



Dynamic Mechanical Analysis of Bio-Based and Synthetic Petroleum Based Polymer Foams with Powder Type Organic Filler at Prolonged Ultra-Violet Exposure

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DOI: <https://doi.org/10.30880/emait.2020.01.01.006>

Received 09 September 2020; Accepted 30 November 2020; Available online 30 December 2020

Abstract: Wood powder filler applied to the bio-based and epoxy polymer foams has the potential to reinforce the polymer foam structure. The 'Meranti' wood filler type was used as the filler in this analysis. In order to observe the pore size of each sample when exposed to different hours of UV exposure using optical microscopy (OM), this study was made. This analysis was conducted to compare the mechanical properties of each sample with different filler ratios of 0 wt%, 5 wt%, 10 wt%, 15wt% and 20 wt% at different UV exposure hours, which is 0 hour to 6000 hours with a 2000 hour rapid increase. Using the DMA Q800 TA unit, the mechanical properties were studied. In order to obtain the product of their mechanical properties, samples having a scale of 40 x 10 x 5 mm were clamped into the machine. The results will show the value of $\tan \delta$, loss modulus and storage modulus from the DMA test. The $\tan \delta$ value shows that the high $\tan \delta$ value will be produced by the higher ratio filler. In contrast to bio-based polymer foams, epoxy polymer foams with powder fillers have the highest $\tan \delta$ value. It shows that the higher filler ratio can be reported with the lower $\tan \delta$ value. As the filler ratio in the polymer foams increased, the consequence of storage and loss modulus was found to increase. The greater the modulus of loss and the modulus of storage, the lower the temperature. As energy is lost as heat during UV irradiation exposure, bio-based polymer foams with a high powder filler ratio can dissipate more energy.

Keywords: Epoxy, Bio-based, Wood Powder Filler, UV Irradiation, Tan Delta, Storage Modulus, Loss Modulus

1. Introduction

To form a foam, polyurethane (PU) foams are made of a blended solid and gas phase. This usually happens by too quickly combining the two stages for the system to react in a smooth fashion. The resulting foam has a polymer matrix, described as either a closed-cell structure or an open-cell structure, containing either air bubbles or air tunnels. Closed-cell foams are usually stronger, whereas open-cell foams are normally flexible. The characteristics of polymer foam can be adjusted by changing the chemical composition of the raw materials, in particular polyol and isocyanate, in which the properties of the polymer mainly depend on the shape of the polymer, such as the functionality and the value of hydroxyl [1]. The reason people are commonly used is that it has a lot of advantages, such as low density and weight, low heat transfer, which make them an excellent insulator and acoustic insulating properties. Other than that, it's also flexible and soft [2].

Moreover, during exposure to the environment, polyurethane foam properties can be affected. Ageing is caused by the air oxygen reaction, which encourages the polymer's photo-oxidation. Via a radical chain process, the photochemical

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reaction in the polymer occurs and depends on the length and intensity of light exposure [3]. It manufactures renewable polymers from natural resources. The use of these tools may reduce the use of petroleum as an ingredient in polymer foam production and may also reduce the pollution of the atmosphere. Vegetable oils, as they are inexpensive, readily available and sustainable, are among the renewable potential sources for polyols in the PU foam market [4-5].

Therefore, bio-based and petroleum-based PU foams will be used for development in this research. To test the mechanical and physical properties and its resistance to ultraviolet (UV) irradiation exposure on polymeric foams, these foams will be applied to the organic wood filler in the foam composite. Using the Optical Microscope (OM) test, the Ultra-Violet (UV) test and the Dynamic Mechanical Analysis (DMA) test, the properties of polymeric foams were studied.

2. Materials and Methods

The polymer foams based on bio-based and synthetic petroleum with organic wood powder filler were prepared in the laboratory. Before undergoing DMA analysis to study the temperature, frequency or time, the polymer foams will be cut into several pieces according to the appropriate dimension. The polymer foams often need to extend exposure to UV irradiation for up to 6,000 hours. Before and after undergoing UV irradiation exposure, morphological examination must be carried out. The morphological test and DMA analysis data were gathered and analyzed.

2.1 Preparation of sample

The second stage in this analysis is sample preparation. In this study, the sample used was bio-based polymer foams and polymer foams based on synthetic petroleum mixed with Meranti wood filler. Research has shown that it is possible to reinforce mechanical and physical polyurethane foams by inserting filler. To create a homogeneous mixture, approximately 5-20 percent of wood fibre was used [6]. Foams were prepared and cut into beams in a cylindrical shape. The polymer foam was 5x40x10 mm in dimension. For synthetic petroleum-based polymers, the foams were called E, E5P, E10P, E15P and E20P, and for bio-based polymer foams, B, B5P, B10P, B15P and B20P.



Fig. 1 - Preparations of samples

| Type of foams | Samples Name | Filler ratio (%wt) |
|---------------|--------------|--------------------|
| Epoxy | E | 0 |
| | E5P | 5 |
| | E10P | 10 |
| | E15P | 15 |
| | E20P | 20 |
| Bio-Based | B | 0 |
| | B5P | 5 |
| | B10P | 10 |
| | B15P | 15 |
| | B20P | 20 |

2.2 Microscopy Analysis of Polymer Foams

Polymer foams must be subjected to optical microscope morphological testing [7]. For the study of the cell structure of foams and the examination of the foam binding filler, this test was essential. After and before exposure to UV radiation, study using an optical microscope was performed. A piece of foam will be placed on the point below the objective lens. The cell structure's diameter was calculated in three repeats. In order to ensure that the filler binder is well connected to the structure, this test further includes an inspection of the binding filler on the foams.

2.3 UV Irradiation Exposure

In urethane production, PU foams are usually one of the most important materials. It is possible to modify the characteristics of PU foam by altering the chemical composition of the raw materials, in particular polyol and isocyanate, where the properties of PU foam depend primarily on the types of polyol, such as functionality and hydroxyl value[8]. Until undergoing morphological analysis using the Optical Microscope, the samples will be exposed to UV radiation. For synthetic petroleum-based polymer foams, approximately 3 to 5 samples of each polymer foam are classified as E, E5P, E10P, E15P and E20P, whereas for bio-based polymer foams, B, B5P, B10P, B15P and B20P. At least 2000 hours of UV radiation must be submitted to each hour of UV irradiation. With an increase of 2000 hours, each sample was exposed to UV radiation from 0 hours to 6000 hours. In addition, during exposure to the environment, PU foam properties may be affected. Light-exposed polymeric materials may lead to their ageing, which is related to the break-up of the polymer chain by the 300-400 nm wavelength action of UV radiation [9].

2.4 Dynamic Mechanical Analysis

In order to determine the relative rigidity and damping properties, dynamic mechanical analysis methods are commonly used to investigate the structures and viscoelastic behaviour of polymeric and composite materials. The storage modulus, loss modulus, and the damping coefficient ($\tan \delta$, ratio modulus to storage modulus) were reported depending on the temperature, frequency or time. Results were typically reported as a graphical loss modulus, storage modulus, and $\tan \delta$ versus temperature graph. DMA offers details on the transition regions in polymers and composites, such as $\tan \delta$, which may be used for quality assurance purposes or for the development of products[10]. DMA Q800 TA was the device involved in this. Table 2 show the parameter setting in a single cantilever bending form on the DMA system, a piece of beam-shaped foam was clamped.

Table 2 - Parameter value for DMA testing

| Parameters | Value |
|------------------|---------------------------------|
| Test frequency | 1 Hz |
| Temperature ramp | 25°C/ min to 180°C |
| Dimension | Rectangular (40mm X 10mm X 5mm) |

3. Result and Discussion

For the polymeric foams which were subjected to UV irradiation for 0 to 6,000 hours, the result of DMA was obtained. The disparity in every 2,000 hours is seen by this outcome.

2.5 Morphological Test Data

In Figure 2, the structure of the epoxy polymer has a transparent surface than the bio-based polymer foams. Biobased polymer foams are stickier than epoxy polymer foams and more brownish. The colour of polymer foams would become more brownish as the polymer foams undergo UV irradiation exposure. Foams are also tougher and more fragile. The average pore size of the unfilled epoxy polymer is shown in Figure 3 at 0, 2000h, 4000h and 6000h upon sustained UV irradiation. When the irradiation of UV exposure is greater, the pore size shrinks [11].



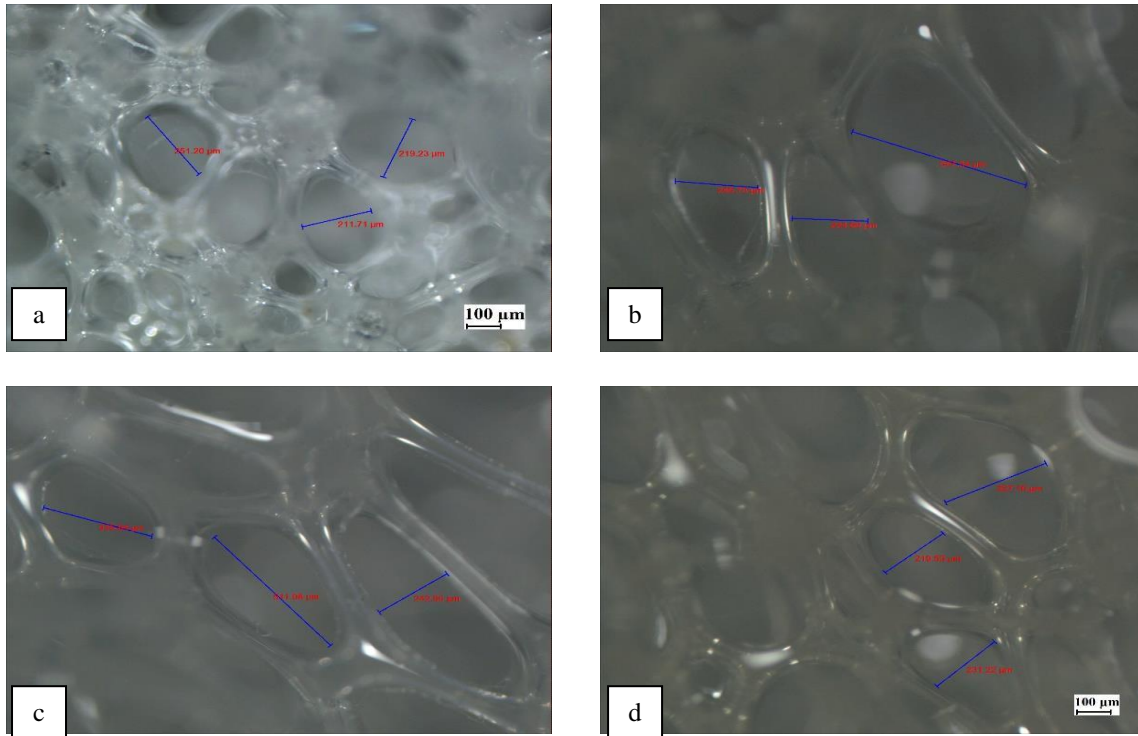


Fig. 3 - Optical microscopy image for unfilled epoxy polymer exposure at (a) unirradiated exposure, (b) 2000h UV, (c) 4000h UV exposure and (d) 6000h UV exposure. Scale bar: 100μ

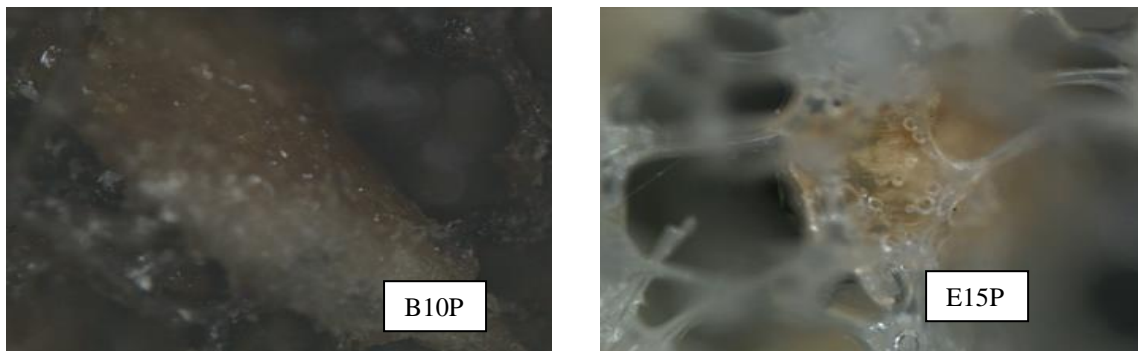


Fig.4 - Microscopic structure of binding filler at samples. Scale bar: 100μ

Table 3 - Pore size of bio-based and epoxy with the respective composite upon prolong UV irradiation exposure

| Composite | wt % | 0 h UV | 2000h UV | 4000h UV | 6000h UV |
|---------------|------|--------|----------|----------|----------|
| Bio-Based (B) | 0 | 431.52 | 36.79 | 59.03 | 213.66 |
| | 5 | 191.07 | 283.99 | 249.90 | 75.86 |
| | 10 | 278.95 | 290.64 | 294.40 | 94.76 |
| | 15 | 218.61 | 296.45 | 230.19 | 277.69 |
| | 20 | 162.87 | 118.22 | 323.67 | 218.28 |
| Epoxy (E) | 0 | 208.00 | 339.25 | 379.64 | 259.30 |
| | 5 | 227.38 | 190.08 | 226.94 | 171.99 |
| | 10 | 350.70 | 162.18 | 209.74 | 212.97 |
| | 15 | 253.49 | 205.65 | 266.30 | 243.62 |
| | 20 | 224.86 | 242.73 | 205.34 | 302.32 |

The B10P and E15P powder fillers bind well to polymer foams, as shown in Figure 4. It is convenient to see epoxy-based polymer foams as having a basic structure rather than bio-based polymer foams. The binding filler's function is to

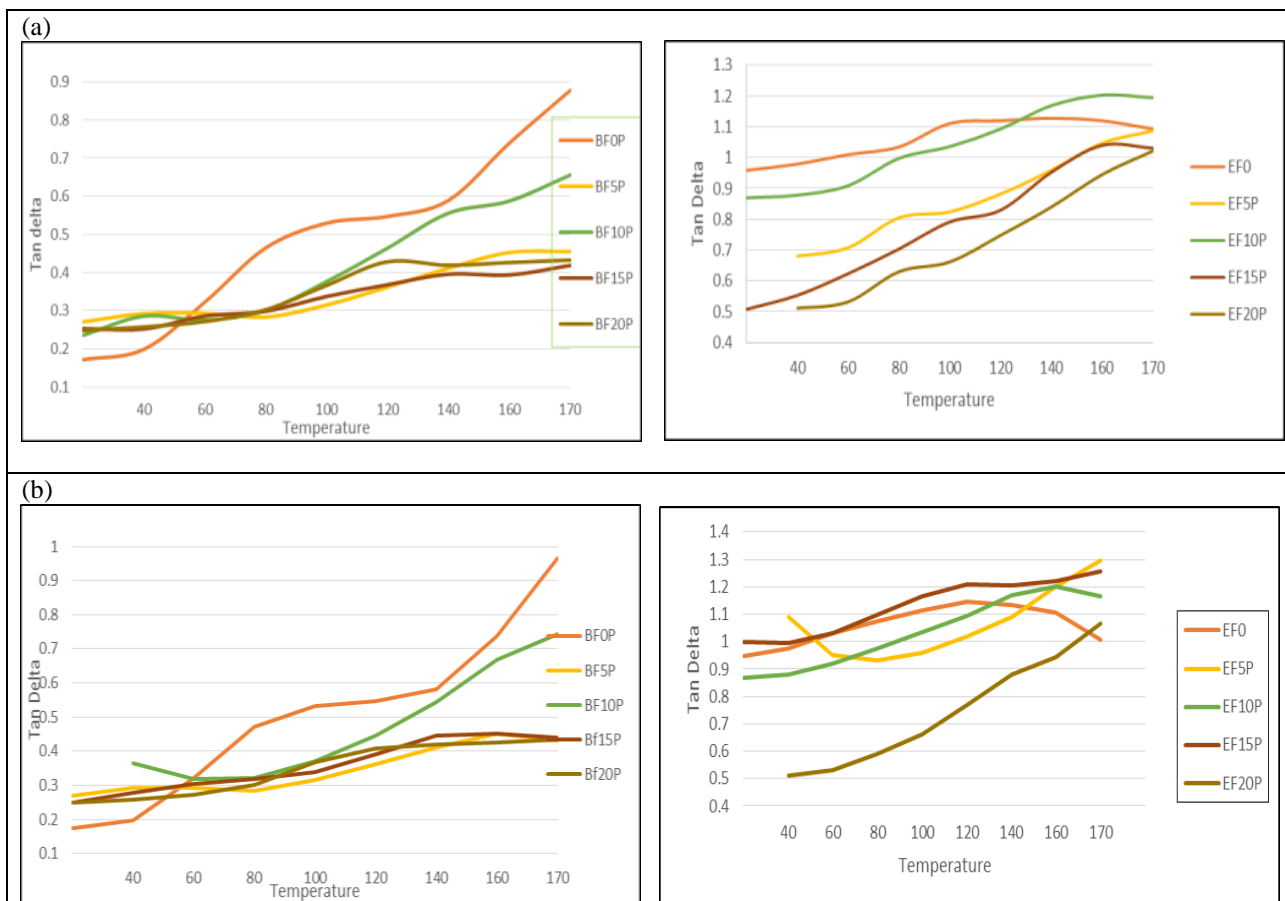
increase the strength of the polymer foams' elasticity. The colour of polymer foams can become more brownish when polymer foams are exposed to UV radiation.

The maximum pore size value calculated from bio-based polymer foams without powder filler at a non-irradiated UV exposure of $431.25 \times 10^{-6} \text{ m}$ is shown in Table 3. However, from a study of bio-based polymer foams without powder filler with a 6000h UV irradiation value of $59.03 \times 10^{-6} \text{ m}$, the smallest was also calculated. The high UV radiation temperature causes the sample pore size to shrink [11].

2.6 Tan Delta (δ)

The tan δ value for bio-based and epoxy and its composite at unexposed UV, 2000h UV, 4000h UV and 6000h irradiation exposure are shown in Figure 5-6. As compared to bio-based composite foams, the epoxy has a higher tan δ value. Unfilled bio-based polymer foams (B) have the highest tan δ value for bio-based foams, whereas unfilled epoxy polymer foams (E) have the highest tan δ value for epoxy when UV irradiation is not exposed, as shown in Figure 6a. The lower the composite chains are, the higher the density of cross-linking. A high filler concentration may lead to a drop in the value of the tan δ [12]. The unfilled bio-based polymer foams (B) have the highest tan δ value for bio-based foams, while epoxy has the highest tan δ value for epoxy polymer foams at 2000h UV irradiation exposure with 15wt% concentration filler (E15P) from Figure 6b. This suggests that E15P has a low crosslink density because, among others, it displayed a higher tan δ value.

Figure 6c shows that unfilled bio-based polymer foams (B) have the highest tan δ value for bio-based foams, while epoxy has the highest tan delta value for epoxy polymer foams at 4000h UV irradiation exposure with 10 wt percent concentration filler (E10P). The low crosslink density in E10P was due to the filler concentration that resulted in a greater tan δ value. When subjected to UV irradiation for 6000 hours, E10P still has the greatest tan δ in Figure 6d. From the findings, loading filler into the PU could give the materials more elasticity. The over filler addition can decrease the composite's tan δ value.



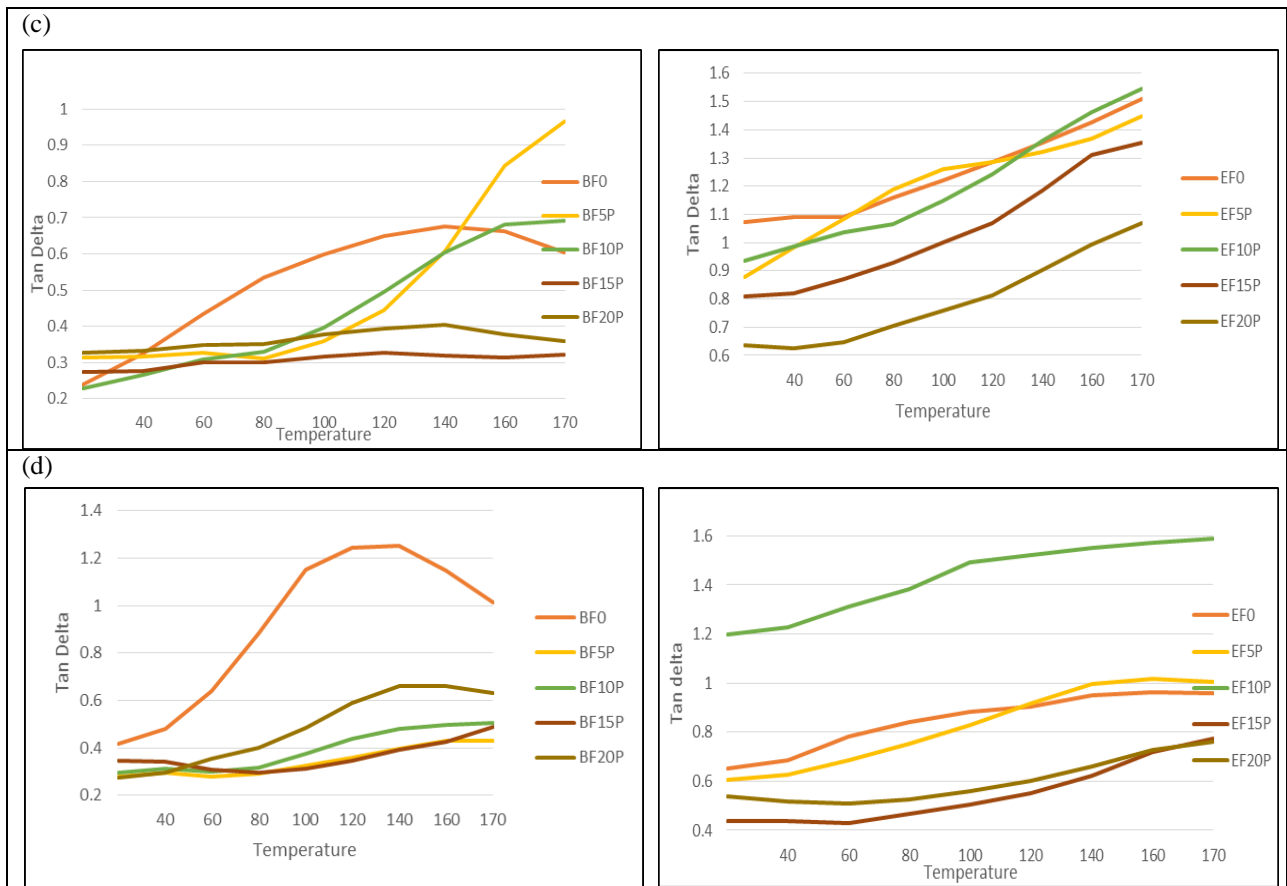


Fig. 5 - A comparison curve for B and E with its composites at (a) unexposed (b) 2000h (c) 4000h and (d) 6000h UV irradiation exposure

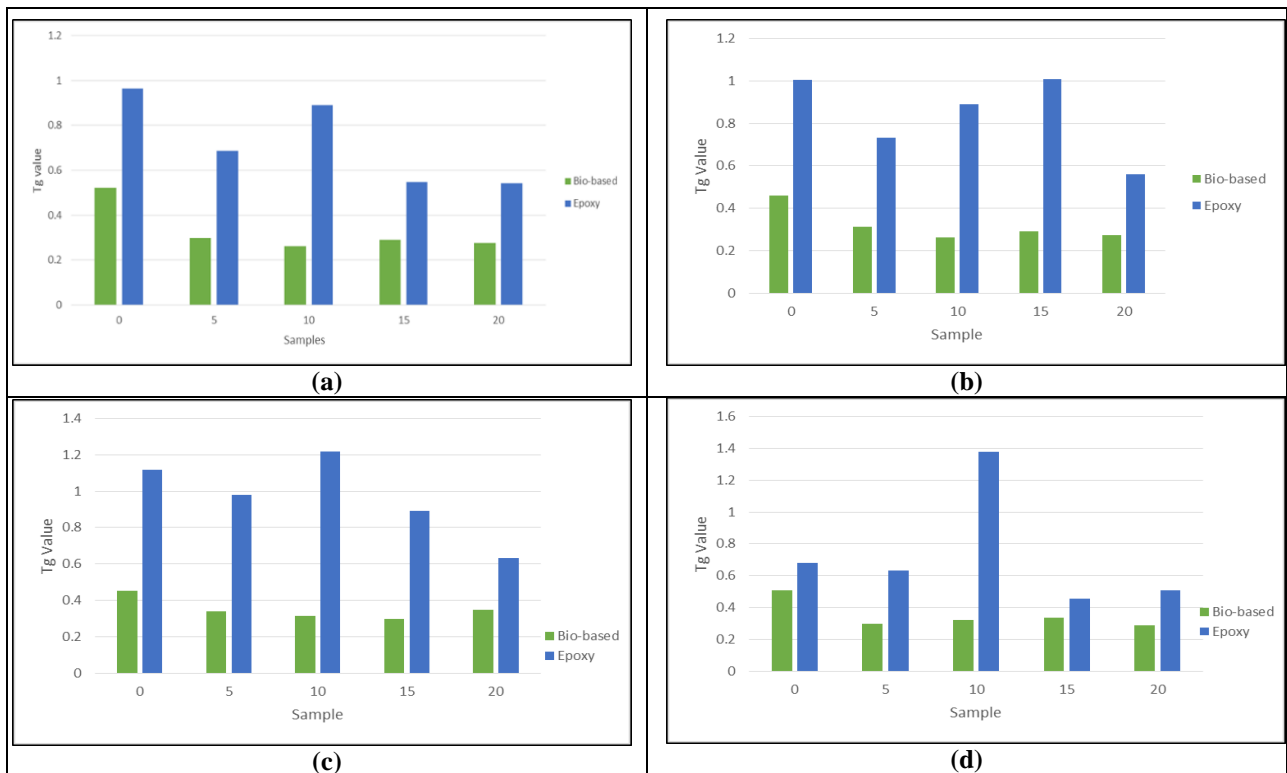
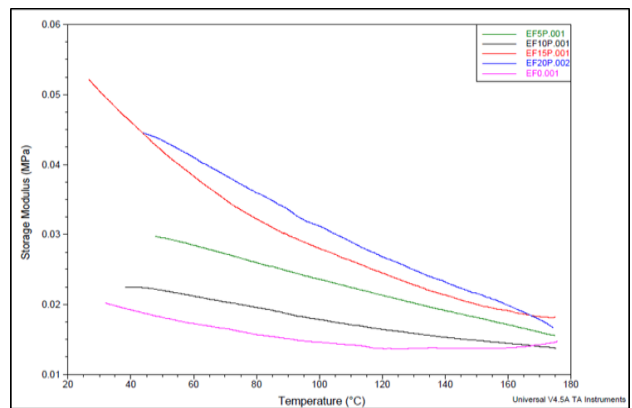
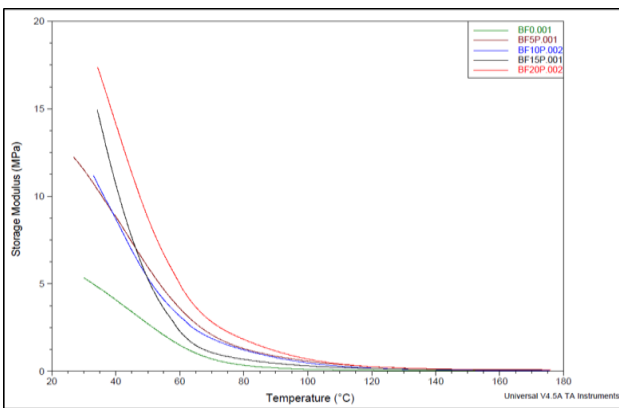


Fig. 6 - Comparison chart of $\tan \delta$ for epoxy and bio-based polymer foams at (a) unexposed UV (b) 2000 hours UV (c) 4000 hours UV and (d) 6000 hours UV

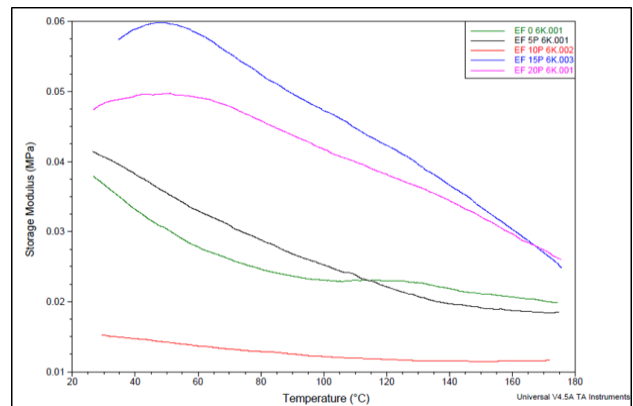
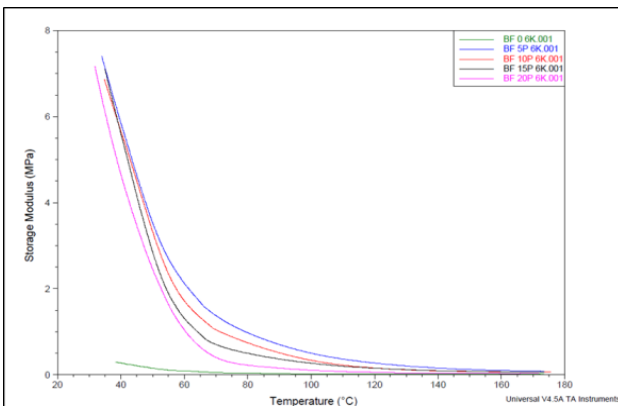
2.7 Storage Modulus

Figure 7-8 shows the data for the bio-based and epoxy storage modulus with its composite when subjected to unirradiated UV irradiation at 2000, 4000, and 6000 hours. The storage modulus is critical for measuring the composite's capacity to store energy. Figure 8a shows that, relative to other epoxies, E15P has the highest storage module value, while B20P has the highest storage module relative to other bio-based composites when not subjected to UV irradiation. Compared to other bio-based composites, B20P samples still have the highest storage modulus in Figure 8b, while E20P correlates with other epoxy composites at 2000h UV irradiation exposure. These findings indicate that a higher storage module value vmay be induced by high filler concentration. [13].

Figure 8c indicates that B15P and E20P have the highest storage modulus value at 4000h UV irradiation exposure relative to other bio-based and epoxy composites. The higher concentration results in higher storage modulus in the composite. Figure 8d indicates that at 6000h UV irradiation exposure, B20P and E15P were indicated with the highest storage modulus. The increase in cross-linking density storage modulus was due to the filler reaction in the composite. Filler concentration can affect the composite in order to store energy.



(a)



(b)

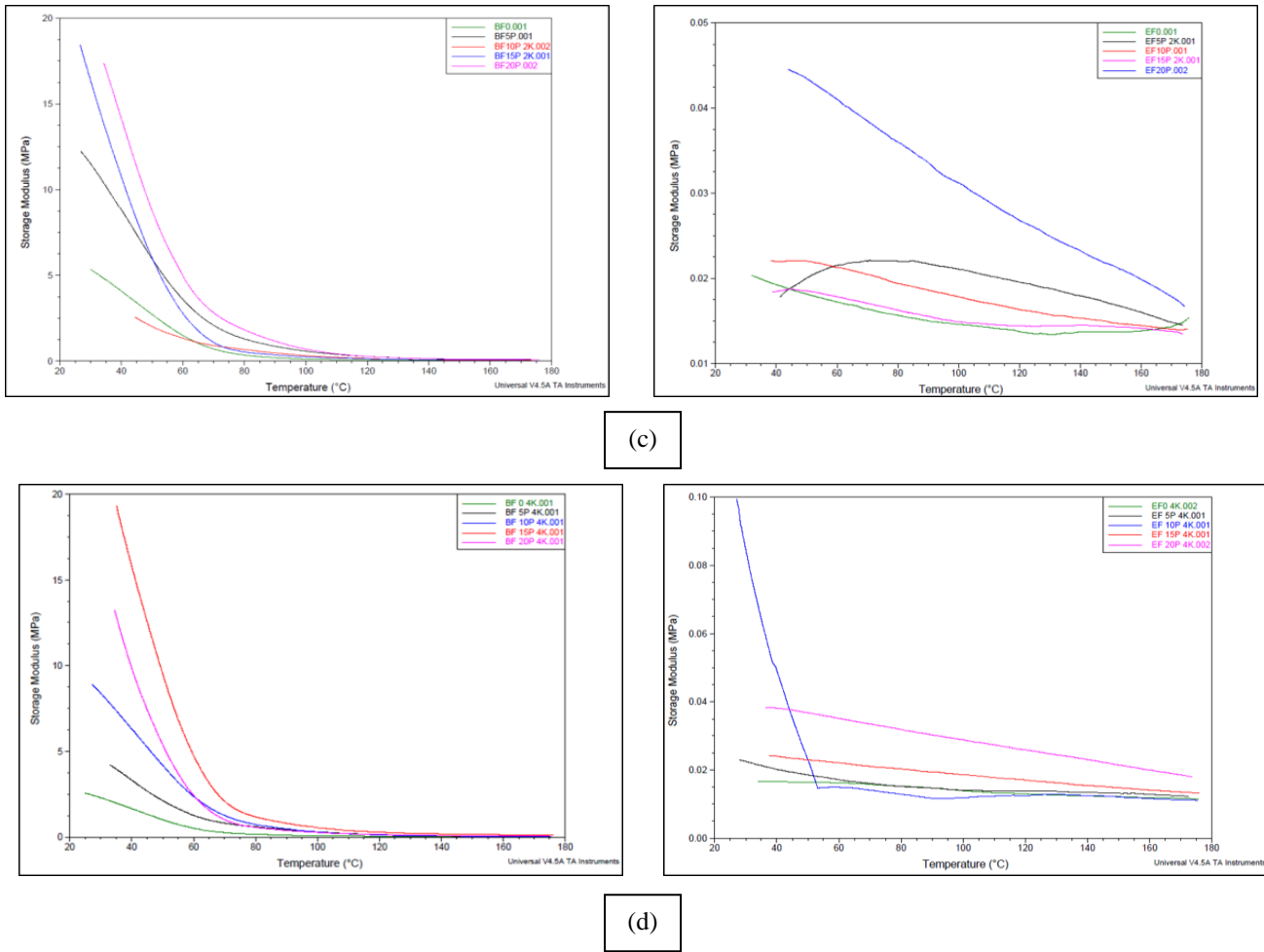
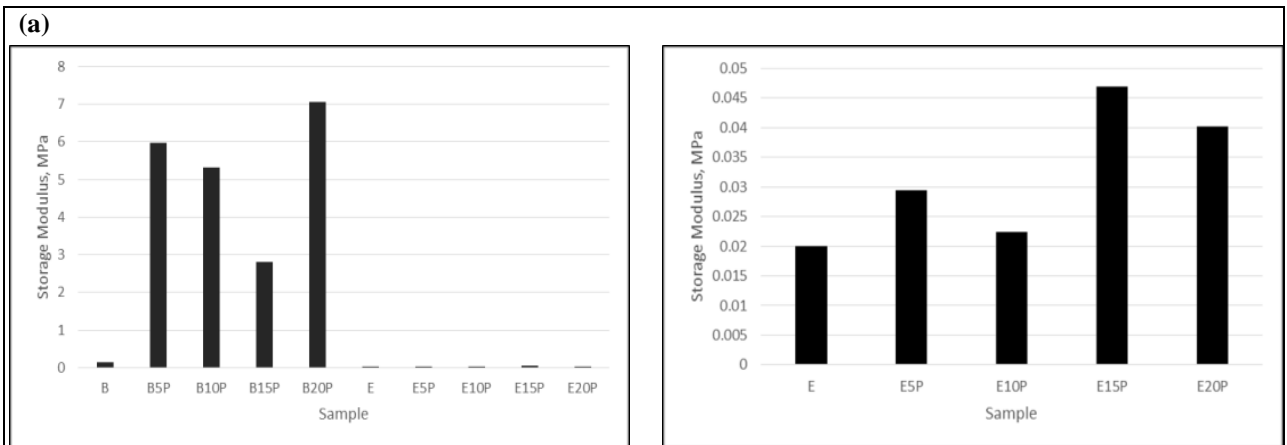


Fig.7 - A comparison of graph of storage modulus for B and E with its composites at (a) unexposed (b) 2000h (c) 4000h and (d) 6000h UV irradiation exposure



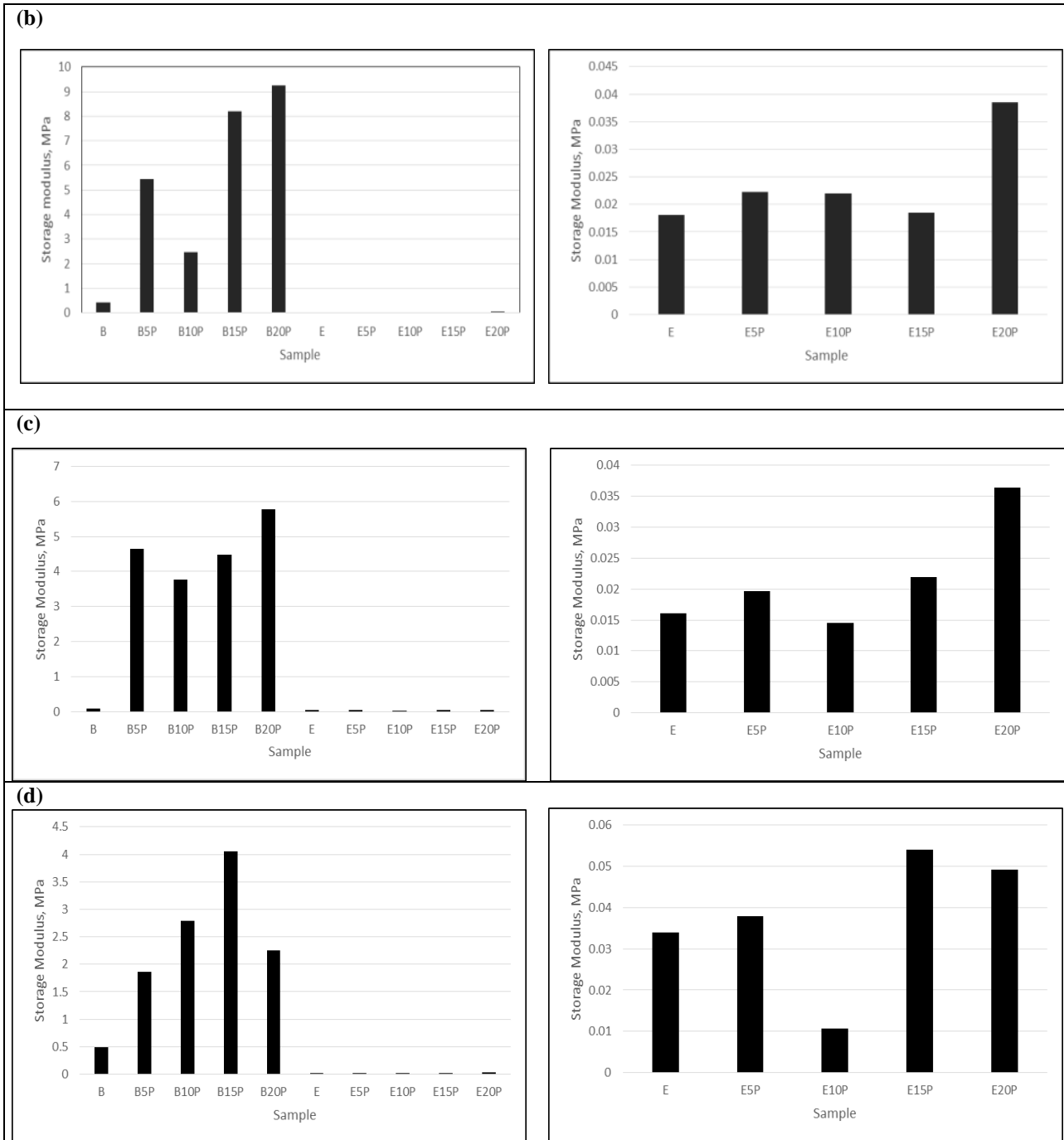


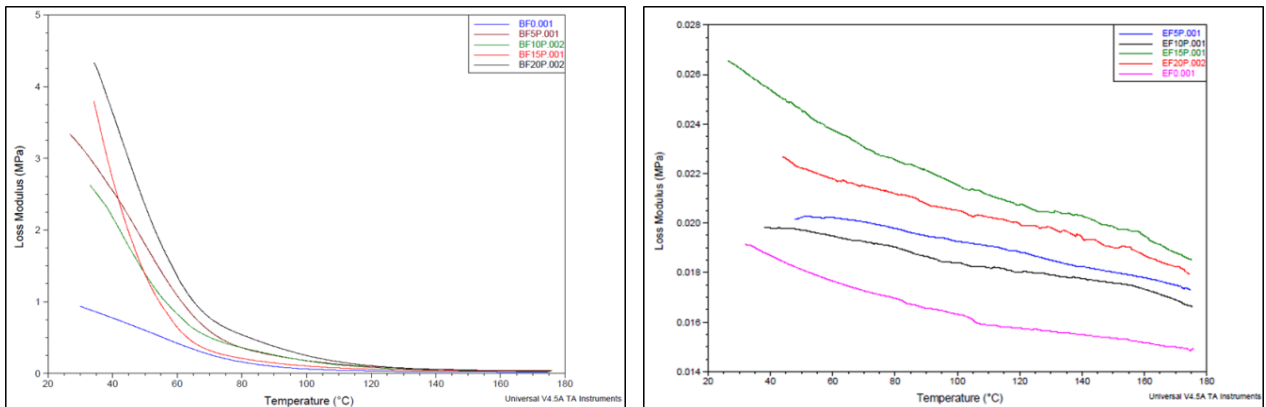
Fig.8 - Comparison curve of storage modulus for bio-based and epoxy with its composites at (a) unexposed UV (b) 2000 hours UV (c) 4000 hours UV and (d) 6000 hours UV

2.8 Loss Modulus

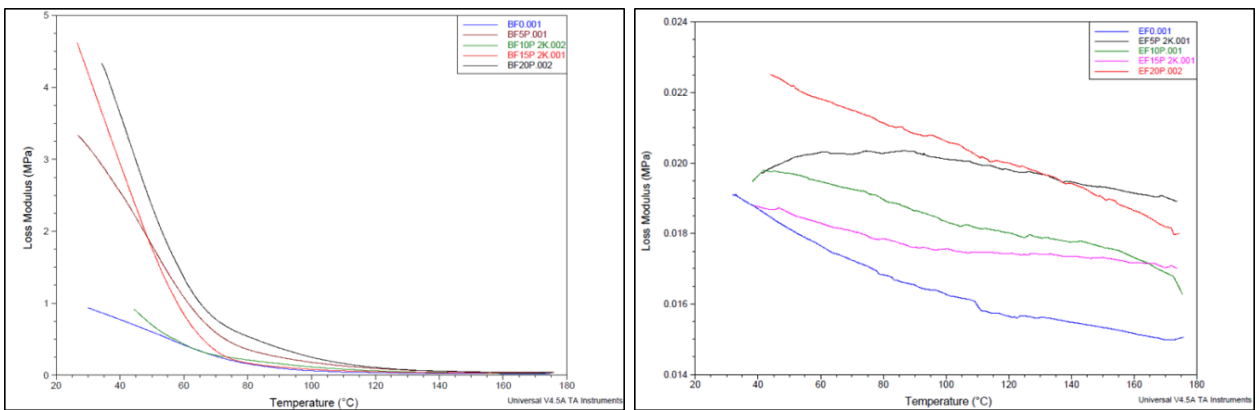
The loss modulus is a material's ability to dissipate energy. It is also known that energy is going to be lost as heat. The loss modulus value at unexposed UV, 2000h, 4000h and 6000h of bio-based and epoxy with its composite is shown in Figures 9 and 10. B20P has the highest loss modulus value among other bio-based composites, from Figure 10a, while E15P has the highest loss modulus with its composite at unexposed UV irradiation compared to other epoxies. When exposed at 2000h UV irradiation, Figure 10b shows bio-based and epoxy with its composite. The B20P and E20P are seen. The increased value of the loss module is due to the higher filler concentration [14].

The B15P sample has the highest loss modulus value compared to other bio-based composites, while E20P also has the highest loss modulus compared with other epoxy composites in Figure 10c at 4000h UV exposure. Figure 10d shows that bio-based and epoxy have the highest loss module value with 15 percent filler concentration. The value of the

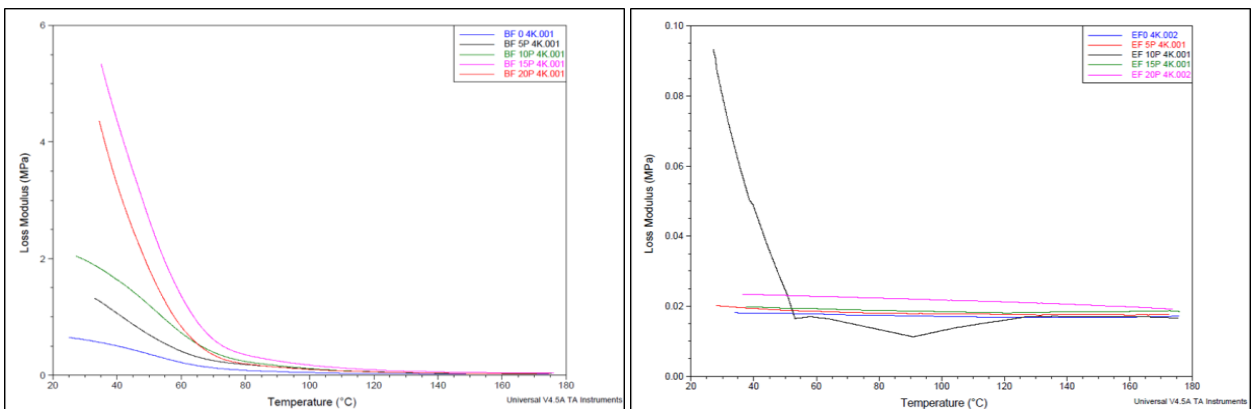
storage modulus has been influenced by the crosslink density in the composite. The higher the filler concentration, the greater the potential for the substance to dissipate the energy as energy that is lost as heat.



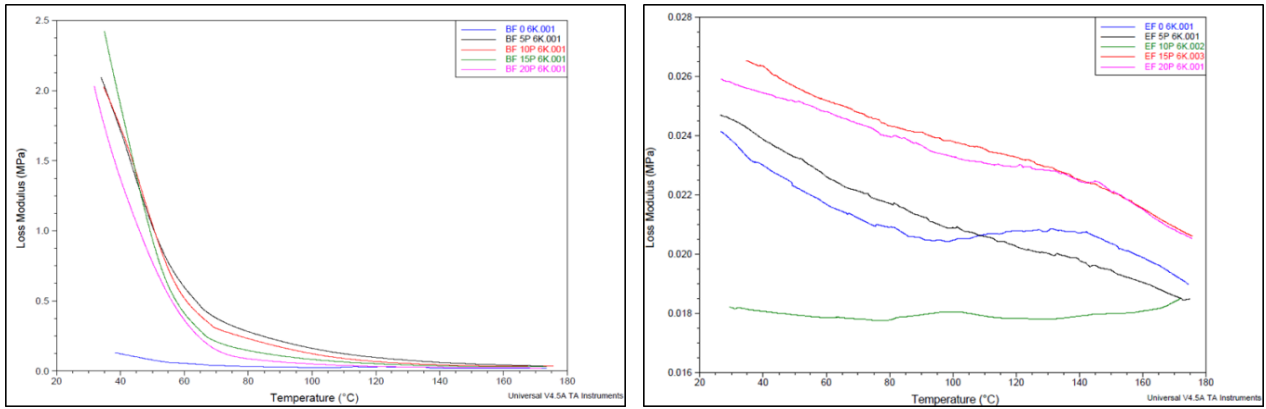
(a)



(b)

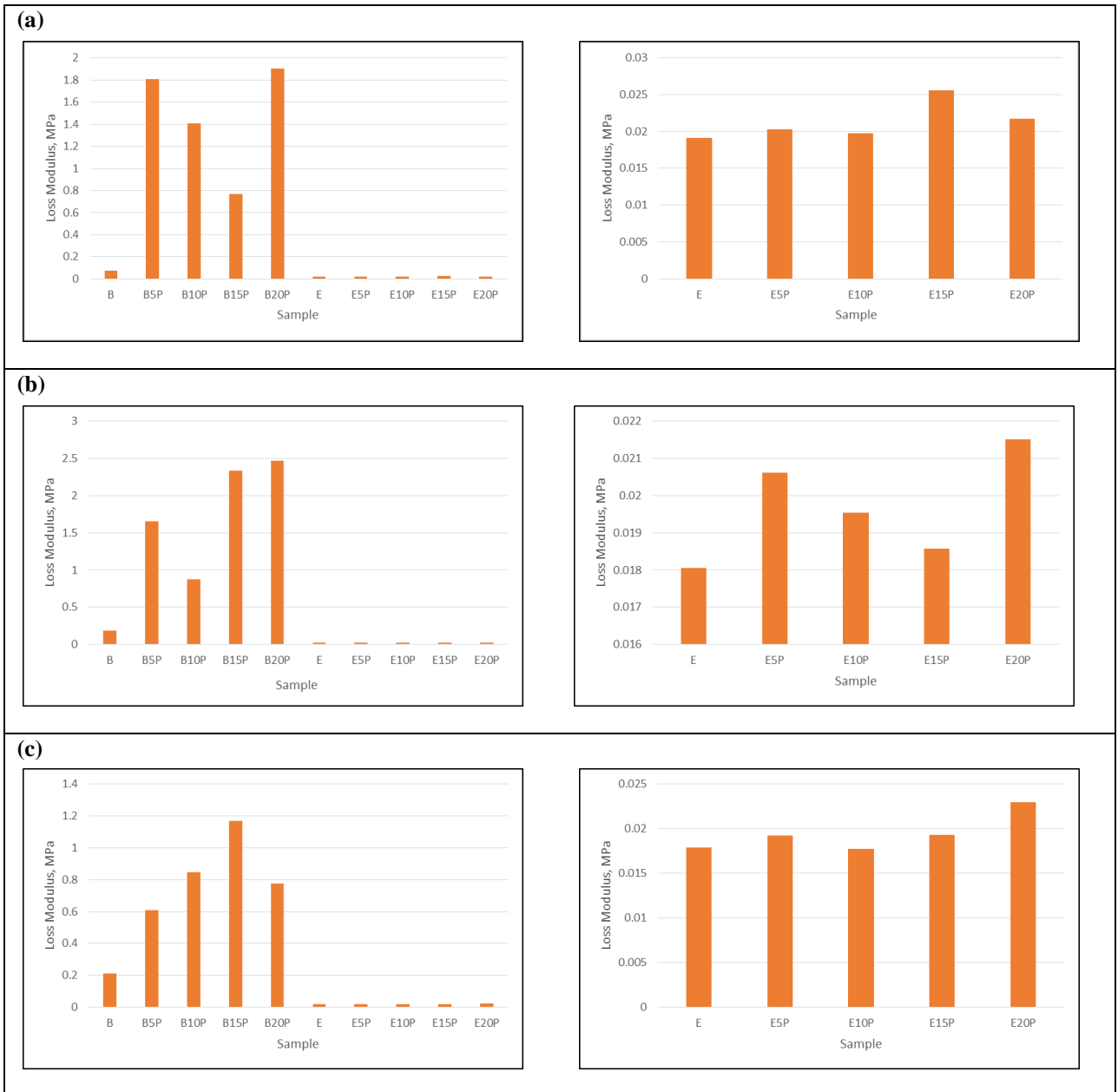


(c)



(d)

Fig. 9 - A comparison of graph of loss modulus for B and E with its composites at (a) unexposed (b) 2000h (c) 4000h and (d) 6000h UV irradiation exposure



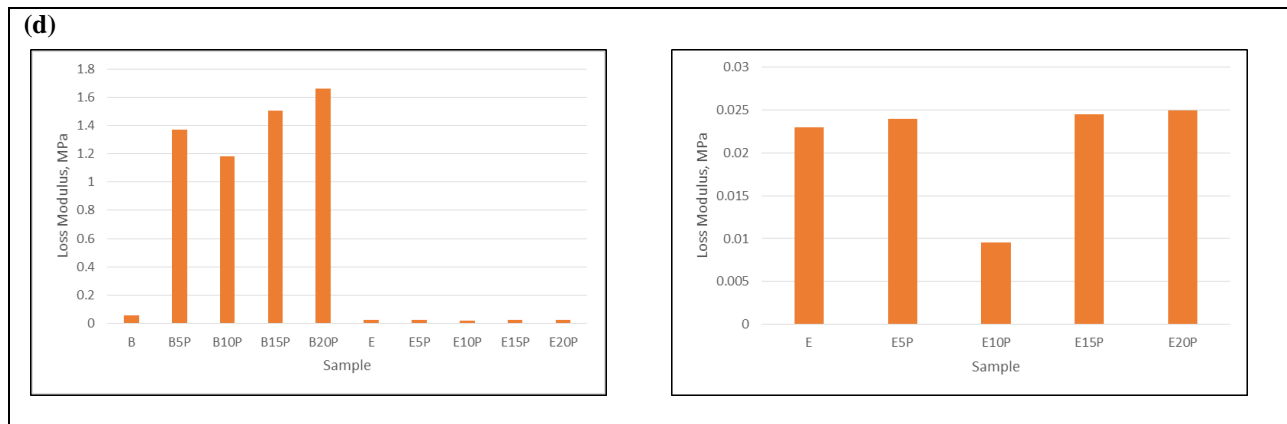


Fig. 10 - Comparison curve of storage modulus for bio-based and epoxy with its composites at (a) unexposed UV (b) 2000 hours UV (c) 4000 hours UV and (d) 6000 hours UV

4. Conclusion

It can also enhance the strength of chemical bonding in polymers and increase the durability of the polymer by adding some filler to polymer foams. It can be inferred that if the sample is subjected to more hours of UV irradiation, the pore size of each sample will decrease. Other than that, since the structure of epoxy polymers is clearer than that of bio-based polymer foams with a brownish colour, the pore size for epoxy polymer foams is easier to measure. The more UV radiation is exposed to, the darker the brown colour of polymer foams.

Compared to bio-based polymer foams, epoxy composites have the highest tan delta value relative to dynamic mechanical analysis (DMA) testing. At E10P with a value of 1.3780, the highest tan δ value was recorded. It demonstrates that the higher the filler ratio, the lower it is possible to record the tan δ value. It can be assumed that, along with increased exposure to UV radiation, the benefit of the storage and loss module is reduced. This also means that if the powder filler ratio increases, the value of the storage and loss modulus would increase. As a consequence, as energy is lost as heat during UV exposure, bio-based polymer foams with a high powder filler ratio can dissipate more energy.

Acknowledgement

The authors would also like to thank the Ministry of Education Malaysia and Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia (UTHM) for support this study.

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