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Prediction of Hyperelastic Material Properties of Nafion117 and Nafion/ZrO_2 Nano-Composite Membrane

F. Nemavhola[1] and R. Sigwadi[2, *]

[1]Department of Mechanical and Industrial Engineering, University of South Africa
Private BagX9, Florida, 1709
[2]Department of Civil and Chemical Engineering, University of South Africa,
Private BagX9, Florida, 1709
*Email: sigwara@unisa.ac.za
Phone: +2711472765; Fax: +27114712765

ABSTRACT

This paper presents constitutive laws suitable for the prediction of mechanical behaviour of nano-composite membrane compared with the commercial membrane Nafion®117. The uniaxial tensile data of commercial Nafion®117 and Nafion®/ Zr-150 nano-composite membrane utilised for fitting hyperelastic models was determined experimentally. Several material models on mechanical behaviour of nano-composite and commercial Nafion® 117 membrane material was fitted to determined accuracy. In order to observe yield and fracture behaviour, the com-mercial Nafion®117 and Nafion®/ Zr-150 nano-composite membranes were loaded in uniaxial direction at a constant strain rate. To obtain the optimal material constants form six different material models considered in this study, the OriginLab® version 9 was used and the Leven-berg-Marquardt (M) optimization logarithm. Hyperplastic material models including Mooney-Rivlin, Yeoh, Ogden, Humphrey, Martins and Veronda-Westmann were selected to use in an inverse method to fit the experimental uniaxial data of nano-composite material. The hyper-plastic material parameters could then be used to simulate material behaviour of nano mem-brane using finite element analysis (FEA) technique. The procedure discussed in this paper could be used to accurately determine the constitutive parameters of various constitutive models of Polymer Nafion presented.

Keywords: Constitutive laws; hyperelastic deformation; mechanical behaviour; uniaxial tests.

INTRODUCTION

Polymer Nafion® has gain interests from scientists and engineers for use in fuel cells application around the globe. The inherent complex mechanical properties of Polymer Nafion® necessitates the development of suitable constitutive models that could be utilised in various industries. The durability of polymer Nafion® plays a vital role in fuel cells application [1]. Therefore, there is a need to conduct computational simulation using simulation technique like finite element analysis to study its behaviour. The computational models as good as the provided constitutive parameters of chosen models. However, without accurate parameters, the accuracy of computational models is compromised. Hence, this study seeks to develop the con-stative parameters of widely used hyperplastic models in polymer Nafion®. The mechanical properties of the modified membrane with metal oxide have become a priority for fuel cell applications, as they must able to reduce the methanol permeability while enhancing the proton conductivity of the electrolyte. Proton exchange membrane fuel cells (PEMFCs) is a favourable contender to substitute internal combustion (IC) engines in vehicle applications [2-4]. The ability of PEMFCs has since have pulled in noteworthy consideration from both the industry and the scholarly world [5]. Recently the main challenge facing the fuel cell industry is the weak strength of thin membranes. In order to meet this challenge, there is a great need to develop high durable proton exchange membranes that has the ability to stand high durability targets of automotive industry [6, 7]. Due to the requirement of performance increase in these membranes, the composite membranes are made to be thinner. However, the thinning of these membranes tends to lower the mechanical properties [8-10]. The mechanical properties of the modified membrane have become a priority for fuel cell applications, as it must endure all the fuel cell operations to prevent crossover of the fuel while still conducting. In this paper, the nano-composite membrane was synthesised by the impregnation method using zirconium oxide as a nano-filler compared to the commercial Nafion117. The mechanical strength including the hyperplastic mechanical properties of Nafion/Zr-150 nano-composite membranes where were compared with the commercial Nafion117 membrane.

Hooke's law was used to study the linear stress-strain relationship of engineering materials since the 17th Century. However, Hooke's law became redundant and irrelevant when Mooney [11] and Rivlin [12] discovered that hyperplastic material behaviours such as rubber and soft tissue. Hyperplastic material models including Mooney-Rivlin, Yeoh, Ogden, Humphrey, Martins and Veronda-Westmann were selected to use an inverse method to fit the experimental uniaxial data of modified membrane and the commercial Nafion117 membrane. Polymer membrane for deformation models based on linear elasticity has been used extensively. Nonetheless, when the polymer membranes undergo hyperactive strains as most polymers do, the application on linear deformation models becomes limited and cannot be applied. As polymers undergo large deformation, they normally require the use of hyperplastic modelling. Elastic models can be characterised by Young's modulus of elasticity or shear modulus. In most polymers, this happens in the linear region of the stress-strain curve. However, a number of material parameters normally called hyperplastic parameters normally characterise polymer exhibiting hyperplastic response. Therefore, this paper seeks to utilise the uniaxial tensile test data (stress-strain curve) to determine the hyperplastic parameters of the hyperplastic models. Finite element methods have been developed enough and are capable of determining and simulating the mechanical behaviour of the polymer nano-composite membrane. However, the accuracy of these finite element models depends highly on the correctness of hyperplastic parameters used in simulating the model.

The theoretical and numerical modelling of elastic mechanical behaviour of nano-composite membrane materials have been not widely perused and under developed. In the engineering perspective, the nano-composite membrane polymers can be regarded as composite materials. Accordingly, the framework of continuum mechanics is normally used to capture the elastic response of soft tissues and rubbers. Additionally, the definition of a strain-energy function expressed in terms of kinematic invariants is further used in capturing of the purely elastic response of these materials. While several works has been done in constitutive modelling of soft tissue behaviour [13] little work has been done in the mechanical behaviour of nano-composite membranes. However, several mechanical behaviours of Nafion117 has presented no application of constitutive laws [14].

Furthermore, it is vital to have an accurate constitutive model that is fully capable of mathematically describing the mechanical behaviour of nano-composite membranes.

In addition, the full understanding of mechanical influences on the nano-composite membrane is vital to be further applied into finite element simulations. The evaluation of the mechanical behaviour of nano-composite material is critical due to the harsh conditions that this material could be subjected to in the field. Therefore, precise mathematical descriptions of the mechanical behaviour of nano-composite material continue to be the limiting factor in the advancement of accurate modelling. The constitutive response of nano-composite membrane is an important requirement for investigation of mechanical behaviour. Although the behaviour of nano-composite polymer is complex and often difficult to characterise, well-organised several materials models could be determined to test their suitability. Mechanical behaviour of hyperplastic materials remains an import matter in the area of non-linear mechanics. Constitutive laws remain relevant and important in studying the mechanical behaviour of solid structures under loadings. Hyperplastic models are commonly used to analysed or model the mechanical behaviour for rubber-like and soft tissue materials. These hyperplastic models could also be used in predicting the mechanical behaviour of nano-composite membrane materials as they exhibit non-linear behaviour under loading.

In the past decade, numerous hypothetical constitutive models have been presented to describe the mechanical behaviour of rubber and soft tissues observed in the experiments. Hyperplastic material models including Mooney-Rivlin, Yeoh, Ogden, Humphrey, Martins and Veronda-Westmann were selected to use an inverse method to fit the experimental uniaxial data of nano-composite material. Hyperplastic parameters of polymer Nafion® are normally determined by plotting the experimental data of stress-strain to a well or chosen strain energy function [15, 16]. The method of determining the materials constants by fitting curves using the known function is referred to as inverse procedure [17, 18]. The constitutive parameters of known strain energy can be determined by minimising the sum of the squares of the deviations between the experimental data and calculated data. The experimental data collected during uniaxial tensile testing was utilised for fitting into the selected material models. In this paper, six hyperplastic constitutive models suitable for rubber and soft tissue were used to fit the experimental data. A physically motivated constitutive model is important to help better understand the mechanical behaviour of nano-composite membrane polymer. The major objective of this study is to shed lights on the suitability of hyperplastic constitutive model to mechanical behaviour of nano-composite membrane material. This is achieved by conducting a systematic study of mechanical properties of commercial Nafion117 and Zr150 based on continuum theory of non-linear deformation elasticity.

EXPERIMENTAL SETUP

The commercial Nafion117 extruded thin films had an equivalent weight of 1100, and a nominal thickness of 0.18 mm were treated according to the standard procedure:1 hour in boiling 3% solution of hydrogen peroxide; 1 hour in boiling 0.5 M sulphuric acid; 1 hour in boiling distilled water. The nano-composite membranes were prepared by extending the Nafion 117 membranes over a petri-dish, adding a required amount of ZrO_2 (5wt %) nanoparticles in methanol solution. The nanocomposites membranes were repeatedly impregnated (up to 5 times) at room temperature [19]. In order to remove any air from the membrane pores, the sol and immersed membranes were heated up to 100 °C, then slowly cooled down to room temperature and kept in the solution for 24 hours. After drying, these membranes were stored in de-ionised water. The uniaxial mechanical properties of nano-composite membranes and commercial Nafion117 membrane were captured using a uniaxial testing system (see Figure 1). The length, width and thickness of samples were measured using a Vernier calliper and recorded prior to testing. The testing area of the membrane samples was 4 mm × 10 mm in dimension. To allow the clamping area, the sample were prepared in such a way that they will be clamped both sides and still allow the testing area to be 4 mm ×10 mm.

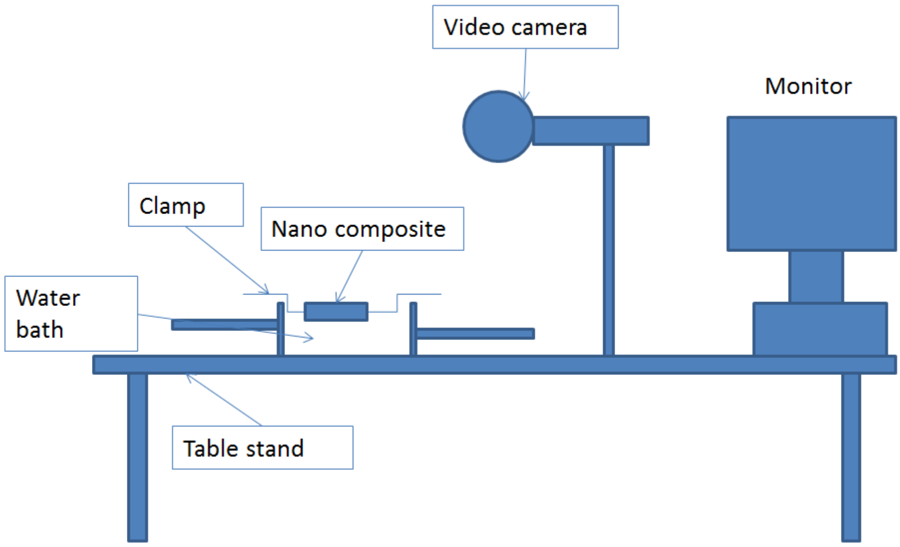


Figure 1. Schematic of the experimental set-up.

The length, width and thickness of samples were measured using a Vernier calliper and recorded before testing. The thickness of 0.18 mm of the nano-composite membrane was used in analysing the stress applied to the sample. Most Nafion nano-composite membranes are between 0.12 mm and 0.2 mm [20, 21]. The tensile strength of modified Nafion membranes was measured using CellScale Ustretch device dried at 25 °C and actuator speed of 5 mm per min. The tensile tests were conducted using CellScale Ustretch device, and the samples were stretched up to 40% strain. The 40% strain was applied in each sample of Nafion117 to avoid any breakage. The 40% strain was determined by first conducting a sample test. The 40% strain has translated to the maximum applied force of 25 N and 6 mm displacement (See Figure 2).

Hyperelastic Material Models

A hyperplastic material model relies upon the definition of the strain-energy function, which assumes different forms according to the material or class of materials considered. This function is obtained from symmetry, thermodynamic and energetic considerations. In this paper, six hyperplastic models were considered, namely: Mooney-Rivlin, Yeoh, Ogden, Humphrey, Martins and Veronda-Westmann. The mathematical derivation of all considered hyperplastic models are clearly stated and will not be repeated in this paper [13].

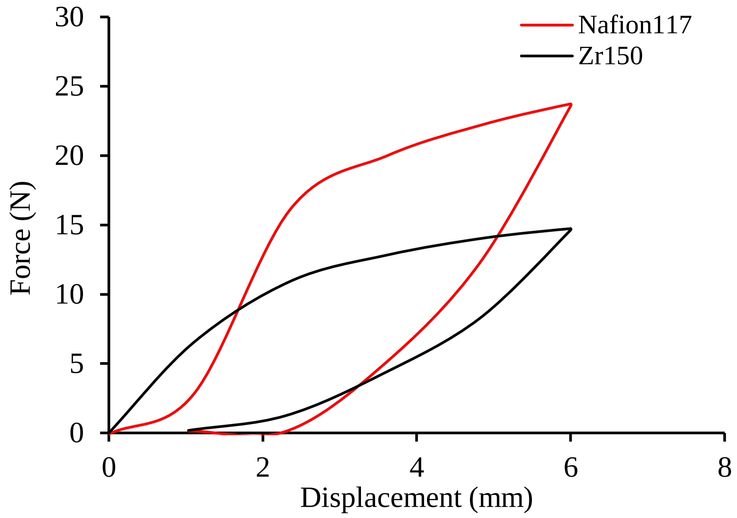


Figure 2. Force-displacement loading and unloading curve in the uniaxial direction of Nafion117 and Nafion®/ ZrO_2 nano-composite membrane

Theoretical Consideration

Mooney-Rivlin material model

The Mooney-Rivlin model has the ability to predict accurately the behaviour of non-linear isotropic material like rubber. As seen in the literature, the strain-energy function of the Mooney-Rivlin material model is often seen to be written as follows:

$$W=\frac{\mu_1}{2}(I_1-3)-\frac{\mu_2}{2}(I_2-3) \tag{1}$$

W represents the strain energy function. The material properties can be replaced by *a* and *b*, and the expression becomes:

$$W=\sum_{i=1}^{2} g_i(I_i-3) \tag{2}$$

Ogden material model

W represents the strain energy function. The Ogden materials model has the following general form:

$$W=\sum_{i=1}^{N}\frac{\mu_i}{\alpha_i}(\lambda_1^{\alpha_i}+\lambda_2^{\alpha_i}+\lambda_3^{\alpha_i}-3) \tag{3}$$

W represents the strain energy function. The Nx2 notation can be represented using the following form:

$$W=\sum_{i=1}^{3}\frac{g_{(2i-1)}}{g_{2i}}(\lambda_1^{g_{2i}}+\lambda_2^{g_{2i}}+\lambda_3^{g_{2i}})-3 \tag{4}$$

Humphrey material model

Humphrey material model has the following strain energy function:

$$W=g(\exp^{Q}-1) \quad (5)$$

Because Q is the right Cauchy-Green tensor, the isotropic form of Q is chosen to be as follows:

$$W=a\left(\exp^{b(I_1-3)}-1\right) \quad (6)$$

Where *a* and *b* are the material parameters, an I_1 is the first invariant of the Right-Cauchy tensor.

Martin's material model

The strain-energy function of the Martins material model is chosen to be as follows:

$$W=a\left(\exp^{b(I_1-1)}-1\right)+c\left(\exp^{d(\lambda-1)^2}-1\right) \quad (7)$$

Veronda-Westmann material model

It is understood that Veronda-Westmaan material model depends on all three variants including I_1, I_2 and I_3.

$$W=a\left[\exp^{\alpha(I_1-3)}-1\right]-b(I_2-3)+g(I_3) \quad (8)$$

Because the material is assumed to be incompressible, therefore, $I_3 = 1$ and $g(I_3) = 0$.
The following format is adopted:

$$W=a\left[\exp^{b(I_1-3)}-1\right]-\frac{ab}{2}(I_2-3) \quad (9)$$

Yeoh material model

In 1990, the Yeoh material model was introduced for simulating the rubber-like material which is incompressible. This model only uses the first strain invariant to describe its strain energy function. Therefore, the material constants *a, b and c* are to be fitted in the experimental data:

$$W=\sum_{i=1}^{3} g_i(I_i-3)^i \quad (10)$$

Uniaxial tension tests

The uniaxial stress derivation of all models considered is taken from [22]. In this study, it has been assumed that the modified nano-composite membrane and commercial Nafion117 has a similar mechanical behaviour that is similar to incompressible hyperplastic materials. Following the work done by [23], the following equations for uniaxial stress as a function of the stretch ratio is adopted for all considered material hyperplastic models.

Mooney-Rivlin model:

$$\sigma_{Uniaxial\_Mooney}=2\left(\lambda^2-\frac{1}{\lambda}\right)\left(a+b\frac{1}{\lambda}\right) \quad (11)$$

Yeoh material model [24]:

$$\sigma_{Unixial\_Yeoh}=2\left(\lambda^2-\frac{1}{\lambda}\right)(a+2b(I_1-3)+3c(I_1-3)^2) \quad (12)$$

But $I_1=\lambda^2+\frac{2}{\lambda}$ (13)

Therefore:

$$\sigma_{Unixial\_Yeoh}=2\left(\lambda^2-\frac{1}{\lambda}\right)\left(a+2b\left(\left(\lambda^2+\frac{2}{\lambda}\right)-3\right)+3c\left(\left(\lambda^2+\frac{2}{\lambda}\right)-3\right)^2\right) \quad (14)$$

Ogden material model:

$$\sigma_{Uniaxial\_Ogden}=a\left(\lambda^b-2^{-1+b}\lambda^{\frac{-b}{2}}\right)+c\left(\lambda^d-2^{-1+d}\lambda^{\frac{-d}{2}}\right)+e\left(\lambda^f-2^{-1+f}\lambda^{\frac{-f}{2}}\right) \quad (15)$$

Humphrey material model:

$$\sigma_{Humprey}=2\left(\lambda^2-\frac{1}{\lambda}\right)a.bexp^{b\left(\left(\lambda^2+\frac{2}{\lambda}\right)-3\right)} \quad (16)$$

Martins material model:

$$\sigma_{Unixial\_Martins}=2\left(\lambda^2-\frac{1}{\lambda}\right)a.bexp^{a\left(\left(\lambda^2+\frac{2}{\lambda}\right)-3\right)}+2\lambda(\lambda-1)c.dexp^{c(\lambda-1)^2} \quad (17)$$

Veronda-Westmann material model:

$$\sigma_{Uniaxial_{Veronda}\text{-}Westmann}=2\left(\lambda^2-\frac{1}{\lambda}\right)a.b\left(exp^{b\left(2\left(\lambda^2-\frac{1}{\lambda}\right)-3\right)}-\frac{1}{2\lambda}\right) \quad (18)$$

$$R^2=1-\frac{\sum_{i=1}^{n}[\sigma-\sigma^{\psi}]_i^2}{\sum_{i=1}^{n}[\sigma-\mu]_i^2} \quad (19)$$

$$\mu=\frac{1}{n}\sum_i^n[\sigma]_i \quad (20)$$

$$\varepsilon=\frac{\sqrt{\frac{\chi^2}{(n-q)}}}{\mu} \quad (21)$$

RESULTS

The statistical analysis was implemented to assess the correlations between the commercial Nafion117 and Nafion/Zr-150 nano-composite membrane. The commercial Nafion117 membrane shows strong nonlinear properties under tensile loading. Figure 1 shows the uniaxial loading of stress-strain curve for Nafion 117 and modified membranes materials. The tensile test was conducted according to the standard DIN 53504: 1994. A Univert CellScale® mechanical tester with 200 N load cell, as shown in Figure 1 tested the tensile mechanical property. The specimens were rectangular, about 10 mm in width and about 30 mm in length. We used sandpaper to adhere on the two surfaces of the clamp, which prevent the slip of the specimen during the testing. The crosshead speed was set as 3 mm/min, and the load was applied until the ultimate fracture of the specimen. The elastic modulus was calculated as the slope of the initial linear portion of the force-strain curve. The tensile strength was determined as the maximum point of the force-strain curve. To obtain the optimal material constants form six different material models considered in this study, the OriginLab® was used. The OriginLab® uses the Levenberg-Marquardt (M) optimisation logarithm.

The experimental data obtained from the tensile test is the force displacement presented. As a result, there a need to calculate the associated stress-strain of the experimental data. The average cross-sectional area of each polymer Nafion® was calculated. The average stress is calculated as follows:

$$\sigma_i=\frac{F_i}{A_i} \tag{22}$$

To calculate the strain (Eq. (23)) and stretch (Eq. (24)); the following relationships were used:

$$\varepsilon=\frac{l_i-l_o}{l_o} \tag{23}$$

$$\lambda=\varepsilon+1 \tag{24}$$

The force-displacement loading and unloading curve in the uniaxial direction of Nafion117 and Nafion®/ ZrO2 nano-composite membrane is shown in Figure 2. Similarly, Figure 3 shows the variation of the stretch ratio with time as the nanocomposite membrane is stretched in a uniaxial direction. Using the force and cross-sectional area of the nanomembrane stress-stretch ratio curve was determined in Figure 4, showing the typical stress-stretch ratio curve of Nafion117 and Nafion/ Zr-150 nano-composite membranes. There is high strength associated with Zr150 nanocomposite membrane when compared with commercial Nafion117 membrane.

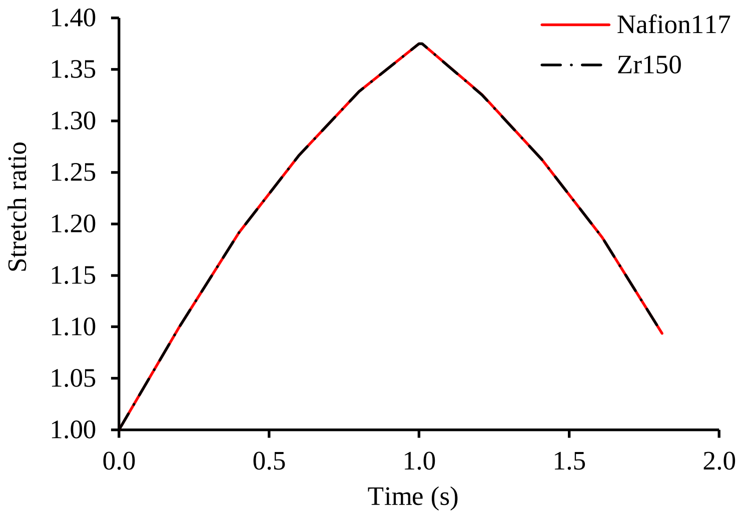


Figure 3. Variation of the stretch ratio with time as the nanocomposite membrane is stretched in a uniaxial direction.

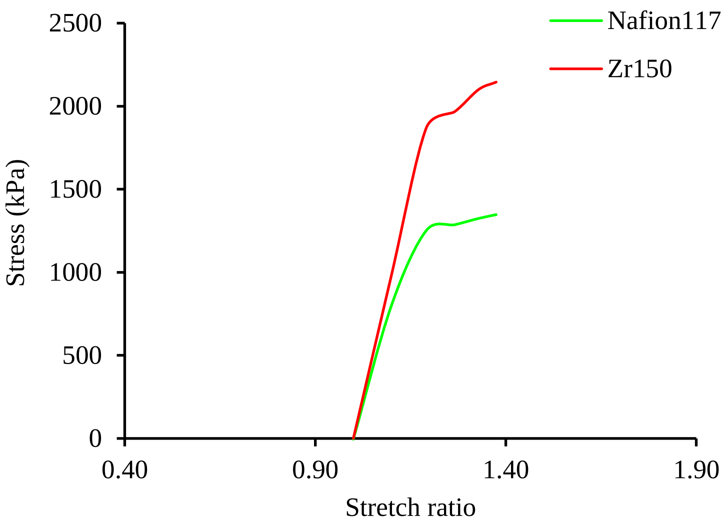


Figure 4. Stress-stretch ratio curve of Nafion117 and Nafion/ Zr-150 nano-composite membranes.

It is observable that the hyperplastic materials models considered in this study are relevant in explaining the mechanical behaviour of modified membrane material. The coefficient of determination (also referred to as R^2) was used to measure the distance between the data and the fitted regression line. This R^2 is also useful as it provides the proportion of the variance (fluctuation) of one variable that is predictable from the other variable. Furthermore, the R^2 was considerable for each material model considered in this study. Figure 5 shows the stress-stretch curve of the fitted models of commercial Nafion117 membrane. Figure 5 shows that all six material models observed in this study are able to capture the hyperplastic behaviour of Nafion117 membrane material. As shown in Figure 6, the stress-stretch curve of Nafion/ Zr-150 nano-composite membrane material has a higher strength when compared to Nafion117. However, it can conclude that the materials models considered sufficiently fit the hyperplastic material behaviour of Nafion/ Zr-150 nano-composite membrane.

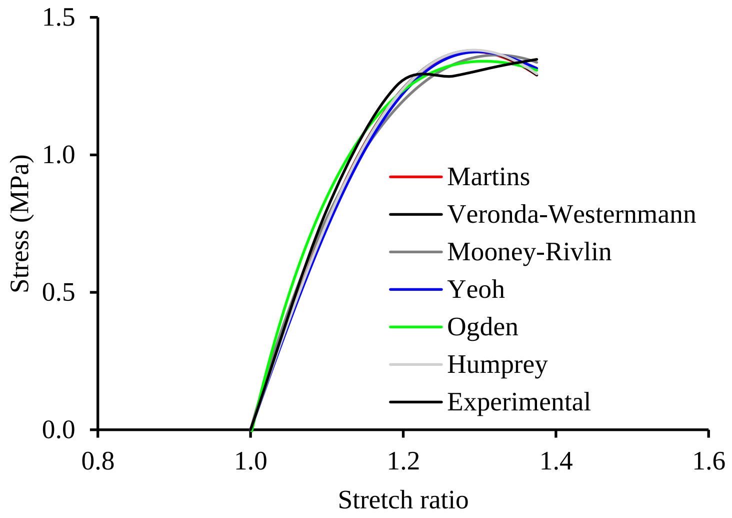


Figure 5. Stress-stretch curve for Nafion117 membrane.

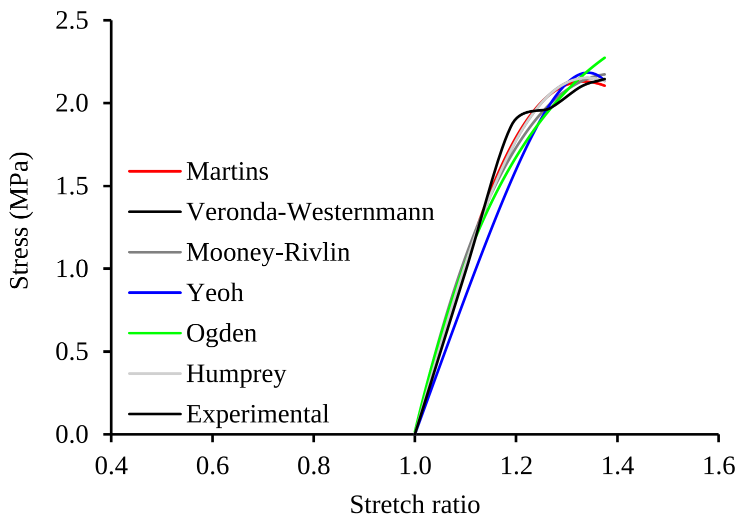


Figure 6. Stress-stretch curve for Nafion/ Zr-150 nano-composite membrane

Table 1 shows the material parameters of the Nafion/ Zr-150 nano-composite membrane that were determined using six models considered. On the other hand, Table 2 shows the material parameters of Nafion 117 that were determined using six models considered. When looking at Nafion/ Zr-150 nano-composite membrane, Martins, Veronda-Westmann and Humphrey models had the highest R-squared of greater than 0.99. However, Mooney model also shows an R-squared of 0.988. Yeoh and Ogden models of Nafion/ Zr-150 nano-composite membrane showed an R-squared of less than 0.988 (See Table 1). When looking at Nafion 117, Martins, Ogden, Mooney and Humphrey models had the highest R-squared of greater than 0.99. However, Humphrey, Yeoh and Veronda-Westmann models show an R-squared of greater than 0.988 (Table

2). This means that the Nafion 117 material had better-fitted models when compared to the Nafion/ Zr-150 nano-composite membrane material.

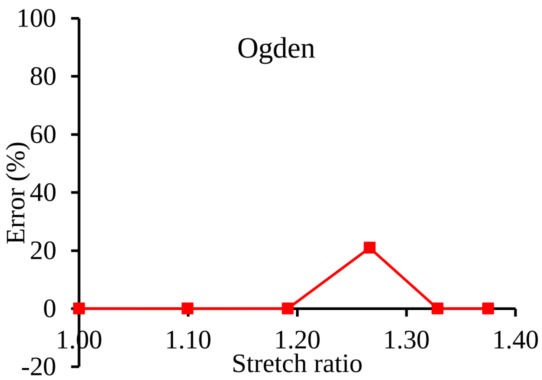
The error analysis of hyperplastic models is presented in Figure 7. Generally, the error is lower in the region between 1< λ >1.2 and higher in the region 1.2< λ >1.4. This means that contrary to the rubber and soft tissue materials; the Nafion117 and Nafion/ Zr-150 nano-composite membrane exhibits small errors in the region between 1< λ >1.2 and higher in the region 1.2< λ >1.4 (See Figure 7). Table 3 shows the number of iterations of all six material models considered in both Nafion117 and Nafion/ Zr-150 nano-composite membrane. When considering a single material model like Martins, it is clear that the number of iteration is independent of either Nafion117 or Nafion/ Zr-150 nano-composite membrane as they have exhibited an equal number of iterations. Humphrey model for Nafion/ Zr-150 nano-composite membrane has 7 iterations while Nafion 117 had 8 iterations. This is the only model where the number of iterations is different in two materials considered in this paper (see Table 3). However, Humphrey, Yeoh and Veronda-Westmann models show an R-squared of greater than 0.988 (See Figure 8). This means that the Nafion 117 material had better fitted models when compared to Nafion/ Zr-150 nano-composite membrane material.

Table 1. Optimised materials constants from different hyperplastic models (Nafion/ Zr-150 nano-composite membrane).

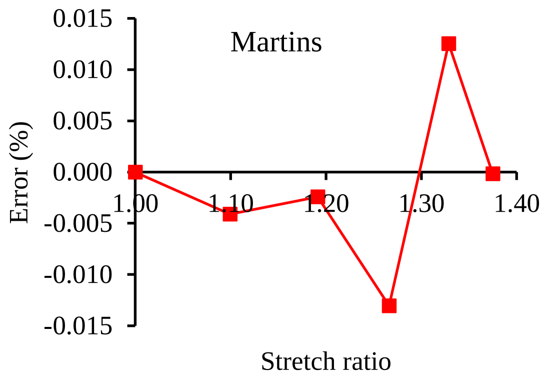
	Constant	Parameters	R-squared	Reduced chi-square
Martins	*a*	-3.4	0.9923	0.007
	b	-0.3434		
	c	-3.15		
	d	-0.606		
Veronda-Westmann	*a*	-0.92	0.9913	0.006
	b	-1.962		
Mooney-Rivlin	*a*	-2.45	0.9883	0.009
	b	4.65		
Yeoh	*a*	1.4	0.9624	0.027
	b	-0.244		
	c	-0.88		
Ogden	*a*	2.04	0.9781	0.02
	b	-0.66		
	c	-5		
	d	-6.379		
	e	5.252		
	f	-0.66		
Humprey	*a*	-0.92	0.9913	0.006
	b	-1.962		

Table 2. Optimised materials constants from different hyperplastic models Nafion117 membrane.

	Constants	Parameters	R. Squared	Reduced Chi-Square
Martins	*a*	-2.9	0.99	0.0035
	b	-0.4273		
	c	-2.54		
	d	-0.1248		
Veronda-Westmann	*a*	-0.524	0.9894	0.003
	b	-2.56915		
Mooney-Rivlin	*a*	-2.25	0.9924	0.0022
	b	3.88334		
Yeoh	*a*	1.3	0.9884	0.0032
	b	-1.5		
	c	0.841		
Ogden	*a*	2.1872	0.9947	0.018
	b	4.9871		
	c	-5		
	d	-2.35295		
	e	-3.29606		
	f	4.2454		
Humphrey	*a*	-0.526	0.9894	0.003
	b	-2.55265		



(a)



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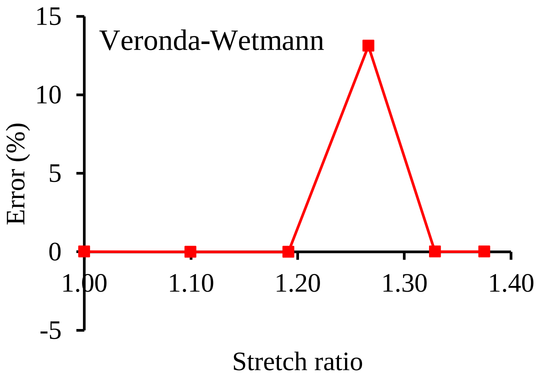

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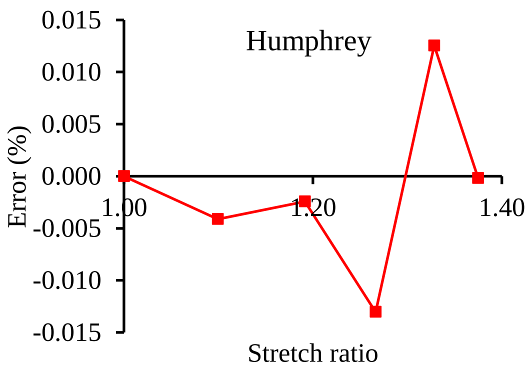

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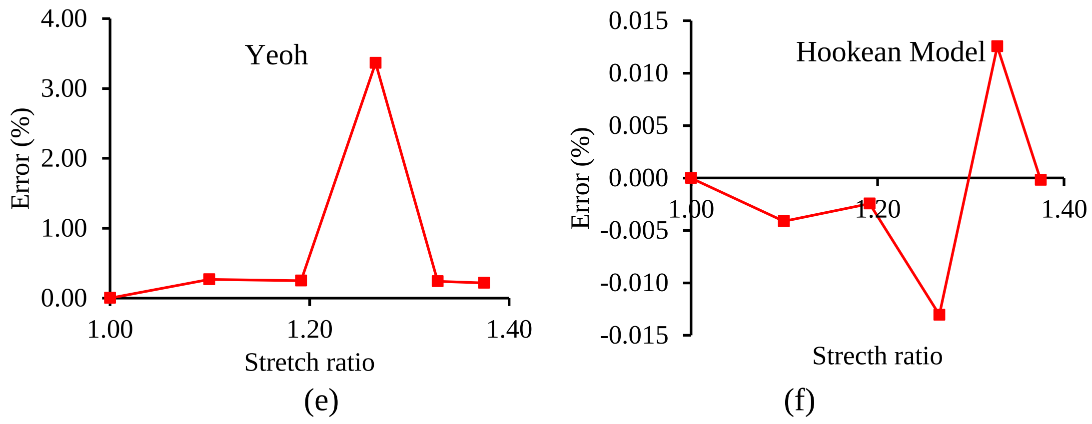

Figure 7. Comparison of error between the experiment and fitted data.

Table 3. Number of iterations per hyperplastic model in commercial Nafion117 and Nafion/ Zr-150 nano-composite membrane materials.

	Nafion®/Zr150	Nafion117	Reduced Chi-Square
Martins	4	4	0
Veronda-Westmann	7	7	0
Mooney-Rivlin	3	3	0
Yeoh	3	3	0
Ogden	8	8	0
Humprey	7	8	0

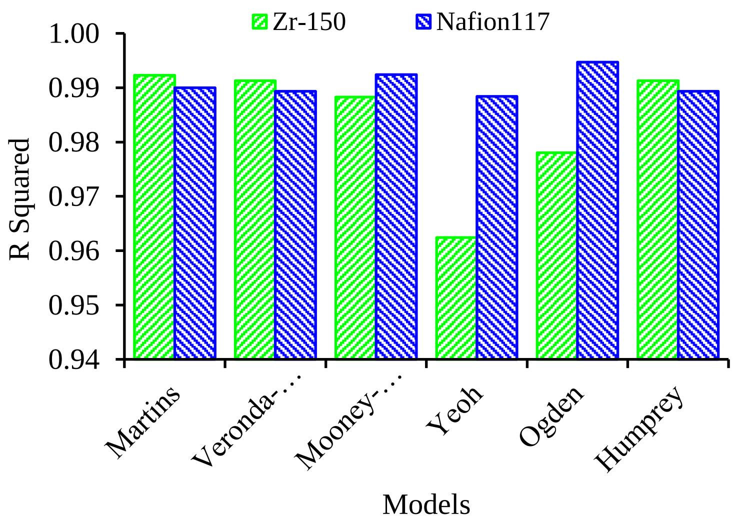

Figure 8. Comparison of R^2 of different models for Nafion/ Zr-150 nano-composite and Nafion 117 membrane materials.

DISCUSSION

The mechanical properties of the modified membrane have become a priority for fuel cell applications, as it must endure all the fuel cell operations (to prevent crossover of the fuel while still conducting) [25]. These properties could be used in predicting the material deformation to prevent crossover of the fuel while still conducting. The hyperplastic material properties can be further used for assessing the development of high strength nanocomposite materials [26]. The suitability of models for nanomembranes plays an important role in the development of computational models. In this paper, various suitable models were compared to check the suitability. This was achieved by randomly selecting the related mathematical models that were utilised in similar materials. The best fit models were chosen with further input. In this paper, the nanocomposite membrane was synthesised by the impregnation method using zirconium oxide (Zr150) as a nanofiller compared to the commercial Nafion 117. The mechanical strength, including the hyperplastic mechanical properties of Nafion/Zr-150 nano-composite membranes where were compared with the commercial Nafion117 membrane. It is vital to have an accurate constitutive model that is fully capable of mathematically describing the mechanical behaviour of nano-composite membranes. Also, the full understanding of mechanical influences on the nano-composite membrane is vital to be further applied into finite element simulations. The evaluation of the mechanical behaviour of nano-composite material is critical due to the harsh conditions that this material could be subjected to in the field. Therefore, precise mathematical descriptions of the mechanical behaviour of nano-composite material continue to be the limiting factor in the advancement of accurate modelling.

The error analysis of hyperplastic models is presented in Figure 4. Generally, the error is lower in the region between $1< \lambda >1.2$ and higher in the region $1.2< \lambda >1.4$. These findings contradict with what has been presented by [23]. In the paper [23], hyperplastic parameters of rubber and soft tissue were determined by fitting the tensile uniaxial data [22, 27]. This means that contrary to the rubber and soft tissue materials, the Nafion 117 and Nafion/ Zr-150 nano-composite membrane54redsaz1 exhibit small errors in the region between $1< \lambda >1.2$ and higher in the region $1.2< \lambda >1.4$ (See Figure 4).

When comparing the material parameters of commercial Nafion 117 and Nafion/ Zr-150 nano-composite membrane, a significant difference between the two materials is observed. For example, when looking at Martin's hyperplastic model, the material parameters a, b, c and d of commercial Nafion 117 are -2.9, -0.4273, -2.54 and -0.1248 MPa, respectively. These material parameters are significantly different when considering the hyperplastic Martin's model material parameters that are -3.4, -0.3434, -3.15 and -0.606 MPa, respectively. In addition, the material parameters using the Mooney-Rivlin model when considering commercial Nafion 117 and Nafion/ Zr-150 nano-composite membrane are -2.25, 3.88 MPa and -2.45, 4.65 MPa, respectively. From this data, it can be seen that the material parameters of the Mooney-Rivlin of commercial Nafion 117 are lower than Nafion/ Zr-150 nano-composite membrane materials. However, when looking at the Humphrey model, the magnitude of the material parameter of commercial Nafion 117 is higher than that of the Nafion/ Zr-150 nano-composite membrane material.

In this paper, six hyperplastic models were fitted using the tensile uniaxial data of commercial Nafion 117 and Nafion/ Zr-150 nano-composite membrane material. In these six hyperplastic material models, only five models are suitable (>0.98) for mechanical behaviour of Nafion/ Zr-150 nano-composite membrane and six models are suitable for commercial Nafion 117. Generally, the suitability of hyperplastic models on the commercial Nafion 117 has been found to be better than that of the Nafion/ Zr-150 nano-composite membrane material. For Nafion/ Zr-150 nano-composite membrane, the best fit models (with >0.99) obtained was in Martins, Veronda-Westmann and Humprey model. For commercial Nafion 117 membrane material, the best fit models (with >0.99) are Martins, Mooney-Rivlin, Ogden. Martins model was used in this paper to fit the experimental data for both the commercial Nafion 117 and Nafion/ Zr-150 nano-composite membrane materials. This model shows to have good correlations for both commercial Nafion 117 and Nafion/ Zr-150 nano-composite membrane materials. It is to be noted that the accuracy of the model fit is more is observed in the non-linear region ($1.2< \lambda >1.4$). The high accuracy is achieved in a high strain region [28].

The systematic study of the fitting of stress-stretch equations using a non-linear least squares optimisation method hyperplastic constitutive law. The experimental data of uniaxial tensile of commercial Nafion 117 and Nafion/ Zr-150 nano-composite membrane materials were used to determine the material parameters using various selected models. Furthermore, a concerted effort was made to focus on determining the relative errors of fitted data based on selected models. It must be noted that several sets of optimal material parameters were obtained especially in Ogden and Martins strain-energy functions based on the initial guess and initial estimate of the parameter. The problem of numerous optimum sets of material parameters was not encountered based on the selected model like Ogden was mentioned in previous studies.

CONCLUSION

In this paper, six hyperplastic models were fitted using the tensile uniaxial data of commercial Nafion® 117 and Nafion®/ Zr-150 nano-composite membrane material. The results presented here could be useful for the strength optimisation of improved nano-composite membrane materials. The hyperplastic material parameters could then be used to simulate material behaviour of nanomembrane using finite element analysis (FEA) technique. The procedure discussed in this paper could be used to accurately determine the constitutive parameters of various constitutive models of Polymer Nafion® presented. Our future research will focus on the fatigue properties of Polymer Nafion®. This will allow us to simulate the mechanical behaviour of the Polymer Nafion® of various mechanical strength. In these six hyperplastic material models, only five models are suitable (>0.98) for mechanical behaviour of Nafion/ Zr-150 nano-composite membrane and six models are suitable for commercial Nafion 117. Martin's model has exhibited the best fit and could be used to best model Nafion®/Zr150 materials.

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