A Constitutive Law for Poly(butylene terephthalate) Nanofibers Mats

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ABSTRACT: A three-dimensional structural constitutive equation is proposed to describe the mechanical properties of poly(butylene terephthalate) nanofibers mats. The model is formulated under the assumption that the mechanical response of the fibrous mat is determined by the individual fibers. The inelasticity, which has been observed when subjecting the fibrous mat to tensile tests, is assumed to be due to the gradual breakage of linear elastic fibers. The constitutive relation also takes the material anisotropy associated with the fibers' architecture into account. Uniaxial experimental data were used to assess the proposed model. The results demonstrate that the model is well suited to reproduce the typical tensile behavior of the fibrous mat. In agreement with the empirical observations, the model predicts that almost all the fibers fail when the poly(butylene terephthalate) fibrous mat sample breaks. Nevertheless, multiaxial stress–strain data and quantification of the fibers' orientation are required to completely validate the constitutive law. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5280–5283, 2006

Key words: fibers; failure; inelasticity; poly(butylene terephthalate); modeling

INTRODUCTION

The electrospinning technique continues to reveal numerous advantages in manufacturing nanoscales polymeric fibers. It enables to generate fibers with diameters in the range of nanometers, with large surface area to volume ratios, and with high strength. These nanofibers can be engineered by electrospinning various types of polymer solutions or melts. These fibers have potential use in composite reinforcements, tissue engineering, filtration application, and protective clothing industry.[1] Despite the large field of applications, the mechanical properties of the electrospun polymer fibers mat remain poorly understood.

Predominantly, nonwoven structures with randomly oriented nanofibers have been fabricated through the electrospinning process. Few investigators attempted to produce assemblies that possess highly aligned electrospun nanofibers.[2–5] The speed of the rotating cylinder collector, which is part of the electrospinning apparatus, has been reported to influence the orientation of the nanofibers in nonwoven structures. Recently, Mathew et al.[5] fabricated highly oriented poly(butylene terephthalate) (PBT) nanofibers mats and investigated their mechanical properties by conducting tensile tests. They found that the tensile strength, the tangent modulus, and the ultimate strain depend strongly on the arrangement of the fibers.

In the present work, a structural three-dimensional constitutive equation for PBT fibrous mat is proposed. Thus, the microstructure is assumed to govern the gross mechanical response of the material. The equation is formulated by taking into account the inelastic properties of the PBT nanofibers mat as exhibited in the experimental studies.[5] The inelastic behavior was assumed to be due to the gradual failure of linear elastic PBT nanofibers. The description of the anisotropy, which was observed in the aforementioned experiments, is also included in the model.

The validity of the proposed model is demonstrated by assuming that the deformation of PBT nanofibers mat is homogeneous, isochoric, and axysymmetric, and that the nanofibers are perfectly aligned along the axial direction of loading. Only three parameters are needed to reproduce the tensile response of the PBT nanofibrous mat. Although the current results are promising, multiaxial experimental data coupled with quantification of the PBT fibers' orientation are needed to completely estimate the performance of the proposed model.

Model formulation

A general three-dimensional constitutive law for the mechanical properties of PBT nonwoven fabric is presented. The fibrous mat is treated as a hyperelastic

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material and, hence, the existence of a strain energy function to define the stress tensor is assumed. Following the structural approach for soft planar tissues,[6,7] the strain energy of the mat is defined as the sum of the strain energies of the individual fibers. The PBT fibers are assumed to be linearly elastic fibers with a stretched-controlled failure criterion. Each fiber contributes to the gross mechanical behavior only under tension. Thus, fiber compressive and bending energies are ignored. The fibers are idealized as straight and they are arranged along different directions. Both the fibers' orientation and failure stretches are stochastically defined by two probability density functions.

By assuming the PBT fibrous mat to be incompressible, nonlinear, and hyperelastic, the first Piola-Kirchhoff stress tensor can be expressed as[88]

$$\mathbf{P} = -p\mathbf{F}^{-\mathrm{T}} + 2\mathbf{F} \cdot \frac{\partial W(\mathbf{C})}{\partial \mathbf{C}}, \tag{1}$$

where "·" denotes the dot product, p is an indeterminate pressure that enforces the incompressibility assumption, $\mathbf{F}$ is the deformation gradient tensor, $\mathbf{F}^{\mathrm{T}}$ is the transpose of $\mathbf{F}$, $\mathbf{F}^{-\mathrm{T}}$ is the inverse transpose of $\mathbf{F}$, $\mathbf{C} = \mathbf{F}^{\mathrm{T}} \cdot \mathbf{F}$ is the right Cauchy-Green deformation tensor, and $W(\mathbf{C})$ is the strain energy function of the PBT fibrous mat.

The strain energy function of the overall structure, $W(\mathbf{C})$, is assumed to be the sum of the strain energies of the individual fibers, $w(\Lambda)$, where (Λ) denotes the fiber stretch. Thus, it can be defined as[6,7]

$$W(\mathbf{C}) = \int_{\Sigma} R(\mathrm{N}) w(\Lambda(\mathbf{C},\mathbf{N}))\, d\boldsymbol{\Sigma}, \tag{2}$$

where Σ is the set of all unit vectors in the reference configuration, and $\mathbf{N}$ an element of such set. $R(\mathbf{N})$ is the probability density function for fibers to be oriented along the direction $\mathbf{N}$ in the reference configuration, subjected to the constrain

$$\int_{\Sigma} R(\mathbf{N})\, d\boldsymbol{\Sigma} = 1, \tag{3}$$

with

$$\Lambda(\mathbf{C},\mathbf{N}) = \sqrt{\mathbf{N}\cdot\mathbf{C}\cdot\mathbf{N}}. \tag{4}$$

It must be explicitly noted that eq. (4) states that the fiber stretch, Λ, is a tensorial transformation of the mat deformation, $\mathbf{C}$, in the fiber direction $\mathbf{N}$. This assumption is justified by the presence of interconnections among the nanofibers in the tissue.

After defining the stress–stretch relation for fibers that are aligned along $\mathbf{N}$ as

$$\sigma = \frac{d}{d\Lambda} w(\Lambda(\mathbf{C},\mathbf{N})), \tag{5}$$

and noting that

$$\frac{\partial w}{\partial \mathrm{C}} = \frac{dw}{d\Lambda}\frac{\partial \Lambda}{\partial \mathbf{C}}, \tag{6}$$

the constitutive law (1) becomes

$$\mathbf{P} = -p\mathbf{F}^{-\mathrm{T}} + \mathbf{F}\cdot \int_{\Sigma} R(\mathbf{N}) \frac{\mathbf{NN}}{\Lambda(\mathbf{C},\mathbf{N})} \sigma(\Lambda(\mathbf{C},\mathbf{N}))\, d\boldsymbol{\Sigma}. \tag{7}$$

The stress–stretch relation for the fibers along the direction $\mathbf{N}$ is defined as

$$\sigma(\Lambda) = \frac{1}{n}\sum_{i=1}^{n} \sigma^{(i)}, \tag{8}$$

where $\sigma^{(i)}$ is given by

$$\sigma^{(i)} = \begin{cases} 0 & \text{if } \Lambda \le 1, \\ K(\Lambda - 1) & \text{if } \Lambda < \Lambda^{(i)}{}_f, \\ 0 & \text{if } \Lambda \ge \Lambda^{(i)}{}_f, \end{cases} \tag{9}$$

where K is the fiber tangent modulus and $\Lambda_f^{(i)}$, are the failure stretches that are assumed to be distributed randomly according to the two-parameter Weibull cumulative distribution, i.e.,

$$\Lambda_f^{(i)} = 1 + \beta\left[-\ln(1 - G_f^{(i)})\right]^{\frac{1}{\alpha}} \qquad (i = 1 \ldots n) \tag{10}$$

where $G_f^{(i)}$ are random numbers such that $0 < G_f^{(i)} < 1$ $\alpha > 0$, and $\beta > 0$ are the shape parameter and the scale parameter of the Weibull distribution, respectively.

Model implementation

Some assumptions concerning the deformation and the orientation distribution of the PBT fibrous mat specimens are made hereafter to evaluate the constitutive model with the available uniaxial experimental data.[5]

The PBT fibrous mat is assumed to undergo a homogeneous, isochoric, and axisymmetric deformation defined by the following deformation gradient tensor

$$\mathbf{F} = \lambda_1 \mathbf{e}_1\mathbf{E}_1 + \frac{1}{\sqrt{\lambda_1}}\mathbf{e}_2\mathbf{E}_2 + \frac{1}{\sqrt{\lambda_1}}\mathbf{e}_3\mathbf{E}_3, \tag{11}$$

where λ_1 is the axial stretch, the sets of vectors, $\{\mathbf{E}_1, \mathbf{E}_2\ \mathbf{E}_3\}$ and $\{\mathbf{e}_1, \mathbf{e}_2\ \mathbf{e}_3\}$, define orthonormal bases in the current and reference configurations, respectively. The vectors $\mathbf{E}_1$ and $\mathbf{e}_1$ coincide with the axial loading directions. Consequently, the right Cauchy-Green deformation tensor has the form

$$\mathbf{C} = \lambda_1^2 \mathbf{E}_1\mathbf{E}_1 + \frac{1}{\lambda_1}\mathbf{E}_2\mathbf{E}_2 + \frac{1}{\lambda_1}\mathbf{E}_3\mathbf{E}_3. \tag{12}$$

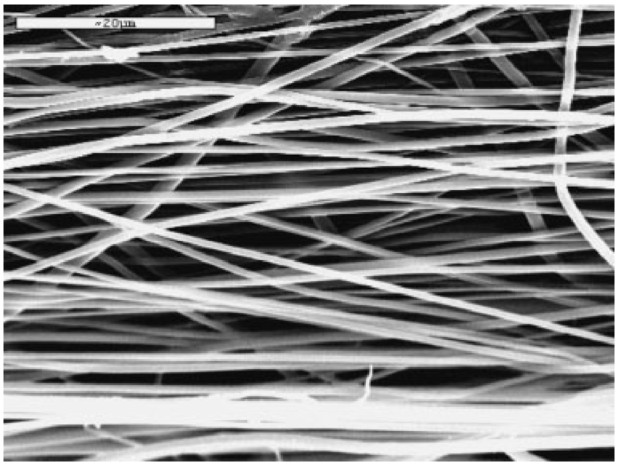

Figure 1 Field emission scanning electron microscopy image of the PBT elecrospun fibrous mat that is collected by a drum rotating at a speed 1200.

The constitutive model is implemented under the assumption that all the fibers in the PBT nonwoven fabric specimens are oriented along the loading direction $\mathbf{E}_1$ in the reference configuration. This assumption is reasonable since the specimen that has been utilized to collect the experimental stress–strain data contained highly oriented PBT fibers. Figure 1 illustrates the orientation of the nanofibers as observed by a field emission-scanning electron microscope. Therefore, for the experimental data considered herein, the fiber orientation distribution is assumed to be

$$R(\mathbf{N}) = \delta(\mathbf{N} - \mathbf{E}_1), \tag{13}$$

where δ denotes the Dirac delta function and $\mathbf{E}_1$ is the fiber direction in the reference configuration.

Under the conditions defined by eqs. (11)–(13) it follows from eq. (1) that the nonzero components of the first Piola-Kirchhoff stress tensor are given by

$$\mathrm{P}_{11} = -p\lambda_1^{-1} + \sigma(\lambda_1), \tag{14}$$

$$\mathrm{P}_{22} = \mathbf{P}_{33} = -p\lambda_1^{-1/2}, \tag{15}$$

where σ is defined by eqs. (8)–(10) with $\Lambda = \lambda_1$. Moreover, the sample strips are assumed to have traction-free boundaries and, therefore, $p = 0$. Finally, the only nonzero component of the first Piola-Kirchhoff stress tensor has the following form

$$\mathrm{P}_{11} = \sigma(\lambda_1). \tag{16}$$

The three parameters, $\{K, \alpha, \beta\}$, which appear in the definition of the stress σ, can be determined by curve fitting eq. (16) to the experimental stress–strain curves.

RESULTS

Stress–stretch experimental data were obtained by subjecting strips of highly aligned PBT fibrous mat to tensile tests. Detailed on the experimental procedures can be found in Mathew et al.[5] Briefly, the fibrous mat was generated via the electrospinning process with a drum collector apparatus rotating at a speed of 1200 rpm (corresponding linear velocity at drum surface was 12.9 m/s). The specimens were excised from a unidirectional aligned nonwoven PBT fabric at different angles with respect to the main fibers' orientation. The experimental findings demonstrated a variation of the tensile strength, tangent modulus, and ultimate strain with the fibers' orientation.

The structural parameters, $\{K, \alpha, \beta\}$, were evaluated by curve fitting the constitutive eq. (16) to the collected uniaxial experimental data. To this end, the Downhill Simplex method was implemented to minimize the sum of the squared differences between the theoretical and experimentally measured stresses.[9] In the numerical computation of the theoretical stresses, the uniform deviates, $G_f^{(i)}$, were generated by using Park and Miller's Minimal Standard generator with an additional shuffle.[9,10] These were converted in Weibull distributed deviates by means of eq. (10). It needs to be noted that the number n of fibers was varied during the computation and it was fixed to be 50,000 since no significant changes were observed for greater values.

The model was fitted to the stress–stretch data that were collected from the sample with highly aligned fibers along the loading direction. A good agreement between the theory and the experiments was attained with $K = 868$ MPa, $\alpha = 0.31$ and $\beta = 0.014$ ($R^2 = 0.95$). Figure 2 illustrates the experimental stresses, the theoretical stresses, and the cumulative distribution function (CDF) for the best fitting parameters. The CDF describing the failure of the mat allows computing the percentage of broken fibers for each value of the

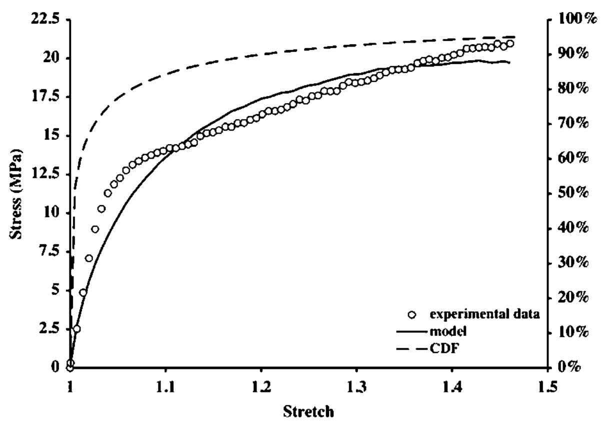

Figure 2 Experimental stress-stretch curve (circles), model curve fit (continuous line), and prediction of broken fiber fractions (dotted line) at best fitting parameters.

stretch. As the figure shows, the model predicted that 95% of the fibers fail when the entire specimen ruptures under load.

CONCLUSIONS

A constitutive law is proposed for the characterization of the mechanical properties of the PBT fibers mat. The macroscopic mechanical response of the mat is assumed to be the result of the fibers' architecture. The anisotropy of the material observed in the experimental studies is incorporated in the model by following Lanir's structural approach for soft tissues.[6,7] The nonlinearity of the stress–strain curve is attributed to the progressive failure of the fibers. The failure process is defined stochastically by a two-parameter Weibull distribution.

The constitutive relation provides a good fit to the results of the tensile experiments. Because the parameters in the model are physically meaningful, they have the advantage of providing useful information on the microstructural changes occurring in the fibrous mat during the deformation. By using the proposed model and the experimentally determined macroscopic stress–strain curve, the tangent modulus of the PBT nanofiber is predicted to be $K = 868$ MPa. Although such value is inferior to 2 GPa, which is the value reported in the literature for PBT, it compares well with the tangent modulus computed by carrying out atomic force microscopic experiments on a PBT nanofiber.[11]

The failure behavior of the fibers has been related to the mechanical response of the mat under tension. It is demonstrated that the 95% of the fibers break when the rupture of the sample occurs during tensile testing. Thus, it is speculated that after a certain percentage of fibers break, the failure of the fibrous mat become catastrophic because of the presence of some flaws in the tissue.

In the experimental study,[5] tensile tests have been performed on specimens that possess highly aligned PBT nanofibers at different directions with respect to the applied load. As the misalignment of the fibers with the loading direction increases, the tensile strength and the tangent modulus decrease while the ultimate strain increases. The rotation of fibers during tensile tests and the variation in the number of fibers gripped by the testing apparatus are responsible for these findings. Biaxial experiments need to be designed to better characterize the mechanics of these nonwoven fabrics.

To apply the constitutive model to the available experimental stress–stretch curve for PBT fibrous mat, the Dirac delta function has been assumed to define the nanofibers' layout in the reference configuration. Thus, all the fibers in the sample have been assumed to be oriented along the loading direction. It must be emphasized that this assumption can be removed when information of the fibers' orientation distribution become available. It is envisaged that the anisotropy of the PBT fibrous mat could be measured by using optical technique and incorporated in the model.[4]

In closing, this study suggests the potential use of the proposed constitutive model to elucidate the mechanics of the PBT nanofibrous assemblies. The material parameters in the model are physically meaningful and, hence, they help in understanding the effects of the fibrous architecture on the gross mechanical response. However, multiaxial experiments and quantification of the tissue's anisotropy are necessary to completely verify the validity of the constitutive law.

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