

Journal Pre-proof

Effect of cellulosic filler loading on mechanical and thermal properties of date palm seed/vinyl ester composites

Nagaraj Nagaprasad, Balasubramaniam Stalin, Venkataraman Vignesh, Manickam Ravichandran, Nagarajan Rajini, Sikiru Oluwarotimi Ismail



PII: S0141-8130(19)37586-5

DOI: <https://doi.org/10.1016/j.ijbiomac.2019.11.247>

Reference: BIOMAC 14183

To appear in: *International Journal of Biological Macromolecules*

Received date: 18 September 2019

Revised date: 5 November 2019

Accepted date: 14 November 2019

Please cite this article as: N. Nagaprasad, B. Stalin, V. Vignesh, et al., Effect of cellulosic filler loading on mechanical and thermal properties of date palm seed/vinyl ester composites, *International Journal of Biological Macromolecules*(2018), <https://doi.org/10.1016/j.ijbiomac.2019.11.247>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Effect of cellulosic filler loading on mechanical and thermal properties of date palm seed / vinyl ester composites

Nagaraj Nagaprasad¹, Balasubramaniam Stalin^{2*}, Venkataraman Vignesh³,
Manickam Ravichandran⁴, Nagarajan Rajini^{5*}, Sikiru Oluwarotimi Ismail⁶

¹*Department of Mechanical Engineering, ULTRA College of Engineering and Technology, Madurai- 625 107, Tamil Nadu, India.*

^{2*}*Department of Mechanical Engineering, Anna University, Regional Campus Madurai, Madurai- 625 019, Tamil Nadu, India.*

³*Department of Mechanical Engineering, Sethu Institute of Technology, Pulloor, Kariapatti – 626 115, Tamil Nadu, India.*

⁴*Department of Mechanical Engineering, K.Ramakrishnan College of Engineering, Tiruchirappalli- 621 112, Tamil Nadu, India.*

⁵*Department of Mechanical Engineering, Kalasalingam University, Krishnankoil, Virudhunagar- 626126, Tamil Nadu, India.*

⁶*Department of Engineering, School of Engineering and Computer Science, Centre for Engineering Research, University of Hertfordshire, Hatfield, Hertfordshire AL10 9AB, England, United Kingdom.*

*Correspondence Author: Nagarajan Rajini; Email: rajiniklu@gmail.com and B. Stalin; Email: stalin1312@gmail.com

Abstract

There are numerous better applications of fibre reinforced polymer composites today, when compared with metals and alloys. Many studies have been conducted to further improve the inherent mechanical and thermal properties of the composite materials, especially with sustainable, environmental friendly, recyclable and biodegradable reinforcements. Consequently, in this current study, the composites were prepared by combining bio solid waste (date seed filler) and vinyl ester to enhance the properties of polymer composites. The date seed filler reinforced vinyl ester (DSF-VE) composites were prepared by using conventional compression moulding technique with varying fillers loadings from 5% to 50%. The mechanical (tensile, flexural, impact

and hardness), water absorption and thermal (heat deflection temperature and thermo-gravimetric analysis) properties of the DSF-VE composites were experimentally evaluated. Scanning electron microscopic analysis was carried out to analyse the surface characteristics and fractured surface of the DSF-VE composites. It was evident from the results obtained that 30 wt% of the DSF-VE composites exhibited the highest mechanical properties: impact, tensile, hardness and flexural of 17.03 KJ/m², 40.3 MPa, 51 and 149 MPa, respectively, among the fabricated composites. Similarly, the heat deflection temperatures of DSF-VE composites increased by 58.49%, when compared with the neat, pure vinyl ester resin. The thermo-gravimetric analysis showed that the natural filler-based (DSF-VE) composites possessed thermal stability up to 400.2 °C, which was within the polymerisation process temperature. Furthermore, the DSF-VE composites have been successfully utilised for various potential applications, such as fabrication of a table fan blade, an engine guard for two-wheelers and self-motor guard for four wheelers.

Keywords: Cellulosic filler; date palm seed; vinyl ester; thermal and mechanical properties.

1. Introduction

In recent years, the researchers all over the world have been studying to incorporate the inorganic nanoparticles or fillers into the polymer matrix. This work has attracted increasing interest of the researchers, because of the improved mechanical, thermal stability, electrical, optical and wear resistance properties of several filler based composites when compared with various neat polymers. Selection of material is of paramount importance for any engineering design to achieve a low cost successful sustainable product. Physical and metaphysical properties of the products are the keystones for customer's satisfaction along with the mechanical properties. Considering these aspects of engineering, product design, performance and recyclability have been given higher priority [1-3].

The large amount of waste date seeds available in gulf region necessitates the utilisation of bio waste as a filler in polymer matrices, which has gained attention today. Addition of bio filler into the polymer matrix enriches the mechanical and thermal properties

of the fabricated composites [4]. Most of the researches have focused on the naturally available fillers like sawdust, rice husk, coconut shell powder, egg shell powder, wood flour, fly ash and red mud, because of their cost effectiveness and abundance. Carbon nanotubes, nanoclay, silicon carbide, talc and calcium carbonate are some of the inorganic fillers that are mostly or widely used reinforcements for polymer matrix. Also, in the rubber industry, different varieties of fillers have been incorporated to enhance the properties of various composites for various applications [5,6]. Vinod et al. [7] have conducted a comparative investigation of gigantea stem filler filled jute epoxy composite of 5 to 10 wt% and without filler, using hand lay-up method. Their results showed that 10 wt% of gigantea stem powder filled composite produced better results of both mechanical and thermal properties, because of higher filler loading. Fiore et al. [8] have analysed the tensile, flexural and dynamic mechanical properties of arundo donax filler filled epoxy composite and reported a decrease in tensile and flexural strength, due to the addition of arundo donax filler. Above the glass transition temperature, the storage module and the loss moduli showed some significant changes. In addition, coconut shell powder [9], calcium carbonate, phenolic hollow microspheresthese [10] and Clay [11] fillers have been added to fibres, not only to reduce the cost of polymers, but also to improve the dimensional, mechanical and thermal behaviours of their composite.

Furthermore, Jayabal et al. [12] comparatively analysed termite mound soil, rice husk, groundnut shell and boiled egg shell particles reinforced vinyl ester composite. From their study, it was observed that the rice husk filled vinyl ester composite exhibited a better tensile strength of 32 MPa, flexural strength of 38 MPa and maximum impact strength of 53 kJ/m² for termite mound soil particles filled composite. Another similar attempt has been made by using coconut shell and wood apple shell particulate filled epoxy composite. It has been observed that wood apple shell particulate filled composite exhibited a better tensile strength

of 43.6 MPa and flexural strength of 78.19 MPa than coconut shell particulate composite [13]. Rosamah et al. [14] fabricated and tested the mechanical and thermal properties of kenaf–coconut–kenaf fiber mat hybrid composite filled with varying oil palm shell nanoparticles with 1 wt%, 3 wt% and 5 wt% reinforced polyester composite. Their results showed that 3 wt% of oil palm shell nanoparticles filled composite produced a better physical, mechanical, and thermal properties than the other composite counterparts. Prabu et al. [15] studied mechanical, damping and chemical resistance properties of hybrid untreated and treated (with NaOH and silane) banana fibre polyester composites, with the effect of red mud as a filler. These composites established that products can be made with a better resistant to various chemicals. Another impressive work on *jatropha curcas L.* whole seeds, seed shells and seed kernels reinforced with epoxy composite have been investigated by Ruggiero et al. [16] and concluded that composite made with 20% seed kernels produced a greater wear resistance than the whole seed and the seed shells filled composites.

Moreover, the tamarind seed filler reinforced vinyl ester composite has been investigated in the recent work of Stalin et al. [17]. The results have shown that addition of tamarind seed filler increased the impact, tensile and flexural strengths by 21.5%, 39% and 55%, respectively. Babu et al. [18] developed coir powder filled polyester micro-composites, using hand lay-up method. The authors investigated mechanical, thermal and dynamic behaviour of micro coir powder filled composites. They concluded that composites with 4 wt% coir powder filled composites produced a better tensile flexural strength and storage modulus.

From the literature survey, it is evident that an addition of date seed filler improves the mechanical, thermal properties and water absorption behaviour of the polymer composites. Some of the extant studies on date seed filler reported that it was reinforced in polyester and poly (butylene), but there are no reported works on vinyl ester resin as a matrix

and thermal and water absorption behaviours of DSF reinforced composites. Significantly, vinyl ester resin has several advantages, such as a low viscosity, better impact resistance, water resistance, less shrinkage on curing, chemical/corrosion resistance, better cross bonding and sensitive nature to ambient conditions (temperature and humidity), when compared with other commonly used matrices. In addition, vinyl ester resin imparts superior properties of toughness, chemical resistance, mechanical, thermal elongation and interface strength to the composite, when compared with epoxy and polyester. Vinyl ester resin is cheaper than epoxy resin and stronger than polyester resin [19,20,36,37]. It is evident from literature that several fillers improve the mechanical, thermal and dynamic properties of polymer composites. In this regard, this paper shed light on the mechanical and thermal behaviours of the date seed filler reinforced vinyl ester composite. The date seed filler reinforced vinyl ester (DSF-VE) composites with different filler loadings were fabricated using compression moulding technique, and mechanical (tensile, flexural, impact and hardness) and thermal (thermo-gravimetric analysis and heat deflection temperature) characteristics of the DSF-VE fabricated composites were studied. In addition, water absorption behaviour of the composites were tested in accordance with the ASTM standard; to analyse the water uptake percentage. Moreover, a scanning electron microscopic (SEM) examination of the fractured surfaces of DSF-VE composite were extensively analysed.

2. Experimental details

2.1. Materials

The date fruit (*Phoenix dactylifera L.*) has been the main crop in gulf regions of the world. It is an essential part of the economic and social lives of the people in the region. After the technological transformation of date fruit, the date palm seeds remain the waste products of many industries. For instance, Tunisia is one of date processing countries with about

100,000 tons of annual yield of date fruits. From this, around 1000 tons of waste date seeds are extracted. Focusing on this experimental study, a 5 kg of date seeds was procured from Naveen agro traders, Madurai, Tamil Nadu, India. The seeds were cleaned by distilled water to remove the excess fruit pulp adhered to them. Then, excess water in their surfaces was removed by using tissue paper. Finally, they were dried in an oven for 24 hours at 60 °C. The dried seeds were milled in a ball mill, and an excellent morphology of 30 – 60 µm was obtained and therefore, ready to be used as a reinforcement. Commercially available industrial bisphenol-A-epoxy vinyl ester resin (styrene - 45%) with a density of 1.145 g/cm³, viscosity of 400 cps, and specific gravity of 1.09, along with N-dimethylaniline (C₈H₁₁N - promoter), methyl ethyl ketone peroxide (C₈H₁₈O₆ - catalyst) and cobalt 6% naphthenate (C₂₀H₃₄CoO₄ - accelerator) were purchased from Covai Seenu and Company, Coimbatore, Tamilnadu, India [17]. Without any treatment, vinyl ester resin was used as a matrix.

2.2. *Fabrication of composites*

In this current work, the compounding of date seed filler and vinyl ester has been carried out in a conventional compression moulding technique. Different filler loadings between 5% and 50% with a mould of dimension of about 200 mm long, 200 mm width, and 3 mm thick were used for fabrication of specimens. The stages of preparation of the date seed filler is shown in the Fig. 1. The cavity surface of the mould was coated with wax for easy removal of the composite plate. Then, for each percentage, the calculated amount of date seed filler was mixed into a measured vinyl ester resin and stirred for 30 minutes to get a homogeneous mixture and to reduce the air bubble generation. Dimethylaniline accelerator of 1.5 %, methyl ethyl ketone peroxide catalyst of 1.5% and cobalt naphthenate promoter of 1.5% were added to the mixture, as recommended by the supplier. Then, the mixture was gently poured into the mould cavity until it completely filled and kept closed with the

matching die. It is compressed with a constant pressure of 100 kPa for 24 hours at a room temperature for adequate curing. The hardened DSF-VE composite plate was removed from the mould cavity. A similar procedure has been adopted to prepare the DSF with different filler loadings. Fig. 2 shows the fabricated composites with different filler loadings.

2.3. *Mechanical testing*

A saw cutter was used to cut the fabricated composite plates to the desired shapes for different test specimens. Tensile and flexural tests were performed at a room temperature, using a universal testing machine (Tinius OlsenH50K). To check the repeatability of the results obtained, three specimens with respect to each weight percentage were tested. According to ASTM D638 (165 x 10 x 3 mm) test standard, tensile test was performed on specimens, using a set crosshead speed of 1 mm/min [24]. The flexural test was performed using three-point bending method, with a capacity 50 kN and a crosshead speed was fixed at 2 mm/min for all the specimens with a dimension of 127 mm long, 12.7 mm wide and 3 mm thickness according to ASTM D790-10 standard [23]. The ability of reinforced vinyl ester composites to absorb energy from impact load without breaking is referred to as impact strength. The magnitude of impact strength mainly depends on the interfacial adhesion between the filler and matrix, voids present, filler influence and testing conditions. The impact strength was evaluated using the Charpy test method in accordance with ASTM D-256 (65 x 13 x 3 mm) standard [15]. Also, hardness was measured using Barcol Hardness tester (Model: VBH2), according to ASTM 2583 standard [17].

2.4. *Thermal studies*

Thermal properties of date palm seed filler reinforced vinyl ester composites were analysed by heat deflection temperature (HDT) test, thermo-gravimetric thermal analysis

(TGA) and differential thermal analysis (DTA). The heat deflection temperature test was performed and a standard test bar of 60 x 12 x 3 mm deflected under a load of 0.455 MPa. The specimen was kept in a silicone oil bath. The temperature at which the bar deflected was recorded as a heat deflection temperature, according to ASTM D648 standard [33,39]. The rate of change in the weight and amount were measured as a function of temperature or time in a controlled environment, using thermo-gravimetric analysis (Model STA449 F3, Netzsch, Germany). About 10 milligrams of powder specimen of DSF-VE composite was placed in an alumina crucible with a precision balance. To predict their thermal stability, the specimens were gradually heated from the room temperature to 1000 °C with heating rate of 10 °C/min in nitrogen (20 mL/min) atmosphere [21].

2.5. *Water absorption behaviour*

The water absorption of the fabricated DSF-VE composites was evaluated in accordance with ASTM D570-99 standard (39 mm x 10 mm x 3 mm). Initially, the specimens were dried in an oven at 60 °C until a constant weight was obtained. Five replicas of each specimen were immersed in four different environments: normal water, cold water, salt water and hot water. A known weight (W_i) of each specimen was immersed in water for 24 hours one after the other. After, the specimens were taken out and moisture in the surface was wiped off using absorbent paper. Immediately, the weight of the specimen was measured [25]. The water absorption percentage was determined by finding the weight difference between the dry specimens and specimens immersed in water by Eq. (1).

$$\text{Water absorption percentage, } w\% = \frac{(W_f - W_i)}{W_i} \times 100\% \quad (1)$$

Where $W\%$ is the moisture present in percentages; W_f is the weight of the specimen in particular time; and W_i is the weight of the specimen before immersing in water.

2.6. *Microstructure analysis*

The microstructure morphology of the fractured tensile, impact and flexural DSF-VE composite specimens were recorded, using JEOL model scanning electron microscope with different magnifications. Before the examination of the fractured surfaces of the specimens, they were placed in a vacuum chamber, where the 10 mm height specimen was coated with a thin film of platinum for better conductivity during the examination.

3. **Results and discussion**

3.1. *Elemental analysis*

The chemical composition of date seed filler has been determined by SEM equipped with energy dispersive X-ray analysis (JEOL-JSM-5610LV). The elements present is shown in Fig. 3. The plot depicts that significant elements in DSF were carbon of 61.32 wt% and oxygen of 35.90 wt%. The other constitutions of filler materials were nitrogen, magnesium, and potassium. Similarly, Vimalanathan et al. [5] and Rosamah et al. [34] observed and reported carbon and oxygen as major elements in Shorea robusta natural filler and oil palm shell nanoparticles, respectively.

3.2. *Mechanical properties*

3.2.1. *Tensile strength*

The specimens of DSF-VE composites fabricated with various filler weight percentages were tested for tensile strength. Fig. 4 shows the average results of tensile strength of the DSF-VE composites as a function of filler loading weight percentages. The ultimate tensile strengths of 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50% of DSF-VE composites were 28.1, 32.1, 34.9, 25.4, 33.3, 40.3, 11, 15.5, 9.9 and 11.7 MPa, respectively. At 5 wt% filler, the improvement on tensile strength was 15% higher than that of pure vinyl ester resin.

Meanwhile, when it was increased from 5 wt% to 10 wt%, the tensile strength was slightly increased from 28.1 MPa to 32.2 MPa, respectively. At 15 wt% filler weight, the improvement on tensile strength was 42.45% higher than that of pure vinyl ester resin. The tensile strength was suddenly reduced between 34.9 to 25.1 MPa at 20 %wt. This was because of the distorted bonding properties between the filler and the matrix and also due to the presence of voids. However, the tensile strength of the DSF-VE composite was improved from 25.1 to 33 MPa by varying the filler weight percentage from 20 to 25%wt. The high tensile strength of DSF-VE composite was 40.3 MPa at 30%wt and it was observed as an optimum value. Also, it was 64.49% higher than that of pure vinyl ester resin. Fig. 5 depicts the tensile stress-strain curves for various filler weight percentages. Moreover, DSF-VE composites showed an increasing trend in the filler weight percentage up to 30%. This condition can be attributed to the distribution of the developed stress within the filler under tensile load by the matrix, and the filler reinforcement carried the tensile load which was more effective to withstand the matrix breakage. It has a higher stiffness and strength. Hence, it was observed that when filler weight percentage was increased beyond 30%wt, the strength of DSF-VE composites decreased. This continued in sinusoidal pattern with the further increase in filler weight percentage. This can be attributed to the insufficient bonding between the filler and vinyl ester matrix at a higher filler percentage. It resulted to voids and weaker strength during tensile testing.

Fig. 6 depicts the tensile load-displacement curves for the various filler weight percentages. The percentage of elongation between 5 and 50%wt ranged from 1.67 to 3.9%. The tensile modulus is a measure of stiffness of an elastic material and a quantity to characterise materials. Moreover, the addition of filler weight from 5 wt% to 50 wt% increased or enhanced the modulus value from 0.9 GPa to 2.14 GPa. Optimum tensile strength of 40.3 MPa of DSF-VE composites was close to that of coconut shell powder

reinforced epoxy, oil palm shell powder reinforced polyester, oil palm shell powder and kenaf–coconut–kenaf fibre reinforced polyester composites. But, it was higher than the tamarind seed filler reinforced vinyl ester composites of 34.1 MPa, date palm wood flour and glass fibre reinforced polypropylene composite of 25 MPa, boiled egg shell powder and coir fibre reinforced vinyl ester composite of 24 MPa, and groundnut powder and coir fibre reinforced vinyl ester composite of 29.5 MPa. This comparative analysis on mechanical behavior (tensile and other properties) of the DSF-VE composite shows that the DSF-VE composite is a promising materials for engineering structures. Summarily, a detailed comparison of mechanical properties of the DSF-VE composite with other fillers and fibres-based composites are shown in Table 1.

3.2.2. Flexural strength

Fig. 7 shows bending test results obtained on variations in the flexural characteristics obtained for the DSF-VE composites, with the effect of filler loadings. The neat resin recorded flexural strength and flexural modulus of 78 MPa and 3.64 GPa, respectively. When compared with pure vinyl ester resin, the flexural strength of the composites increased with filler loadings of 5, 10, 15, 20, 30 and 40%. The flexural modulus also followed the same trend and it increased with an increased DSF content. When compared with the neat VE resin, the average flexural strength of the DSF-VE composites increased with an increase in filler loading. It was evident that 5 and 10% DSF-VE filler loaded composites produced an increased flexural strength of 1.62 and 1.69 times higher than neat VE resin, respectively. Then, an increased trend was evident from the test results obtained from 15 to 20% filler loadings. The flexural modulus remained almost constant with the DSF-VE composites manufactured with filler loading of 15 and 20%. A severe increase in flexural strength was observed in 25% of the DSF loading. The flexural strength was 1.6 times higher than the pure

resin for the filler loading of 25%. The optimum flexural strength of 30% DSF-VE reinforced composite was 149 MPa, and it was about 1.91 times higher than that of vinyl ester resin. Admittedly, the flexural modulus was observed to be highest for 30% filler loading. There was a sinusoidal decrease in flexural strength with filler loadings higher than 30%, due to the agglomeration and incompatibility between higher quantity of DSF and vinyl ester resin [5].

Furthermore, it can be significantly observed that the trend of flexural strength of DSF-VE reinforced composites was similar to the tensile strength for various filler loadings. Fig. 8 shows flexural stress-strain curves of the DSF-VE composites with different filler loadings. The flexural strength of the DSF-VE composites produced a higher maximum value of 149 MPa than the tamarind seed filler/vinyl ester composites of 121 MPa, arundo donax fillers/epoxy composite of 88 MPa, wood apple shell/epoxy of 79 MPa and arundo donax fillers/poly lactic acid of 87 MPa, among other natural filler reinforced polymeric composites.

3.2.3. Impact strength

Un-notched DSF-VE composites were held in Izod Charpy instrument and broken by a pendulum. The recorded average impact energy values of the DSF-VE composites with different filler loadings are present in Fig. 9. These experiments showed that the impact strength of DSF-VE composites increased with an increase in the filler loading. When adding 5% of filler content, there was a slight increase of 5.24% in the impact energy. Importantly, the DSF-VE composites exhibited a maximum impact strength of 17.03 kJ/m² at 30% of filler loading, and it was 43.96% higher than the pure vinyl ester resin. When compared with neat vinyl ester resin, the DSF-VE composites were capable of absorbing high energy to stop crack propagation. The higher impact strength of DSF-VE composites recorded was due to the excellent homogeneous dispersion of filler in the matrix, and it produced an excellent interfacial adhesion. Hence, the crack propagation was prevented and energy was easily

absorbed, thus improving impact strength. On the other hands, poor dispersion of filler increased the tendency to agglomerate the particle, thus minimising their surface areas. Therefore, the crack propagation was increased, and the energy absorption was also less. The phenomenon has explained the decrease in impact strength of 5%, 10%, 45%, and 50% DSF weight loadings of the composites. An increase in impact strength was more pronounced when the filler loading was increased.

3.2.4. Barcol hardness

Fig. 9 depicts the barcol hardness values of the DSF-VE composites with respect to different filler loadings. It was inferred that the DSF was well dispersed all over the matrix and produced an excellent surface roughness. Hence, the hardness increased with an increase in the filler loading. The hardness was 26.33 for the pure vinyl ester resin. In particular, the hardness for 30% addition of DSF increased by 1.94 times that of the neat resin. A similar trend of results was followed by Prabhu et al. [29], as reported on rice husk reinforced with polyester and epoxy. Admittedly, an increasing values of hardness property was produced by increasing the filler loadings, especially between 0% (neat with no filler) and 10% as well as between 15% and optimal threshold filler loading of 30% (Fig. 9).

3.3. Thermal properties

3.3.1. Heat deflection temperature

Heat deflection temperature was performed for the DSF-VE composites, and the test results obtained are shown in Fig. 10. From the results obtained, DSF-VE composite with a filler weight of 5%wt recorded HDT value up to 53 °C. Significantly the HDT was further increased when adding filler content up to the optimum value of 30 wt% at 84 °C. This was 58.49 % higher than that of pure vinyl ester resin. Moreover, after 30 wt% filler weight, the

HDT decreased to 72, 65, 58 and 56 °C with filler weights of 35, 40, 45 and 50 wt%. Evidently, the optimum DSF-VE composite was achieved with a filler weight of 30 wt% from all the tested mechanical properties, such as tensile, flexural, impact and hardness measurements.

3.3.2. TGA and DTA analyses

Thermal degradation profiles of TG and DTA curves of DSF-VE composites are shown in Fig. 11. TGA analysis was carried out continuously since DSF-VE composite specimen reached the nearest millionth of a gram and it was heated to a temperature up to 1000 °C. As the temperature increased, the various components of the specimen burnt off and the residual mass loss % of each can be measured. From Fig. 11, three stages of thermal degradation can be observed; first stages was dehydration (<150 °C), followed by second stage (150 – 400 °C) and the final stage (>400 °C). The initial stage of thermal degradation occurred at 90.2 °C and 120 °C with 10.2% and 8.2% minor weight loss at 5%wt and 30%wt filler, respectively. It was corresponded to the evaporation of moisture in the DSF-VE composites. More significant weight loss took place during the second stage of the process. This second stage process occurred between the temperatures of 150 - 400 °C. At the second stage of degradation, peak temperature was observed at 382 °C and 400.2 °C. This represented a thermal decomposition and de-polymerisation of the DSF-VE composites with the weight loss of 52% and 40% at filler weight of 5%wt and 30%wt, respectively. From the DTA curve, the final degradation of fillers took place at temperatures of 620 °C and 683 °C, with a residual mass loss of 16.87% and 12.83% at 5%wt and 30%wt filler, respectively. It confirmed the thermal de-polymerisation of fixed carbon percentages present in DSF-VE composites. It was significantly evident that the DSF-VE composite withstood more temperature at 30%wt when compared with 5 % wt, and weight loss percentage was lesser at

30% wt when compared with 5 % wt, due to the addition of more filler content into the VE composites [37].

3.3.3. SEM analysis

The SEM micrographs of the tensile fracture surface of DSF-VE composites are shown in Fig. 12. In Fig. 12(a), a certain number of crack formation can be highlighted on the fractured surfaces of the DSF-VE composites with filler loading of 35%, showing a significant evidence of weak filler-matrix adhesion. In Fig. 12(b), few micro-voids were present, due to filler pullout. It can be observed clearly that the filler was evenly distributed in the matrix. Consequently, an improved mechanical strength of the DSF-VE composites was obtained at filler loading of 30% than other composite counterparts and pure resin.

Fig. 13 shows SEM micrographs of fractured flexural DSF-VE composite test specimens with filler loadings of 30% and 35%. Fig. 13(a) indicated that the filler and the matrix were firmly embedded to improve the mechanical strength of the DSF-VE composites with a filler loading of 30%. It was evident from Fig. 13(b) that the DSF-VE composite specimen with a filler loading of 35% was characterised with de-bonding and voids, due to weak interfacial bonding and filler pullout in some fractured surfaces or areas. Consequently, this led to the earlier and greater failure of the composite with a filler loading of 35%.

Similarly, the SEM images of the fractured impact specimens of 30% and 45% of the DSF-VE composites were examined, as shown in Fig. 14. The micrographs obtained at filler loadings of 30% and 45% are presented in Figs. 14(a) and (b), respectively. The filler loading of 30% shows once again a better bonding characteristics with the matrix. When the filler content was increased, less amount of matrix was present in the DSF-VE composite specimens. Therefore, numerous pores were observed and it was also evident from the SEM

micrographs of the DSF-VE composites that optimum weight percent occurred at a filler loading of 30%.

3.3.4. *Water absorption behaviour*

Fig. 15 shows the percentage of water absorption curves for the DSF-VE composites; with average data of three specimens of different filler loadings after immersing the composite specimens in normal, cold, salt and hot water. From Fig. 15, it was evident that an increase in the filler loading percentage in the composites resulted to an increase in the water absorption percentage, because of the hydrophilic nature of the filler material. A similar trend was observed in different natural filler/fibre reinforced composites [31-32]. There was no water absorption for the pure vinyl ester resin at aforementioned four different environments, due to the hydrophobic nature of the resin. It was evident that the hot water environment absorbed more water than the other three environments. The hot water increased the diffusivity phenomenon of the DSF-VE composites. Consequently, micro-crack formation occurred in the filler-matrix interface region [31]. Above loading filler of 30%, the DSF-VE composites absorbed more water in all four different environments, due to the presence of micro voids in composites. At filler loading of 40% and above, the DSF-VE composites contained a lesser amount of matrix, and this led to an increase in the formation of voids. However, a lowest water absorption was recorded with salt water environment when compared with other three environments, because of the presence of large salt (notably sodium chloride) molecules in seawater. The slow penetration of large molecules into the composites produced a smallest moisture absorption percentage [17].

3.4 *Potential Applications*

In the automotive industry, plastics and glass fibre reinforced composites are used as potential materials for automotive and construction parts. Plastics and glass fibres are not biodegradable materials, hence they are harmful to the environment [33]. Moreover, natural filler reinforced polymer composites possess excellent mechanical strength, lightweight, low cost and biodegradability over their synthetic counterparts. Therefore, the present work demonstrated the viability of utilization and feasibility of usefulness of DSF in lightweight automobile applications and home appliances. Figs. 16(a)-(f) show different views of various engineering products of the DSF-VE composites; table fan blade, engine guard for two-wheelers and self-motor guard for four-wheelers were fabricated by using DSF-VE composites.

4. Conclusions

An experimental investigation into the effect of filler loading on mechanical and thermal properties of date palm seed filler reinforced vinyl ester composites has been successfully carried out. Based on the promising results obtained from this study, the following conclusions are subsequently drawn.

- The mechanical and thermal properties of the DSF-VE composites were observed to be dependent on the filler weight percentages, and an optimum filler weight percent was 30%.
- The maximum tensile strength and modulus of DSF-VE composites were around 40.3 MPa and 1.03 GPa, respectively.
- In addition, the flexural and impact tests performed on the DSF-VE composite with a filler loading of 30% exhibited a maximum strength of 149 MPa and 17.03 kJ/m², respectively. The barcol hardness of the pure vinyl ester resin was 26.33 and addition of DSF loading of 30% increased it by 1.94 times that of the neat VE resin.

- The thermal stability tests showed that the heat deflection temperature of the DSF-VE composites increased by 58.49%, when compared with neat, pure vinyl ester resin.
- Furthermore, the water absorption test showed that the lowest and highest percentages of water absorptions were recorded in saltwater and hot water environments, respectively. Also, the percentages of the water absorption increased with an increase in the filler loadings.
- Therefore, with impact strength, tensile, flexural and hardness of the DSF-VE composites increased by 44%, 64.5%, 91% and 93.67%, respectively when compared with the neat, pure vinyl ester resin, it was significantly evident that the DSF-VE composite with a filler content of 30 wt% is a promising and potential material for automotive applications and home appliances. These include, but are not limited to, a table fan blade, an engine guard for two-wheelers and self-motor guard for four wheelers, as demonstrated within the scope of this study.

Acknowledgments

The authors wish to express their sincere appreciations to the management of the ULTRA College of Engineering and Technology, Anna University, Regional Campus Madurai and Sethu Institute of Technology.

References

- [1] Alamri H, Low IM. Effect of water absorption on the mechanical properties of nano-filler reinforced epoxy nanocomposites. *Mater Des* 2012;42:214-22.
- [2] Sun H, Fang Z, Li T, Lei F, Jiang F, Li D, Sun D. Enhanced mechanical and tribological performance of PA66 nanocomposites containing 2D layered α -zirconium phosphate nanoplatelets with different sizes. *Adv. Compos. Hybrid Mater* 2019;407–422.

- [3] Essabir H, Hilali E, Elgharad A, El Minor H, Imad A, Elamraoui A, Al Gaoudi O. Mechanical and thermal properties of bio-composites based on polypropylene reinforced with Nut-shells of Argan particles. *Mater Des* 2013;49:442-8.
- [4] Mittal V, Chaudhry A. U, Matsko N. B. True biocomposites with biopolyesters and date seed powder: Mechanical, thermal, and degradation properties. *Journal of Applied Polymer Science* 2014, 131:1–15.
- [5] Vimalanathan P, Venkateshwaran N, Santhanam V. Mechanical, dynamic mechanical and thermal analysis of shorea robusta dispersed polyester composite. *Inter J Polym Analys Character* 2016;21:314-26.
- [6] Ismail H, Othman N, Komethi M. Curing characteristics and mechanical properties of rattan-powder-filled natural rubber composites as a function of filler loading and silane coupling agent. *J Appl Polym Sci* 2012;123:2805-11.
- [7] Vinod A, Vijay R, Lenin Singaravelu D. Thermo-mechanical characterization of calotropis gigantea stem powder-filled jute fibre-reinforced epoxy composites. *J Nat Fibres* 2017;15:648-57.
- [8] Fiore V, Scalici T, Vitale G, Valenza A. Static and dynamic mechanical properties of Arundo Donax fillers-epoxy composites. *Mater Des* 2014;57:456-64.
- [9] Kumar PAU, Suresha B, Rajini N, Satyanarayana KG. Effect of treated coir fibre/coconut shell powder and aramid fibre on mechanical properties of vinyl ester. *Polym Compos* 2018;39:4542-50.
- [10] Yusriah L, Mariatti M, Abu Bakar A. Mechanical properties of particulate-filler/woven-glass-fabric-filled vinyl ester composites. *J Vinyl Addit Technol* 2010;:16:98-104.
- [11] Chandradass J, Kumar MR, Velmurugan R. Effect of clay dispersion on mechanical, thermal and vibration properties of glass fibre-reinforced vinyl ester composites. *J Reinf Plast Compos* 2008;27:1585-1601.

- [12] Jayabal S, Ramprasath R, Prithivirajan R, Sathiyamurthy S, Christal K. Mechanical performance of bio particulated natural green husk coir fibre-vinyl ester composites. *Inter J Chem Tech Res* 2016;9:65-9.
- [13] Shakuntala O, Raghavendra G, Acharya SK. A comparative investigation of bio waste filler (wood apple-coconut) reinforced polymer composites. *Polym Compos* 2014;35:180-5.
- [14] Rosamah E, Hossain MdS, Abdul Khalil HPS, Dungani R, Omar AKM. Properties enhancement using oil palm shell nanoparticles of fibers reinforced polyester hybrid composites. *Adv Compos Mater* 2016;26:259-72.
- [15] Prabu VA, Uthayakumar M, Manikandan V, Rajini N, Jeyaraj P. Influence of redmud on the mechanical, damping and chemical resistance properties of banana/polyester hybrid composites. *Mater Des* 2014;64:270-9.
- [16] Ruggiero A, Valasek, M. Muller, D'Amato R. Tribological investigation of epoxy/seed particle composite obtained from residues of processing *Jatropha Curcas L.* fruits, *Compos B Eng* 2019;167:654-67.
- [17] Stalin B, Nagaprasad N, Vignesh V, Ravichandran M. Evaluation of mechanical and thermal properties of tamarind seed filler reinforced vinyl ester composites. *J Vinyl Addit Technol* 2019;25: E114-28.
- [18] Babu NBK, Muthukumaran S, Arokiasamy S, Ramesh T. Thermal and mechanical behaviour of the coir powder filled polyester micro-composites. *J Nat Fibres* 2018 doi:10.1080/15440478.2018.1555503.
- [19] Javaid U, Khan Z. M, Khan M. B, Bassyouni M, Abdel-Hamid S. M. S, Abdel-Aziz M. H, Ul Hasan S. W. Fabrication and thermo-mechanical characterization of glass fiber/vinyl ester wind turbine rotor blade. *Composites Part B: Engineering* 2016;91: 257–66.

- [20] Suresha B, Chandramohan G. Three-body abrasive wear behaviour of particulate-filled glass-vinyl ester composites. *Journal of Materials Processing Technology* 2008;200:306–11.
- [21] Boopalan M, Niranjanaa M, Umapathy MJ. Study on the mechanical properties and thermal properties of jute and banana fibre reinforced epoxy hybrid composites. *Compos B Eng* 2013;51:54-7.
- [22] Ashori A, Kiani H, Mozaffari SA. Mechanical properties of reinforced polyvinyl chloride composites: Effect of filler form and content. *J Appl Polym Sci* 2011;120:1788-93.
- [23] Stalin B, Athijayamani A. The performance of bio waste fibres reinforced polymer hybrid composite. *Inter J Mater Eng Innov* 2016;7:15-25.
- [24] Vignesh V, Balaji AN, Karthikeyan MKV. Effect of wood sawdust filler on the mechanical properties of Indian mallow fibre yarn mat reinforced with polyester composites. *Inter J Polym Analys Character* 2017;22:610-21.
- [25] Ben Daly H, Ben Brahim H, Hfaied N, Harchay M, Boukhili R. Investigation of water absorption in pultruded composites containing fillers and low profile additives. *Polym Compos* 2007;28:355-64.
- [26] Nabinejad O, Sujana D, Rahman ME, Davies IJ. Effect of oil palm shell powder on the mechanical performance and thermal stability of polyester composites. *Mater Des* 2015;65:823-30.
- [27] Behzad K. Influence of maleic anhydride on the flexural, tensile and impact characteristics of sawdust flour reinforced polypropylene composite. *World Appl Sci J* 2011;12:1014-6.
- [28] Fiore V, Botta L, Scaffaro R, Valenza A, Pirrotta A. PLA based biocomposites reinforced with *Arundo donax* fillers. *Compos Sci Technol* 2014;105:110-7.

- [29] Prabu VA, Johnson RDJ, Amuthakkannan P, Manikandan V. Usage of industrial wastes as particulate composite for environment management: Hardness, tensile and impact studies. *J Environ Chem Eng* 2017;5:1289-301.
- [30] Petchwattana N, Covavisaruch S, Chanakul S. Mechanical properties, thermal degradation and natural weathering of high density polyethylene/rice hull composites compatibilized with maleic anhydride grafted polyethylene. *J Polym Res* 2012;19:9921-6.
- [31] Velusamy K, Navaneethakrishnan P, Rajeshkumar G, Sathishkumar TP. The influence of fibre content and length on mechanical and water absorption properties of *Calotropis gigantea* fibre reinforced epoxy composites. *J Ind Text* 2019;48:1274-90.
- [32] Ganeshan P, Kumuran SS, Raja KR, Venkateswarlu D. An investigation of mechanical properties of madar fibre reinforced polyester composites for various fibre length and fibre content. *Mater Res Express* 2019;6:1-11.
- [33] Karthikeyan MKV, Balaji AN, Vignesh V. Effect of rope mat and random orientation on mechanical and thermal properties of banana ribbon-reinforced polyester composites and its application. *Inter J Polym Analys Character* 2016;21:296-304.
- [34] Rosamah E, Hossain MdS, Abdul Khalil HPS, Dungani R, Omar AKM. Properties enhancement using oil palm shell nanoparticles of fibres reinforced polyester hybrid composites. *Adv Compos Mater* 2016;26:259-72.
- [35] AlMaadeed MA, Kahraman R, Khanam PN, Madi N. Date palm wood flour/glass fibre reinforced hybrid composites of recycled polypropylene: Mechanical and thermal properties. *Mater Des* 2012;42:289-94.
- [36] Rajesh M, Jeyaraj P, Rajini N. Mechanical, dynamic mechanical and vibration behavior of nanoclay dispersed natural fiber hybrid intra-ply woven fabric composite. *Nanoclay Reinforced Polymer Composites* 2016: 281-296.

- [37] Hu Z, Liu Y, Xu X, Yuan W, Yang L, Shao Q, Huang Y. Efficient intrinsic self-healing epoxy acrylate formed from host-guest chemistry. *Polymer* 2019; 164:79–85.
- [38] Najafi SK, Hamidinia E, Tajvidi M. Mechanical properties of composites from sawdust and recycled plastics. *J Appl Polym Sci* 2006;100:3641-45.
- [39] Wanjun L, Drzal LT, Mohanty AK, Misra M. Influence of processing methods and fibre length on physical properties of kenaf fibre reinforced soy based biocomposites. *Compos B Eng* 2007;38:352-9.

Journal Pre-proof

List of Table

Table 1. Comparison of mechanical properties of the date seed filler/vinyl ester (DSF-VE) composite with other fillers and fibres-based composites.

List of Figures

Fig. 1. Preparation of date seed filler (a) date tree (b) date fruit pulp (c) date seed and (d) date seed filler.

Fig. 2. Fabricated composite plates with different filler loadings.

Fig. 3. Chemical composition of the DSF.

Fig. 4. Effect of filler loadings on tensile strength and tensile modulus of the DSF-VE composites.

Fig. 5. Effect of filler loadings on tensile stress and tensile strain of the DSF-VE composites.

Fig. 6. Effect of filler loadings on tensile load and displacement of the DSF-VE composites.

Fig. 7. Effect of filler loadings on flexural strength and flexural modulus of the DSF-VE composites.

Fig. 8. Effect of filler loadings on flexural stress and flexural strain of the DSF-VE composites.

Fig. 9. Effect of filler loadings on impact strength and hardness of the DSF-VE composites.

Fig. 10. Effect of filler loadings on heat deflection temperature of the DSF-VE composites.

Fig. 11. Effect of filler loadings of (a) 5% and (b) 30% on TGA and DTA of the DSF-VE composites.

Fig. 12. SEM images of the fractured tensile the DSF-VE composite specimen with filler loadings of (a) 35% and (b) 30%, at same magnification of 500 μm .

Fig. 13. SEM micrographs of the fractured flexural surfaces of the DSF-VE composite specimens with filler loadings of (a) 30% and (b) 35%, at magnifications of 200 and 100 μm , respectively.

Fig. 14. SEM micrographs of the fractured impact surfaces of the DSF-VE composite specimens with filler loadings of (a) 30% and (b) 45%, at magnifications of 100 and 50 μm , respectively.

Fig. 15. Effect of filler loadings and water treatments/conditions on water absorption behaviour of the DSF-VE composites.

Fig. 16. The fabricated DSF-VE composite products; showing (a) and (b) table fan blade, (c) and (d) engine guard for two-wheelers and (e) and (f) self-motor guard for four-wheelers.

Journal Pre-proof

Materials	Manufacturing process	Tensile strength	Flexural strength	Impact strength	Hardness	Ref.
-----------	-----------------------	------------------	-------------------	-----------------	----------	------

Journal Pre-proof

Table 1. Comparison of mechanical properties of the date seed filler/vinyl ester (DSF-VE) composite with other fillers and fibres-based composites.

				(MPa)	(MPa)	(KJ/m ²)		
Date seed filler/vinyl	Compression			10.5 –	46 – 149	9.43 –	20.33 –	Present
robusta filler/polyester	Hand lay-up			12 – 15	25 – 26	–	–	[5]
Calotropis gigantea	Hand lay-up			35 – 49	115 –	–	60 – 67	[7]
Arundo donax	Hand lay-up			20 – 48	50 – 88	–	–	[8]
Date palm wood	Injection			15 – 25	–	–	35 – 60	[10]
Boiled egg/coir/vinyl	Compression			24	26	39.5	–	[12]
Alumina/coir/vinyl	Compression			27	31	40.5	–	[12]
Groundnut/coir/vinyl	Compression			29.5	34	42	–	[12]
Termite mount	Compression			30	36	46	–	[12]
Rice husk/coir/vinyl	Compression			32	39	53	–	[12]
Wood apple	Hand lay-up			18 – 44	41 – 79	–	–	[13]
Coconut shell/epoxy	Hand lay-up			18 – 41	41 – 68	–	–	[13]
Oil palm shell/kenaf–	Hand lay-up			30 – 38	60 – 77	–	–	[14]
Tamarind seed	Compression			9 – 34.1	47 – 121	7 – 14	23 –	[17]
wood flour/pulp	Injection			6 – 17	18 – 42	–	–	[22]
Oil palm shell	Hand lay-up			29 – 41	43 – 62	–	–	[26]
Sawdust	Injection			25 – 30	50 – 54	–	–	[27]
Arundo donax	Melt			31 – 50	62 – 87	–	–	[28]
Rice hull/polyethylene	Injection			19 – 26	19 – 30	11 – 16	–	[30]
Nano oil palm	Compression			30 –	60 –	10 –	–	[34]
shell/kenaf coconut Nanoclay/	moulding Compression			37.56 15 –	60.15 34 –	13.17 –	–	[36]
Sawdust/recycled	Compression			9 – 13	21 – 35	–	–	[38]

as



Figure 1

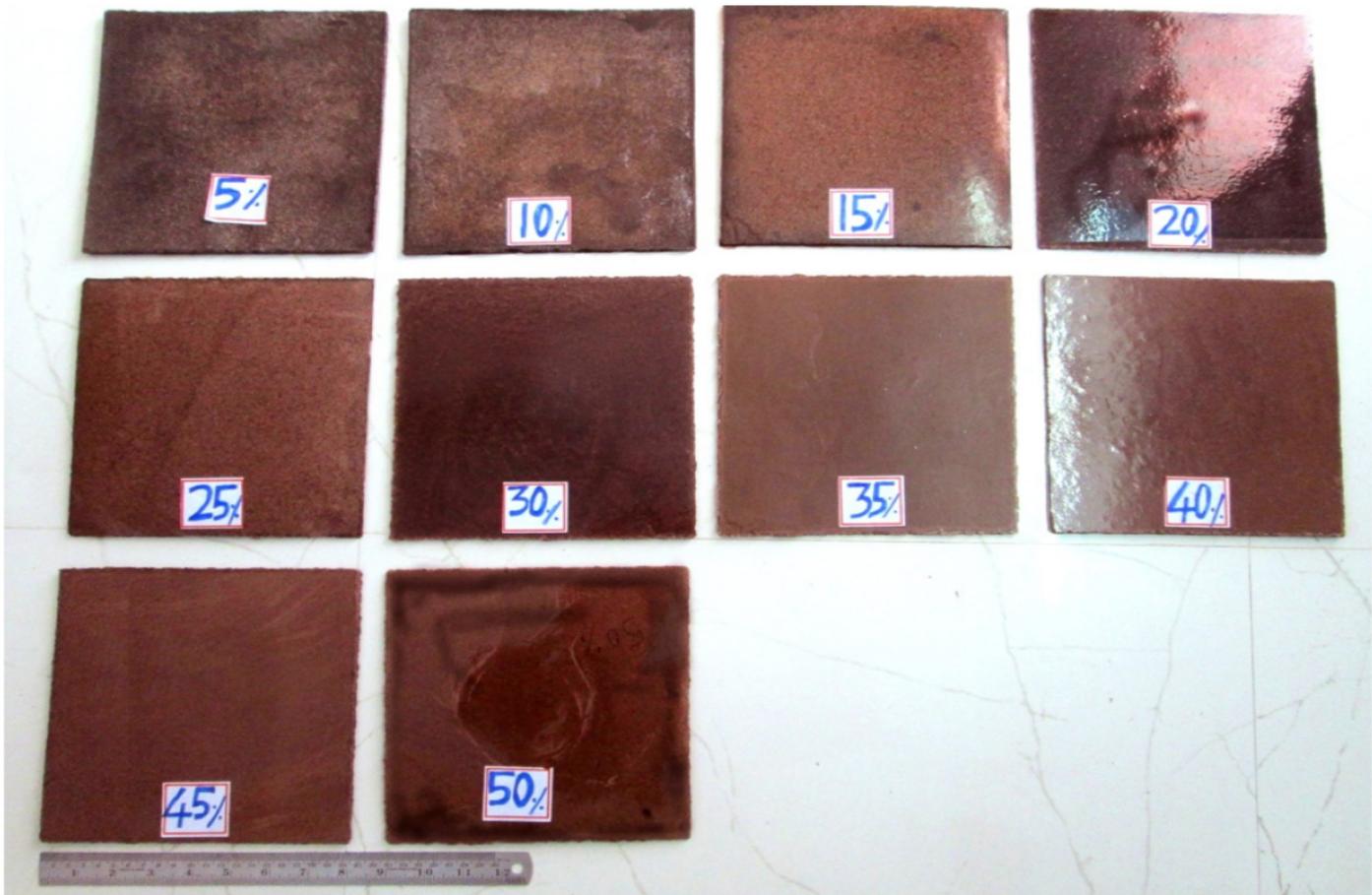


Figure 2

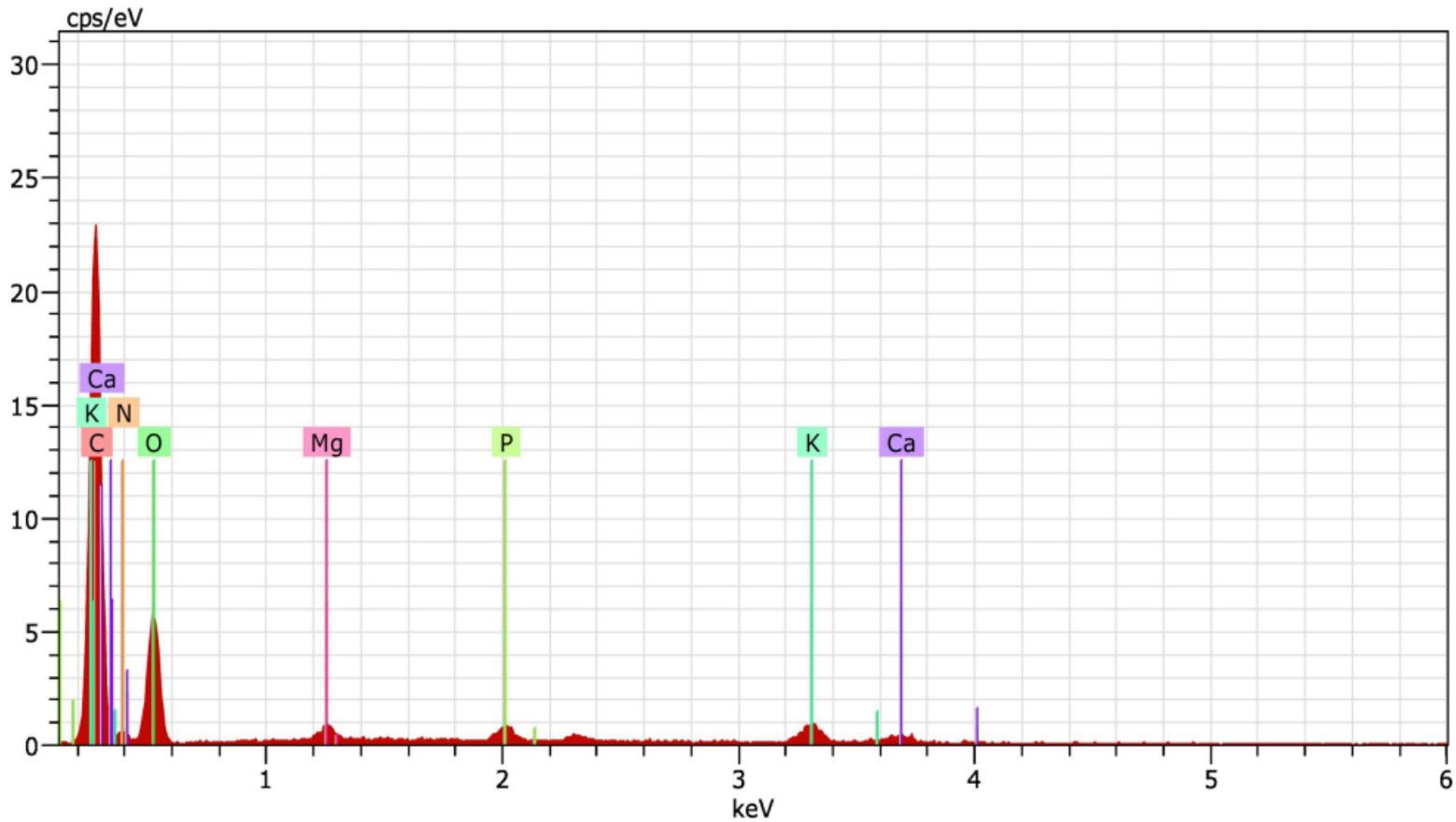


Figure 3

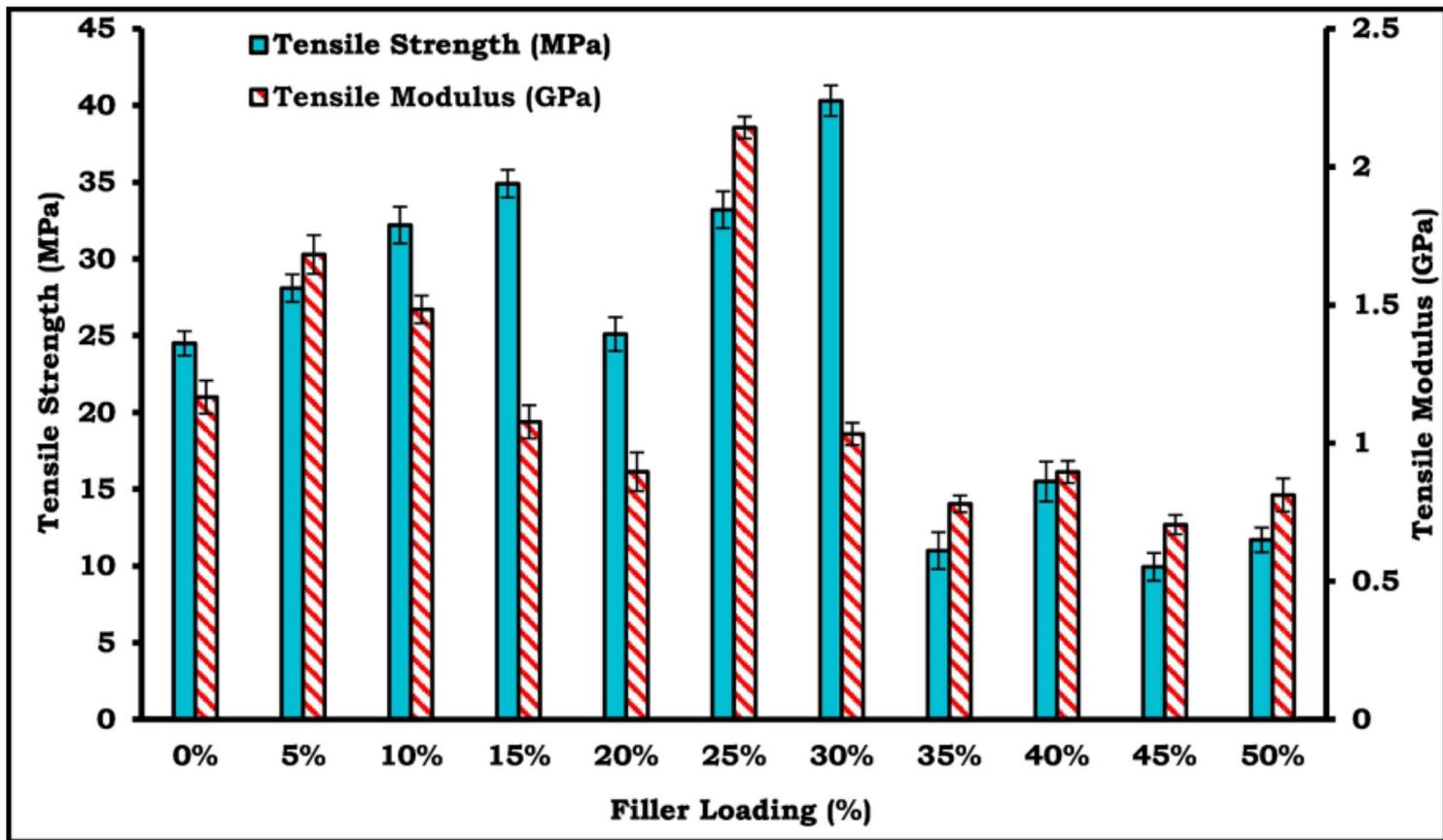


Figure 4

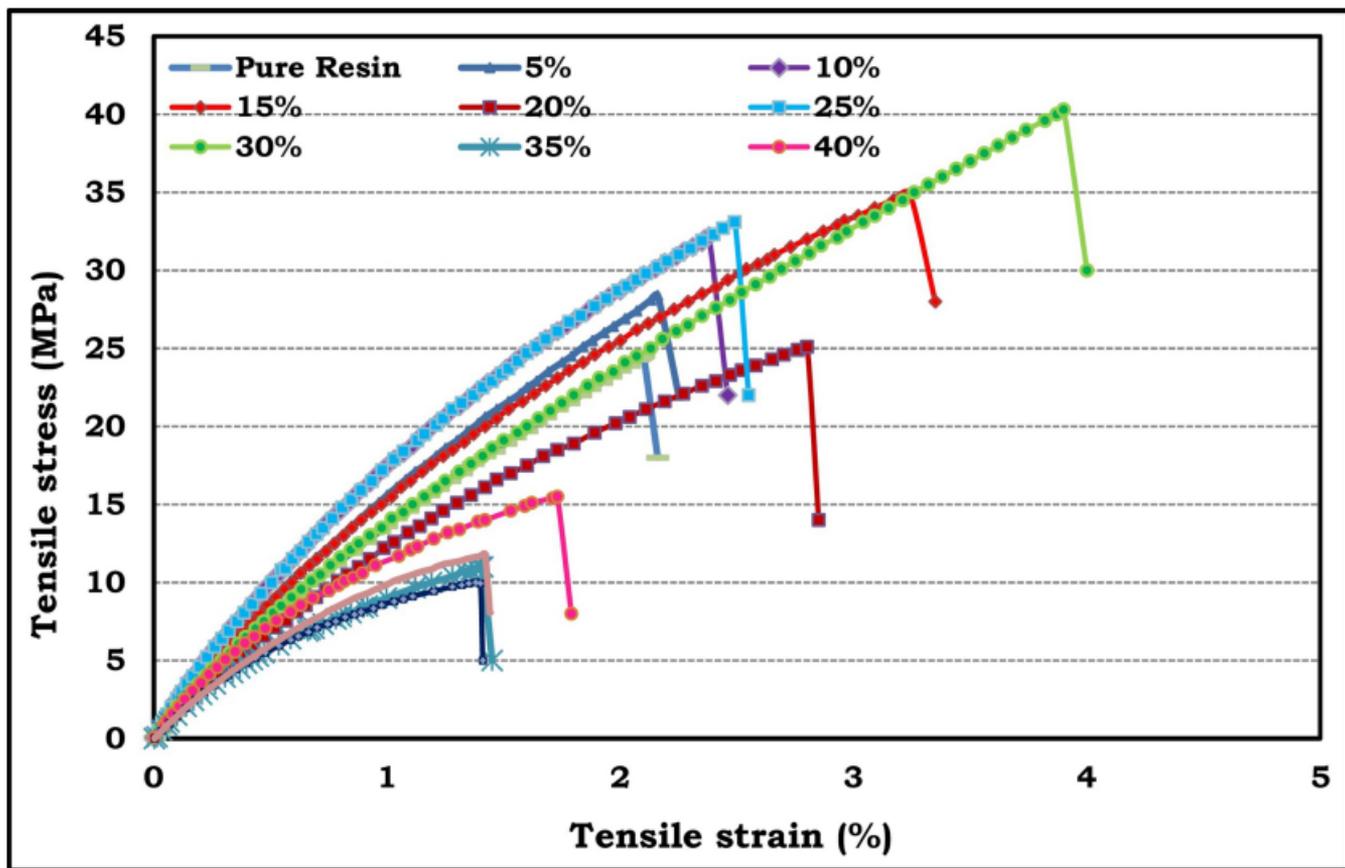


Figure 5

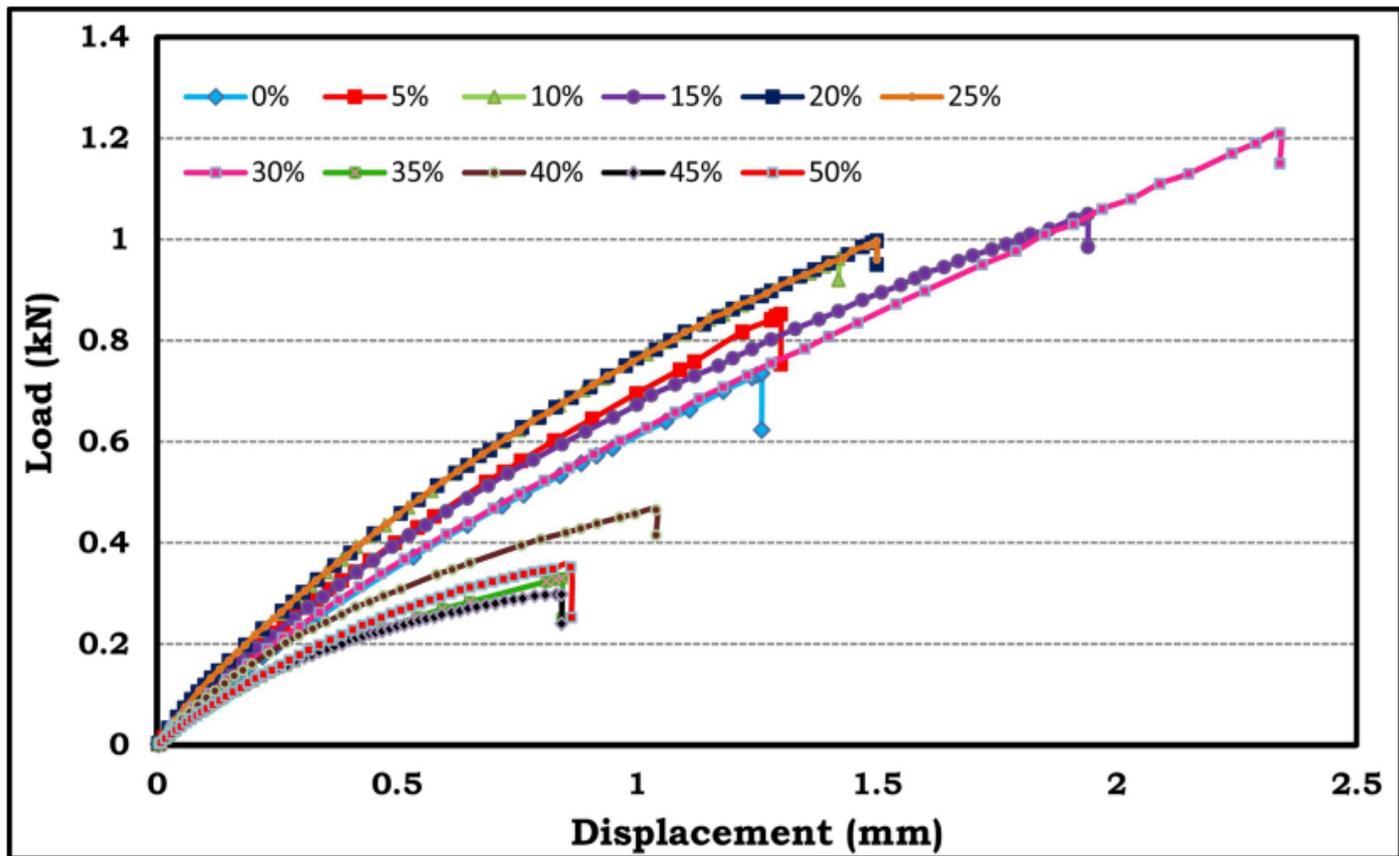


Figure 6

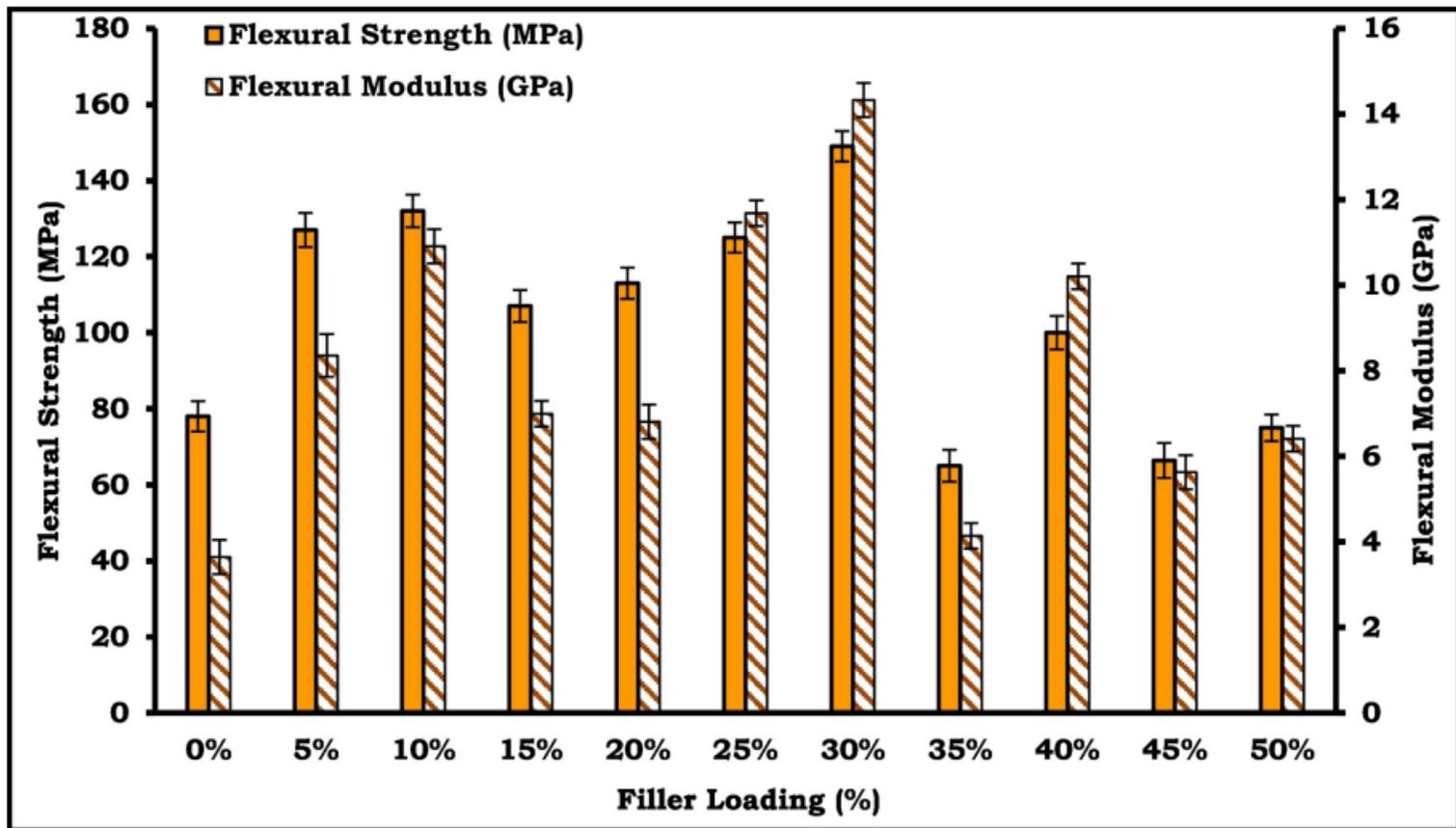


Figure 7

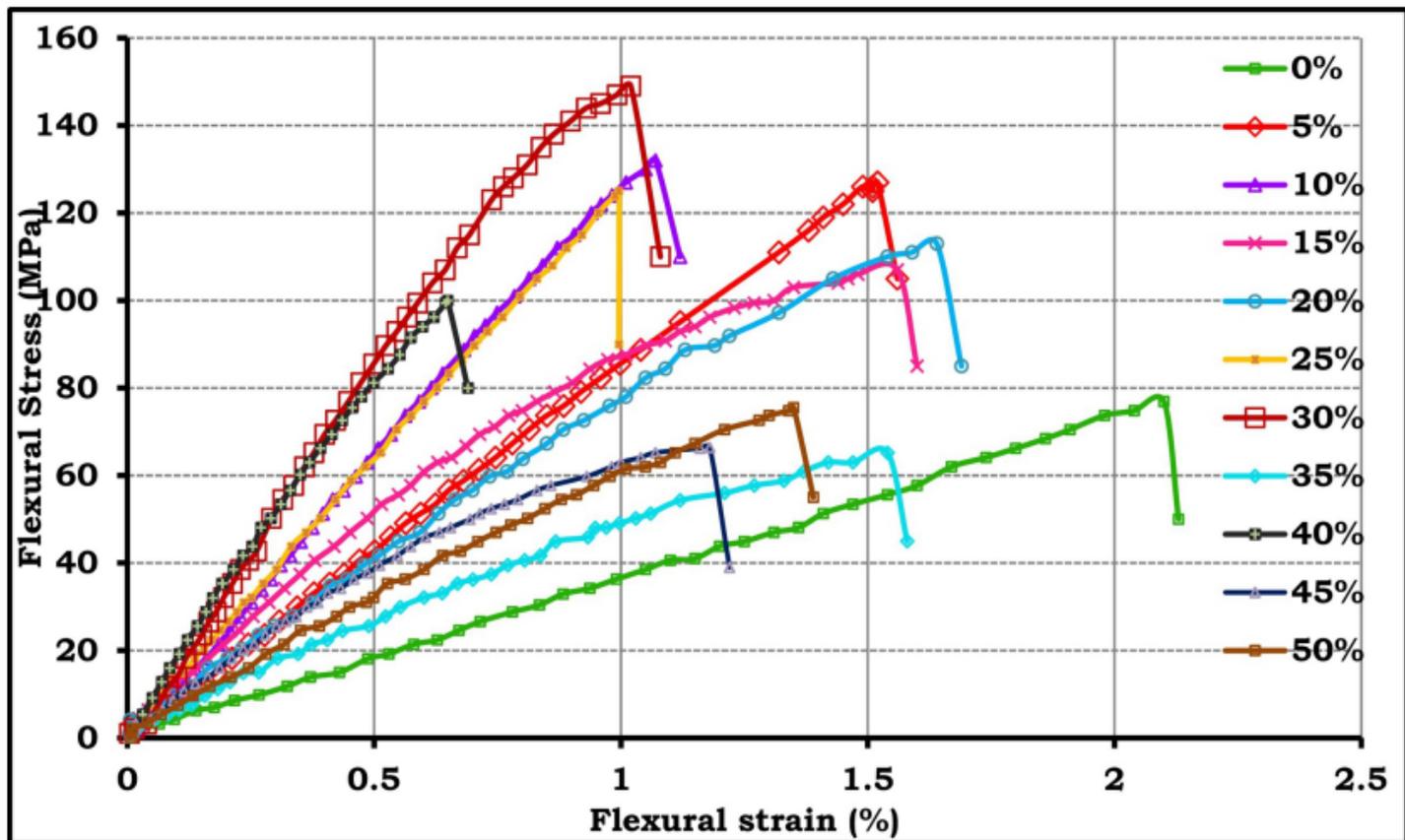


Figure 8

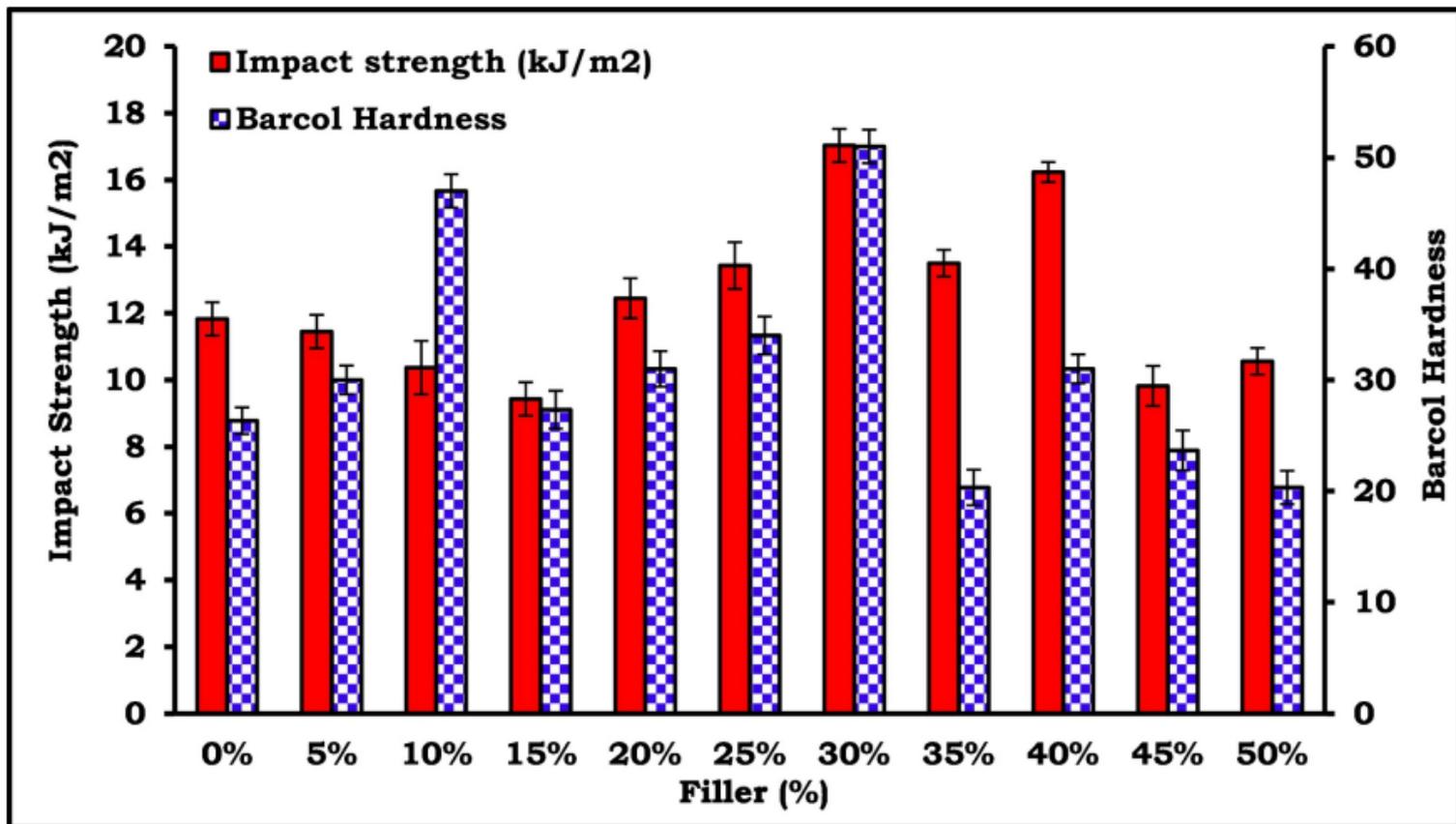


Figure 9

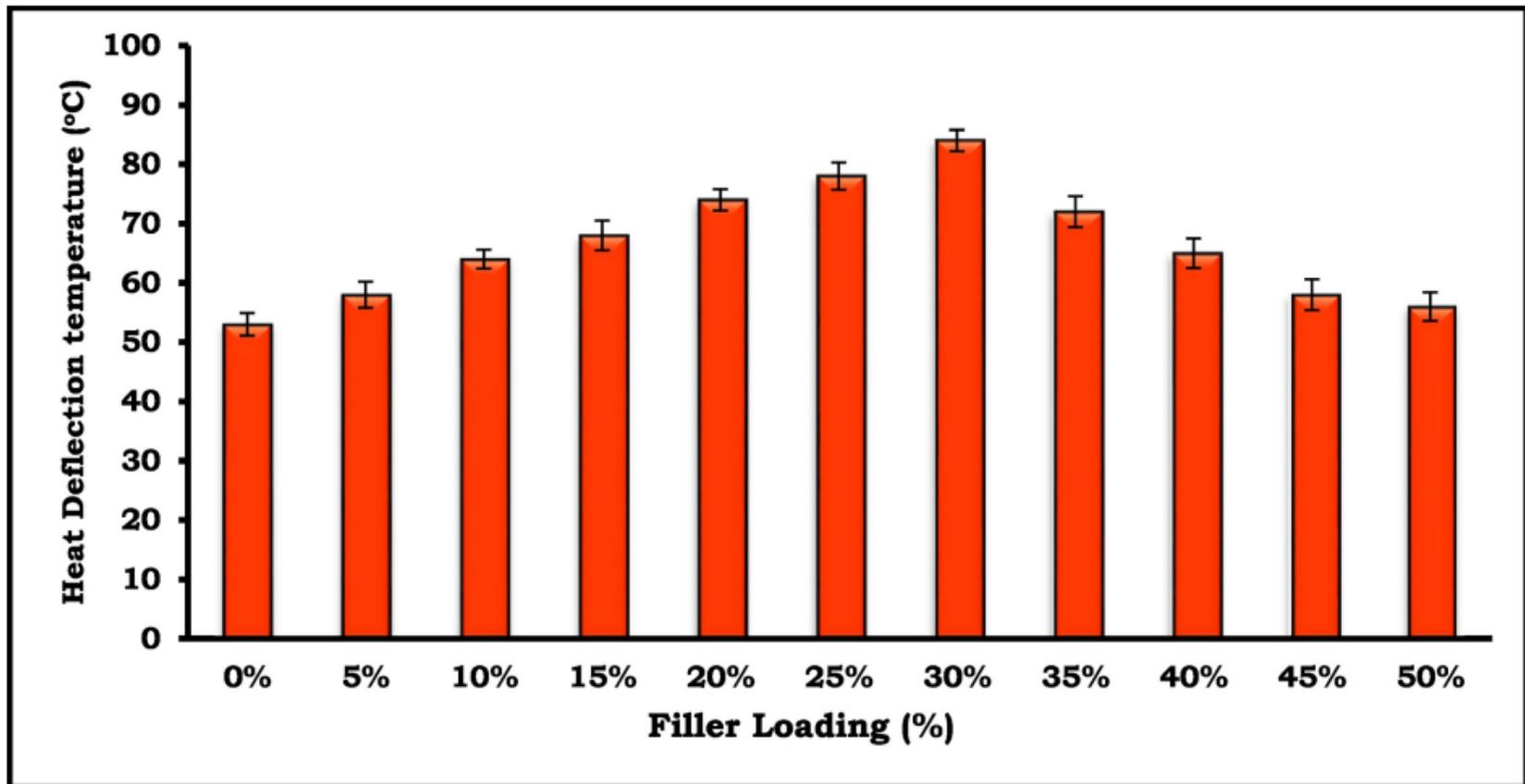
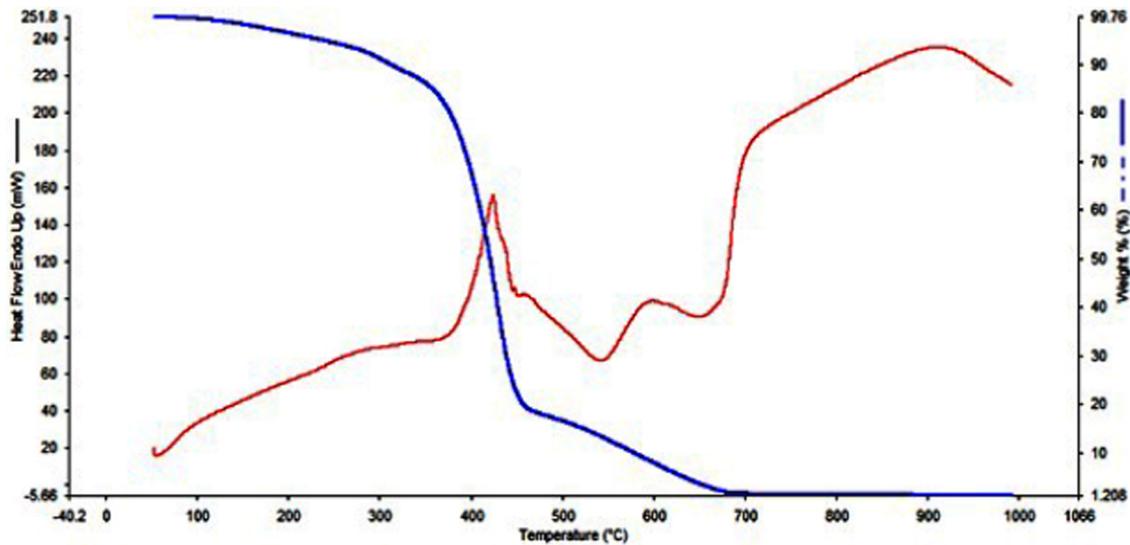
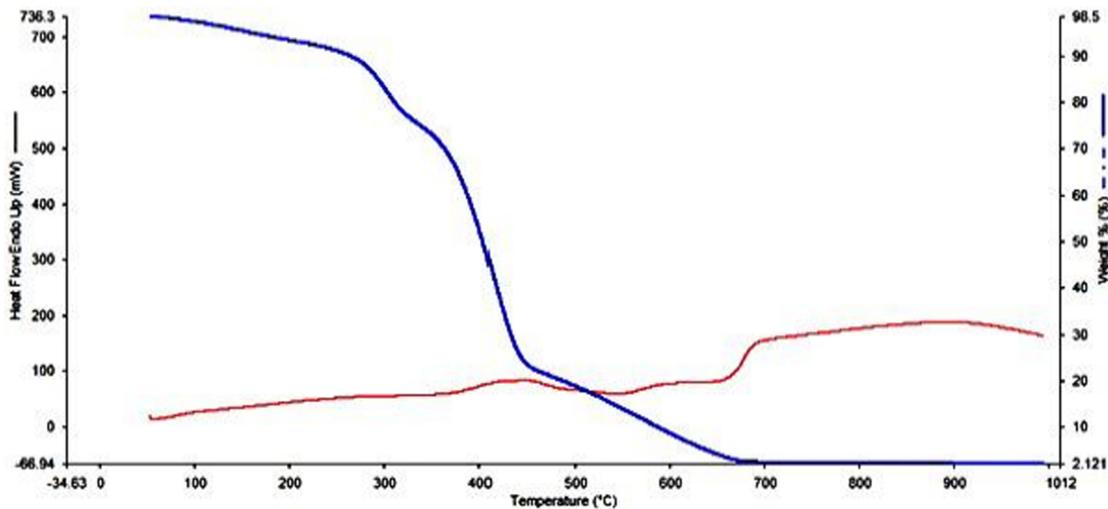


Figure 10



(a)



(b)

Figure 11