 390; 50% mango wood/50% shorea robusta wood/epoxy	Around 3750; 50% KF/phenolic	Around 2750; 30% PALF/70% PLA
Peak loss modulus (MPa)	Around 250; 25% kenaf fiber/PP	Around 500; Jute 25%/sisal 75%/polyester	-	Around 210; 50% KF/phenolic	Around 410; Neat PLA
Peak tan delta	Around 0.07; 25% kenaf fiber/PP	Around 0.55; Jute 75%/sisal25%/ polyester	Around 0.45; 75% mango wood/25% shorea robusta wood/epoxy	Around 0.08; 70% PALF/30% KF/phenolic	1.1; Neat PLA
T_g from loss modulus(^oC)	Around 10; 12.5% kenaf/12.5% wood floor/PP	85; Jute 25%/sisal 75%/polyester	-	106.1; PALF/phenolic	65; 15% PALF/ 15% coconut fiber / 70% PLA
T_g from tan delta (^oC)	Around 10; 12.5% kenaf/12.5% wood floor/PP	94; Jute 25%/sisal 75%/polyester	Around 80; 25% mango wood/75% shorea robusta wood/epoxy	124.82; KF/phenolic	Around 70; 15% PALF/ 15% coconut fiber / 70% PLA

Table 9. Reported works on DSC properties of chemically treated natural fiber hybrid composites

Details of composite	Details of chemical treatment	Significant effect	Reference
i. Jute/epoxy (untreated, alkali treated and combined treated); ii. Jute/sisal/epoxy (untreated, alkali treated and combined treated); iii. Jute/ramie/epoxy (untreated, alkali treated and combined treated); iv. Jute/curaua/epoxy (untreated, alkali treated and combined treated).	**i. Alkali treatment:** Two grams of NaOH mixed with 100 ml of water for 1hr. **ii. Combined treatment** The alkali treated fibers immersed in 2% of silane solution for 1hr; pH of 5.	• Endothermic and exothermic temperature (°C) of untreated fiber composites ranged between 169.5 to 208.4 and 351.6 to 374.8 respectively. • Endothermic and exothermic temperature (°C) of alkali treated fiber composites ranged between 163.3 to 207.9 and 357.4 to 372.8 respectively. • Endothermic and exothermic temperature (°C) of combined treated fiber composites ranged between 149.9 to 208.3 and 359.9 to 372.9.	(Neto et al., 2019)
a) jute/*Sansevieria cylindrica*/epoxy; b) fiber ratio = 1:1; c) fiber length = 1, 2, 3 and 4cm.	5% NaOH; 1hr	• Mechanical properties improved when increasing the fiber length from 1cm to 2cm. • Two exothermic peaks were observed for treated and untreated fiber composites. • The first exothermic peak of untreated and treated fiber composites observed at 355°C. • The second exothermic peak of untreated and treated fiber composites observed at 375°C and 479°C respectively.	(Kumar & Ramachandra Reddy, 2014b)

	• Endothermic peak of untreated and treated fiber composites observed at 366°C and 375°C respectively.

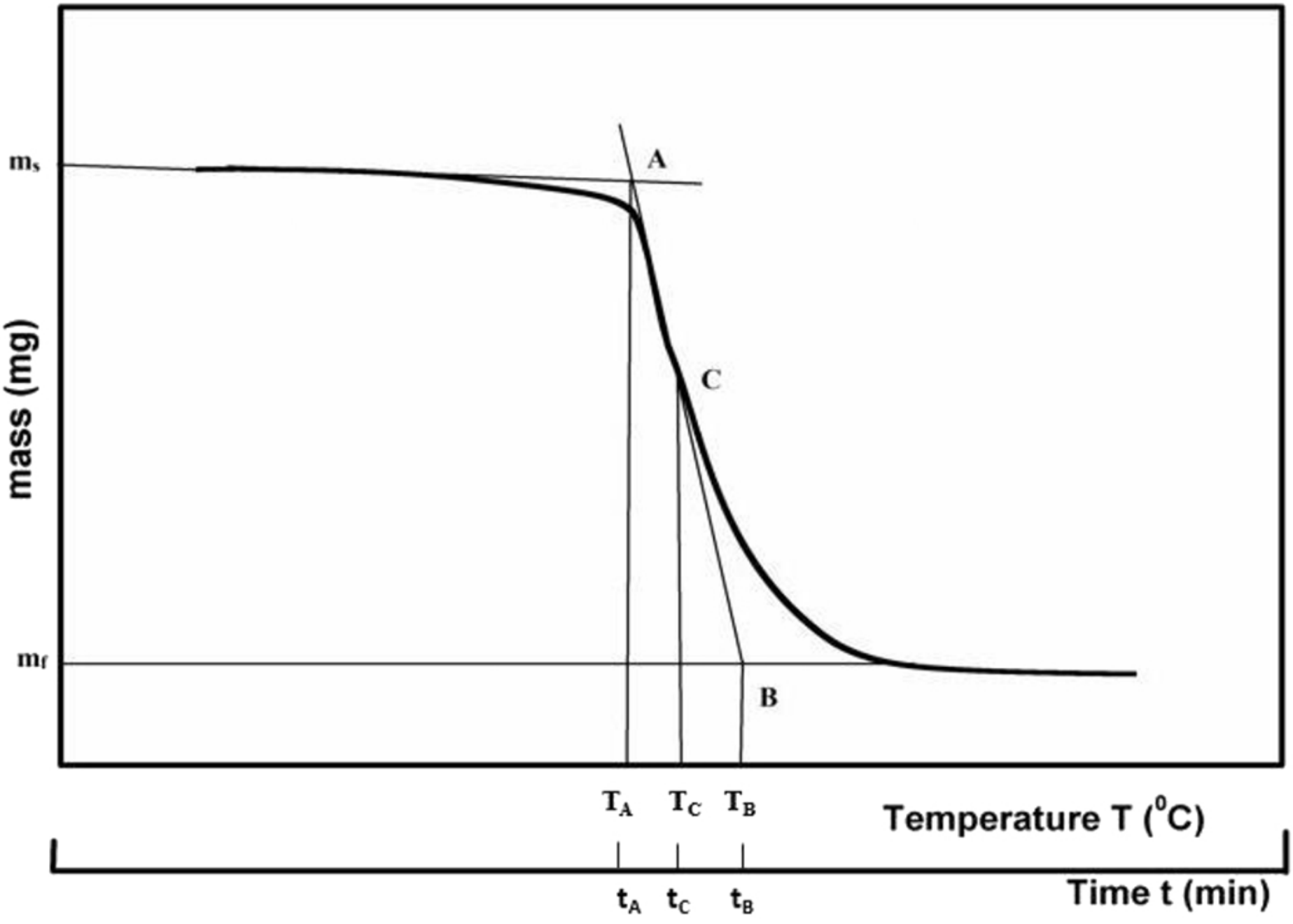
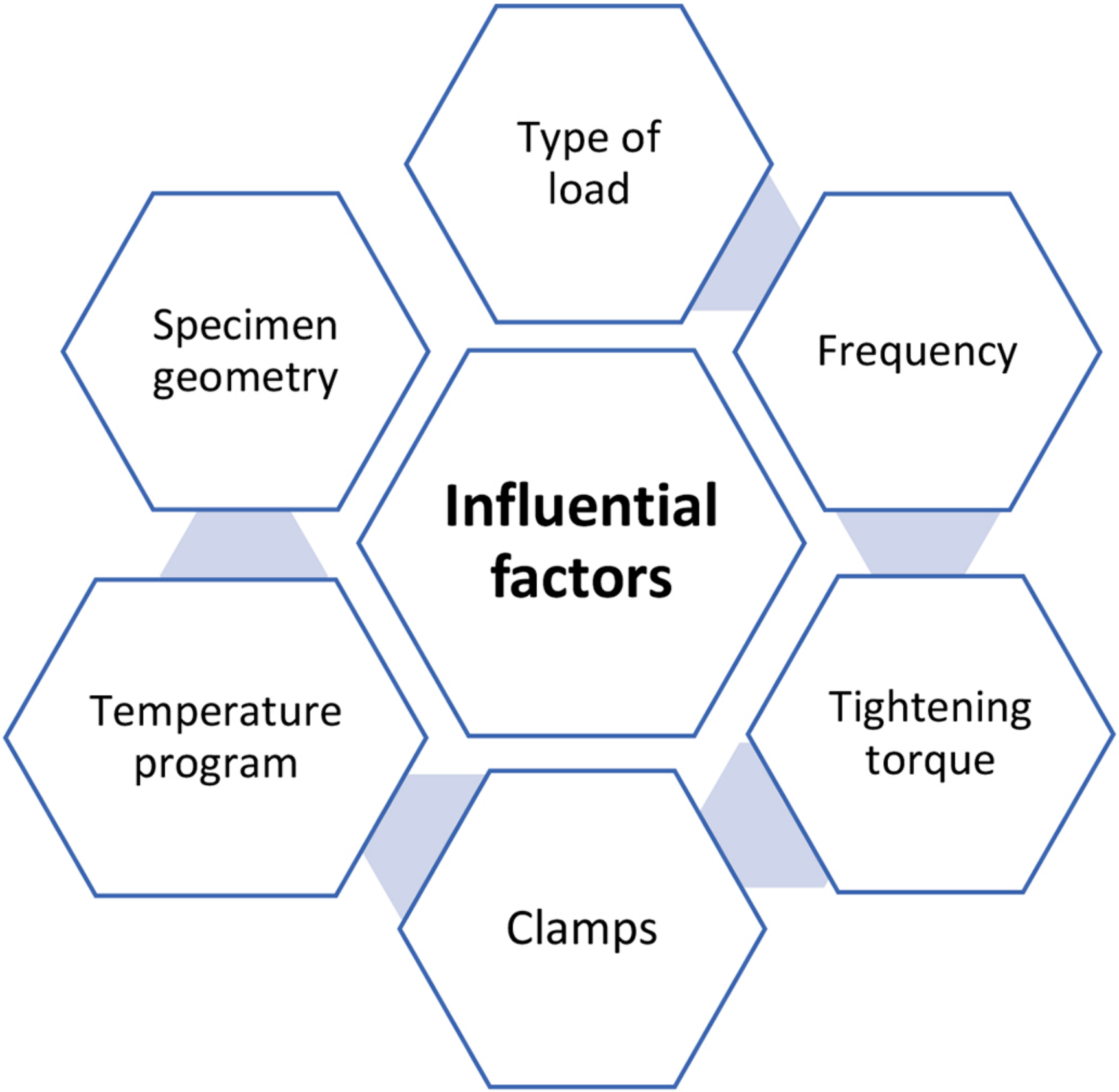


Figure 1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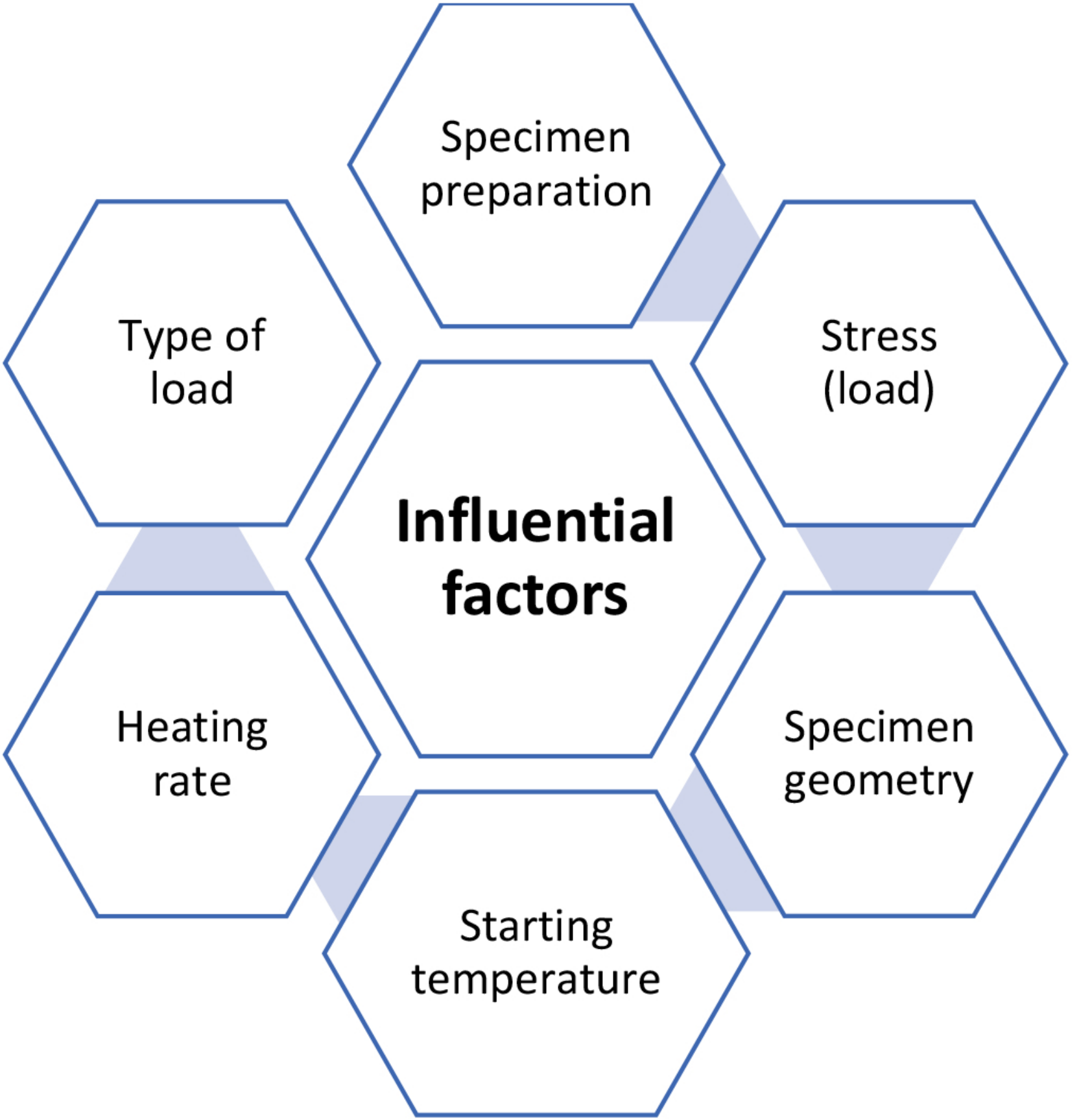
Specimen geometry
Frequency
Influential factors
Temperature program
Tightening torque
Clamps

Figure 2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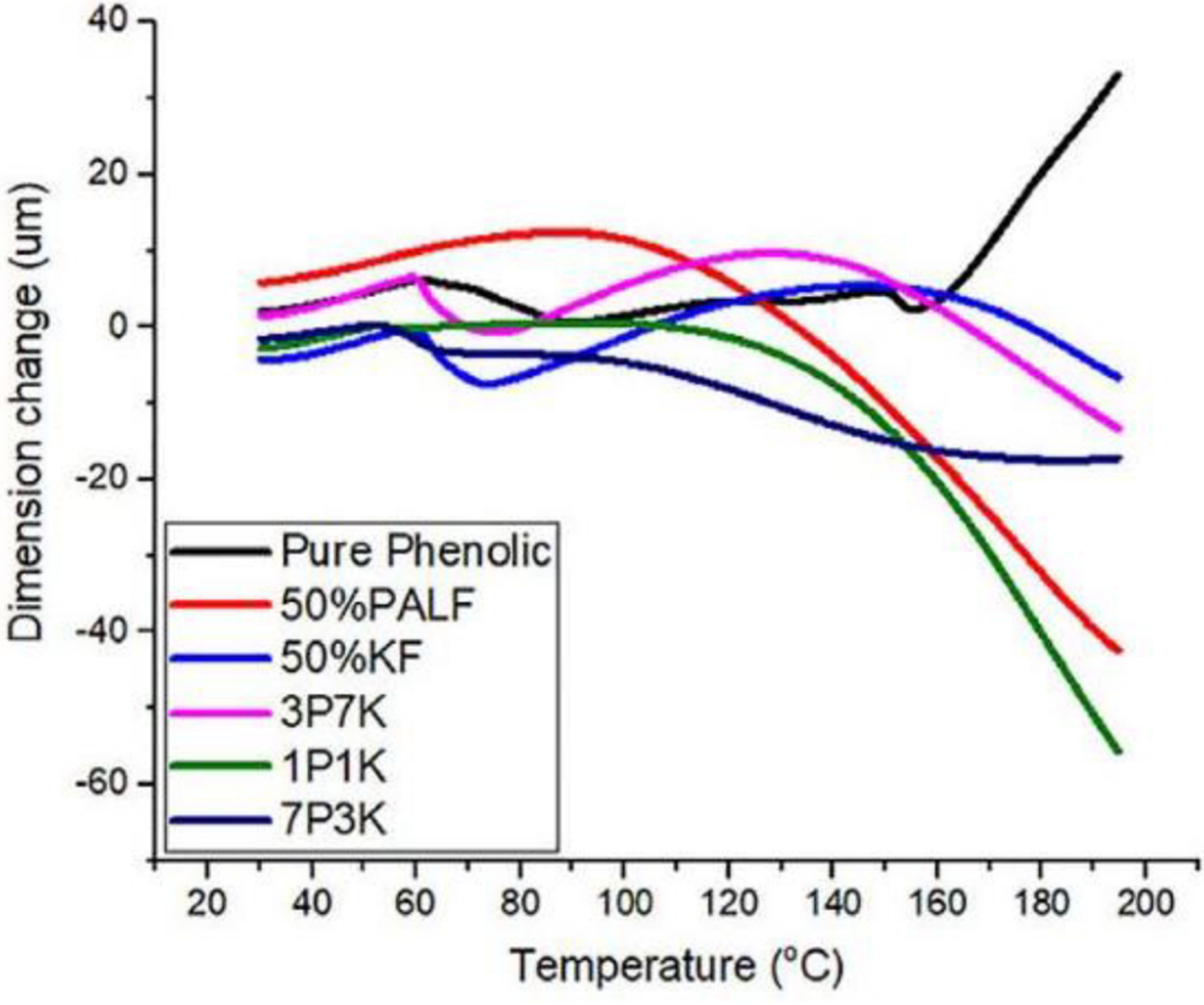
Influential factors
Heating rate
Specimen geometry
Starting temperature

Figure 3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1P1K
7P3K

Figure 4

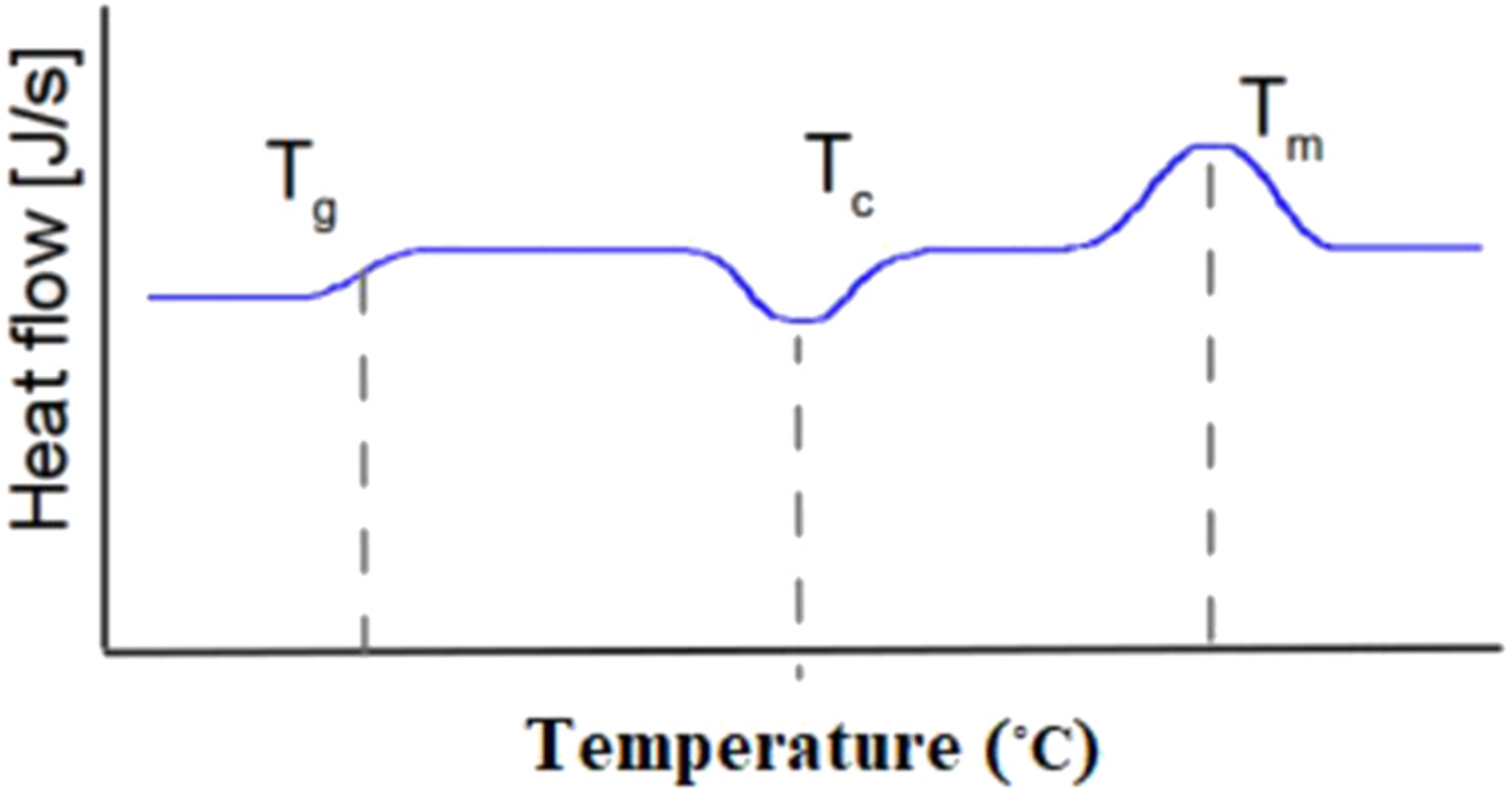

Figure 5