Modified Burgers-Reimschuessel model for moisture-sensitive polymers

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Abstract

Viscoelastic properties of moisture-sensitive polymers can be significantly affected by moisture in the ambient environment, resulting in drastic changes in the properties as the absorbed moisture content increases. In this paper, a simple yet important modification to the Reimschuessel model is introduced by considering both plasticization and anti-plasticization induced by water molecules. The proposed model is validated against the results of four different polymers obtained by Onogi et al., which demonstrates its capability of describing the available data. This model can be used to estimate the performance and service life of products produced using moisture-sensitive polymers. It also reveals that small amounts of diffused moisture might have a stiffening effect on the mechanical properties of hydrophilic polymers.

1   Introduction

Polymers are one of the most common engineering materials used in our daily lives.[1] Mechanical properties of polymers are crucial in their applications. Almost all polymers exhibit viscoelasticity, and their time-dependent properties must be considered when used as a structural components under long-term loading.[2] This becomes more critical for hydrophilic polymers, whose viscoelastic properties are typically sensitive to moisture. A number of studies have reported that, viscoelastic properties of hydrophilic polymers can be significantly affected by moisture, resulting in drastic changes in the deformation as moisture content increases.[3–20] However, to the best of our knowledge, modeling the moisture effect on viscoelastic properties has been limited, which calls for further investigations. [4,8–11]

At molecular level, the effect of moisture is originated by the interaction between the molecular chains and the water molecules.[8] When small molecules, like water, penetrate the hydrophilic polymer's molecular structure, they can increase the inter-chain distance and break the physical bonds between the chains. As a result, the polymers are softened.[21] These small molecules are commonly referred to as plasticizers and the softening phenomenon is referred to as plasticization. The plasticization phenomenon induced by water has been widely observed in a variety of polymers such as polyamide 6 (Nylon 6)[8], polyvinyl alcohol (PVA)[22] and polylactic acid (PLA).[23] On the other hand, water molecules can also form hydrogen bonds with the polar groups on the polymer chains.[24] These water molecules become immobilized between the polymer chains, restricting their mobility. The reduced molecular mobility can cause stiffening of the polymers, known as the anti-plasticization effect,[25] which has been indirectly observed in the literature. For example, Schmid et al.[26] reported that, in low RH (3-10%) environment, there was an increase in the resonance frequency of SU-8, a hydrophilic polymer commonly used in the fabrication of micro-resonators. This increase in the resonance frequency at low moisture content

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was attributed to the increased stiffness of SU-8 due to water's anti-plasticization effect while the decrease of the resonance frequency at high moisture content was caused by the plasticization effect.

It is important to understand and be able to predict the effect of both plasticization and anti-plasticization on moisture-sensitive polymers prior to any design and structural applications. In the literature, attempts have been made to model the effect of moisture on the mechanical behaviors of polymers, among which the time-moisture superposition (TMS) principle is the most widely used. TMS states that for a time-dependent property such as creep compliance or stress relaxation modulus, the effect of increasing moisture content is equivalent to that of extending the time scale.[18,19] Mathematically, the principle can be represented by

$$K(t, C_0) = K(\frac{t}{a_C}, C) \tag{1}$$

where $K(t, C_0)$ is the property at a reference moisture content C_0, $K(t, C)$ is the property at moisture content C, and $a_C = f(C)$ is the moisture shifting factor. C is usually defined as the ratio between the weight of the absorbed moisture and the original weight of the dry polymer. **Equation (1)** implies that when plotting the time-dependent property with respect to time in logarithmic scale, the curves corresponding to different C values can be collapsed into a single master curve by a horizontal shift.[9] Therefore, knowing a_C and the curve under C_0, the time-dependent property under other moisture contents can be predicted. Fujita et al. reported that, for a linear amorphous polymer above its second-order transition temperature, material softening with increased moisture content was solely due to plasticization whereas the anti-plasticization effect was negligible at high temperature.[19] As a result, the TMS principle held. Onogi et al. attempted to apply the TMS principle to PVA and Nylon 6 at room temperature (20-25°C).[18] The TMS principle was found to work well for the stress relaxation modulus of Nylon 6 while it failed to provide a good fit for PVA

at very low moisture content. It is highly possible that the poor agreement was due to the omission of anti-plasticization effect which could be significant for PVA at room temperature. Later, Emri et al. proposed that, to adopt the TMS principle in real applications, the shift factor a_C may follow the Williams-Landel-Ferry (WLF) function:[9,27]

$$\ln a_C = \frac{-B_1(C - C_0)}{B_2 + C - C_0} \tag{2}$$

where B_1 and B_2 are empirical parameters to be determined by fitting experimental data. Emri et al. successfully applied the WLF function to fit the shear creep compliances measured for cylindrical specimens of polyvinyl acetate (PVAc) containing different moisture contents.[9] Ishisaka et al. also attempted to use the WLF function on the storage modulus of Nylon 6 and epoxy.[7] Although the shift factor in the form of **Equation (2)** worked for Nylon 6, it did not hold for epoxy. A possible explanation could be that the covalent bonds between the epoxy chains restricted the molecular mobility. Consequently, water molecules cannot significantly increase the inter-molecular distance and plasticize the material. The authors also discovered that the glass transition temperature was not significantly lowered even after the moisture absorption, suggesting that the plasticization effect is rather limited.[7] This study agreed with the findings by Onogi et al. where the TMS principle was only applicable to Nylon 6.[18] Under the framework of TMS, Maksimov et al. proposed a second order polynomial for the relation between $\ln a_C$ and C.[10] This relation was successfully applied to predict the creep compliance of polyester, although to the best of our knowledge it has not been used for any other polymers due to the lack of physical interpretation. Widiastuti et al. used Burgers model to describe the viscoelasticity of a PLA-based polymer while considering moisture-dependent parameters.[28] The WLF function was used to predict the retardation time while other parameters were assumed to be polynomials of moisture

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content C. At the highest C (6 wt%), more than 25% of discrepancy was observed for the creep compliance between the model prediction and experimental results.[28]

Reimschuessel proposed a model for the change of Young's modulus E with respect to moisture,[8] based on the tensile test results of Inoue and Hoshino.[29] One underlying assumption was that the sample was fully saturated and the moisture was uniformly distributed during the tests. This was a reasonable assumption given that the time scale of the tensile tests (~30 s) was two orders of magnitude smaller than that of moisture diffusion (~8000 s).[29] Experimentally for Nylon 6, E was found to decay faster at low moisture content and slower at high moisture content, eventually approaching a limiting value. Based on those observations, Reimschuessel proposed the relation in **Equation (3)** to describe the change of E with respect to C:

$$E(C) = E_f + \left(E_0 - E_f\right)\exp(-k_E C) \tag{3}$$

where k_E is a positive constant, E_0 is the Young's modulus of dry Nylon 6 and E_f is the limiting value for large C. This relation was explained by water plasticization causing the breakage of secondary bonds between the polymer chains and the increase of inter-molecular distance.[8] Garces et al. successfully applied this model to predict the Young's modulus of one type of polyurethane-based shape memory polymer.[30] However, in Reimeschuessel's work, it was found that the agreement between model and experiments was poor at intermediate moisture levels.[8] In particular, the experimental value of E was approximately 19% higher than the prediction at $C = 2$ wt%.[8] This suggests the overestimation of the plasticization effect, or the lack of consideration on anti-plasticization, by the Reimschuessel model.

In this paper, we introduce a simple, yet important, modification to the Reimschuessel's model, by considering both plasticization and anti-plasticization induced by water molecules. Isothermal condition is assumed, to avoid the coupled effect of temperature and moisture. The model is

validated by the experimental stress relaxation data presented by Onogi et al. for four different types of polymers, namely PVA with degree of polymerization (DP) 600, PVA with DP 2060, original Nylon 6, and heat-treated Nylon 6.[18] The proposed modified Reimschuessel model predictions compare well with the aforementioned experimental data for the stress relaxation moduli of the materials for a range of moisture content (0 to 16 wt%). The proposed model can provide valuable information for critical uses of other types of moisture-sensitive polymers when their performance and service life under ambient conditions need to be predicted prior to design.

2   Model

A great amount of work has been done to model the viscoelasticity of polymers and the majority of them were based on phenomenological mechanical analogs consisting of elastic and viscous elements.[25,31] The present work adopts and modifies the Burgers model since it is one of the simplest models that capture the essential features of polymer viscoelasticity.[32] The behaviors of the elastic and viscous elements are considered to change with moisture. The change is mathematically described by considering plasticization and anti-plasticization caused by two different forms of water that exists in moisture-sensitive polymers: free water and bound water. [33–37]

2.1   Burgers model

The Burgers model is schematically shown in **Figure 1** and quantitatively described by **Equation (4)**, where $\varepsilon(t)$ and $\sigma(t)$ are strain and stress, respectively.[38] Although generally considered as a phenomenological model, the parameters (E_1, E_2, μ_1 and μ_2) in the Burgers model, to some degree, capture the molecular responses of the polymers.[2] The elastic parameters E_1 and E_2 represent the ability of the polymer chains to recover from a deformation.[2] They are affected by the fraction of closely compacted crystalline region (crystallinity) and the number of topological entanglements between the polymer chain coils within the amorphous regions.[21,25,32] The viscous

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parameters μ_1 and μ_2 represent the resistance caused by the non-covalent bonds between the polymer chains when they slide past one another under the external load.[21] The free volume within the polymers and the number of the inter-chain non-covalent bonds affects these viscous parameters.[2,21]
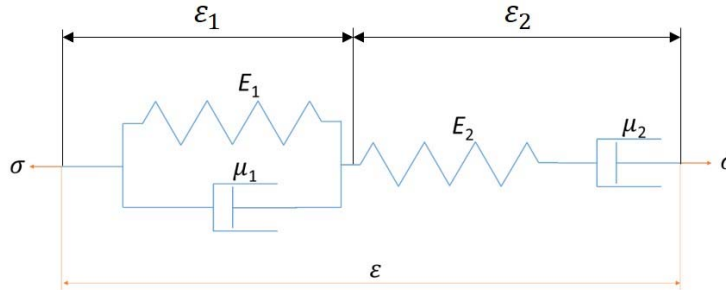

Figure 1. Schematic representation of Burgers model

$$\frac{\mu_1\mu_2}{E_1}\frac{d^2\varepsilon}{dt^2} + \mu_2\frac{d\varepsilon}{dt} = \frac{\mu_1\mu_2}{E_1E_2}\frac{d^2\sigma}{dt^2} + \left(\frac{\mu_1}{E_1} + \frac{\mu_2}{E_1} + \frac{\mu_2}{E_2}\right)\frac{d\sigma}{dt} + \sigma \tag{4}$$

2.2 Plasticization caused by free water

Water molecules has little effect on the crystalline regions due to their closely compacted nature.[8] Under constant temperature, when water molecules enter the amorphous regions, it can exist in two forms, free and bound as shown in **Figure 2** (a) and (b), respectively.[33,39,40] Free water corresponds to molecules that do not have significant interaction with the polymer chains and therefore are free to move within the network. They usually form clusters as illustrated by the blue filled circles in Figure 2 (a), and can increase the inter-molecular distance, leading to increased free volume.[22,33,36] As a result, the polymer is softened by the enhanced molecular mobility.[19]
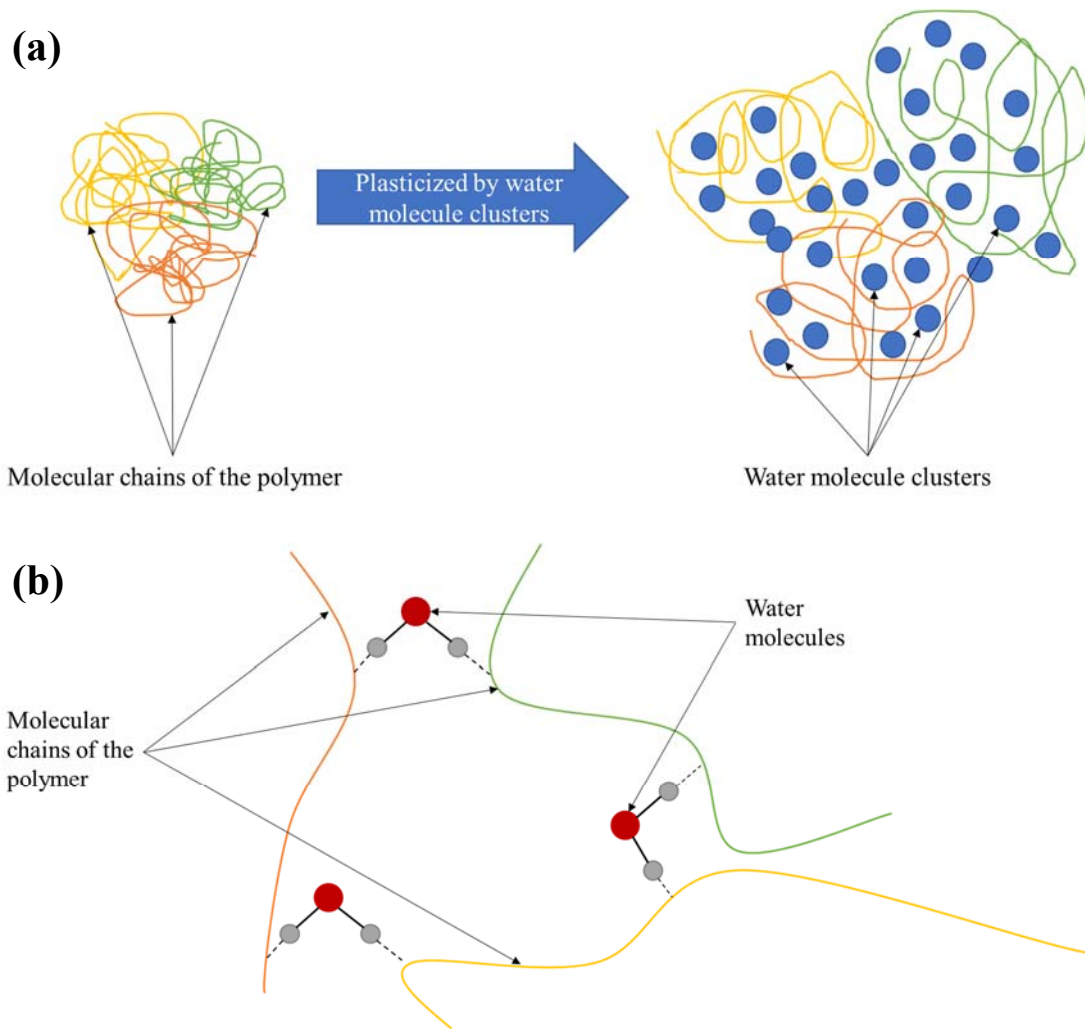
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(a)

Plasticized by water
molecule clusters

Molecular chains of the polymer

Water molecule clusters

(b)

Water
molecules

Molecular
chains of the
polymer

Figure 2. Schematic representation of (a) free water clusters and (b) bound water bridges within the polymer network.[22,33]

The effect of free water on the Burgers model parameters are qualitatively illustrated by the red curve in **Figure 3**. E_1 and E_2 mainly represent the enthalpic elasticity of the crystalline region and the entropic elasticity of the amorphous region, which are affected by the crystallinity and topological entanglements within the polymer. Water molecules that diffuse into the polymer network can increase the free volume and release some of the topological entanglements, causing the elastic moduli to decrease. However, E_1 and E_2 may not decrease to zero even if there is a

significant amount of absorbed moisture. This is because of the finite number of topological entanglements that can be released, the existence of entropic elasticity of the polymer coils, the little impact free water has on the closely compacted crystalline regions, and the residual non-covalent interactions between the polymer chains such as van der Waals force and water bridges (to be discussed in section 2.3). Therefore, as in the Reimschuessel model[8], **Equation (5)** is proposed to describe the change of elastic parameters with respect to moisture content C, under the effect of plasticization:

$$\frac{dE_i(C)}{dC} = -k_{Ei}(E_i(C) - E_{if}) \tag{5}$$

where $i = 1, 2$; k_{Ei} are positive constants; and E_{if} are the limiting values for large C. The initial condition, corresponding to the dry polymer, is given by **Equation (6)**:

$$E_i(C = 0) = E_{i0} \tag{6}$$

which renders the following solution to Equation (5):

$$E_i(C) = E_{if} + (E_{i0} - E_{if})\exp(-k_{Ei}C) \tag{7}$$

The viscous parameters μ_1 and μ_2 are affected by free water in a similar way, where the increased inter-molecular distance reduces the probability of forming non-covalent bonds between chains. As a result, μ_1 and μ_2 are expected to decrease with moisture content and approach their respective limiting values at large C. Therefore, as proposed by Reimschuessel[8], μ_1 and μ_2 change with C in the following form

$$\mu_i(C) = \mu_{if} + (\mu_{i0} - \mu_{if})\exp(-k_{\mu i}C) \tag{8}$$

where $i = 1, 2$; $k_{\mu i}$ are positive constants; μ_{if} are the limiting values at large C; and μ_{i0} are the viscous parameters of the dry polymer.

2.3 Anti-plasticization caused by bound water

Some of the water molecules that diffuse into the polymer network do not form clusters with other water molecules. Instead, they become immobilized due to their interactions with the polymer chains[22,33,40], and hence are referred to as bound water.[33] For example, the hydrogen and oxygen atoms on a water molecule can form hydrogen bonds with polar groups on the polymer chains.[7,39,41] Through the hydrogen bonds, water molecules can establish bridge-like links between the polymer chains shown in **Figure 2** (b) and restrain these chains' relative motions. This phenomenon, referred to as the water-bridge-anti-plasticization (WBAP) effect, has been found in microcrystalline cellulose by Hancock et al.,[42] as well as in Nylon 6 by Inoue and Hoshino.[29] In both works it was reported that the decreasing rate of Young's modulus with respect to C is smaller at low C.

The WBAP effect caused by water bridges shown in **Figure 2** (b) slows down the plasticization caused by water clusters shown in **Figure 2** (a) and provides a stiffening mechanism. To capture this effect, we propose to add a single term to the Reimschuessel model given by **Equations (7)** and **(8)**. At low C, the bridges formed by bound water molecules in **Figure 2** (b) act as weak cross-links between polymer chains and occupy some of the free volume.[42–44] As a result, the chain mobility is restrained, and the Burgers model parameters are expected to increase with C. Higuchi and Iijima[37] discovered that when the amount of water that diffuses into the polymer network is small, the majority of the water molecules are bound water and forming bridges between the polymer chains. Consequently, the number of water bridges and hence the term describing the WBAP effect are approximated to be linear in C for small C. As C increases, the probability of forming water clusters becomes larger, which increases the inter-chain distance and can break the existing water bridges, weakening the anti-plasticization.[43] Therefore, the stiffening mechanism will eventually decrease, reaching a constant value at high moisture content. The effect of bound

water can be qualitatively illustrated by the green curve in Figure 3. Based on these physical considerations, the WBAP effect is captured by introducing a term, varying non-monotonically with C, to each elastic (E_i) and viscous (μ_i) parameter:

$$E_{i-WBAP} = (k_{AEi}C)\exp(-k_{DEi}C)$$
$$\mu_{i-WBAP} = (k_{A\mu i}C)\exp(-k_{D\mu i}C)$$

(9)

In **Equation (9)** k_{AEi} and $k_{A\mu i}$ are coefficients that describe the approximately linear relation at small C, whereas k_{DEi} and $k_{D\mu i}$ describe the exponential decay that occurs at larger C. All these parameters are positive constants for a given material under isothermal condition. Equation (9) predicts, for each parameter, an increasing branch at low C, a skewed peak at intermediate C, and a decreasing branch at large C. It is recognized that the term associated with the WBAP effect does not necessarily decay to zero at high C. However, any residual contribution from the WBAP effect can be captured by the limiting values, E_{if} and μ_{if} in Equations (7) and (8), when the plasticization and WBAP effects are combined. Therefore, to minimize the number of parameters in the model, no additional constants are introduced in Equation (9). Performing Taylor series expansion on Equation (9), near $C = 0$, Equation (9) is reduced to $E_{i-WBAP} = (k_{AEi}C) + O(C^2)$ and $\mu_{i-WBAP} = (k_{A\mu i}C) + O(C^2)$, which captures the anticipated linear variation of the moduli with respect to C at small C. At large C, Equation (9) is dominated by the exponential decay, representing the diminishing of anti-plasticization as water bridges break. The exponential decay is a characteristic of first-order kinetics, used in many empirical models such as the original Reimschuessel model. Compared with the polynomial form suggested by Maksimov et al.[10] and Widiastuti et al.,[28] Equation (9) proposed here is simple (containing only a single term instead of a series), has stronger physical interpretations (linear increase for small C and exponential decay

for large C), and can be readily integrated into the existing Reimschuessel model which possesses terms in similar forms.
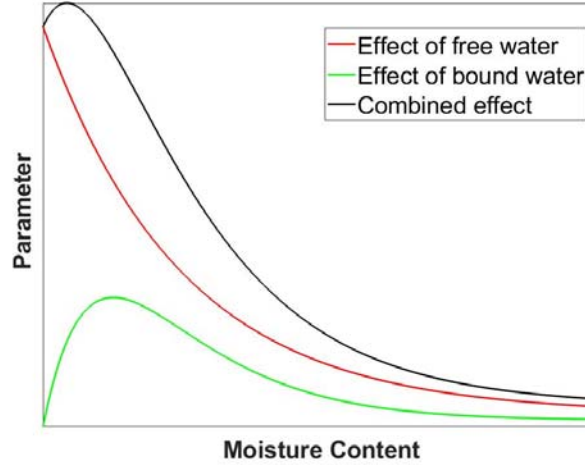

Figure 3. Illustration of the effects of free and bound water on the Burgers model parameters

2.4 Modified Burgers-Reimschuessel model

Combining the formulations in sections 2.2 and 2.3, the change of any of the model parameters P (E_1, E_2, μ_1 or μ_2) with respect to moisture content under isothermal condition can be described by the modified Burgers-Reimschuessel model below

$$P(C) = P_f + \left(P_0 - P_f\right)\exp(-k_p C) + (k_A C)\exp(-k_D C) \qquad (10)$$

where $P(C)$ is the value of the parameter as a function of C; P_0 corresponds to the dry polymer; P_f is the limiting value at large C; k_p is a positive constant that describes the exponential decay due to plasticization; and k_A and k_D are positive constants that describes the WBAP effect. The overall trend of $P(C)$ is illustrated by the black curve in **Figure 3**.

With **Equation (10)** and the constitutive relation given in Equation (4), the viscoelastic behavior of the polymer under different loading and moisture conditions can be predicted. Two quantities of general interest are the creep compliance $J(t)$ and the stress relaxation modulus $G(t)$,

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which can be respectively extracted from creep and stress relaxation tests. Similar to the original Reimschuessel model used for the Young's modulus extracted from tensile tests, it is assumed that the creep and relaxation tests were either much faster than moisture diffusion or performed under well controlled humidity condition. As such, the moisture can be considered uniformly distributed within the sample during the tests, and spatial variations of the creep compliance or stress relaxation modulus are neglected. In a creep test, an instantaneous stress σ_0 is applied at $t = 0$ and the strain ε is measured with respect to time. The creep compliance is given by $J(t) = \varepsilon(t)/\sigma_0$, and for the Burgers model it is given by **Equation (11)**[38]

$$J(t) = \frac{t}{\mu_2} + \frac{1}{E_2} + \frac{1}{E_1}\left[1 - \exp(-\frac{E_1}{\mu_1}t)\right], \qquad t \geq 0 \tag{11}$$

In a stress relaxation test, an instantaneous strain ε_0 is applied at $t = 0$ and the stress σ is measured with respect to time. The stress relaxation modulus is given by $G(t) = \sigma(t)/\varepsilon_0$, which for the Burgers model is given by[38]

$$G(t) = \frac{1}{\sqrt{p_1^2 - 4p_2}}[(q_1 - q_2 r_1)\exp(-r_1 t) - (q_1 - q_2 r_2)\exp(-r_2 t)], \qquad t \geq 0 \tag{12}$$

where

$$r_1 = \frac{p_1 - \sqrt{p_1^2 - 4p_2}}{2p_2}$$

$$r_2 = \frac{p_1 + \sqrt{p_1^2 - 4p_2}}{2p_2}$$

$$p_1 = \frac{\mu_1}{E_1} + \frac{\mu_2}{E_1} + \frac{\mu_2}{E_2} \tag{13}$$

$$p_2 = \frac{\mu_1 \mu_2}{E_1 E_2}$$

$$q_1 = \mu_2$$

$$q_2 = \frac{\mu_1 \mu_2}{E_1}$$

3   Validation and Discussion

The above modified Burgers-Reimschuessel model is validated against the data obtained by

Onogi et al.[18] In their work, four different types of materials were used, namely PVA with DP

600, PVA with DP 2060, original Nylon 6 and heat-treated Nylon 6. PVA films were fabricated by

solvent casting and Nylon 6 films were fabricated by inflation method. Some of the Nylon 6

samples were heat-treated for 8 min under 150-155°C, leading to increased crystallinity and

slightly decreased molecular weight. All samples were conditioned under constant temperature

(20°C for PVA with DP 600; 25°C for PVA with DP 2060, original Nylon 6 and heat-treated Nylon

6) in chambers with different relative humidity until an equilibrium moisture content was reached.

Thus, the samples were fully saturated with moisture and there was no spatial heterogeneity. Then,

stress relaxation test was conducted on each sample in the same chamber where it was conditioned,

so that the moisture content in the sample stayed uniform and at the equilibrium level during the

test. Stress relaxation modulus as a function of time was plotted with respect to time for different

moisture content.

Since the constitutive relations for the tested polymers were not provided in Onogi et al.[18],

the stress relaxation modulus was fitted using **Equation (12)** to extract the elastic (E_1 and E_2) and

viscous (μ_1 and μ_2) parameters under different C. Then Equation (10) was used to extract P_0, P_f,

k_p, k_A and k_D in the modified Burgers-Reimschuessel model. **Table 1** lists the values of these

parameters and the adjusted R^2 for the fittings. All the adjusted R^2 values are greater than 0.98,

suggesting the good quality of the fit. P_0 for the dry polymers are of similar magnitude to what was

reported for PVA[45] and Nylon 6[46], confirming that the results were physically reasonable. As

expected, the limiting values P_f for all polymers are either 0 or significantly lower than the

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corresponding P_0 values, indicating the dominance of the plasticization effect at large C. The coefficients k_A all have similar order of magnitude to the corresponding P_0, emphasizing the significance of the anti-plasticization effect at small C. As an example, the fitting of E_2 using both Reimschuessel model and the modified Reimschuessel model proposed in this work is shown in **Figure 4** for heat-treated Nylon 6 and PVA with DP 2060. Consistent with what was reported, the original Reimschuessel model underestimated the values at lower C,[8] which was corrected by the modified Reimschuessel model.
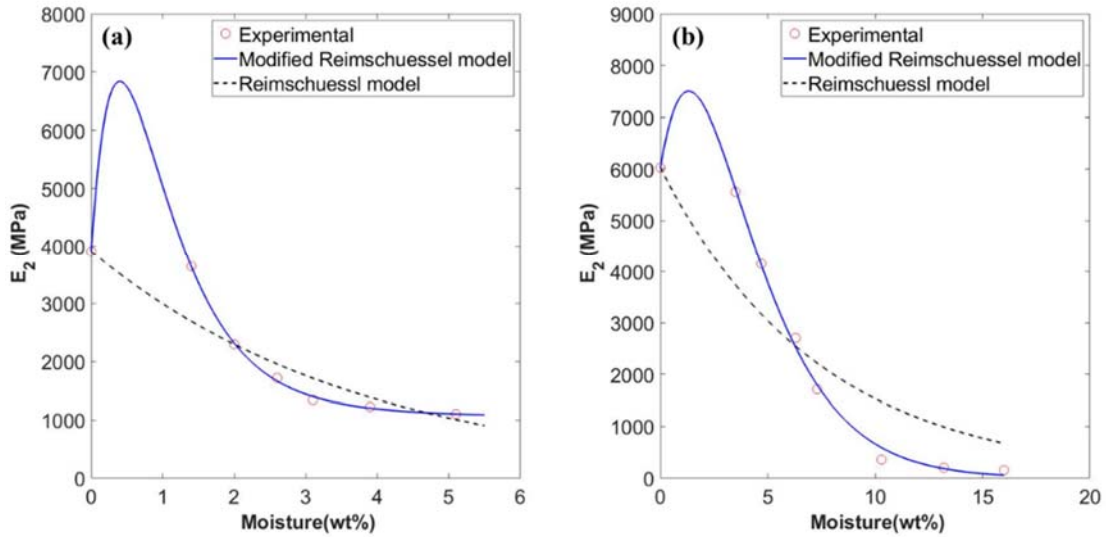

Figure 4. Comparison between Reimschuessel's model in[8] and the modified Reimschuessel model proposed in this work for (a) E_2 of heat-treated Nylon 6, (b) E_2 of PVA with DP 2060.

Table 1. Fitted model parameters and quality of fitting

	P_0 (unit)	P_f (unit)	k_p (1/wt%)	k_A (unit/wt%)	k_D (1/wt%)	Adjusted R^2
				PVA with DP 600		
E_1 (MPa)	20637	422.3	0.7191	37720	0.7177	
E_2 (MPa)	5590	61.48	0.9989	10100	0.4987	
μ_1 ($\times 10^6$ MPa·s)	1.819	0	0.9790	8.981	0.9880	0.98949
μ_2 ($\times 10^6$ MPa·s)	127.6	2.857	0.5134	497.1	0.9519	
				PVA with DP 2060		
E_1 (MPa)	25679	414.5	7.076	367300	1.087	
E_2 (MPa)	6030	0	1.001	8462	0.4848	
μ_1 ($\times 10^6$ MPa·s)	4.018	0	0.9663	17.92	0.9901	0.99737
μ_2 ($\times 10^6$ MPa·s)	225.4	1.456	0.6437	1453	1.059	
				Original Nylon 6		
E_1 (MPa)	47311	0	1.797	3665	0.1821	
E_2 (MPa)	4233	617.5	0.3613	1029	15.76	
μ_1 ($\times 10^6$ MPa·s)	5.466	0.2258	2.504	0.09683	21.26	0.99234
μ_2 ($\times 10^6$ MPa·s)	310.3	0	9.961	44.42	0.2412	
				Heat-treated Nylon 6		
E_1 (MPa)	153890	5792	4.063	7501000	4.578	
E_2 (MPa)	3910	1055	0.8116	21110	2.052	
μ_1 ($\times 10^6$ MPa·s)	107.25	0	2.227	0.06016	0	0.99225
μ_2 ($\times 10^6$ MPa·s)	514.05	0	1.042	29.59	0.1902	

Parameters in Table 1 were used to generate the time-dependent stress relaxation modulus predicted by the modified Burgers-Reimschuessel model. **Figure 5** shows the comparisons between the model and experimental results. Unlike the TMS principle adopted by Onogi et al.[18], which failed to predict the behavior of PVA at low moisture content, all the model predictions in **Figure 5** are accurate which demonstrates the capability of the model to capture the change of viscoelastic properties with moisture content. The only exception is heat-treated Nylon 6 under 2.0 wt% moisture, for which a discrepancy of 17% was observed between the model prediction and experimental results. However, this discrepancy is still smaller than the model proposed by Widiastuti et al., which is more than 25%.[28] The discrepancy found in this particular case (heat-treated Nylon 6 containing 2.0 wt% moisture) arises from the relatively poor fitting of μ_2 (**Figure 6**). Since this deviation was not observed in other types of polymers, there is a high probability that the deviation is caused by the heat treatment. According to Onogi et al., the heat treatment of Nylon 6 films was conducted at 150-155°C for 8 min.[18] The treatment might have induced imperfect crystallites[47,48], which could have allowed water molecules to penetrate into them and affect the viscoelasticity of the material in a different way. In addition, the cooling process after the heat treatment was not reported in Onogi et al.[18] which, if not well controlled, could have induced residual stresses in the samples. The diffusion of water molecules might release the residual stress and change the conformation of the polymer chains. These potential factors are not considered in the modified Burgers-Reimschuessel model.
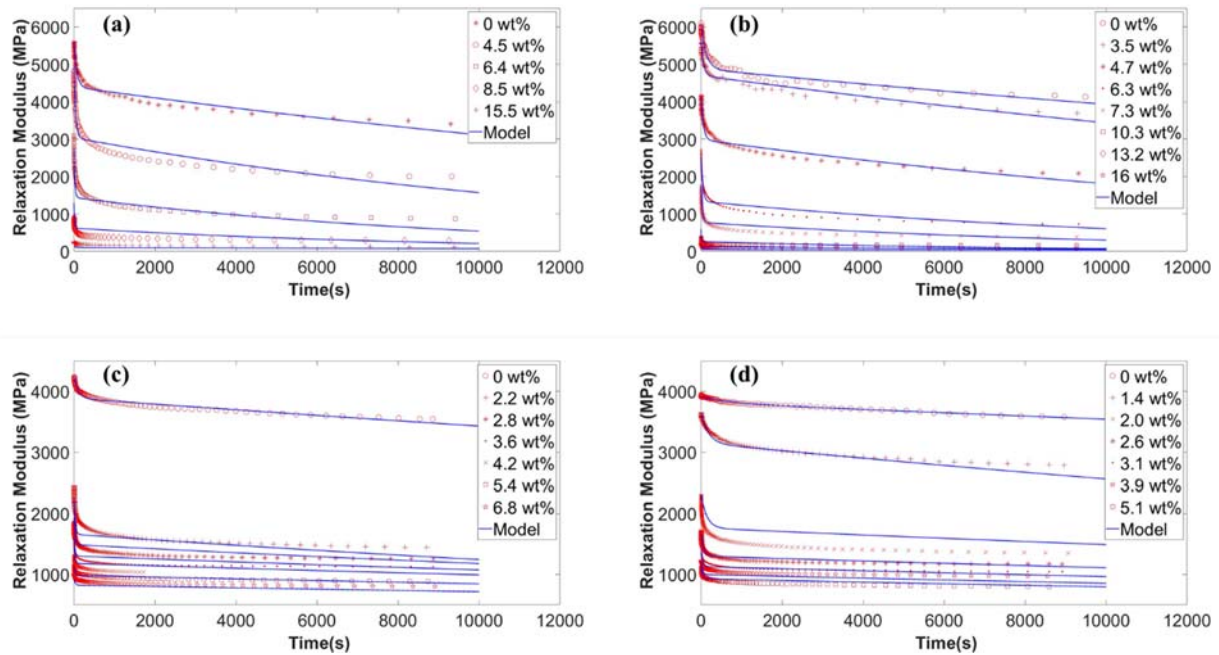
Figure 5. Stress relaxation modulus with different moisture content for (a) PVA with DP 600, (b) PVA with DP 2060, (c) Original Nylon 6, (d) Heat-treated Nylon 6. Red symbols represent experimental data from Onogi et al.[18] and blue solid curves are predictions using the proposed modified Burgers-Reimschuessel model.
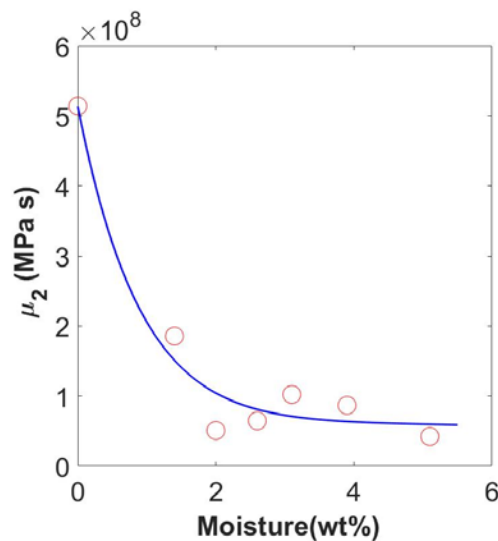

Figure 6. Change of μ_2 with respect to moisture for heat-treated Nylon 6. Red circles represent values obtained from fitting the Burgers model to stress relaxation data, and blue solid curve is prediction using the proposed modified Burgers-Reimschuessel model.

Compared with other models reviewed in the Introduction, the greatest advantage of the modified Burgers-Reimschuessel model is its simplicity. The WBAP effect is included by a simple modification as given in Equation (9), and all the Burgers model parameters have the same form as shown in Equation (10). Wide applicability of this model presents another advantage. In contrast to the TMS principle coupled with the WLF function, whose success has been limited to few polymers such as Nylon 6, the current model can be applied to a variety of hydrophilic polymers.

Hydrophilic polymers have been widely used in a broad range of engineering applications that may be subject to humid or aqueous environment. For example, PVA is a hydrophilic polymer that has a well-documented history to be used as load-bearing components in tissue engineering scaffolds[49], surgical thread[50], and vascular stents.[51] PVA have been reported to show deteriorations in mechanical properties as moisture content increases, which could affect the performance of these products.[7,18] With the modified Burgers-Reimschuessel model, the performance and service life for these polymer products under given working condition can be estimated. Since the model establishes a relation between the moisture content and the viscoelastic parameters, if the moisture content of a polymer product can be determined as a function of time, the material parameters can be predicted after exposure to the ambient environment for a period of time. Taking the data of PVA with DP 600 as an example, **Figure 7** shows the prediction of the Burgers model parameters normalized by the respective values of the dry counterpart. The intersects between the blue curves and the black horizontal lines correspond to moisture content at which the Burgers model parameters reduce to 20% of their original values. If 80% of reduction is a critical level at which the polymer product can no longer support its designed load, then one can conclude that the service life of this PVA product is at the time when the moisture content of the product reaches around 5 wt%, which can be estimated from the rate of diffusion of water in PVA.
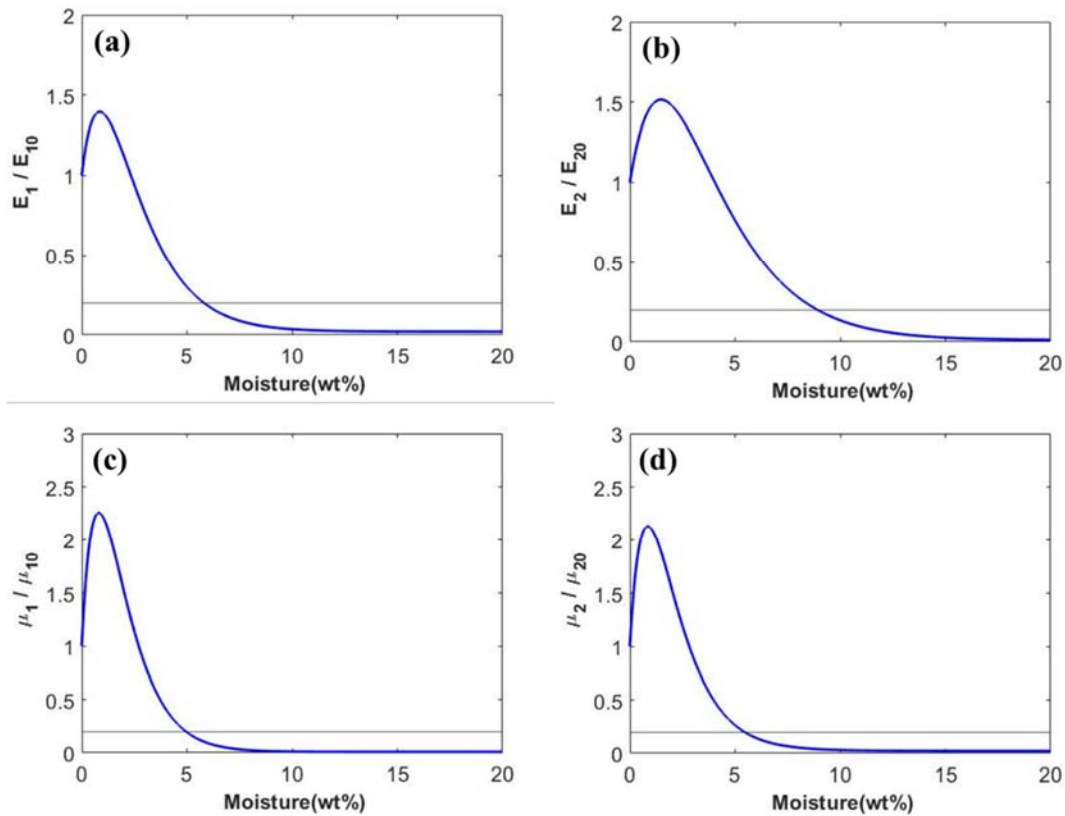
Figure 7. Prediction of the Burgers model parameters of PVA with DP 600, normalized by the respective values of the dry PVA (a) E_1/E_{10}, (b) E_2/E_{20}, (c) μ_1/μ_{10}, (d)μ_2/μ_{20}

This study may also provide guidance on how to manufacture polymer products to reduce the effect of moisture. The most apparent approach is to increase the limiting values P_f , which can be achieved by creating more entanglements between the polymer chains during synthesis and manufacturing, by increasing the crystallinity of the material with added nucleating agents, by properly selecting the processing parameters, or by using manufacturing techniques such as injection molding instead of extrusion so that the polymer chains are in a more compacted structure. Compacting the polymer network has another advantage, namely it increases the anti-plasticization effect. More closely compacted polymer chains have their polar groups located closer to each other. Thus, it is potentially easier for water molecules to find anchor points to form bridges. The

probability that water molecules gather together to form clusters and cause plasticization is also decreased.

In industry, mechanical properties of some intrinsically brittle materials such as polyvinyl chloride (PVC) and PLA are tailored by adding compatible plasticizers, which reduce the hardness and stiffness of the polymers by increasing the inter-molecular distance and decreasing the amount of secondary bonds such as hydrogen bonds and van der Waals forces.[21,52,53] Li et al. discovered that less than 10 wt% of polyethylene glycol (PEG) with molecular weight of 400 g/mol could significantly reduce the stiffness of PLA.[52] On the other hand, Gedde pointed out the presence of anti-plasticization effect for a variety of polymers and plasticizers which was caused by interaction between the low molecular weight plasticizers and the polymer chains.[25] A similarity can be recognized between the role of these small plasticizers and that of moisture. Therefore, the model proposed here may be able to describe the effect of plasticizers, with the moisture content C replaced by the weight percentage of the plasticizers.

It is worth pointing out a few limitations of this model and future perspectives. First, the model is based on the isothermal assumption, and validated against experiments performed under a constant temperature. The effect of temperature on the constitutive relation of the polymers is not included. In practical applications, especially in outdoor environments, both temperature (T) and C can influence the viscoelastic properties of polymers and their effects are often coupled. Huber et al.[4] pointed out that the increase of T could increase the vibration of water molecules, which might further increase the free volume within the polymer network and lead to increased plasticization. Baschek et al.[54] reported that at T below 0°C, water within the polymer network could provide a reinforcing effect since the free water was frozen. Future work can be done to describe the coupled effect of T and C, by introducing T-dependent parameters $k_p(T)$, $k_A(T)$, etc, and/or adding terms as functions of both T and C to Equation (10).

The model presented here is empirical in nature, i.e., it is developed based on phenomenological description of the influence from free and bound water. Macroscopically, the model captures the anticipated behaviors at small and large moisture contents and supports indirect experimental evidence for anti-plasticization. However, there are microscopic phenomena which are not considered by the model, for example, the release of residual stress during moisture diffusion, or the penetration of water molecules into imperfect crystallites. Future work can be done to study the effects of these microscopic phenomena and provide modifications to the model. The empirical nature of the model also implies that values of the parameters in Equation (10) need to be acquired by fitting experimental data. Efforts can be devoted to study the correlation between these parameters and the intrinsic and extrinsic properties of polymers such as the molecular weight, free volume, and density of polar functional groups on the polymer chains. Such correlation can benefit the design and synthesis of the polymers to achieve desired performance.

Finally, this work revealed the possibility that a small amount of moisture may be able to stiffen the material. In **Figure 7**, when the moisture content is less than 1 wt%, all four Burgers model parameters are larger compared with the dry material. Theoretically, this stiffening effect is possible due to the more likelihood of water molecules to form bridges rather than clusters when their concentration is low. While the lack of data in the low moisture regime (**Figure 4** and **Figure 6**) in Onogi et al.[18] does not provide direct evidence, future testing in this regime may generate insights into this potential transient stiffening.

4   Conclusion

A modified Burgers-Reimschuessel model was proposed to describe the viscoelasticity of moisture-sensitive polymers. Plasticization caused by free water and anti-plasticization induced by bound water were both considered. The proposed model was validated against the data from Onogi

et al.[18] for four different polymers, which demonstrated good accuracy. Due to the anti-plasticization effect, properties of moisture-sensitive polymers may be tailored by a small amount of moisture, or equivalently, a small amount of low molecular weight plasticizers. The model can be used to evaluate the performance and estimate the service life of products made from moisture-sensitive polymers. It can also be used to assist in the design and manufacturing of these polymers.

References

[1]   C. Hall, *Polymer Materials, An Introduction for Technologists and Scientists*, The MacMillan Press Ltd., London, **1981**.

[2]   M. T. Shaw, W. J. MacKnight, *Introduction to Polymer Viscoelasticity*, John Wiley & Sons, Inc., Hoboken, **2005**.

[3]   R. A. Jurf, J. R. Vinson, *J. Mater. Sci.* **1985**, *20*, 2979.

[4]   F. Huber, H. Etschmaier, H. Walter, G. Urstöger, P. Hadley, *Int. J. Polym. Anal. Charact* **2020**, *25*, 467.

[5]   M. B. Satterfiield, J. B. Benziger, *J. Polym. Sci., Part B: Polym. Phys.* **2009**, *47*, 11.

[6]   S. M. Zhou, K. Tashiro, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1638.

[7]   A. Ishisaka, M. Kawagoe, *J. Appl. Polym. Sci.* **2004**, *93*, 560.

[8]   H. K. Reimschuessel, *J. Polym. Sci., Part A: Polym. Chem.* **1978**, *16*, 1229.

[9]   I. Emri, V. Pavsek, *Met.* **1992**, *16*, 123.

[10] R. D. Maksimov, E. A. Sokolov, V. P. Mochalov, *Mech. Compos. Mater.* **1975**, *11*, 334.

[11] I. Widiastuti, I. Sbarski, S. H. Masood, *J. Appl. Polym. Sci.* **2014**, *131*, 1.

[12] P. Myllytie, L. Salmén, E. Haimi, J. Laine, *Cellulose* **2010**, *17*, 375.

[13] O. Starkova, A. Aniskevich, *Mech. Time Depend. Mater.* **2007**, *11*, 111.

[14] E. M. Woo, *Composites* **1994**, *25*, 425.

[15] K. Aniskevich, R. Krastev, Y. Hristova, *Mech. Compos. Mater.* **2009**, *45*, 137.

[16] X. J. Fan, S. W. R. Lee, Q. Han, *Microelectron. Reliab.* **2009**, *49*, 861.

[17] A. Valls-Lluch, W. Camacho, A. Ribes-Greus, S. Karlsson, *J. Appl. Polym. Sci.* **2002**, *85*, 2211.

[18] S. Onogi, K. Sasaguri, T. Adachi, S. Ogihara, *J. Polym Sci.* **1962**, *58*, 1.

[19] H. Fujita, A. Kishimoto, *J. Polym Sci.* **1958**, *28*, 569.

[20] F. Goldschmidt, S. Diebels, *Arch. Appl. Mech.* **2015**, *85*, 1035.

[21] W. D. Callister, D. G. Rethwisch, *Material Science and Engineering, An Introduction*, John Wiley & Sons, Inc., Hoboken, USA, **2010**.

[22] R. M. Hodge, T. J. Bastow, G. H. Edward, G. P. Simon, A. J. Hill, *Macromolecules* **1996**, *29*, 8137.

[23] K. M. Zakir, A. J. Parsons, C. D. Rudd, I. Ahmed, W. Thielemans, *Eur. Polym. J.* **2014**, *53*, 270.

[24] P. Gilormini, J. Verdu, *Polymer* **2018**, *142*, 164.

[25] U. W. Gedde, *Polymer Physics*, Springer, Dordrecht, **1999**.

[26] S. Schmid, S. Kühne, C. Hierold, *J. Micromech. Microeng.* **2009**, *19*.

[27] M. L. Williams, R. F. Landel, J. D. Ferry, *J. Am. Chem. Soc.* **1955**, *77*, 3701.

[28] I. Widiastuti, I. Sbarski, S. H. Masood, *Mech. Time Depend. Mater.* **2014**, *18*, 387.

[29] K. Inoue, S. Hoshino, *J. Polym. Sci. B Polym. Phys.* **1976**, *14*, 1513.

[30] I. T. Garces, S. Aslanzadeh, Y. Boluk, C. Ayranci, *Materials* **2019**, *12*.

[31] R. M. Christensen, *Theory of Viscoelasticity, An Introduction*, Dover Publications Inc., New York, **2003**.

[32] L.H. Sperling, *Introduction to Physical Polymer Science*, John Wiley & Sons, Inc, **2006**.

[33] X. Fan, in *Int. Conf. Therm. Mech. Multi-Phys. Simul. Exp. Microelectron. Microsyst. EuroSimE 2018*, Freiburg, **2008**.

[34] H. Ardebili, E. H. Wong, M. Pecht, *IEEE Trans. Compon. Packaging. Manuf. Technol.* **2003**, *26*, 206.

[35]   Y. J. Chang, C. T. Chen, A. v. Tobolsky, *J. Polym. Sci., Part B: Polym. Phys.* **1974**, *12*, 1.

[36]   W.-I. Cha, S.-H. Hyon, Y. Ikada, *Makromol. Chem.* **1993**, *194*, 2433.

[37]   A. Higuchi, T. Iijima, *Polymer* **1985**, *26*, 1207.

[38]   W. N. Findley, *Creep and Relaxation of Nonlinear Viscoelastic Materials : With an Introduction to Linear Viscoelasticity*, Dover Publications Inc., New York, **1989**.

[39]   B. Yang, W. M. Huang, C. Li, L. Li, *Polymer* **2006**, *47*, 1348.

[40]   R. M. Hodge, G. H. Edward, G. P. Simon, *Polymer* **1996**, *37*, 1371.

[41]   M. Pannico, P. la Manna, *Front. Chem.* **2019**, *7*, 1.

[42]   B. C. Hancock, S. D. Clas, K. Christensen, *Int. J. Pharm.* **2000**, *209*.

[43]   L. Mascia, Y. Kouparitsas, D. Nocita, X. Bao, *Polymers* **2020**, *12*.

[44]   G. Dlubek, F. Redmann, R. Krause-Rehberg, *J. Appl. Polym. Sci.* **2002**, *84*, 244.

[45]   N. Jain, A. Verma, V. K. Singh, *Mater. Res. Express* **2019**, *6*.

[46]   Y. Nakazato, S. Zhu, A. Usuki, M. Kato, *J. Solid Mech.* **2010**, *4*, 856.

[47]   A. L. Simal, A. R. Martin, *J. Appl. Polym. Sci.* **1998**, *68*.

[48]   L. A. de Godoy Oriani, A. L. Simal, *J. Polym. Sci.* **1992**, *46*, 1973.

[49]   M. Teodorescu, M. Bercea, S. Morariu, *Biotechnol. Adv.* **2019**, *37*, 109.

[50]   T. Gaaz, A. Sulong, M. Akhtar, A. Kadhum, A. Mohamad, A. Al-Amiery, D. McPhee, *Molecules* **2015**, *20*, 22833.

[51]   M. C. Lin, C. W. Lou, J. Y. Lin, T. A. Lin, Y. S. Chen, J. H. Lin, *Mater. Sci. Eng. C* **2018**, *91*, 404.

[52]   D. Li, Y. Jiang, S. Lv, X. Liu, J. Gu, Q. Chen, Y. Zhang, *PLoS ONE* **2018**, *13*, 1.

[53]   M. A. Rahman, D. de Santis, G. Spagnoli, G. Ramorino, M. Penco, V. T. Phuong, A. Lazzeri, *J. Appl. Polym. Sci.* **2013**, 202.

[54]   G. Baschek, G. Hartwig, F. Zahradnik, *Polymer* **1999**, *40*, 3433.