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RESEARCH PAPER

Investigation of the Mechanical Properties for Polymer Reinforced by Nanoparticles with Considering Viscoelasticity of the Matrix

Diyar Omar Kaka[1]

[1]Department of Petroleum & Energy, College of Engineering, Sulaimani Polytechnic University- Sulaimaniyah, Iraq.

A B S T R A C T:

Nanomaterials have shown more interests to the field of nanotechnologies. Polymeric nanocomposites combine the lightweight and low cost of manufacturing for polymers with nanoparticles of higher performance properties.

The aim of this paper is to find the mechanical properties of nanocomposite of polymer reinforced by nanoparticles with considering matrix viscoelasticity. The viscoelasticity of the polymer was obtained from the experimental tests for the thermoplastic polymer of Poly ether ether Ketone (PEEK) at a range of temperatures and frequencies. The viscoelasticity of the polymer was confirmed by comparing the experimental results with a finite element model. The approved viscoelasticity was used for the matrix of the nanocomposite numerically.

To obtain the mechanical properties of the nanocomposite, a micromechanical model was developed. It was used to find their homogeneous mechanical properties with range temperatures. It was found that the viscoelasticity have effect on mechanical properties for the nanocomposite, and the modulus of the nanocomposite increases with nanoparticle content. However, it decreases as the temperature increases.

KEY WORDS: Viscoelasticity; Nanoparticles; Nanocomposites; Numerical Analysis; Micromechanical Model.
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1. INTRODUCTION:

In the last decade the industry have inspired to the nanocomposite materials because of their interested properties and their wide range of applications.

Nanomaterials have interested properties, their size is measured in nanometers, they must possess at least one of the dimensions at the nanoscale (Parameswaranpillai et al., 2015). To examine the mechanical properties of the nanocomposites several researches have done researches in this field. For instance, (Yas et al, 2019, Le et al, 2020) have estimated the effect of addition different types of nanoparticles into polymers at various particle content.

Nanosilica is among the most usable nanofillers in polymer composites. Various investigations found that mechanical properties of nanosilica particle reinforced polymer nanocomposites are enhanced significantly at low particle volume fraction (Ou et al, 1998, Wang et al, 2002). Micromechanical methods were used widely to estimate the mechanical properties for the nanocomposites (Boutaleb et al, 2009, Ghasemi et. al, 2021). For instance, (Mahmoodi et el, 2019) have studied the influences of the volume fraction, and diameter of the nanoparticles of nanosilica on the thermal expansion properties of polymer nanocomposite. Liu et al. (2017) have used micromechanical model to consider interphase effect on the nanocomposite properties.

Representative volume element (RVE) method is a micromechanical method that employ to identify the homogenized properties of the nanocomposites (Rouhi et al. 2018, Sanel and

* **Corresponding Author:**
Diyar Omar Kaka
E-mail: diyar.kaka@spu.edu.iq

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Oles, 2019, Azmi et. al. 2014). Reddy et al. (2015) have used representative volume element method with a combination of finite element software of Ansys to find the tensile properties of multi-scale composite reinforced by nanoparticle and fiber. The results were compared with experimental methods and good agreements were observed. The micromechanics based homogenization methods were used to estimate the effective modulus of the nanocomposite that reinforced with some spherical inclusions (Amrai et al, 2018).

The effect of polymer viscoelasticity on the nanocomposite is enormous (Obucina et al., 2016; Koval et al., 2012). Several researchers have considered matrix viscoelasticity in nanocomposites (Gosz et al., 1991; Hashin et al., 1992). (Fischer and Brinson, 2001) have considered the effect of viscoelasticity with micromechanical models to find the effective moduli for composite materials and they found viscoelastic effect on the nanocomposite is observable.

From previous researches, it can be observe that several experimental works were carried out to find mechanical properties of nanocomposite reinforced with nanoparticles. Moreover, several numerical researches have been done to estimate the elastic modulus composite of short fiber composite. However, the majority of researches were used elastic analysis of the polymer. As the polymers are viscoelastic material not elastic, the suitability of RVE for viscoelastic material was not examined, and the effect of nanoparticles on PEEK at temperature range is not known.

In this work, the viscoelastic materials for polymer poly ether ether ketone PEEK were obtained from the experimental tests. The viscoelastic results were used to represent matrix viscoelasticity of the nancomposite. Moreover, based on the equivalent homogeneous material concept, a micromechanical model with Representative Volume Element (RVE) was developed with considering matrix viscoelasticity.

2.THEORY OF VISCOELASTIC MATERIALS

2.1 Viscoelasticity

The materials that can display behavior of viscosity and elasticity are called viscoelastic materials; the elastic portion is instantaneous and is recoverable. However, the viscous is time dependent (Cae et al.,2002). Various materials exhibit viscoelasticity when subjected to deformation load. This property can be found in polymers, and it depends on load, time and temperature. Viscoelastic properties are of two types:

1-Linear viscoelastic:

When the stress vs. strain curve plot of the model is linear, this is called linear viscoelastic. This behavior depends on the deformation rate and temperature.

The Boltzman linear viscoelastic equation is (Yannas, 2004):

$$\varepsilon(t) = \int_{\tau=-\infty}^{\tau=t} D_c(t-\tau)\,\frac{d\sigma(\tau)}{d\tau}\,d\tau \qquad (1)$$

where,

$$D_c(t) = \frac{\varepsilon(t)}{\sigma_0}$$

and

t is period time.

τ is relaxation of period time.

2- Non-linear viscoelasticity:

It is the non-linear stress strain curve of the model. It happens usually when the deformations of the materials are large or if they change their properties under deformations. The nonlinear viscoelasticity is much more complex, and there is no rheological equation can predict the material's response under this kind of deformation. The only approach attempt to establish rheological equation for nonlinear behavior is based on continuum mechanic principle. While continuum mechanics models contain elements inspired by molecular or thermodynamic concepts, they are basically empirical. So, that means their applicability out of the conditions under which their predictions can be tested by experiment is unreliable (Dealy, 2021)

2.2 Viscoelastic Material Model

In finite element analysis software's, the viscoelasticity in the time domain can be employed implementing the Prony series, and the Prony series equations can be derived from the viscoelastic models (Charalambides and Olusanya, 1997; Wu, 2009).

This study is dependent on the generalized Maxwell model equations. The stress-strain relation for the generalized Maxwell model is given by (Roylance, 2001):

$$\sigma(t) = E_{\infty}\varepsilon(0) + \sum_{i=1}^{N} E_i e^{-t/\tau_i}\,\varepsilon(0) \quad (2)$$

Where the relaxation modulus is:

$$E(t) = E_{\infty} + \sum_{i=1}^{N} E_i e^{-t/\tau_i} \quad (3)$$

The relaxation moduli E_i and $\tau_i = n_i/E_i$ relaxation time respectively are for the i-th Maxwell-element.

$$\frac{G_R(t)}{G_0} = 1 - \sum_{i=1}^{N} g^{-p}{}_{i}\left(1 - e^{-\frac{t}{\tau_i}}\right) \quad (4)$$

$$G_0 = G + \sum_{i=1}^{N} G_0 g^{-p}{}_{i} \quad (5)$$

So,

(N) is the number of terms in prony series.
$g^{-p}{}_{i}$ is the relative modulus for the term (i).
τ_i is the relaxation period time for term(i).
G_0 is the instantaneously shear modulus.

2.3 Dynamic Mechanical Thermal Analysis (DMTA)

The variables in Equations 3 and 4 can obtain from the experimental tests, by using dynamic mechanical thermal analysis (DMTA) for the polymer. This test was conducted by placing the specimen between a movable and fixing clamps in thermal chamber. A sinusoidal or constant force was applied to the sample whilst changing the temperature environment around the sample and frequency.

Five variables are change in that tests; time, temperature, force, strain and frequency. The dynamic mechanical thermal analysis can obtain five viscoelastic properties of materials; storage modulus (E'), loss modulus (E"), loss factor (tan δ), glass transition temperature (Tg) and stress relaxation (Zmindak et al., 2011)

3.EXPERIMENTAL PART

3.1 DMTA Test for Polymer Poly Ether Ether Ketone (PEEK)

The PEEK polymer was supplied by VICTREX in the form of granules with 150 g . The PEEK specimen was prepared by injection moulding. The manufacturing processes for the sample was by putting granules of the material to the injection moulder. With the injection moulder was controlled to temperature 400°C and pressure at 1400 bars to melt the polymer. Then, the melted PEEK injected to a mould that heated too and allowed to cool naturally. The solidified specimen had the following dimensions of length, width and thickness with 33.7 mm, 6mm and 3 mm respectively, as shown in Figure 1.

For the DMTA tests, visco analyser testing machine of type MTS 858 table top system with the thermal chamber was used. The viscoelastic properties and master curves for the specimen were obtained with using the visco analyser machine. It was conducted by clamping the polymer sample on the bottom side and applying sinusoidal load on the top side. The temperature and the frequency of the chamber that contain the specimen was controlled and increased gradually to find the specimen behavior. The PEEK specimen was tested under a frequency in axial direction with a condition; dynamic strain with 0.001, temperatures range from 25 to 280 °C with steps of 5°C and frequencies of range 1 to 100 Hz in nine logarithmic steps. The increasing steps of chamber temperature should be in a way to get smooth data and not to be rushed; therefore increasing by 5°C was selected. The values of frequency and the dynamic strain were chosen to avoid resonance and failure in the samples, as several samples were tested.

Figure1: PEEK Specimen.

3.2 PEEK DMTA Results

From the DMTA test, the results of the master curves for the loss factor and storage modulus were obtained at different temperatures and frequencies.

The relationship between the temperature and frequency in the dynamic mechanical thermal analysis (DMTA) is dependent on the principle of “reduced modulus in viscoelasticity” (Witczak, 2004). The modulus and loss factor at different temperature and frequencies are shown in Figure 2.

Using large number of Prony series's term gives better and smooth fit for the results. So, the complex modulus at different frequencies is shown in Figure 3. It shows that the storage modulus increase with frequency gradually, and decrease in loss factor. This is normal for polymers as heating increases the mobility of molecules thereby making the material easier to deform, and that is because an increase in frequency causes more friction in the materials structure which cause more damping and increase in loss factor.

Figure 3 is essential to find the parameters, that used for viscoelastic analysis by finite element software, such as instantaneous shear modulus, so, the experimental results was coded to ansys workbench software to represent matrix viscoelasticity.

From the DMTA analysis, the relation between relaxation modulus with time has been found, which is shown in Figure 4. It is clear that the relaxation modulus dropped with increase in time domain, this proved the polymer relaxation, the viscoelastic materials exhibit increase in strain with time increase when subjected to constant force.

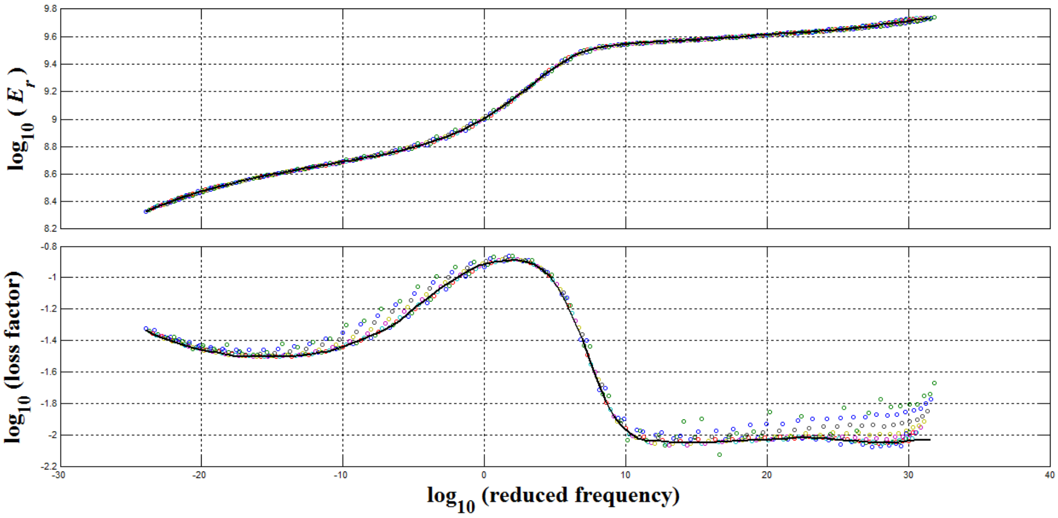

Figure 2: The reduced modulus and loss factor at different frequencies.

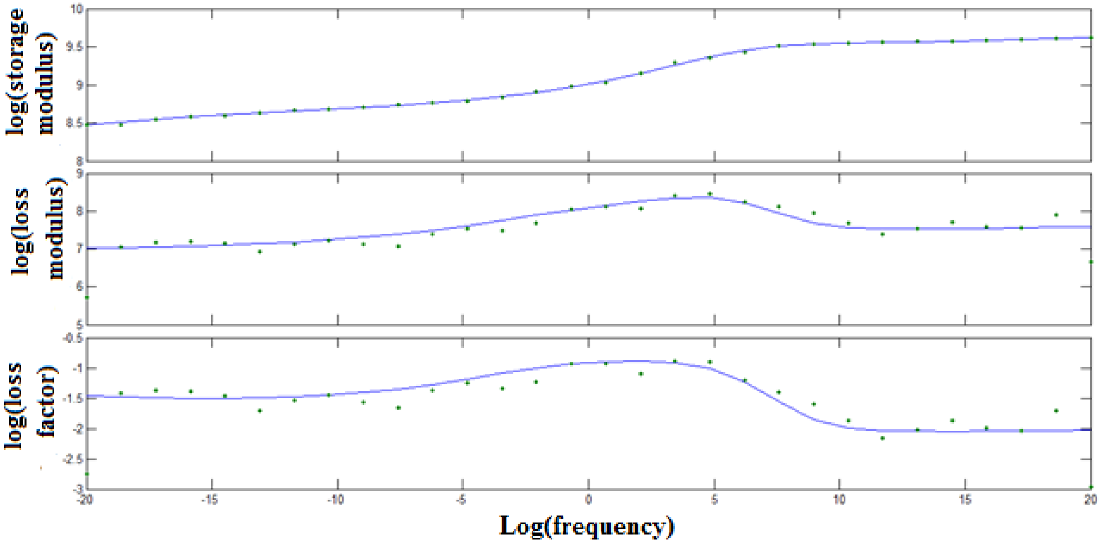

Figure 3: Fitted Prony series parameters to the complex modulus plotted at different frequencies.

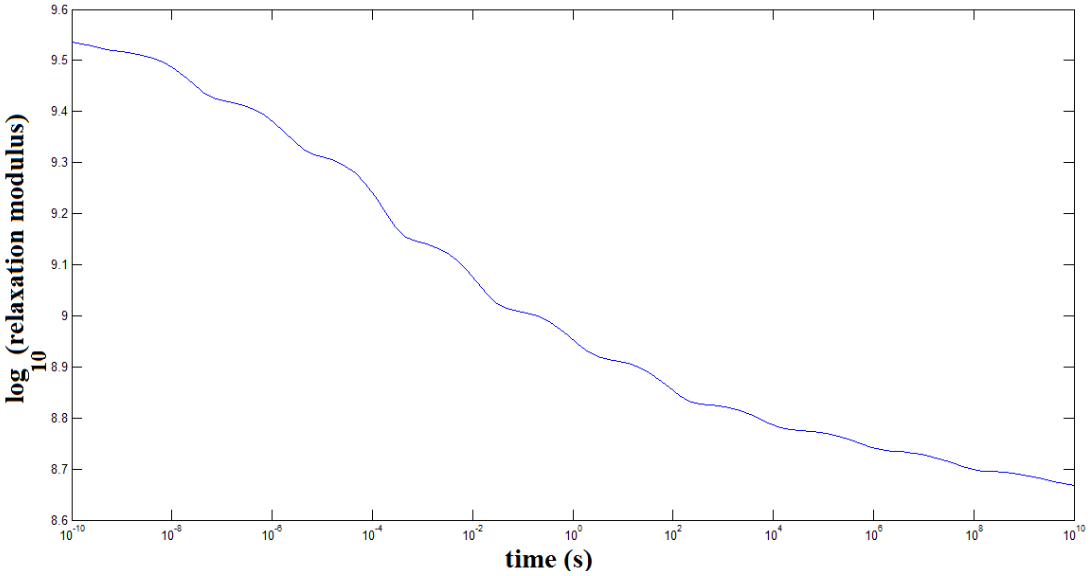

Figure 4: Time domain relation with relaxation modulus.

4. REPRSENTING VISCOELASTICITY IN FEA SOFTWARES

The time parameter of the boundary conditions for the elastic materials is not affecting the solution. However, in viscoelastic materials is dependent on time.

The Viscoelastic properties of the materials can be represent in finite element software through the time domain. For example, in Ansys, the viscoelasticity can implement through the use of prony series (Imaoka, 2008). The relationship between the variables of Young's modulus, shear modulus, Poisson ratio and bulk modulus are as below:

$$G = \frac{E}{2(1+\nu)} \tag{6}$$

$$K = \frac{E}{3(1-2\nu)} \tag{7}$$

The change of values shear modulus, Young's modulus and bulk modulus with time are represented through Prony series. A hyperplastic model of Neo-Hookean was used for the behavior for the matrix. Generally the Poisson ratio of polymers are a complex number changes from 0.33 when the material is glassy to rubbery at value of 0.5. This is due to the viscoelastic effect that is weaker in compression and expansion than in shear. In this work, this difference is neglected.

To approve the numerical results of viscoelasticity, the same sample that used in experiments was modeled in same dimensions and representing viscoelastic behavior through the use of Prony series with using the same boundary conditions of applying sinusoidal displacement on the specimen.

Ansys workbench software was used for the analysis and the simulation. The results showed that at room temperature the material is stiffer; However, at region of glass transition temperature with value 160°C the material possess higher damping and dissipate more energy.

The viscoelastic results were compared with the experimental results of hysteresis loops for PEEK, as shown in Figure 5. The hysteresis loop results for both numerical and experimental shows good compatibility in the dissipated energy in the load-displacement plot, with small differences in the modulus at both temperatures 30 °C and 160°C.

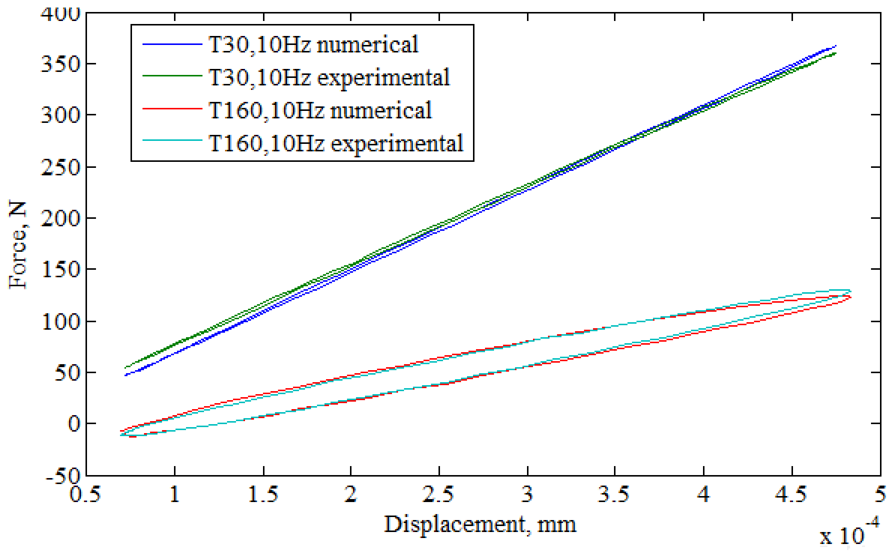

Figure 5: Numerical and experimental hysteresis loops for plain PEEK.

5.NUMERICAL PREDICTION USING REPRESENTATIVE VOLUME ELEMENTS

To predict the homogeneous mechanical properties for nanocomposites reinforced with nanoparticles numerically, the representative volume element (RVE) approach was used. RVE is the smallest size of material that is possible to use for finding the homogenized properties of the model. Also, it should be in large to contain all the information for that model (Gitman et al, 2004). The unit cell for nanocomposite reinforced with nanoparticles is shown in Figure 6.

To find a suitable size and shape of the unit cells, various configurations for the RVE were considered. For analysis, Ansys FEM software was used with suitable meshing. The meshing for the RVE is shown in Figure 7.

For calculation, the boundary conditions that applied were based on equation 9.

$$\begin{aligned} u_1(0,0,0) &= 0 \;, u_4(x,0,z) = 0 \\ u_2(0,0,z) &= 0 \;, u_5(x,y,0) = 0 \\ u_3(0,y,0) &= 0 \;, u_6(x,y,z) = \Delta \end{aligned} \qquad (8)$$

Where x, y, z are the height, width and length of the model, and Δ (delta) is the applied displacement in the z-direction. The input material properties for the nanocomposite was based on Table 1.

To find the effective Young’s modulus for the RVE, the method of curve fitting Young’s modulus of different homogeneous material. In this method, the Young’s modulus of homogeneous material of has changed until the reaction force matches a heterogeneous material. This means that from the resulted reaction forces of different homogeneous materials, unit cells with assuming fixed Poisson ratio of 0.42 was used, which is obtained from the manufacturer of the polymer PEEK. The equation of the resulted reaction forces with Young’s modulus of different homogeneous materials was determined. Then, with using same boundary conditions, the reaction force of the RVE of heterogeneous material was found. The resulted reaction force of the heterogeneous material was put in the equation of homogeneous material of Young’s modulus with reaction forces, in order to determine the Young’s modulus of the RVE of the nanocomposite of heterogeneous material.

Table 1: Mechanical properties for nanocomposite RVE.

Material	Young’s modulus (GPa)	Poisson’s ratio	Diameter (μm)
Nano silica	70	0.23	50
PEEK	3.9	0.42	N/a

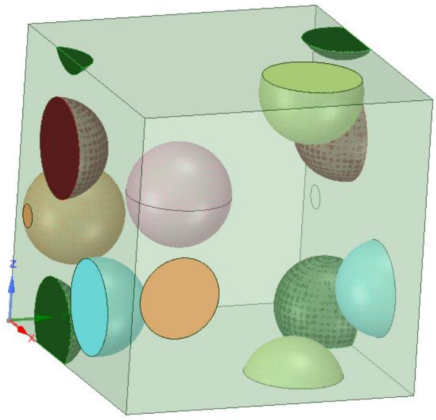

Figure 6: Nanocomposite reinforced with nanoparticles.

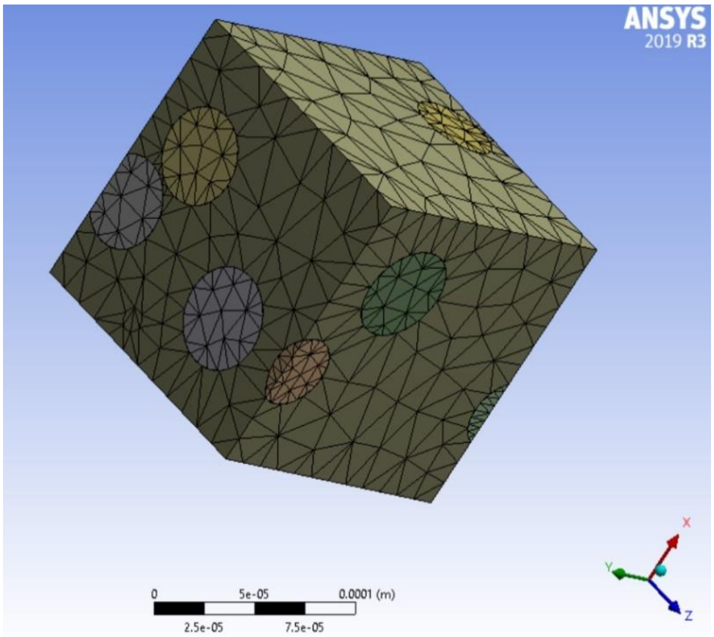

Figure 7: Meshing for the nanocomposite.

6.NANOCOMPOSITE VISCOLASTIC NUMERICAL RESULTS

The results of the viscoelastic numerical analysis for the RVE of nanocomposite that reinforced with random nanoparticles of nanosilica were found from the finite element analysis by ANSYS. To find the temperature effect on the nanocomposite properties numerically, the RVE were subjected to different temperature by using the thermal analysis of Ansys. For the matrix the prony series that obtained from the master curves at specific temperatures was used. The particles were considered in elastic behavior and subjected to the thermal conditions of the RVE. The analysis was conducted at different Prony series that calculated from the master curves. The results of temperatures effect on Young's modulus is shown in Figure 8. It can be observed that the modulus decrease with increasing temperature. At glass transition temperature around 160 °C the declination is steep and the materials lose their majority of the modulus. The reason of that is related to the glass transition region, which is a transition in molecular response that revealed as a change in properties. Materials transition from glassy to leathery to rubbery is with in this temperature range. Also, the modulus is the resistance to deformation; intuitively it seems that storage modulus should decrease with temperature because the of material glassy behavior.

To evaluate the effect of fiber content on the modulus on the nanocomposite, different volume fraction of the nanoparticle were subjected to change in temperature numerically, the results as in Figure 9 were obtained. It can be observe, as the fiber content increased the modulus of the nanocomposite increased gradually. This effect can be seen at different nanoparticle content. That is related to increase in stronger material component in the nanocomposite, which is the nanoparticles which hold the majority of the load by comparing with matrix.

The stress distribution of the RVE can be observed in Figure 10. The results show that higher stress at the bonding area between the particle and the matrix, and that's because of stress concentration in the area of bonding between nanocomposite contents.

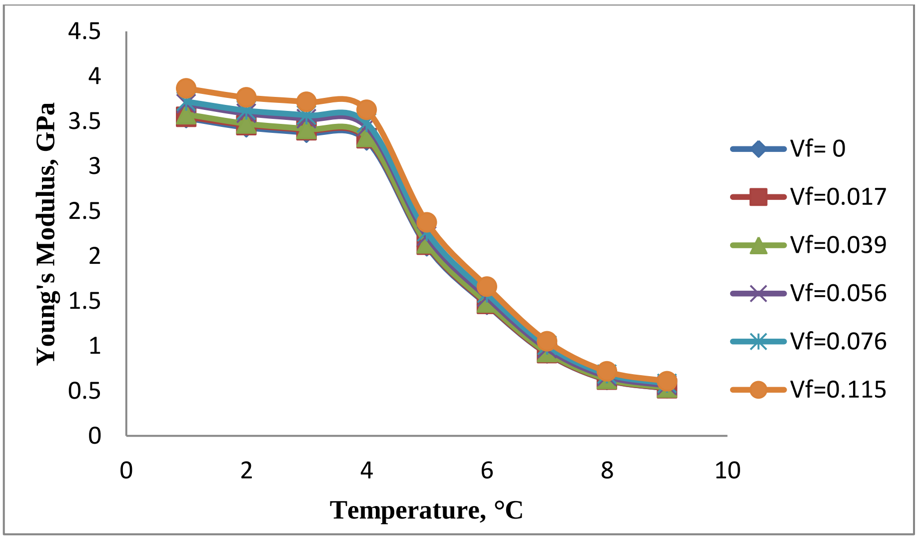

Figure 8: Temperature effect on the modulus of the nanocomposite reinforced by nanoparticle.

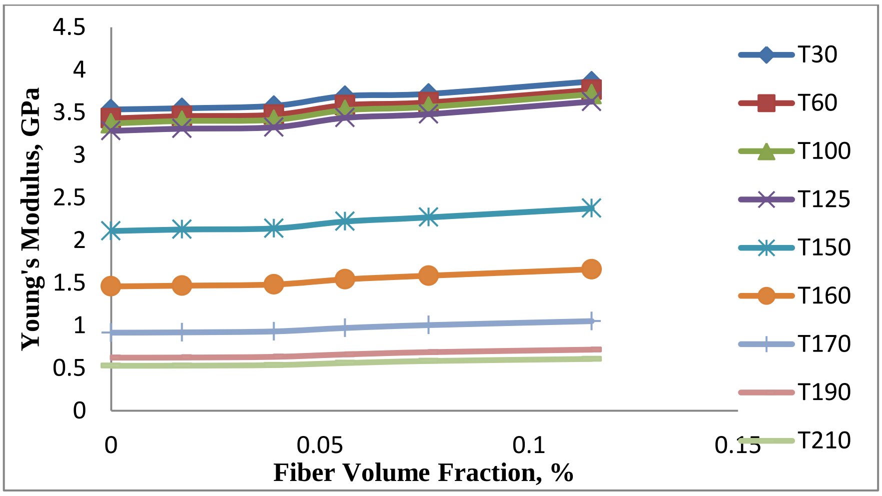

Figure 9: Effect of nanoparticle content on the nanocomposite Modulus.

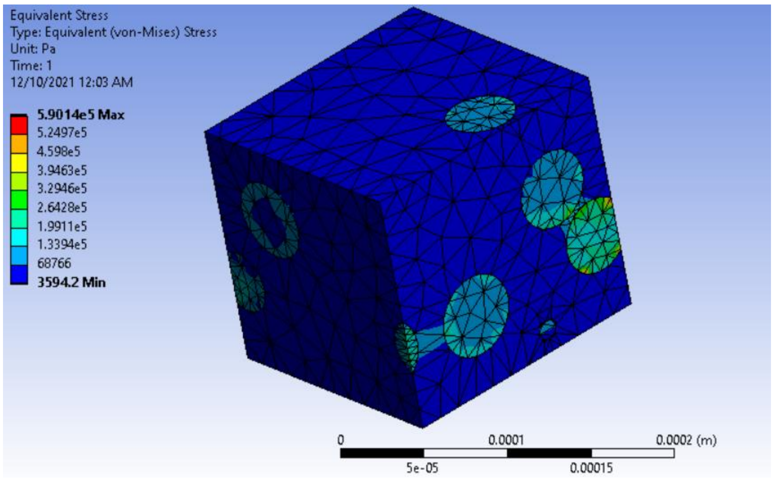

Figure 10: Equivalent stress analysis for the RVE.

7.CONCLUSIONS

The work reported in this paper set out to the following conclusions:

1. The viscoelastic properties for PEEK polymer that found experimentally were compared with numerical analysis, and they exhibited good agreement, which confirm the viscoelastic numerical analysis that conducted by Ansys FEM software.
2. A micromechanical model with RVE with considering matrix viscoelasticity was developed for the nanocomposite of PEEK reinforced by nanoparticles, it was found the temperature have significant effect on the nanocomposite properties while considering polymer viscoelasticity.
3. The effect of temperature on the material properties was predicted at different nanoparticle content; increasing nanoparticles caused increase in modulus.

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Conflict of Interest

The author declares that he has not gained any financial interests or any personal relationship that could influence the work that reported in this paper.

REFERENCE

Parameswaranpillai J., Kurian N. and Yu Y.2015, *Nanocomposite materials: synthesis, properties and applications*, CRC press, Taylor and Francis group.

Yas M, Korani H. and Jouneghani F. 2020. Studying the mechanical and thermal properties of polymer nanocomposites reinforced with montmorillonite nanoparticles using micromechanics method, *Journal of solid mechanics*, 12(1), 90-101, 2020.

Le B. 2020. A review on Nanocomposites Part 1: Mechanical Properties, *Journal of Manufacturing Science and Engineering*, DOI:10.1115/1.4047047.

Ou Y., Yang F., Yu Z. 1998. A new conception on the toughness of nylon 6/silica nanocomposite prepared via in situ polymerization, *Journal of Polymer Scenc. B: Polymer Phyics*, 36, 789–795.

Wang H., Bai Y., Liu S., Wu J. and Wong C. 2002. Combined effects of silica filler and its interface in epoxy resin, *Acta Materials*, 50, 4369–4377.

Boutaleb S. 2009. Micromechanics-based modelling of stiffness and yield stress for silica/polymer Nanocomposites, *International journal of solids and structures*, 46, 1716–1726.

Ghasemi M. et. al. 2021, Micromechanical simulation and experimental investigation of aluminum-based nanocomposites, *Defence technology*, 17, 196-20.

Mahmoodi M. et. al. 2019. Effects of added SiO_2 nanoparticles on the thermal expansion behavior of shape memory polymer nanocomposites, *Journal of intelligent material systems and structures*, 30(1), 32–44.

Liu Z. et. al. 2017. An extended micromechanics method for probing interphase properties in polymer nanocomposites, *Journal of the mechanics and physics of solids*.

Rouhi S., Ansari R., A. Nikkar A. 2018. Finite element modeling of the vibrational behavior of single-walled silicon carbide nanotube/polymer nanocomposites, *Journal of solid mechanics*, 10(4), 929-939.

Sanel S. and Oles R. 2019. Representative volume element for mechanical properties of carbon nanotube nanocomposites using stochastic finite element analysis, *Journal of engineering materials and technology*, 142.

Azmi M., Gitman I., Pinna C. and Soutis C. 2014. Modelling interaction effect of nanosilica particles on nanosilica/ epoxy composite stiffness, *ECCM16*, Seville Spain.

Reddy A. 2015. Effects of adhesive and interphase characteristics between matrix and reinforced nanoparticle of AA5154/AlN nanocomposites," *International journal of advanced research,* 3(9), 703 – 710.

Amrai J. et. al. 2018, Effect of interphase zone on the overall elastic properties of nanoparticle reinforced polymer nanocomposites," *Journal of composite materials*, DOI: 10.1177/0021998318798443.

Obucina M., Dzaferovic E. and Gondzic E. 2016. Numerical analysis viscoelasticity properties composite of wood, *26th DAAAM international symposium of intelligent manufacturing and automation*, Vienna, Austria.

Koval G., Maghous S. and Creus G. 2002. A numerical approach to effective viscoelastic properties of fiber composites, *Mecoom 2002- First south American congress on computational mechanics.* Argentina.

Gosz M., Moran B. and Achenbach J. 1991. Effect of a viscoelastic interface on the transverse behavior of fiber-reinforced composites, *International journal of solids and structures*, 27(14), 1757–71.

Hashin Z. 1992. Extremum-principles for elastic heterogenous media with imperfect interfaces and their application to bounding of effective moduli, *Journal of the mechanics and physics of solids*, 40(4), 767–81.

Fisher F., Brinson L. 2001, Viscoelastic interphases in polymer–matrix composites: theoretical models and finite-element analysis, *Composites science and technology*, 61, 731–748.

Cai C. et. al. 2002. Modelling of material damping properties in ANSYS, *Institute of high Performance Computing*.

Yannas L., Linear viscoelastic behavior," 2004. Available on website http://ocw.mit.edu/courses/health-sciences-and-technology/hst-523j-cell-matrix-mechanics-spring-2004/lecture-notes/lec21_viscoelast.pdf). Accessed on (5/10/2021).

Dealy J., Nonlinear viscoelastic". Available on website (http://www.eolss.net/Sample-Chapters/C06/E6-197-06-00.pdf). Accessed on (12/8/2021).

Charalambides M. and Olusanya A. 1997. The constitutive models suitable for adhesives in some finite element codes and suggested methods of generating the Appropriate Materials Data. NPL Report CMMT(B)130, UK.

Wu Q. 2009. *Creep behaviour o borate-treated stranboard: effect of zinc borate retention, wood species and load*. PhD thesis, Louisiana state university, USA.

Roylance D. 2001. Engineering viscoelasticity, Available online on website (http://web.mit.edu/course/3/3.11/www/modules/visco.pdf). 2001. Accessed on (5/9/2021).

Zmindak M. et. al. 2011, Finite element analysis of viscoelastic composite solids, *The 4th International conference, Modelling of mechanical and mechatronic systems*, technical university of Kosice.

Witczak M. 2004. *Development of a master curve database for lime modified asphaltic mixtures*. PhD thesis, Arizona state university.

Imaoka S. 2008. *Analyzing viscoelastic materials*, Ansys Inc.

I. Gitman I. et. al. 2004. The concept of representative volume for elastic, hardening and softening materials, I*nternational summer school conference in Advance problems in mechanics*, Russia.