

# Effect of Fiber Loadings and Treatment on Dynamic Mechanical, Thermal and Flammability Properties of Pineapple Leaf Fiber and Kenaf Phenolic Composites

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**ABSTRACT:** This study deals with the analysis of dynamic mechanical, thermal and flammability properties of treated and untreated pineapple leaf fiber (PALF) and kenaf fiber (KF) phenolic composites. Results indicated that storage modulus was decreased for all composites with increases in temperature and pattern of slopes for all composites, having almost the same values of  $E'$  at glass transition temperature ( $T_g$ ). The peak of the loss modulus of pure phenolic composites was shown to be much less. After the addition of kenaf/PALF, peaks were higher and shifted towards a high temperature. The Tan delta peak height was low for pure phenolic composites and maximum for 60% PALF phenolic composites. Cole-Cole analysis was carried out to understand the phase behavior of the composite samples. Thermogravimetric analysis (TGA) results indicated that pure phenolic composites have better thermal stability than PALF and kenaf phenolic composites. Vertical and horizontal UL-94 tests were conducted and showed pure phenolic resin is highly fire resistant. The overall results showed that treated KF composites enhanced the dynamic mechanical and thermal properties among all PALF/KF composites.

**KEYWORDS:** Pineapple leaf fiber, kenaf fiber, phenolic resin, dynamic mechanical analysis, thermogravimetric analysis, flammability

## 1 INTRODUCTION

Development of composites reinforced with materials derived from renewable resources has increased during the last few years. Renewable resources are very suitable materials to substitute synthetic compound [1, 2]. Natural fiber composites have specific characteristics such as better formability, renewability, cost effectiveness, light weight, high specific strength and modulus; and possess tool wearing rates, thermal insulation properties, acoustic properties, sufficient energy requirements and are safer towards health [3, 4]. These composites can easily degrade in nature and have the characteristic of being disposable at the end of their life cycle by composting or by retaining their calorific value in a furnace [5].

Natural fibers, such as kenaf, PALF, ramie, flax, jute, and bamboo, are abundant in quantity, very cheap and easily available through an eco-friendly manual process [6]. The mechanical, physical strength and chemical compositions of natural fibers strongly depend on harvesting, climate, location, soil characteristics and weather circumstances. Additionally, the processing of fibers affects their strength, which reveals differences among the same types of fiber composite [7]. However, natural fibers have some disadvantageous characteristics such as high moisture absorption and low thermal resistance [8].

PALF is one of the waste agricultural materials that is produced in tonnes every year and very small proportions are being used as feedstock and in energy production. Usage of natural fibers in biocomposites will enhance degradable products and reduce wastage of renewable materials. Although PALF has high specific strength and stiffness, it is hydrophilic in nature due to its high cellulosic content [9]. KF is known as an industrial fiber, It is commercially

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available and economically cheaper than other natural fiber reinforcing materials due to its rapid growth and environmental sustainability, and can be a substitute of synthetic fibers [10]. The selection of matrix in composites is depend on the application and compatibility between fiber and composite. Phenolic matrix is known for its use in building structural materials and the automobile industry, due to its excellent thermal and fire retardant behavior. Natural fiber reinforced phenolic composites contribute various applications in the automotive sector because of increasing awareness in the use of recyclable natural materials and it reduce density, weight and improve mechanical and thermophysical properties [11]. Thermogravimetric analysis is a process that analyzes the relationship of structure-property and thermal stability of composite materials. The presence of moisture content and volatile component of composite can be determined by using thermal analysis. Some constituents of natural fibers, such as lignin, degrade at a temperature of around 200 °C, whereas cellulose degrades at higher temperatures [12]. Most of the natural fibers degrade in strength above 160 °C [13].

Dynamic mechanical analysis (DMA) has been extensively used for investigating the structure and viscoelastic behavior of various types of polymer composites to observe their influence over stiffness and damping characteristics of various materials. A practical analysis of the dynamic mechanical properties of polymer composites is significant in determining the range of temperatures and frequencies [14]. Building constructions and interior decoration consist largely of flammable polymeric materials that are of critical concern to environmental, safety and health matters. The materials industries are focused on the fire resistance properties of composite materials, and in order to avoid fire incidents and sustain combustion for a long period of time, a regulatory fire test is mandatory [15, 16]. The flammability of a composite not only depends on the matrix polymer and the type of fiber but also on interactions between the matrix polymer and the fiber [16, 17].

Several studies have been reported on the thermal behavior and viscoelastic properties of fiber-reinforced composites. The DMA of the thermal behavior of PALF-reinforced polyethylene composites were studied on various fiber loadings with different types of fiber treatments, and it was found that PALF degrades at high temperature before the polyethylene matrix and storage modulus increased with increasing fiber loading and decreased with increase of temperature [18]. PALF-reinforced phenol formaldehyde (PF) composites have been studied on different fiber loadings; thermal stability of pure PF was higher

than PALF-reinforced PF composites [19]. Chemically modified banana fiber composites were investigated using dynamic mechanical analysis and compared with those of untreated composites and it was found that the dynamic modulus values and damping values decreased, which indicated that silane treatment improved bonding interactions between the fiber and the matrix [20]. Alkali treated and untreated Agave fiber reinforced epoxy composites were analyzed. The thermomechanical properties of the treated composites were considerably good and showed better mechanical properties than untreated composites [8]. Untreated and treated kenaf reinforced epoxy composites were studied by using dynamic analysis, which reported that storage modulus and loss modulus were affected above the glass transition temperature due to alkali treatment [21]. Ramie fiber reinforced epoxy composites showed dynamic-mechanical parameters at various temperatures. It revealed that reinforcement of ramie fibers increased the viscoelastic stiffness of the epoxy matrix and significantly changed the damping modulus after increasing the fiber fraction in composites [22]. Sisal fiber/polypropylene (PP) composite was investigated using a horizontal burning test and a vertical burning test. After addition of fire retardant, flame retardancy and thermal stability of the PP composites were improved without deterioration of their mechanical properties [23].

In previous studies [24], the mechanical and physical properties of untreated and treated PALF and kenaf composites have been investigated and were found to have the highest mechanical properties at 50% fiber loading, and after silane treatment the mechanical properties improved again. This work is an extension of previous work to investigate the thermal, dynamic mechanical and fire resistant behavior of untreated and treated PALF and KF composite at different fiber loadings. It is assumed that treated PALF and KF will improve interfacial bonding with matrix that will help to improve the thermal and dynamic properties of PALF/KF phenolic composites.

## 2 MATERIALS AND METHOD

### 2.1 Materials

Novolac-type phenolic formaldehyde resin (Grade PH-4055) was supplied by Chemovate, Banglore, India. Pineapple leaf fibers (PALFs) (*Ananas comosus*) were harvested in Indonesia and kenaf was harvested from Malaysia and retted. The chemicals used in this research study for treatment is triethoxy(ethyl)silane (96%, Sigma-Aldrich) from Megwena Synergy Supply, Selangor, Malaysia.

## 2.2 Fiber Treatment

The PALF and KF were immersed in distilled water with silane at a concentration of 2% for 3 h. After treatment, the fibers were thoroughly washed with running water several times until pH values were neutralized. Then, the fibers were dried in an oven at 80 °C 48 h. The selection of chemical, chemical concentration and soaking period for fiber treatment was selected from a previous study [10].

## 2.3 Preparation of Composites

PALF and KF were used as filler in fabrication of composites. The PALF and KF were ground into powder with thickness of 0.8–1 mm by using a grinding machine and fibers were maintained at 6–8% moisture content. Kenaf fiber and PALF phenolic composites were fabricated by using a 15 × 15 × 3 mm stainless metal plate. The 3 mm stainless steel plate was placed into a hydraulic hot press at 160° temperature. The stainless steel plate was removed from the press after 8 min and kept for cooling at room temperature, and then samples were cut for testing according to ASTM standard. The formulation of fabricated PALF and KF composites is shown in Table 1.

## 3 CHARACTERIZATION OF COMPOSITES

### 3.1 Thermogravimetric Analysis (TGA)

Thermal stability of PALF/KF composite and hybrid composite samples were characterized using a thermogravimetric analyzer (TGA Q500, TA Instruments, USA). Work on all of the samples was carried out at 20 °C/min under a room temperature in the range of 30–700 °C.

**Table 1** Formulation of KF and PALF in composites.

PALF and KF composites	PF (wt%)	PALF (wt%)	KF (wt%)
Pure phenolic	100	0	0
40% PALF	60	40	0
50% PALF	50	50	0
Treated 50% PALF	50	50	0
60% PALF	40	60	0
50% KF	50	0	50
Treated 50% KF	50	0	50

### 3.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was executed according to ASTM D4065-01 to determine the viscoelastic behavior of untreated and silane treated PALF/KF composites as a function of temperature. DMA testing was performed using a TA Instruments Q800 DMA operating in a three-point bending mode at an oscillation frequency of 1 Hz under controlled amplitude. The temperature was ramped from 30 °C to 150 °C under controlled sinusoidal strain with a heating rate of 5 °C/min. The dimension of samples was 60 × 12.5 × 3 mm<sup>3</sup>.

### 3.3 UL-94

Flammability of pure phenolic and untreated and treated PALF and KF composites was studied by a horizontal UL-94 test and a vertical UL-94 test according to ASTM D635 and ASTM D3801, respectively. For the horizontal UL-94 test, the specimen was fixed horizontally and a flame was applied to one end of the specimen. The time for the flame to travel from 25 mm (from the end) to 100 mm was recorded. Then, burning rates of the composites were calculated as follows:

$$V = 60L/t \quad (1)$$

where  $V$  is the burning rates (mm/min),  $L$  is burned length (mm), and  $t$  is the time of burning (s).

The UL-94 vertical test was carried out by using a test specimen bar 125 mm long, 13 mm wide, and 3 mm thick. Specimen bars were suspended vertically over surgical cotton and ignited with a Bunsen burner. The flammability types were classified from V-0 to V-2. The lower end of the specimen was exposed to the flame for 10 s and then removed. The time was recorded.

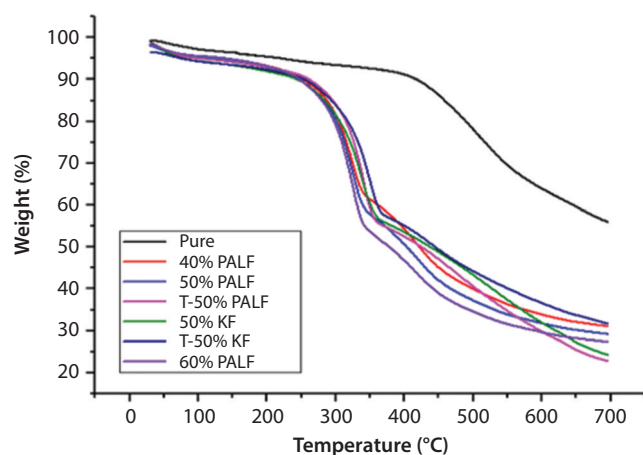
The specimen would then be assigned to class UL-94 V-0 if flaming time is less than 10 s. The lowest flame retardancy rating is V-2 if flaming time is less than 50 s and cotton indicator is ignited by flaming particles or drops. V-1 is the intermediate class of V-0 and V-2; the flaming time should not exceed 30 s and flaming drops could not ignite the surgical cotton below the specimen. The flammable materials which cannot be classified according to this method are marked with code NC (no classification, complete combustion of the specimen).

## 4 RESULTS AND DISCUSSION

### 4.1 Thermogravimetric Analysis (TGA)

The results of TGA analysis on pure phenolic matrix, untreated and silane-treated PALF and KF phenolic

composites on various fiber loadings are shown in Figure 1. Thermal decomposition of each sample was carried out in a programmed temperature range of 30–700 °C. It is observed that higher moisture absorption was found in all natural fiber composites. In the case of PALF and KF composites, the first weight loss between 60 and 100 °C corresponds to vaporization of water molecules from all natural fiber composite samples [13, 25]. The water molecule can easily penetrate into the fiber's cell wall structure or void space at the fiber-matrix interface [26], and water absorption is also responsible for reducing the mechanical strength of natural fiber composites and creating a hurdle in interfacial bonding between fibers and matrix [10]. Pure phenolic composites did not show weight loss at 100 °C temperature, which shows the absence of water molecule. TGA results are summarized in Table 2 for pure phenolic matrix, PALF and KF phenolic composites and show the first and second weight loss in all types of composites, which occurs in most of the



**Figure 1** TGA curve of pure phenolic and PALF/KF fiber loading composites.

lignocellulosic fiber and composites [12, 27]. Pure phenolic shows a 32.16% weight loss at 420.73 °C, and the final remaining residue in pure phenolic was 55.97%, which is much higher due to the presence of more char constituent [3]. The degradation process, accelerated by the presence of phenolic groups adjacent to the methylene bridges, is dependent on the dihydroxy phenyl methane units present in the resin [28]. PALF and KF phenolic composites showed weight loss twice; untreated and treated PALF composite revealed the first weight loss was in the range of 282–303 °C, while untreated and treated 50% KF composites showed first stage thermal degradation at 293.14 and 305.41 °C, respectively. Incorporation of PALF and KF into the phenolic matrix reduced the thermal stability, as evidenced by the TGA analysis in Figure 1. The first weight loss is reportedly due to the thermal decomposition of hemicellulose, lignin, pectin and the glycosidic linkages of cellulose of natural fibers [29–31], while silane-treated PALF/KF composites improved the thermal stability. Sreekala *et al.* [32] reported that alkali and silane treatment increased the thermal stability of the fibers due to thermal depolymerization of hemicellulose and cleavage of the glucosidic linkage of cellulose.

The second weight loss of untreated and treated PALF composites showed a range of 388.7–422 °C and untreated and treated 50% KF composites showed thermal decomposition at 447.99 and 408.58 °C, respectively, due to thermal decomposition of  $\alpha$ -cellulose and depolymerization of matrix [33, 34]. The remaining residue of each sample was calculated and pure matrix showed higher residue of 55.97%, which is higher than untreated and treated PALF/KF composites. The final residue of treated composites was much less than that of untreated composites because most of the chemical composition of, for example, hemicellulose and lignin, was removed during chemical treatments [35, 36].

**Table 2** Thermogravimetric analysis (TGA) results obtained for pure phenolic and PALF/KF fiber loading composites.

Sample	Initial degradation temperature (°C) and weight loss (%)		Final degradation temperature (°C) and weight loss (%)		Final residue (%)
	(°C)	(%)	(°C)	(%)	
Pure phenolic	420.73	32.16	–	–	55.97
40% PALF	282.50	35.17	388.7	25.77	31.07
50% PALF	283.64	38.97	391.38	23.92	29.22
T-50% PALF	303.05	40.52	422.37	26.24	22.76
50% KF	293.14	39.16	447.99	24.91	24.23
T-50% KF	305.41	27.47	408.58	22.78	31.65
60% PALF	283.73	43.75	390.93	21.61	27.33

## 4.2 Derivative Thermogravimetric (DTG) Analysis

Derivative thermogravimetric (DTG) analysis was performed on pure matrix and untreated and treated PALF and KF composites and the results are shown in Figure 2. Decomposition temperature of each component of composites was correlated with peaks of DTG curves. There was only one peak located in the pure matrix at 500 °C in the DTG curve, which showed stages of degradation in the matrix with the maximum rate of degradation at 3.56%/min. PALF and KP/phenolic composites exhibited three peaks; the height of the first peak was lowest, which indicates the presence of water molecules in the hemicelluloses of PALF/KF or the existence of voids that developed during the fabrication of composites. The heights of the second peak of the PALF and KF composites are highest among all peaks. The third peaks were recorded in untreated PALF composites only. The untreated PALF composites decomposed at a slightly lower temperature than the treated PALF/KF composites. For engineering applications, the first degradation of material is very important compared to subsequent degradation [26].

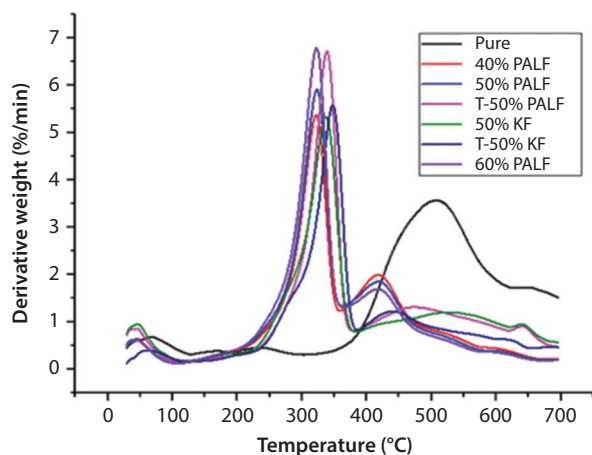
## 4.3 Dynamic Mechanical Analysis

### 4.3.1 Storage Modulus

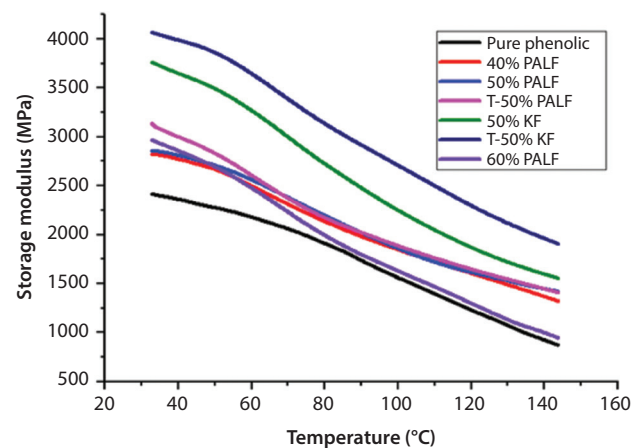
Figure 3 represent the effects of fiber loading and treated fibers on the storage modulus of PALF and KF phenolic composites. Dynamic mechanical analysis reveals knowledge about storage modulus vs. temperature graphs which helps to extract important information about stiffness, degree of crosslinking and fiber/matrix interfacial bonding of materials [37]. Storage

modulus contributes to the elaborate elasticity of the composite's components. Storage modulus has three regions: glassy region, transition region and rubbery region [38]. In the glassy region, composite components are in a frozen state (highly immobile), compact and tightly packed, resulting in high storage modulus [39]. In the glass transition region, the graph of storage modulus falls when it passes through glass transition temperature ( $T_g$ ) due to the increase in mobility of polymer chain above  $T_g$  temperature [40]. The rubbery region is the last phase, where enhancement of temperature makes materials more mobile with loose structural arrangements and no further changes [41].

The variation in storage modulus on different fiber loadings and effects on treated fiber composites were studied. In comparison with the pure phenolic sample, it can be seen that the storage modulus of fiber composites increases with increasing PALF and KF content in the phenolic matrix, and the curve falls with increasing temperature. In the case of the pure phenolic sample, there is a lowest storage modulus. It is due to the increased molecular mobility of the polymer chains above  $T_g$  [42]. However, storage modulus of composites is enhanced after the addition of fibers into the matrix; higher storage modulus represents higher stiffness of composites. Though there was an enhancement of storage modulus after adding fibers, 60% PALF fiber content showed a reduction in modulus. The composites with 60% PALF showed lesser modulus due to weaker fiber/matrix adhesion. It indicated that composites having fibers of more than 50 wt% content cannot be evenly dispersed in the matrix and agglomerate within composite, which reduced the effect of fiber as filler in composite [43]. The 50% PALF and KF phenolic composites showed very high modulus and, among all composites, silane-treated



**Figure 2** DTG curve of pure phenolic and PALF/KF fiber loading composites.



**Figure 3** Storage modulus of pure phenolic and PALF/KF fiber loading composites.

KF composites showed the highest storage modulus, whereas treated PALF also improved. Asim *et al.* [24] studied the tensile properties of PALF and KF fiber loadings and found that 50% fiber loading showed the highest tensile properties and treated 50% fiber loading showed the highest improvement among all samples.

The above findings may be attributed to the fact that untreated and treated 50% PALF and KF fiber composites have better storage modulus because enhanced interfacial adhesion can increase the storage modulus of composites [26].

Silane treatment is considered to enhance the roughness of the fiber surface, which improves the compatibility between the fibers and matrix. The enhanced area of contact between the fibers and matrix binds the material tighter, restricting the molecular mobility upon exposure to higher temperatures. It is also assumed that functional group of the silane forms interpenetrating polymer networks with fibers that can be the cause of changes in the polymer structure [20]. A schematic representation of the interaction between the polymer and the silane-coupling agent is given in Figure 4. Silane treatment of fibers affected the  $T_g$  and improved the rubbery plateau, which means that the thermal mechanical stability of the material at high temperature was improved.

### 4.3.2 Loss Modulus

Figure 5 represents the effect of fiber loading and treated fibers on the loss modulus of PALF and KF phenolic composites. The pure phenolic displays a broader peak in the temperature range of 80–110 °C. The addition of fibers in the matrix shows higher

peaks of loss modulus. The ranges of peak express the diversity of chain segment of polymer three-dimensionally [20]. The loss modulus curve shows that the measure of energy dissipated as heat per cycle under deformation experienced in a viscoelastic material. It is also shows that most of the peaks were shifted towards the lower temperature. The differences among the untreated PALF composites in loss modulus value are marginal and 50% PALF showed higher loss modulus. Addition of PALF and KF in phenolic matrix broadened the loss modulus peaks. The broadening in loss modulus is due to enhancement in chain

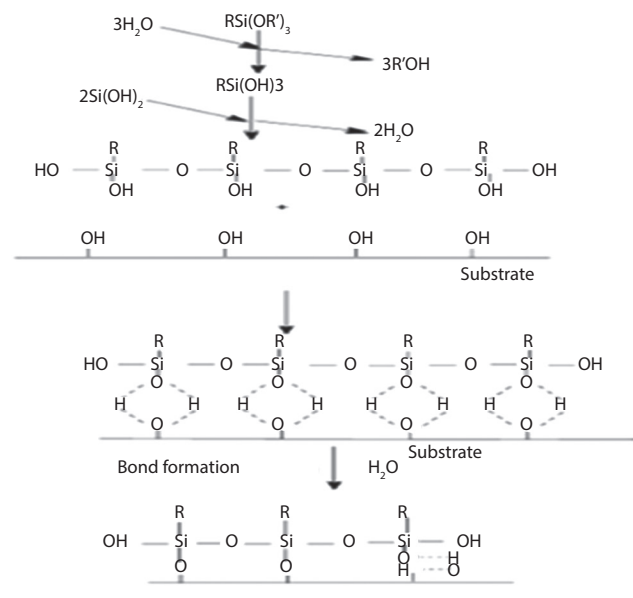


Figure 4 Schematic representation of silane/cellulose interaction.

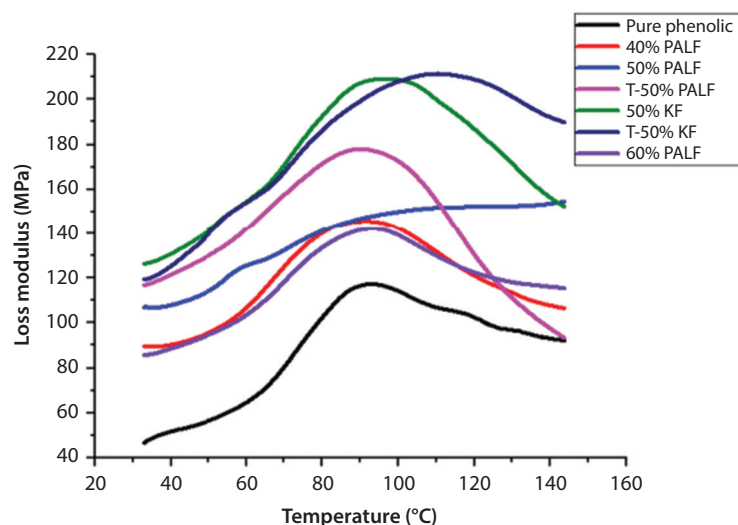


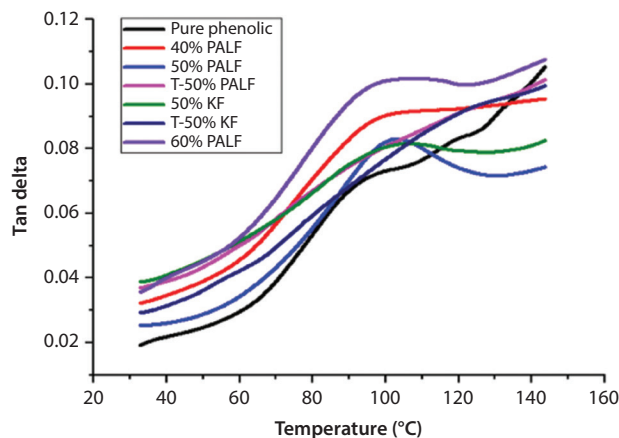
Figure 5 Loss modulus of pure phenolic, PALF and KF phenolic composites.

segment as well as more free volume with the addition of natural fibers [44]. Another reason may be due to the fact that the polymer matrix was surrounded by fibers having a different physical state than the rest of the matrix, which ultimately reduced molecular mobility [39]. The maximum loss modulus occurred at a temperature where loss modulus was indicating the  $T_g$  of the system [3]. The transition region of loss modulus in composites was shown to be much higher than that of pure phenolic, which may be due to an increase in internal friction that enhances the dissipation of energy [40].

The treated KF composite showed the highest loss modulus value, which is much better above the  $T_g$  than untreated PALF and KF phenolic composites, whereas pure phenolic showed the lowest value. It was reported that  $T_g$  values obtained from the loss modulus are more realistic as compared to those obtained from the damping factor [45]. The shifts in the  $T_g$  values of the polymer matrix after the addition of treated fiber indicated that fiber played an important role above  $T_g$ . The highest loss modulus was reported in treated 50% KF composites. The results showed higher loss modulus due to polymer and better compatibility with fibers after silane treatment.

### 4.3.3 Damping Factor

Curve trend changes in the damping factor of the composites and pure phenolic with temperature are shown in Figure 6. Incorporation of fibers into composites influenced damping factor. It was noticed that damping factor goes through a maximum in the transition region and then is reduced in the rubbery region. This phenomenon represented the initial frozen state and then mobility of small groups of materials and molecules within the polymer structure [37]. The higher

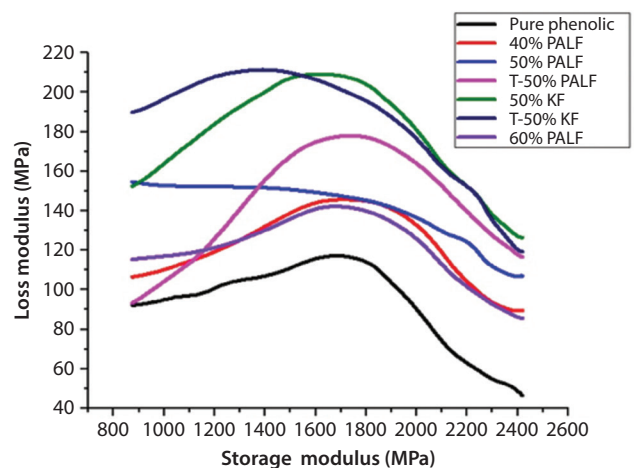


**Figure 6** Damping factor of pure phenolic and PALF/KF fiber loading composites.

peak value of damping factor showed higher degree of molecular mobility [46]. The pure phenolic showed the lowest  $\text{Tan } \delta$  value, indicating a minimum degree of molecular mobility; whereas, incorporation of fibers into phenolic resin substantially increased the viscoelastic damping factor because phenolic resin is known to have great thermal resistance, so it is assumed that pure phenolic minimized the degree of molecular mobility [47, 48]. A lower  $\text{Tan } \delta$  peak was obtained for pure phenolic, treated PALF/KF composites and 50% PALF composites. The incorporation of PALF and KF fiber into phenolic matrix slightly reduced the damping characteristics of the PALF/KF composites. In the case of composites, the damping peak height appears to be due to the fiber's internal energy dissipation between fiber/matrix interphase [49].

### 4.3.4 Cole-Cole Plots

A Cole-Cole curve was plotted to understand the relationship between loss modulus and storage modulus [50, 51]. The smooth and semicircular plotted curves of composites showed the homogeneous behavior of polymeric system [52] and the imperfect or irregular arc indicated the interface effects and heterogeneous dispersion in the polymeric system [51, 53]. Cole-Cole curves displayed the loss modulus data which were plotted as a function of storage modulus for all PALF/KF and pure phenolic composites in Figure 7. The Cole-Cole curve of pure phenolic and 40% PALF composites displayed relatively less heterogeneity than among all other curves. Homogeneous curves are an indicator of poor interfacial bonding between fiber and matrix. The Cole-Cole plot also showed an imperfect semicircle resembling the more heterogeneous ones among untreated and treated 50% PALF/KF composites.



**Figure 7** Cole-Cole plots of pure phenolic and PALF/KF fiber loading composites.

The imperfect semicircle is due to the greater portion of fibers and its interfacial bonding [54], because amount, dimension of incorporated fibers and surface characteristics of the fibers effect the arc shape of Cole-Cole plot, which influence the viscoelastic character as well [55]. Thus the incorporation of treated PALF/KF in phenolic composites greatly affects the shape of Cole-Cole plots, thereby influencing their dynamic mechanical properties with function of temperature.

#### 4.4 Flammability Properties

The vertical and horizontal UL-94 tests were conducted to quantify and rank the flame retardancy of the composites. The results of the UL-94 tests for the pure phenolic and untreated and treated PALF and KF composites are presented in Table 3. It is clear from the vertical UL-94 test that the flame retardancy of pure phenolic was very good and achieved a V-0 grade because its combustion times were less than 10 seconds.

After the addition of untreated and treated PALF, the fire retardancy was reduced up to 60% PALF loading, though 40% PALF loading achieved V-0 grade while 50% and 60% PALF and treated 50% PALF were considered as V-1 grade due to their combustion times being less than 30 seconds. On the other hand, untreated and treated KF composites showed better fire retardancy than PALF composites and their combustion times were less than 10 s, achieving a V-0 grade. No dripping was observed for any of the samples. Reduction in fire retardancy is due to the cellulosic content in the natural fibers and PALF has higher cellulosic content in comparison to KF. After the treatment, the cellulosic content was exposed and reduced the fire retardant properties. Even with this amount of cellulosic content these composites were still considered to be V-0 and V-1 grade because the chemical structure of phenol resin is deformed and forms a

layer of char on the surface of composites that protect the surface from heat [15].

The horizontal UL-94 test showed that the combustion rate of pure phenolic was lowest among all composites; however 60% PALF composites showed the highest combustion rate, as shown in Table 3. In this experiment it can be observed that with the increment of fiber loading and after treatment of fibers, the combustion rate increases. After adding 50% KF, the burning test was reduced compared to 50% PALF composites.

## 5 CONCLUSIONS

Thermogravimetric analysis of pure phenolic and PALF/KF fiber loading revealed that pure phenolic was more stable, whereas 60% fiber loading PALF composite was the least stable due to less proportion of phenolic resin. It was also observed that with incorporation of fiber, thermal properties were reduced. Among all fiber composites, treated 50% KF showed higher  $T_g$  value followed by treated 50% PALF composites, due to good interfacial bonding in which polymer acts as a barrier to prevent the degradation of fibers. In DMA results, it was shown that pure phenolic had the lowest value of storage modulus. After the incorporation of PALF from 40% to 60%, untreated and treated 50% PALF and 50% KF in phenolic composite increased the storage modulus due to the stiff nature of the kenaf fiber and better interfacial adhesion of fiber and matrix. However, after treatment, 50% PALF and KF further improved storage modulus properties. With the addition of PALF and KF, the peaks of loss modulus were higher than with pure phenolic. Untreated and treated KF illustrated the highest peak of loss modulus and peaks were shifted towards high temperature. Tan delta of pure phenolic showed very low modulus, which indicated less mobility in structure; after addition of untreated and treated PALF and KF, composites also showed a curve near

**Table 3** Vertical and horizontal UL-94 test results of untreated and treated PALF and KF composites.

Sample	Vertical UL-94			Horizontal UL-94 (mm/min)
	Flaming drops	Cotton ignited	Classifications	
Pure Phenolic	No	No	V-0	07
40% PALF	No	No	V-0	12
50% PALF	No	No	V-1	15.71
T-50% PALF	No	No	V-1	16.45
60% PALF	No	No	V-1	19.3
50% KF	No	No	V-0	13.6
T-50% KF	No	No	V-0	15



that of pure phenolic composites, whereas 60% PALF showed very high mobility in structure, which may be due to the lack of phenolic resin. Cole-Cole plots showed an imperfect semicircular shape of treated and untreated 50% fiber loading of PALF and KF phenolic composites, indicating heterogeneity of the system that showed good fiber/matrix adhesion. Vertical and horizontal UL-94 testing showed that pure phenolic is highly fire resistant. After the addition of PALF in phenolic composites, the fire resistancy decreased; on the other hand, KF in phenolic composites showed better fire resistancy. The fiber treatment did not help to improve the properties of PALF and KF composites.

It is anticipated from the previous and current work that treated PALF and kenaf fibers have the highest mechanical and thermal stability and these studies will contribute to the optimized use of PALF and KF in the development of unique, cost-effective, advanced composites possessing appropriate stiffness, damping behavior, and thermal stability. Furthermore, the thermal studies on the hybridization of PALF and kenaf will advance the research in developing new cost-effective materials.

## References

1. R. Yahaya, S. Sapuan, M. Jawaid, Z. Leman, and E. Zainudin, Effect of layering sequence and chemical treatment on the mechanical properties of woven kenaf-aramid hybrid laminated composites. *Mater. Des.* **67**, 173–179 (2015).
2. M. Asim, M. Jawaid, K. Abdan, and M. Ishak, Effect of pineapple leaf fibre and kenaf fibre treatment on mechanical performance of phenolic hybrid composites. *Fiber. Polym.* **18**, 940–947 (2017).
3. M. Jawaid, H.A. Khalil, and O.S. Alattas, Woven biocomposites: Dynamic mechanical and thermal properties. *Compos. Part A* **43**, 288–293 (2012).
4. N. Saba, M. Paridah, and M. Jawaid, Mechanical properties of kenaf fibre reinforced polymer composite: A review. *Constr. Build. Mater.* **76**, 87–96 (2015).
5. H.Y. Cheung, M.P. Ho, K.T. Lau, F. Cardona, and D. Hui, Natural fibre-reinforced composites for bioengineering and environmental engineering. *Compos. Part B* **40**, 655–663 (2009).
6. M. Jawaid and H.P.S. Abdul Khalil, Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review. *Carbohydr. Polym.* **86**, 1–18 (2011).
7. S. Banik, M. Basak, D. Paul, P. Nayak, D. Sardar, S. Sil, B. Sanpui, and A. Ghosh, Ribbon retting of jute—a prospective and eco-friendly method for improvement of fibre quality. *Ind. Crops. Prod.* **17**, 183–190 (2003).
8. K. Mylsamy and I. Rajendran, The mechanical properties, deformation and thermomechanical properties of alkali treated and untreated Agave continuous fibre reinforced epoxy composites. *Mater. Des.* **32**, 3076–3084 (2011).
9. M. Asim, K. Abdan, M. Jawaid, M. Nasir, Z. Dashtizadeh, M. Ishak, and M.E. Hoque, A review on pineapple leaves fibre and its composites. *Int. J. Polym. Sci.* **2015**, Article ID 950567 (2015).
10. M. Asim, M. Jawaid, K. Abdan, and M.R. Ishak, Effect of alkali and silane treatments on mechanical and fibre-matrix bond strength of kenaf and pineapple leaf fibres. *J. Bionic. Eng.* **13**, 426–435 (2016).
11. E. Rojo, M.V. Alonso, M. Oliet, B. Del Saz-Orozco, and F. Rodriguez, Effect of fiber loading on the properties of treated cellulose fiber-reinforced phenolic composites. *Compos. Part B* **68**, 185–192 (2015).
12. W. Liu, A. Mohanty, L. Drzal, P. Askel, and M. Misra, Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers as reinforcements for polymer matrix composites. *J. Mater. Sci.* **39**, 1051–1054 (2004).
13. K.M. Nair, S. Thomas, and G. Groeninckx, Thermal and dynamic mechanical analysis of polystyrene composites reinforced with short sisal fibers. *Compos. Sci. Technol.* **61**, 2519–2529 (2001).
14. L.A. Pothan, Z. Oommen, and S. Thomas, Dynamic mechanical analysis of banana fiber reinforced polyester composites. *Compos. Sci. Technol.* **63**, 283–293 (2003).
15. H.T. Chiu, S.H. Chiu, R.E. Jeng, and J.S. Chung, A study of the combustion and fire-retardance behaviour of unsaturated polyester/phenolic resin blends. *Polym. Degrad. Stab.* **70**, 505–514 (2000).
16. R. Kozłowski and M. Władyska-Przybylak, Flammability and fire resistance of composites reinforced by natural fibers. *Polym. Adv. Technol.* **19**, 446–453 (2008).
17. S. Chapple and R. Anandjiwala, Flammability of natural fiber-reinforced composites and strategies for fire retardancy: A review. *J. Thermoplast. Compos. Mater.* **23**, 871–893 (2010).
18. J. George, S. Bhagawan, and S. Thomas, Thermogravimetric and dynamic mechanical thermal analysis of pineapple fibre reinforced polyethylene composites. *J. Therm. Anal.* **47**, 1121–1140 (1996).
19. R. Mangal, N. Saxena, M. Sreekala, S. Thomas, and K. Singh, Thermal properties of pineapple leaf fiber reinforced composites. *Mater. Sci. Eng. A* **339**, 281–285 (2003).
20. L.A. Pothan, S. Thomas, and G. Groeninckx, The role of fiber/matrix interactions on the dynamic mechanical properties of chemically modified banana fiber/polyester composites. *Compos. Part A* **37**, 1260–1269 (2006).
21. V. Fiore, G. Di Bella, and A. Valenza, The effect of alkaline treatment on mechanical properties of kenaf fibers and their epoxy composites. *Compos. Part B* **68**, 14–21 (2015).
22. F.M. Margem, S.N. Monteiro, J. Bravo Neto, R.J.S. Rodriguez, and B.G. Soares, The dynamic-mechanical behavior of epoxy matrix composites reinforced with ramie fibers. *Matéria (Rio J.)* **15**, 164–171 (2010).
23. R. Jeenchan, N. Suppakarn, and K. Jarukumjorn, Effect of flame retardants on flame retardant, mechanical, and thermal properties of sisal fiber/polypropylene composites. *Compos. Part B* **56**, 249–253 (2014).
24. M. Asim, M. Jawaid, K. Abdan, and M. Ishak, The effect of silane treated fibre loading on mechanical properties

- of pineapple leaf/kenaf fibre filler phenolic composites. *J. Polym. Environ.* 1–8 (2017).
25. D. Puglia, M. Monti, C. Santulli, F. Sarasini, I.M. De Rosa, and J.M. Kenny, Effect of alkali and silane treatments on mechanical and thermal behavior of *Phormium tenax* fibers. *Fiber. Polym.* **14**, 423–427 (2013).
  26. M. Ridzuan, M.A. Majid, M. Afendi, M. Mazlee, and A. Gibson, Thermal behaviour and dynamic mechanical analysis of *Pennisetum purpureum*/glass-reinforced epoxy hybrid composites. *Compos. Struct.* **152**, 850–859 (2016).
  27. P. Gañan, S. Garbizu, R. Llano-Ponte, and I. Mondragon, Surface modification of sisal fibers: Effects on the mechanical and thermal properties of their epoxy composites. *Polym. Compos.* **26**, 121–127 (2005).
  28. Y.K. Lee, D.J. Kim, H.J. Kim, T.S. Hwang, M. Rafailovich, and J. Sokolov, Activation energy and curing behavior of resol- and novolac-type phenolic resins by differential scanning calorimetry and thermogravimetric analysis. *J. Appl. Polym. Sci.* **89**, 2589–2596 (2003).
  29. S.S. Kumar, D. Duraibabu, and K. Subramanian, Studies on mechanical, thermal and dynamic mechanical properties of untreated (raw) and treated coconut sheath fiber reinforced epoxy composites. *Mater. Des.* **59**, 63–69 (2014).
  30. A. Arbelaz, B. Fernández, J. Ramos, and I. Mondragon, Thermal and crystallization studies of short flax fibre reinforced polypropylene matrix composites: Effect of treatments. *Thermochim. Acta* **440**, 111–121 (2006).
  31. M. Nasir, O. Sulaiman, R. Hashim, K. Hossain, A. Gupta, and M. Asim, Rubberwood fiber treatment by laccase enzyme and its application in medium density fiberboard. *J. Pure Appl. Microbiol.* **3**, 2095–2100 (2015).
  32. M. Sreekala, M. Kumaran, and S. Thomas, Oil palm fibers: Morphology, chemical composition, surface modification, and mechanical properties. *J. Appl. Polym. Sci.* **66**, 821–835 (1997).
  33. F. Shukor, A. Hassan, M.S. Islam, M. Mokhtar, and M. Hasan, Effect of ammonium polyphosphate on flame retardancy, thermal stability and mechanical properties of alkali treated kenaf fiber filled PLA biocomposites. *Mater. Des.* **54**, 425–429 (2014).
  34. K. Fung, X. Xing, R. Li, S. Tjong, and Y.W. Mai, An investigation on the processing of sisal fibre reinforced polypropylene composites. *Compos. Sci. Technol.* **63**, 1255–1258 (2003).
  35. Z. Azwa and B. Yousif, Characteristics of kenaf fibre/epoxy composites subjected to thermal degradation. *Polym. Degrad. Stab.* **98**, 2752–2759 (2013).
  36. M. Kabir, H. Wang, K. Lau, F. Cardona, and T. Aravinthan, Mechanical properties of chemically-treated hemp fibre reinforced sandwich composites. *Compos. Part B* **43**, 159–169 (2012).
  37. S. Joseph, S.P. Appukuttan, J.M. Kenny, D. Puglia, S. Thomas, and K. Joseph, Dynamic mechanical properties of oil palm microfibril-reinforced natural rubber composites. *J. Appl. Polym. Sci.* **117**, 1298–1308 (2010).
  38. N. Saba, M. Jawaid, O.Y. Allothman, and M. Paridah, A review on dynamic mechanical properties of natural fibre reinforced polymer composites. *Constr. Build. Mater.* **106**, 149–159 (2016).
  39. M. Jacob, B. Francis, S. Thomas, and K. Varughese, Dynamical mechanical analysis of sisal/oil palm hybrid fiber-reinforced natural rubber composites. *Polym. Compos.* **27**, 671–680 (2006).
  40. N. Hameed, P. Sreekumar, B. Francis, W. Yang, and S. Thomas, Morphology, dynamic mechanical and thermal studies on poly(styrene-co-acrylonitrile) modified epoxy resin/glass fibre composites. *Compos. Part A* **38**, 2422–2432 (2007).
  41. M. Jawaid and H.A. Khalil, Effect of layering pattern on the dynamic mechanical properties and thermal degradation of oil palm-jute fibers reinforced epoxy hybrid composite. *Bioresources* **6**, 2309–2322 (2011).
  42. D. Romanzini, H.L. Ornaghi, S.C. Amico, and A.J. Zattera, Influence of fiber hybridization on the dynamic mechanical properties of glass/ramie fiber-reinforced polyester composites. *J. Reinf. Plast. Compos.* **31**, 1652–1661 (2012).
  43. A. Etaati, S. Pather, Z. Fang, and H. Wang, The study of fibre/matrix bond strength in short hemp polypropylene composites from dynamic mechanical analysis. *Compos. Part B* **62**, 19–28 (2014).
  44. M.A. López-Manchado, J. Biagitti, and J.M. Kenny, Comparative study of the effects of different fibers on the processing and properties of ternary composites based on PP-EPDM blends. *Polym. Compos.* **23**, 779–789 (2002).
  45. M. Akay, Aspects of dynamic mechanical analysis in polymeric composites. *Compos. Sci. Technol.* **47**, 419–423 (1993).
  46. M. Sepe, *Dynamic Mechanical Analysis for Plastics Engineering*, William Andrew (1998).
  47. M.M. Hirschler, Chemical aspects of thermal decomposition of polymeric materials, in *Fire Retardancy of Polymeric Materials*, pp. 27–79, A.F. Grand and C.A. Wilkie (Eds.), CRC Press, Boca Raton, FL (2000).
  48. A. Horrocks and B. Kandola, Flammability and fire resistance of composites, in *Design and Manufacture of Textile Composites*, A.C. Long (Ed.), pp. 330–363, Woodhead Publishing, Cambridge, England (2005).
  49. S. Dong and R. Gauvin, Application of dynamic mechanical analysis for the study of the interfacial region in carbon fiber/epoxy composite materials. *Polym. Compos.* **14**, 414–420 (1993).
  50. O.J. Yoon, C.Y. Jung, I.Y. Sohn, H.J. Kim, B. Hong, M.S. Jhon, and N.E. Lee, Nanocomposite nanofibers of poly(D, L-lactic-co-glycolic acid) and graphene oxide nanosheets. *Compos. Part A* **42**, 1978–1984 (2011).
  51. M. Joshi, B. Butola, G. Simon, and N. Kukaleva, Rheological and Viscoelastic Behavior of HDPE/Octamethyl-POSS Nanocomposites. *Macromolecules* **39**, 1839–1849 (2006).
  52. L.U. Devi, S. Bhagawan, and S. Thomas, Dynamic mechanical analysis of pineapple leaf/glass hybrid fiber reinforced polyester composites. *Polym. Compos.* **31**, 956–965 (2010).
  53. M. Jawaid, H.A. Khalil, A. Hassan, R. Dungani, and A. Hadiyane, Effect of jute fibre loading on tensile and dynamic mechanical properties of oil palm epoxy composites. *Compos. Part B* **45**, 619–624 (2013).

54. N. Saba, M. Paridah, K. Abdan, and N. Ibrahim, Dynamic mechanical properties of oil palm nano filler/kenaf/epoxy hybrid nanocomposites. *Constr. Build. Mater.* **124**, 133–138 (2016).
55. M. Sreekala, S. Thomas, and G. Groeninckx, Dynamic mechanical properties of oil palm fiber/phenol formaldehyde and oil palm fiber/glass hybrid phenol formaldehyde composites. *Polym. Compos.* **26**, 388–400 (2005).