Effect of Visco-Elastic Parameters and Activation Energy of Epoxy Resin Matrix Reinforced with Sugarcane Bagasse Powder (SCBP) Using Dynamic Mechanical Analyzer (DMA)

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Abstract: A sugar cane bagasse powder (SCBP) reinforced epoxy resin composite was developed at low cost using the hand lay-up method. The viscoelastic parameters and activation energies of the composites were evaluated using dynamic mechanical analyzer (DMA) in a temperature range from 30°C to 120°C at 10Hz oscillating frequency. It was observed that 30wt% and 40wt% SCBP/Epoxy composites are the stiffest composite materials because of their higher values of storage modulus of 950MPa and 997MPa in comparison to about 800MPa of the neat epoxy matrix. Our findings also revealed that loss modulus decreases with increase in temperature and incorporation of SCPB fiber content caused broadening of the curves which depicts an increase in thermal stability of composite materials in comparison with neat epoxy matrix. There was a gradual decrease in damping coefficients as the SCBP content increases which could be attributed to the reinforcing effect of the fiber. The decrease in activation energies of 293.013, 286.836 and 201.103KJ/mol for 20wt%, 40wt%, and 50wt%SCBP/Epoxy resin composites proved that the activation energy values are in agreement with the storage modulus which suggests an improved stiffness of the composites.

Keywords: Viscoelastic Nature, Sugarcane Bagasse Powder (SCBP), Epoxy Resin, Dynamic Mechanical Properties

1. Introduction

Epoxy resin is currently one of the most leading matrices that are commonly used worldwide for fiber-reinforcement in advanced composite materials due to its unique properties. These properties include relatively high strength, low shrinkage, better resistance to moisture, better mechanical properties, processing flexibility and better handling [1]. Because of the increasing environmental awareness, numerous researches have been conducted on natural fibers as reinforcement of composites in substitution for synthetic fiber [2]. Basically, natural fiber in composites provides environmental advantages which include increase dependences on non-renewable energy ratio of material sources, low pollutant, and toxic chemical emissions, low greenhouse gas emissions, enhanced energy recovery and end of life biodegradability of components. Such superior environmental performances are an important driver of increased future use of natural fiber composite [3]. Polymers can be divided into two classes, namely thermoplastics and thermo-settings. The epoxy resin is one of the most commonly used thermosetting matrix, other examples include phenolic and polyester resins while thermoplastic materials include polypropylene (PP), polyethylene, and polyvinyl chloride (PVC) are also used as matrices for bio-fibers [4]. In recent decades, natural fibers as an alternative reinforcement in polymer composites have attracted the attention of many researchers and scientists due to their advantages over conventional glass and carbon fibers [5, 6]. Dan-Asabe in 2016 published a reputable work on the thermo-mechanical properties of banana particulate reinforced PVC composite as piping material [7]. Dynamic

mechanical analyzer (DMA) is a thermal analysis instrument that gives information on the viscoelastic parameters of material either as a function of a linear heating rate or as a function of time (frequency) and temperature. The glass transition temperature Tg can be measured with high sensitivity by monitoring the visco-elastic response of either the storage modulus (E'), loss modulus (E"), or loss factor (tanδ) as a function of temperature [8]. The storage modulus is proportional to the energy stored per cycle which depicts the elastic behavior of the material [9]. The loss modulus is proportional to the lost or dissipated energy per cycle which depicts the viscous behavior of the material [8]. The ratio of energy dissipated to energy stored is the tangent of the phase angle called tan delta, which depicts the viscoelastic nature of a material. However, the DMA tests can be used to determine shift factors of a composite material with the storage modulus curves only, thereby ignoring other visco-elastic parameters. Furthermore, the effect of frequency on the dynamic mechanical response of polymers was reported in the literatures. By implications, an increase in test frequency will shift the tan delta peak to a higher temperature in the curve [10, 11]. This behavior is as a result of the fundamental relationships between temperature and the frequency of molecular conformational changes in polymers [10, 11]. Similarly, the effect of temperature on the frequency of molecular reorganization, which includes the glass transition of relaxation usually explained using the Arrhenius relationship. The activation energy of the glass transition (E_a) is the energy barrier that must be overcome for the occurrence of molecular motions causing the transition [12]. Particulate natural fibers are also widely used to improve the properties of matrix materials so as to modify the thermal, electrical conductivities, and improve performance at elevated temperatures. Sugarcane bagasse fibers are often regarded as agricultural and environmental waste after the extraction of the sugar content. Hence, they are now being utilized as fillers in forming polymer composites which convert waste to wealth. The main aim of this research is to assess the influence of SCBP addition on the viscoelastic parameters and activation energies of the epoxy resin matrix.

2. Experimental

2.1. Materials

Fresh Sugarcane bagasse was obtained from Samaru cane center, Zaria, Kaduna State, Nigeria while the epoxy resin (grade 3554A) and hardener (grade 3554B) were purchased from Juneng Nigeria Limited, Nsukka of Enugu State.

2.2. Methods

2.2.1. Sugar Cane Bagasse Powder (SCBP) Preparation

The bagasse was thoroughly washed with distilled water so as to remove both excess sugar and dirt particles, then later sun-dried for two weeks. The dried sample was pulverized into powder using a laboratory mill machine and sieved to 72µm particle size using digital high-frequency sieve shaker model in the Department of Geology, Ahmadu Bello University, Zaria [13]. In this research, there was no chemical treatment or fiber modification done to the sugar cane bagasse powder.

2.2.2. Composite Preparation

A wooden mold was used in casting the composite sheet. The composites were fabricated at the chemistry department laboratory, ABU Zaria. In preparing the composite, hand lay-up technique was used via manual mixing using a stirring rod, and the composition of the SCBP and epoxy resin were varied. The weight percent of reinforcement was prepared for 0wt% (control), 10wt%, 2wt0%, 30wt%, 40wt% and 50wt% of SCBP while the epoxy matrix was prepared in the ratio of 2:1 amount by weight of epoxy resin and hardener as shown in Table 1. The measured matrix was thoroughly mixed in a container and stirred at low speed for 15 minutes until the mixture became uniform. For easy removal of the composite sheets or demolding, petroleum jelly was used as a releasing agent which was applied to the surface of the mold before pouring the mixture of the matrix into the mold. Thus, it prevents the composite from sticking to the mold and as well aided the removal of the composite after curing. The composite was allowed to cure for 24 hours at room temperature before demolding, then cut into suitable dimensions for further analysis based on the ASTM standards. The standard weight of the composite sample was 100g.

Table 1. The composition of the materials.

| Composite | Ratio | Matrix(gram) 2:1 | | Fiber(g) |
		Epoxy Resin	Hardner	
0wt%SCBP	100:0	66.60	33.30	0
10wt%SCBP	90:10	60.00	30.00	10
20wt%SCBP	80:20	53.20	26.60	20
30wt%SCBP	70:30	46.60	23.40	30
40wt%SCBP	60:40	40.00	20.00	40
50wt%SCBP	50:50	33.30	16.60	50

2.3. Dynamic Mechanical Analysis

DMA analysis was carried out using DMA 243E machine in the strength of materials laboratory, Mechanical Engineering Department, ABU Zaria in accordance with

ASTM D7028 standard method [14]. The viscoelastic test parameters were initially configured via Proteus software using a personal computer. Instruments set up included the sample holder (3-point bending), furnace temperature at the range of 30-120°C, dynamic force/load at 2.18N, the

frequency range of 10Hz and heating rate of 5K/min were configured. Sample dimension of 40x12x5mm was produced for each test. The sample was loaded on to the machine using the three-point bending sample holder, then locked into the furnace for the commencement of the analysis. The storage modulus, loss modulus and tan delta results output in MS Excel (.csv) were plotted against increasing temperature based on SCBP fiber loading using a MATLAB software. The activation energy was calculated from the tan delta peaks at 10Hz according to the Arrhenius relationship (Eq 1.) using the proteus thermal analysis software.

$$\log f = \log f_\circ + \frac{E_a}{2.303 \cdot R \cdot T} \qquad (1)$$

Where f frequency of the analysis is, $f_\circ$ is the experimental constant, E_a is the activation energy (Jmol^{-1}), R is the ideal gas constant (8.314 Jmol^{-1}K^{-1}) and T is the tan delta peak temperature (K).

3. Results and Discussions

3.1. Storage Modulus

The storage modulus of a composite material describes how materials are stiffer. Figure 1 displays the variation in storage modulus with increasing temperature at a 10Hz oscillation frequency of SCBP/Epoxy Composites. In this Figure, it was observed that the storage modulus increase with an increase in SCBP fiber loading up to 40wt%, then decreases as a result of

improper adhesion between the fiber and the matrix [15]. There was a gradual drop in storage modulus with increasing temperature because of the stiffness loss at elevated temperatures. As such, it can be deduced that storage modulus decrease with increase in temperature. This could be attributed to the relaxations in the polymer matrix associated with the glass transition temperature (Tg) from crystalline to amorphous state [16]. It is obvious that 30wt% and 40wt% SCBP/Epoxy composites are the stiffest composite materials because of their higher values of storage modulus of 950MPa and 997MPa in the glassy region when compared to other composites. This occurs as a consequence of the strong interfacial adhesion, which indicates superior dynamic mechanical properties for this composite in comparison [17]. The decrease in the storage modulus for 20wt%, 10wt%, and 50wt%SCBP/Epoxy composites may be attributed to the low stiffness which tends to reduce the viscoelasticity of the epoxy matrix [18]. It was observed that the 40wt%SCBP/Epoxy resin composite had the highest value of storage modulus in the rubbery region which means that the composite revealed better interface bonding than other composites. Note that the storage modulus is directly proportional to the adhesion between fibers and matrix [19]. Similarly, 10wt%SCBP/Epoxy had its lowest because of the increase in molecular mobility at higher temperatures. Hence, it could also be observed that the storage modulus of the SCBP was not close to each other which is because of the contribution of the fibers to impart to the material at higher temperature [20].
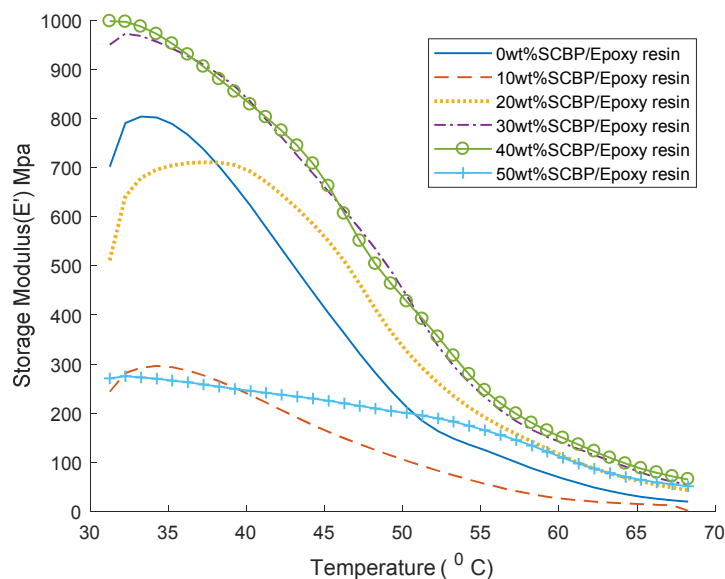

Figure 1. Storage modulus of the SCPB/Epoxy resin composites at oscillation frequency of 10Hz.

3.2. Loss Modulus

Loss modulus is defined as the highest energy dissipated by composite materials during deformation. It is the viscous response of the composite which depends upon the motion of polymeric molecules in the composite [21-23]. Figure 2 shows the loss modulus variation with increasing temperature at 10Hz oscillation frequency. From the graph,

it was observed that the loss modulus decreases with increase in temperature and the neat epoxy resin (0wt%SCBP) has the highest loss modulus of 193MPa. Among the composites, the loss modulus of 40wt%SCBP/Epoxy composite was the highest followed by 30wt%, 20wt%, 10wt% and 50wt% SCBP/Epoxy respectively. However, incorporation of SCPB fiber content triggered curve broadening which depicts an increase in

thermal stability of composite materials in comparison with neat epoxy modules. The higher thermal stability could be related to the decrease in mobility of matrix [24]. Therefore, it can be deduced that the loss modulus increases with increase in SCBP fiber loading.

3.3. Damping Parameters

The ratio between the loss modulus and the storage modulus is called the mechanical loss factor, or Tan Delta. The damping properties of the material give the balance between the elastic and viscous phases in a polymeric structure [25]. It depends upon adhesion between the fibers and matrix. Better fiber-matrix adhesion is attributed to lower damping and vice-versa [26]. This fact can be elucidated as strong fiber-matrix adhesion could decrease the mobility of the polymer chain thereby decreasing damping [21]. As such, lower damping

coefficients indicates good load bearing capacity of the composite [21]. Figure 3 shows the tan δ variation with temperature for different weight percent of sugar cane bagasse powder reinforced epoxy composites at 10Hz oscillation frequency. In this figure, the neat epoxy has the highest damping coefficient of 1.056 while 50wt%SCBP/Epoxy has the lowest of 0.153. Hence, there is a gradual increase in damping coefficients as the SCBP content decreases. Basically, composites have considerably less damping in the transition region compared to neat resin because the fibers carry a greater amount of the load and allow only a small part of it to strain the interface [27]. Therefore, energy dissipation will occur in the polymer matrix at the interface and a stronger interface allows less dissipation. This may be due to a restriction of the movement of the polymer molecules due to the incorporation of the stiff fibers [5].
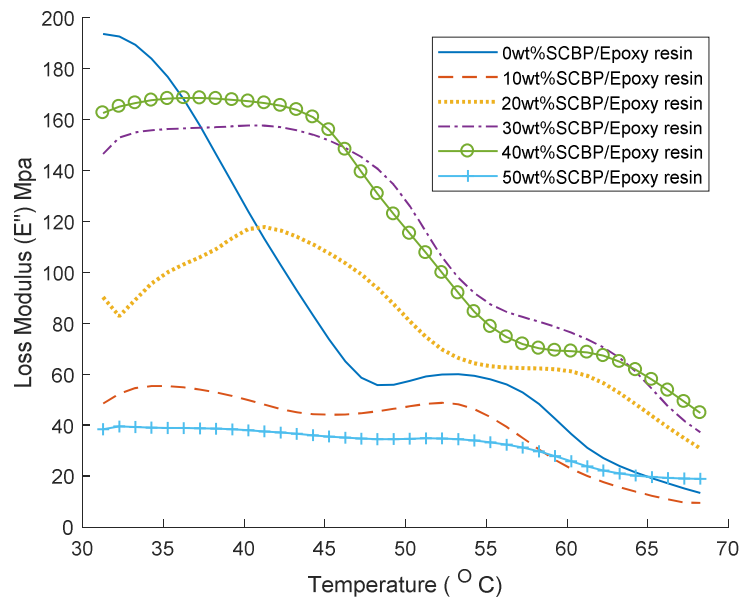

Figure 2. Loss modulus of the SCPB/Epoxy resin composites at 10Hz oscillation frequency.
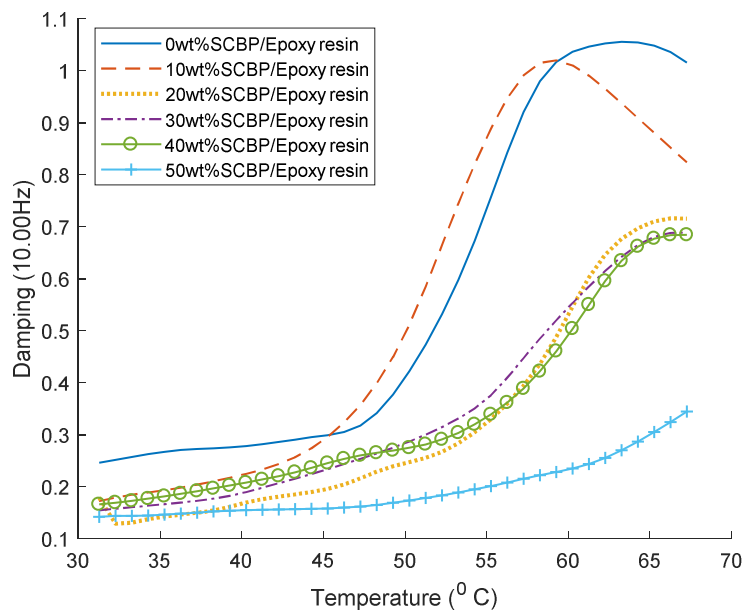

Figure 3. Damping variation of the SCPB/Epoxy resin composites at 10Hz oscillation frequency.

3.4. Arrhenius Plots

The Arrhenius plots of all composites were obtained by plotting logarithmic frequency dependence of the loss factor (tanδ) against inverse absolute temperature in Kelvin using Proteus® thermal software of dynamic mechanical analyzer (DMA) and the activation energy (Ea) is given as the slope of the linear fit through the data points. The activation energy of the glass transition is the energy barrier that must be overcome for the occurrence of molecular motions causing the transition [28]. In other words, it provides approximate energy required to promote the initial movement of some molecular segments in the polymer backbone [29]. Figure 4 illustrates the Arrhenius curve of neat epoxy (0wt%SCBP/Epoxy) with an activation energy of 306.260KJ/mol.
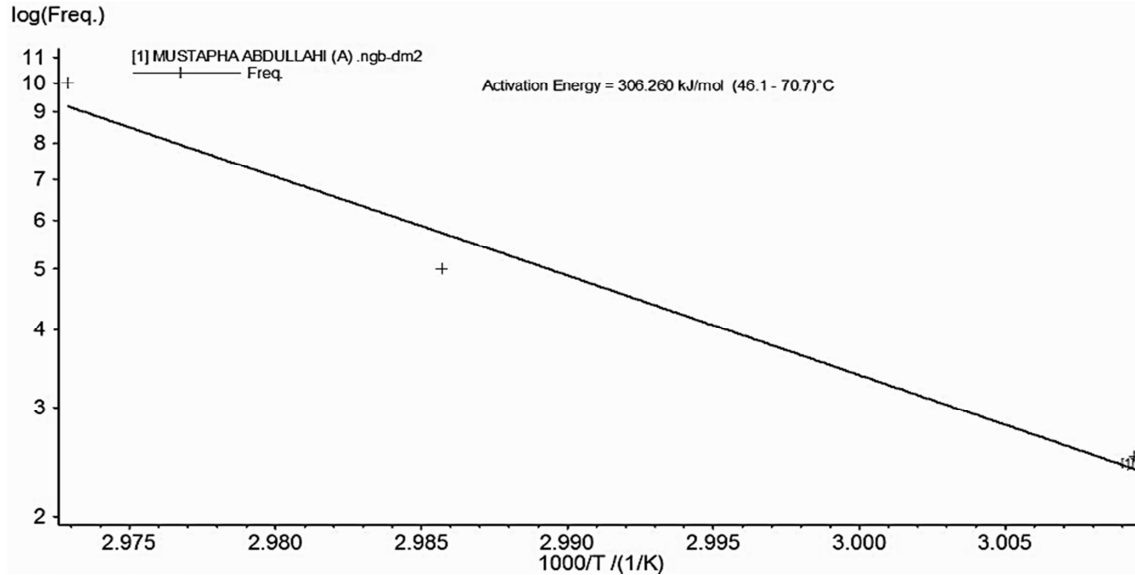

Figure 4. Arrhenius plot of the neat epoxy resin matrix.

Incorporation of the 10wt%SCBP to epoxy resin matrix increases the activation energy to 334.565KJ/mol as depicted in Fig 5. This is due to the higher matrix/fiber interaction. However, decrease in activation energies of 293.013, 286.836 and 201.103KJ/mol for 20wt%, 40wt%, and 50wt%SCBP/Epoxy resin composites was observed respectively (Figure 6, 7 and 8). These suggest improved interfacial adhesion of SCBP/Epoxy matrix which increased the stiffness of the composites. In this study, the activation energy values are in agreement with the storage modulus and mechanical test results. Figure 9 displays the Arrhenius curve of 30wt%SCBP/Epoxy matrix composite with the highest activation energy of 430.976KJ/mol. This clearly shows that more energy is needed to initiate the movement of the molecular segment in the matrix [31]. A similar observation has been reported other authors [32, [33].
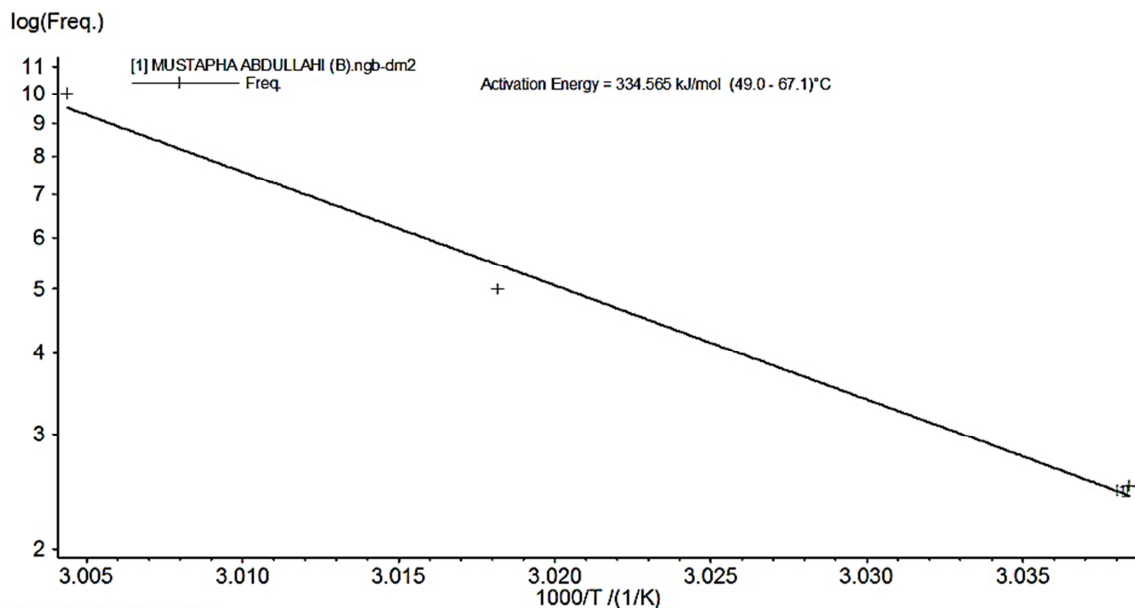

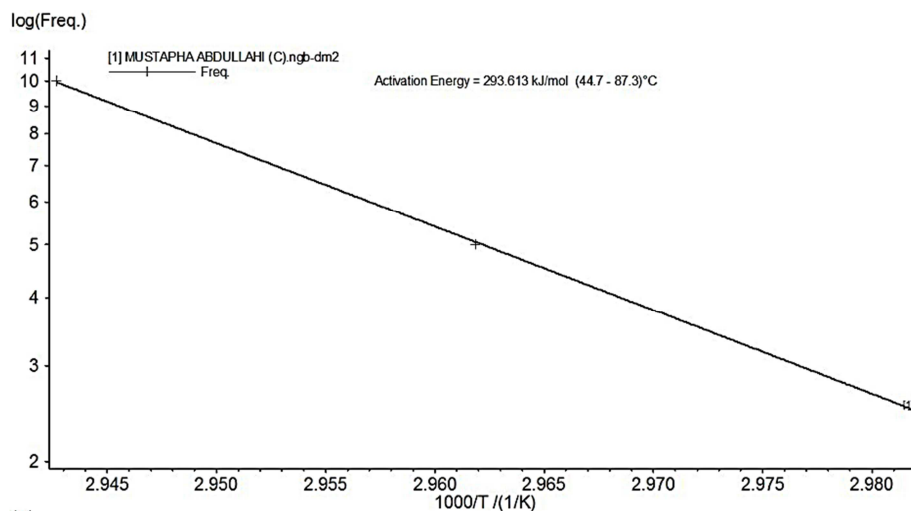*Figure 5. Arrhenius plot of 10wt% SCBP/Epoxy resin composite.*

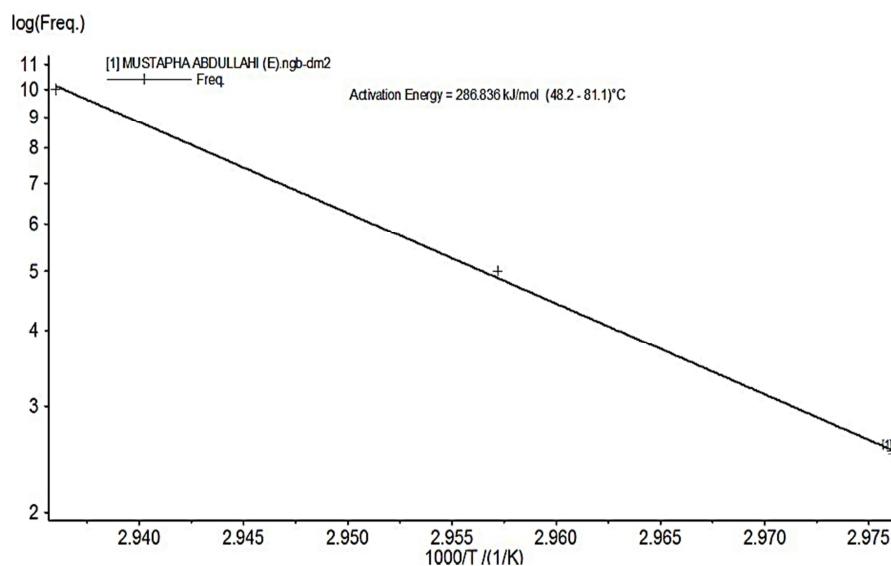**Figure 6.** *Arrhenius plot of 20wt% SCBP/Epoxy resin composite.*

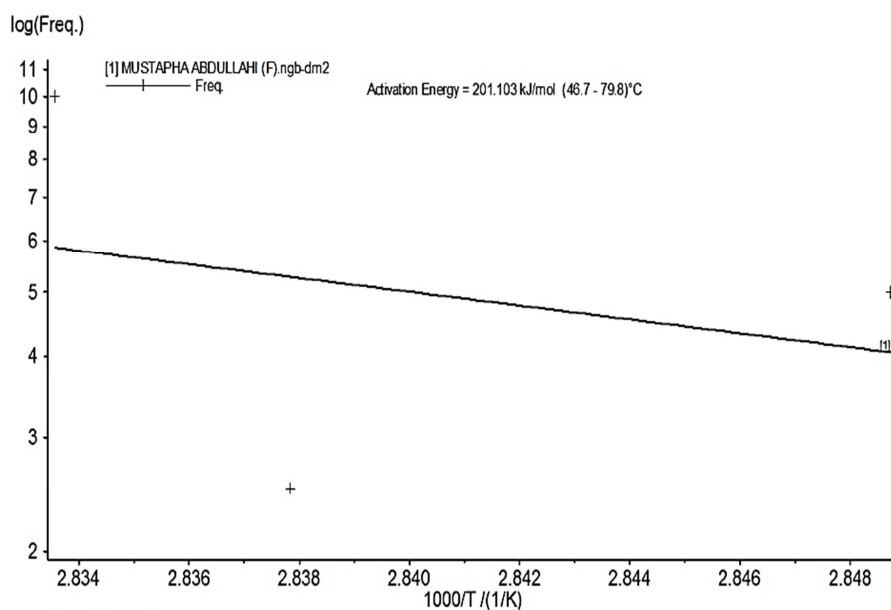**Figure 7.** *Arrhenius plot of 40wt% SCBP/Epoxy resin composite.*

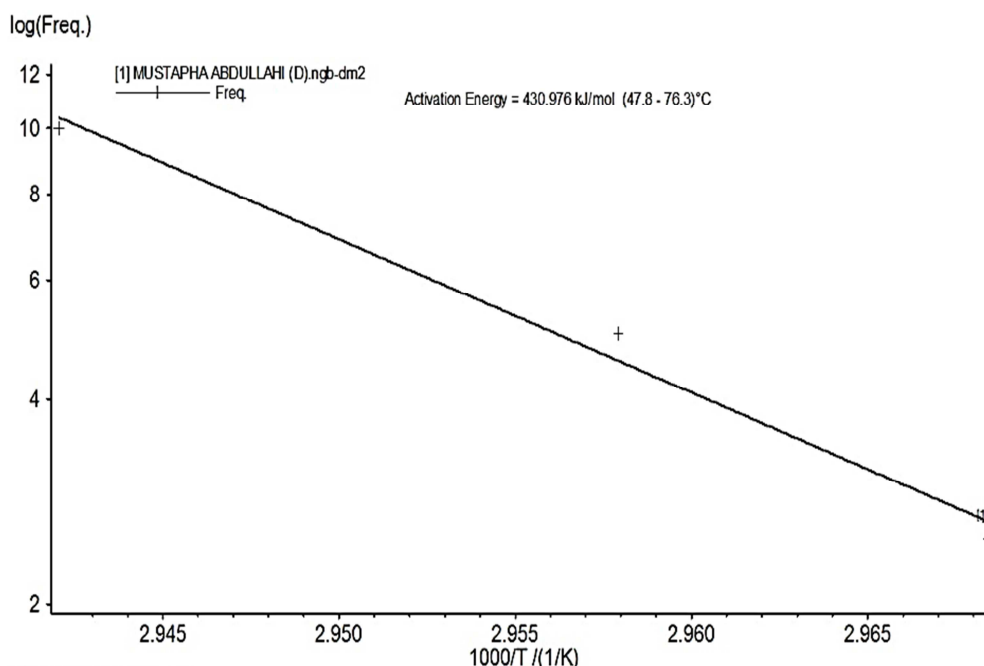**Figure 8.** *Arrhenius plot of 50wt% SCBP/Epoxy resin composite.*

Figure 9. Arrhenius plot of 30wt% SCBP/Epoxy resin composite.

4. Conclusion

The viscoelastic parameters and activation energy of SCBP/Epoxy resin composites were successfully evaluated at 10Hz oscillation frequency. The storage modulus was found to be maximum for 30wt% and 40wt% SCBP/Epoxy composites which are the stiffest materials. Hence, storage modulus increase with an increase in weight percentage of SCBP content and decreases with increase in temperature for all composites. Our findings revealed that incorporation of SCPB fiber content caused curve broadening which depicts an increase in thermal stability of composite materials in comparison with neat epoxy matrix. An irregular trend of the activation energy values was observed. Thus, incorporation of 10wt% and 30w% SCBP to epoxy resin matrix increased the activation energy to 334.565KJ/mol and 430KJ/mol respectively. However, the decrease in activation energies of 293.013, 286.836 and 201.103KJ/mol for 20wt%, 40wt%, and 50wt%SCBP/Epoxy resin composites respectively proved that the activation energy values are in agreement with the storage modulus which suggests an improved stiffness of the composites

Acknowledgements

Conflicts of Interest

The authors declared no conflict of interest in this research work.

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